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Design of Well-Defined Mesoporous Silicas via Surfactant Templating Method Enhanced by the Use of Swelling Agents

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Design of Well-Defined Mesoporous Silicas via Surfactant Templating Method Enhanced by the Use of Swelling Agents

by

Tiffany Man

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree in Doctor of Philosophy, The City University of New York

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Approval Page

This manuscript has been read and accepted for the Graduate Faculty in Chemistry

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Abstract

Design of Well-Defined Mesoporous Silicas via Surfactant Templating Method Enhanced by the Use of Swelling Agents

by

Tiffany Man

Advisor: Dr. Michal Kruk

Surfactant-templated ordered mesoporous materials continue to attract tremendous attention as these materials are characterized by reproducibility and predictability of their synthesis as well as their wide range of potential applications, which serve as future opportunities for additional advancement. The main purpose of this dissertation is to advance the understanding how to control the structural features and properties in the synthesis of well-defined porous materials via surfactant templating method, while keeping in mind that the uniformity of pore size and structural ordering are essential characteristics for these well-defined materials. The work was primarily focused on the issue of the unit-cell size and pore size adjustment in the large-pore domain (that is, for pore diameters above 12 nm) for two-dimensional hexagonal silica structures with cylindrical pores (referred to as SBA-15 silicas). The use of common poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO, surfactants, commercially known as Pluronics® in combination with appropriate hydrophobic micelle swelling agents was pursued. The main hypothesis was that it is possible to
judiciously select surfactant/swelling agent pairs to achieve optimal structural adjustment capabilities. Moreover, it was hypothesized that different surfactant/swelling agent pairs may work most effectively in certain temperature intervals. The choice of Pluronic tri-block copolymer as main templating agent, the selection of micelle expanders, the adjustment of initial synthesis temperature (including room temperature conditions), and the adjustment of the amount of silica precursor (tetraethylorthosilicate) can systematically affect the structure of porous silica materials formed via the surfactant-micelle-templating synthesis approach. The advancement in pore size tailoring discussed in this dissertation focuses on the above aspects. In particular, considerations based on the extent of solubilization of organic compounds in Pluronic surfactants paved the way to the identification of new excellent swelling agent for the synthesis of large-pore SBA-15. Ordered SBA-15 silica with d_{100} interplanar spacing of up to about 30 nm has been successfully synthesized. Modifications in the synthesis approach in terms of shortening the duration of the synthesis to as little as six hours and eliminating the need for temperature control to carry out the SBA-15 synthesis were found effective for the synthesis around room temperature. Highly ordered face-center-cubic silica materials have also been synthesized using surfactants with moderate content of the hydrophilic PPO domains challenging our current understanding of viable selections of surfactants for the synthesis of materials with spherical mesopores. These materials exhibited increased mesopore volumes when compared to the silicas obtained via the traditional synthesis of materials with spherical pores involving block copolymers with a high fraction of the hydrophilic PEO domains. Overall, the dissertation demonstrates that the synthesis mixture composition and synthesis conditions can be predictively selected to achieve particular structural properties (such as unit-cell size) or to observe formation
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Dedication

This dissertation is dedicated to my incredible spouse, Mark Tiu, who had unconditionally provided me love and support; our cheerful and lovable sons, Christopher Tiu, Curtis Tiu, and Connor Tiu, who always give me motivation and hopes; and lastly, my faithful and encouraging parents, who are always there for me.
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1.

Introduction: Overview of Structure and History of Synthesis, and Design of Ordered Mesoporous Silicas
1.1. Overview of Mesoporous Materials

1.1.1. History of Ordered Mesoporous Materials

By definition established by International Union of Pure and Applied Chemistry (IUPAC), mesoporous materials are classified as a category of porous materials, in which the pore diameter ranges from 2 to 50 nm. Microporous and macroporous materials are porous materials with pore diameters between 0.2 to 2 nm and 50 to 1000 nm, respectively. Although the definition does not specifically indicate the extent of structure ordering of these materials, such a trait is an important feature of some porous materials. While some mesoporous materials can be ordered on the atomic scale, the possible ordering is typically related to periodic arrangement of the mesopores in these materials. The most prominent method to synthesize ordered mesoporous solids is based on templating of the pores by micelles of surfactants. The method was initially referred to as liquid crystal templating, because of the fact that the materials contained arrangements of micelles akin to those in liquid-crystal surfactant phases of surfactants in solutions. However, the surfactant-templating or micelle-templating term is now used more commonly. Silicas with ordered mesopores were developed first, and still constitute a crucial group of ordered mesoporous materials, because of their often straight-forward syntheses, structural diversity and adjustability, and a wide range of potential applications. By using surfactant-templating approach, there have been quite a few types of well-known ordered mesoporous silicas developed over the years.

1) 2-D hexagonal (honeycomb) structures: MCM-41 silica and FSM-n silicas, which appear to be nearly the same. In addition, SBA-15 silica that differs from MCM-41 and FSM-n in that such a material is templated by a block-copolymer surfactant (rather than small-molecule
surfactant) and that microporosity in its wall is expected to be present due to the formation involving the condensation of silica around the hydrophilic blocks of the surfactant;\(^8\)

2) Cubic Ia3d structures: MCM-48\(^3,4\) silica, and KIT-6\(^9,10\) silica, and so forth;

3) Body-centered cubic structures (Im3m symmetry): SBA-16\(^7\) silica;

4) Face-centered cubic structure (Fm3m symmetry): FDU-12\(^11,12\), KIT-5\(^13\), and related close-packed structure FDU-1\(^14,15\), including 3-D hexagonal structure (P6\(_3\)/mmc symmetry) SBA-2\(^16\);

5) Cubic Pm3n structure: SBA-1\(^17\) and SBA-6\(^18\)

In addition, there have been quite many disordered surfactant-templated silicas with rather narrow pore size distribution: HMS\(^19\); MSU-x\(^20\), x=1,2,3 (which includes the first work involving Pluronics surfactants); as well as KIT-1\(^21\)

The reproducibility and predictability of the synthesis approaches for these types of materials give great advantages and gained enormous popularity in the scientific community over the years. The earliest known procedure for the preparation of ordered mesoporous silica was developed and patented in 1971 [V. Chiola, J.E. Ritsko, C.D. Vanderpool, US Patent 3 556 725, 1971],\(^22\) but the obtained material was referred to as a low bulk density silica and its fascinating nano-scale structure was not known until late 1990s.\(^22\) Consequently, this earlier work did not have any impact on the development of ordered mesoporous materials. Then, Kuroda’s group\(^23\) from Japan and the scientists from Mobil Research and Development Corporation,\(^3\) in 1990 and 1992, respectively, reported surfactant-templated materials with controlled pore size,\(^3,23\) including MCM-41\(^3\) materials that feature 2-dimensional hexagonal arrays of uniform mesopores. These materials were prepared using cationic alkylammonium surfactants, such as
hexadecyltrimethylammonium, as structure directing agents. The Mobil scientists also reported other types of materials templated by cationic alkylammonium surfactant: lamellar, called MCM-50; and cubic, called MCM-48 (space group Ia3d) (Scheme 1).³ The field of Materials Science has changed ever since, as developments in ordered mesoporous silicas (OMSs) opened many opportunities for research and advancement in ordered mesoporous materials due to their beneficial properties, such as high surface areas and large pore volumes, periodic mesostructures with accessible uniform pores, diverse chemical composition, rich array of achievable surface functional groups, various particle morphologies, and so forth. In particular, OMSs are suitable for applications that include separations of large molecules, biosensors, catalysis, adsorption, microelectronics, optics, and the fabrication of novel nano-objects.²⁴⁻³⁶

Scheme 1. Three types of surfactant-templated silicas reported by Mobil Scientists. In the case of cubic Ia3d structure, the scheme depicts the arrangement of surfactant micelles that template the materials and thus the morphology of pore structure of the material.

Ionic surfactants, and cationic surfactants in particular, were used in the first successful cases of the surfactant-templated syntheses of OMSs.³,⁴,²³,³⁷ Under appropriate alkaline conditions, deprotonated anionic silica precursors and cationic surfactant molecules can form
one-dimensional (1-D) lamellar (denoted MCM-50), two-dimensional (2-D) hexagonal (MCM-41), and three-dimensional (3-D) cubic (MCM-48) structures, in which 1-D, 2-D, and 3-D indicate the periodicity in one, two, or three directions, respectively. A few years later, anionic surfactants under acidic conditions were also investigated to effectively synthesize OMSs.\textsuperscript{17} Though successful, ionic-surfactant-templated OMSs typically have the limitation of producing small mesopores with sizes in the range of 2-7 nm due to moderately long hydrophobic tails. Moreover, their small head groups facilitate the formation of relatively thin walls. Thus, the limited sizes of pores and a low hydrothermal stability stemming from small pore wall thickness somewhat limited the potential applications of these OMSs.

In 1998, Zhao et al.\textsuperscript{6,7} reported a new OMS named SBA-15, which possesses highly ordered, two-dimensional hexagonal structure (space group \textit{p6mm}) (with interconnections in the walls)\textsuperscript{8,38} of cylindrical pores of diameter from 4.6 nm to 30 nm (the initially stated upper limit of the pore size will be discussed below). They used amphiphilic triblock copolymers, which were commercially available Pluronics surfactants, featuring a hydrophobic center block and two hydrophilic end blocks, in acidic medium to direct the organization of polymerizing silica species. In fact, neutral surfactants like synthetic amphiphilic block copolymers with high molecular weight have great advantages in tailoring pore structure due to the fact that their hydrophobic blocks to hydrophilic blocks mass ratios can be synthetically adjusted by using different copolymers of varying block lengths\textsuperscript{6,7} or the copolymermixtures.\textsuperscript{39} In addition, by changing the reaction conditions, such as the selection of initial synthesis temperature, adjusting pH of the reaction medium, and introducing additives such as micelle expanders, one can systematically tune the pore size of the block-copolymer-templated OMS.
Zhao et al.\textsuperscript{6,7} first reported that the pore diameter of SBA-15 silica templated by Pluronic P123 surfactant (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) can be enlarged from its typical size (~9 nm) to 30 nm using 1,3,5-trimethylbenzene (TMB) as a swelling agent. Nonetheless, it was shown later\textsuperscript{40} that as the amount of TMB is increased, there is a limit in the enlargement of the pore diameter (up to 12 nm) with retention of the SBA-15 structure.\textsuperscript{40} Beyond that limit, the pore size increase ability was complicated by a change of the pore geometry to spherical to form a new material, referred to as a silica mesocellular foam (MCF).\textsuperscript{40} MCFs typically exhibit narrow pore size distributions, but the structures are weakly ordered or completely disordered.\textsuperscript{41} Subsequently, there were no further published works that successfully documented the extension of the pore diameter of SBA-15 materials significantly beyond 12 nm using TMB as the micelle expander.

Since then, several strategies were reported that extended the pore diameters of SBA-15 beyond 12 nm. These approaches included the use of either custom-made amphiphilic block copolymers, or additives (swelling agents or alcohols), or a combination of the above. Early work by Goltner et al.\textsuperscript{42} in the synthesis of 2-D hexagonal structures of cylindrical pores involved poly(ethylene-co-butylene)-poly(ethylene oxide) surfactants, but the structural identification of the product was based only on transmission electron microscopy (TEM) and is not fully convincing. In 2000, Feng et al.\textsuperscript{43,44} employed concentrated solutions of commercially available Pluronic F127, EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}, in combination with appropriate co-solvents (butanol, pentanol, hexanol), and in some cases, swelling agents (octane). It should be noted that Pluronic F127 has about the same size of the hydrophobic poly(propylene oxide) PPO block as Pluronic P123, EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}, but has much larger hydrophilic poly(ethylene oxide) PEO blocks. This synthetic approach afforded SBA-15 silicas with large values (up to 17 nm) (100) interplanar spacing (d\textsubscript{100}), which is the distance between two adjacent planes of pores in the (100)
orientation, see Scheme 2). In 2002, Li et al.\textsuperscript{45} reported their synthesis of SBA-15 materials having $d_{100}$ of about 15 nm using 1,3,5-triisopropylbenzene (TIPB) as the swelling agent and P104 as a surfactant, but the characterization data provided are difficult to discern. In 2005, Sun et al.\textsuperscript{46} discovered the benefits of the use of hexane and other linear hydrocarbons as swelling agents in SBA-15 synthesis. They obtained SBA-15 materials with $d_{100}$ of up to 15 nm. In 2006, Lin et al.\textsuperscript{47} published their work on the synthesis of poly(methyl acrylate)-poly(ethylene oxide)-poly(methyl acrylate) copolymers $[(\text{MA})_x(\text{EO})_{77}\text{MA})_x$ ($x = 33$–$70$) via atom transfer radical polymerization (ATRP) and their use as templates for the synthesis of SBA-15 with (100) interplanar spacings up to 17 nm, and BJH pore diameters up to 20 nm. The increase in the size of the hydrophobic block (PMA) resulted in a fairly systematic pore diameter increase. Similar work was published in 2003\textsuperscript{48}, but the characterization was not fully complete. The authors published a more complete account of their work in 2009\textsuperscript{49} with new details to extend their previous findings. In 2009, we\textsuperscript{50} reported the work using 1,3,5-triisopropylbenzene (TIPB) as a swelling agent and Pluronic P123 as a surfactant that afforded SBA-15 with $d_{100}$ up to as large as 26 nm and pore diameter up to as large as about 26 nm. An improvement of this synthesis pathway was reported more recently.\textsuperscript{51} A summary of the reported syntheses of large-pore SBA-15 silica is listed in Table 1.
Scheme 2. Illustration of $d_{100}$ interplanar spacings and unit cell parameter of SBA-15 materials.

Table 1. Summary of reported syntheses of large-pore SBA-15 silicas.

<table>
<thead>
<tr>
<th>Ref. #</th>
<th>Surfactant</th>
<th>Swelling Agent</th>
<th>Results</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>Pluronic P123</td>
<td>Trimethylbenzene</td>
<td>Pore diameters of up to 12 nm were achieved.</td>
<td></td>
</tr>
<tr>
<td>43,44</td>
<td>Pluronic F127</td>
<td>Octane</td>
<td>$d_{100}$ of up to 17 nm were achieved.</td>
<td>Alcohols used as additives</td>
</tr>
<tr>
<td>45</td>
<td>Pluronic P104</td>
<td>1,3,5-triisopropylbenzene</td>
<td>$d_{100}$ of ~15 nm were reported.</td>
<td>Lack of complete characterization data</td>
</tr>
<tr>
<td>46</td>
<td>Pluronic P123</td>
<td>Hexane and other linear hydrocarbons</td>
<td>$d_{100}$ of up to 15 nm were achieved.</td>
<td></td>
</tr>
<tr>
<td>47,48,49</td>
<td>poly(methyl acrylate)-poly(ethylene oxide)-poly(methyl acrylate) copolymers and PMA-PEO</td>
<td>None</td>
<td>$d_{100}$ of up to 17 nm were achieved; BJH pore diameters up to 20 nm were achieved.</td>
<td></td>
</tr>
<tr>
<td>50,51</td>
<td>Pluronic P123</td>
<td>1,3,5-triisopropylbenzene</td>
<td>$d_{100}$ of up to ~30 nm were achieved; Pore diameters up to ~30 nm were achieved.</td>
<td>The degree of structural ordering was low for $d_{100}$ approaching 26 nm$^{50}$ or 28 nm$^{51}$</td>
</tr>
</tbody>
</table>
1.1.2. Synthesis of Ordered Mesoporous Materials

The synthesis of ordered mesoporous silica (OMS) primarily relies on the soft-templating method (Scheme 3).\textsuperscript{35,36} Surfactants, for instance amphiphilic molecules with long alkyl chains or block copolymers, aggregate in solutions and form micelles or their ordered mesostructures that can direct ordered silica framework formation.\textsuperscript{52} Initially, the Mobil scientists\textsuperscript{3,4} proposed a liquid-crystalline templating mechanism, which suggested that the surfactant forms the periodic liquid-crystalline structure, which can efficiently template the silica mesostructure. Silica precursors were thought to deposit onto the hydrophilic head group layer of the micelles, condensing to form a silica network, which frames the preset geometry based on the surfactant liquid-crystalline phase arrangement (Scheme 4). However, under conditions typically used in the synthesis of OMSs, a liquid-crystalline surfactant phase does not exist due to the fact that the concentration of surfactant is not high enough.\textsuperscript{52} Therefore, the mechanism of formation of OMS needed to be revisited. According to the cooperative self-assembly formation mechanism,\textsuperscript{17,53} the surfactant molecules interact with the silica precursor forming ion-pairs, and the surfactant-silica species self-assemble into the liquid-crystalline phase, in which periodically arranged surfactant micelles template the mesopores in the periodic silica framework (Scheme 3). The strategy is applicable to other framework precursors.
Scheme 3. Pathways that describe the synthesis of OMS via soft and hard templating methods.\textsuperscript{36}


Considering that both mechanisms just described are valid for the synthesis of mesoporous materials, it is important to understand which of these mechanisms can indeed be operational within a particular reaction mixture. Variables in the reaction mixture include the chemical structure of the surfactant template, initial synthesis temperature, components of the reaction mixture, and their concentrations including pH and the concentration of additives (if they are present). These parameters determine the formation of ordered materials in the form of lamellar, cubic, 2-D hexagonal phases, and so on. It is expected that the true liquid-crystalline templating is operational only in concentrated surfactant solutions.\textsuperscript{52}

As far as surfactant templates are concerned, there are two main groups categorized according to their electrical charge: ionic surfactants and neutral (non-ionic) surfactants. Ionic surfactants include anionic and cationic surfactants. Anionic surfactants contain negatively charged head groups, for example, carboxylate, phosphate, sulfate, and so on.\textsuperscript{17} Cationic surfactants possess positively charged head groups like quaternary ammonium.\textsuperscript{3,4,17,18} Neutral surfactants are the ones that hold no charges in their head groups and some of them are poly(ethylene oxide)/(propylene oxide) diblock or triblock copolymers, alkyl polyethers, alkyl amines, and so on.\textsuperscript{35}

The initial synthesis temperature is usually chosen above the critical micelle temperature (CMT) of the surfactant due to its temperature-dependent self-association in aqueous solutions.\textsuperscript{54} The process of self-association of surfactant in solution can be induced by either adjusting the concentration of the surfactant to the value above the critical micelle concentration (CMC) and/or adjusting the temperature to exceed CMT.\textsuperscript{55-60} For ionic surfactants, the CMC is determined by two competing factors: repulsion between the polar head groups that opposes the formation of micelles and the hydrophobic effect.\textsuperscript{61} The hydrophobic effect is related to the
situation in which there is an introduction of a surfactant (or other hydrophobic species) to water. This results in a loss in entropy for water, because water molecules have to orient to some extent around the surfactant unimers while preserving their hydrogen-bonded network. The formation of micelles composed of many unimers eases the disruption of the hydrogen-bonded network for water, as micellization reduces the number of surfactant unimers that would have to be accommodated by water with concomitant decrease in entropy. The micelles are arranged in such a way that water would primarily interact with the hydrophilic parts of the surfactant, hence the hydrophobic parts of the surfactant would form the core of the micelles. Therefore, the formation of well-defined aggregates (micelles) from unimers in water causes an increase in entropy, because the entropy decrease upon surfactant aggregation is exceeded by the entropy gain related to the removal of hydrophobic parts of the surfactant from the aqueous environment.

In ionic surfactants, the charged head groups have a strong affinity for water owing to their electrostatic attraction to the water dipoles and are capable of pulling fairly long hydrophobic hydrocarbon chains into the solution, eventually forming micelles surrounded by charged head groups and excluding the hydrophobic chains from water. For non-ionic surfactants, the hydrophilic PEO blocks, which have high affinity for water, would surround the hydrophobic PPO block to reduce unfavorable interactions. The micelle structure is likely to be held in place (even though the exchange of surfactant unimers among micelles is highly likely) through the hydrophobic effect. Hydrogen bonding between polar PEO units and water molecules takes place on the periphery of the micelle.\textsuperscript{62,63} Induced dipole-induced dipole interaction with some contribution of dipole-dipole interactions occur between the PPO units in the hydrophobic core of the micelles. The silica precursor forms the covalently bonded silica framework once it is introduced. The hydrolyzed and possibly positively charged silicon species
may form hydrogen bonding with the hydrophilic PEO region of the surfactant prior to their condensation into the silica framework.\textsuperscript{63}

The pH values are selected to provide conditions that promote interactions between the framework precursor and the surfactant. For instance, cationic surfactants are often used under basic conditions under which silica precursors form negatively charged silicates. The pH values in the syntheses under acidic conditions (as in the case of SBA-15) govern the rate of hydrolysis of tetraalkoxysilane silica precursors. In the synthesis of SBA-15, acidic condition will facilitate the reaction of silanol groups from the hydrolyzed silicon alkoxide (Scheme 5), to condense and form a silica network (Scheme 6). The hydrolysis of silicon alkoxides under acidic conditions is likely to start with an alkoxide group being protonated in a rapid first step (Scheme 5, Step 1).\textsuperscript{64} Electron density is withdrawn from the silicon atom, making it more electrophilic, and such species is more susceptible to attack by water. This results in the formation of a penta-coordinate transition state with significant S\textsubscript{N}2-type character. The transition state decays by the displacement of an alcohol and the inversion of the silicon tetrahedron (Scheme 5, Step 2). As for the condensation of silanol groups that follows, the mechanism involves the protonation of silanol species (Scheme 6, step 1). While monomeric silanol and condensed silanol species coexist in the solution and both are susceptible to protonation under acidic medium, Brinker\textsuperscript{65} suggested that the more basic monomeric silanol species are more prone to being protonated than the condensed silanol species. The protonation of the silanol makes the silicon more electrophilic and thus susceptible to nucleophilic attack by an unprotonated monomeric silanol species (Scheme 6, Step 2).\textsuperscript{64,65}
Scheme 5. Acid-catalyzed silicon alkoxide hydrolysis: Step (1), protonation of silicon alkoxides in a rapid first step; and Step (2), the attack of nucleophile (water) forming a penta-coordinated intermediate state that decays to silicon tetrahedron, including a silanol (Si-OH) species.\textsuperscript{64}
Scheme 6. Condensation of silanol groups in the formation of the silica network: Step (1), the hydrolysis of a monomeric silanol species; and Step (2), the attack of a nucleophilic unprotonated silanol on another silicon atom forming a dimeric, condensed silanol species.\textsuperscript{64} Step (3) shows a protonated dimeric silanol species undergoes another condensation reaction.

Salts, alcohols, and catalysts of framework condensation (ammonium fluoride, \(\text{NH}_4\text{F}\)), have been additional components added to the synthesis mixtures of OMSs. It was reported\textsuperscript{54} that the addition of inorganic salts to the synthesis of SBA-15 allows one to decrease the synthesis
temperature from 35 – 55 °C to as low as 15 °C. On the other hand, Teixeira et al.\textsuperscript{66} reported that the micelle properties and the dynamics of the formation of SBA-15 were clearly dependent on the presence of salt based on their study of the kinetics of the mesophase formation, the initial value of the cell parameters, and the extent of long-range order with the salt addition in the synthesis. Specifically, they observed that there is a general ion effect that causes a local dehydration of the hydrophilic PEO block of the surfactant, thus inducing the micelle growth. NH\textsubscript{4}F, which at first appears to be just another salt additive, is known as the hydrolysis/condensation catalyst in the synthesis of OMS,\textsuperscript{67} and therefore is added to the synthesis mixture in small quantities, unlike typical salts (e.g., KCl). NH\textsubscript{4}F is used in some of the most important syntheses of large-pore SBA-15.\textsuperscript{46,50,68} It has been shown that the synthesis of SBA-15 is significantly slower in its absence\textsuperscript{67}, which can be explored in tuning the size of ordered domains, which may increase with the decrease of the rate of the formation process. The explanation is likely due to the fluoride ions. Fluoride ions may assist in the participation in the attachment to the silicon species and the facilitation of the displacement of the oxygen containing groups via a S\textsubscript{N}2 mechanism\textsuperscript{65,69} (Scheme 7). Moreover, fluoride ions have the ability to increase the coordination of silicon atom above 4, like in the case of SiF\textsubscript{6}\textsuperscript{2-}.\textsuperscript{65} In fact, hydrofluoric acid, HF, is well-known to etch silicas and undergoes a similar mechanism (Scheme 7) that disrupts the Si-O bond. In a recent publication, Cao and Kruk\textsuperscript{70} reported that highly ordered mesoporous SBA-15 silica with platelet particles with large ordered domains of large pores (diameter of 18 nm; nominal BJH pore diameter ~22 nm) and short pore length (~500 nm) was synthesized using 1,3,5-triisopropylbenzene (TIPB) as the swelling agent in the absence of NH\textsubscript{4}F by employing short initial stirring time at 17 °C followed by static aging at 17 °C.
1. \[
\begin{array}{c}
\text{F}^- + \text{RO-Si-OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{RO-Si-OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{F-Si-OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{F-Si-OR} + \text{ROH} + \text{H}_2\text{O} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\]

2. \[
\begin{array}{c}
\text{H}_2\text{O} + \text{F-Si-OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H+O-Si-OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{HO-Si-OR} + \text{H}_3\text{O}^+ + \text{F}^- \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array}
\]

Scheme 7. The hydrolysis of TEOS catalyzed by fluoride ion.\textsuperscript{65}

1.1.3. Design of Mesoporous Materials

As described in the previous section, the use of surfactants of different molecular size is a well-established strategy for pore size tailoring in OMSs. Block copolymer surfactants have recently attracted much attention because of their large molecular size (opening an avenue to larger pore sizes), convenience of use and often low cost.\textsuperscript{6,7} The block lengths of copolymeric surfactants can be synthetically adjusted to introduce larger or smaller hydrophobic and hydrophilic parts as one desires. In particular, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymer surfactants, commercially available as Pluronics from BASF, are available in tens of different molecular weights and mass ratios of the hydrophilic (PEO) to hydrophobic (PPO) blocks.\textsuperscript{71} PEO-based copolymers with hydrophobic
blocks other than PPO, for instance poly(methyl acrylate) (PMA) or polystyrene (PS), can be conveniently synthesized and hold promise in the synthesis of large-pore ordered mesoporous silicas.\textsuperscript{47,48,72,73} Possibilities are seemingly endless as long as appropriate reaction conditions can be identified for the formation of the desired mesoporous materials. Besides, there are many other advantages of copolymer-templated OMSs. First, the synthesis of such OMSs can be very straight-forward and well-reproducible, as it is in the case of normal SBA-15 silica with pores about 10 nm in diameter. The syntheses of SBA-15 typically utilize commercially available Pluronic P123 and ordinary silica precursors (mainly tetraethyl orthosilicate) under acidic conditions.\textsuperscript{6,7} Second, pore diameters can be much larger (up to 40 nm)\textsuperscript{50,72,74} than those previously achieved using ionic surfactants as templates, including MCM-41 (up to ~7 nm)\textsuperscript{75,76} and MCM-48 silicas. Moreover, the pore diameters can be further modified by variations in the hydrothermal treatment conditions. Third, copolymer-templated OMS has thick walls between the ordered mesopores, so it is more hydrothermally stable than the alkylammonium-surfactant-templated MCM-41 and MCM-48 silicas.\textsuperscript{6,7} Fourth, the mesopores of block-copolymer-templated materials are usually connected with adjacent mesopores by inter-wall micropores or mesopores, due to the occlusion of the poly(ethylene oxide) blocks of the template in the silica framework (Scheme 8).\textsuperscript{8,38,77,78} The latter feature creates many opportunities for the use of SBA-15 and other copolymer-templated materials as templates for the synthesis of ordered arrays of connected nanowires\textsuperscript{79}, and nanotubules\textsuperscript{80}. 
Scheme 8. Micropores resulting from the occlusion of hydrophilic blocks of the surfactant lead to the interconnections between adjacent mesopores in block-copolymer-template silicas.\textsuperscript{8,38}

Another useful strategy is the use of co-surfactants, or mixtures of two surfactants. Interestingly, this strategy can lead to the synthesis of SBA-15 materials with spherical morphology. Katiyar et al.\textsuperscript{81} reported that SBA-15 (with pore diameter between 2.8 and 12.7 nm) with spherical particles (size ranging from 4 to 10 μm) were synthesized using Pluronic P123 along with cetyltrimethylammonium bromide (CTAB) as a co-surfactant in the presence of ethanol. In addition, they employed the swelling agent TMB to obtain the largest pore diameter for SBA-15 silica particles they reported. Pluronic P123 appears to template the ordered mesopores while the ionic surfactant may stabilize spherical particles.

The incorporation of a swelling agent in the surfactant-templated synthesis of OMS\textsuperscript{3,4} remains the most attractive strategy in tailoring the pore size due to its convenience. The pore
size tailoring in OMSs via this approach can be compared to blowing bubbles. One has to ensure that the micelles and eventually the pores of the micelle-templated material will enlarge evenly and not excessively. Otherwise, the structural orderings will be disrupted, like delicate bubbles can become non-uniform or even pop. It is known that the enlargement of the pore diameter is usually accompanied by the lowering of the degree of structural ordering. Therefore, one has to select an appropriate swelling agent for the OMS synthesis to avoid certain undesired characteristics of the resulting materials. It may seem trivial as there are so many possible micelle swelling agents. However, over many years of studies involving hypothesis testing as well as trial and error, promising leads have emerged just recently. The first question is what kind of a compound is appropriate to use as a swelling agent. A crude answer is that it must be a hydrophobic compound, as it is meant to solubilize in the hydrophobic domains of the surfactant. The second question is what state(s) of matter a swelling agent should be in. In most cases, the micelle swelling agents are liquids including ones with very low boiling point, but Huo et al. have used a solid swelling agent (octanoic acid) with some success (however, based on our study discussed below, solids are less promising than liquids). The third question is whether a given swelling agent is universally applicable to micelle-templated syntheses or its choice is dependent on the pore structure morphology and/or the surfactant structure. Based on our earlier studies and the work of other group members, the selection of swelling agents is dependent on the structure of the surfactants that are used to template the porous materials. For PEO-PPO-PEO surfactants (Pluronics) with a relatively small fraction of the hydrophobic domain in comparison to the hydrophilic domains, the appropriate swelling agent should exhibit a strong solubilization in the hydrophobic core. On the other hand, for surfactants with a large fraction of hydrophobic domains, swelling agents with moderate or perhaps even weak
swelling ability would facilitate efficient enlargement of the pores.\textsuperscript{50} While the selection of the surfactant is an important factor in determining the pore structure morphology of the porous materials, a swelling agent is chosen based on the surfactant structure, particularly relating to the fraction of the hydrophobic domain, rather than based on the pore structure morphology. This conclusion emerges from earlier studies (Huang, L.; Kruk, M., manuscript in preparation) and is additionally supported by the research presented in this Dissertation. Organic compounds such as alcohols,\textsuperscript{43} aliphatic hydrocarbons,\textsuperscript{46} and aromatic hydrocarbons,\textsuperscript{50} are suitable swelling agents as they offer a predictable range of solubilization in surfactants dependent on the carbon chain length or number and size of substituents on the aromatic ring. It is essential to identify particularly good swelling agents and to learn how to optimize the synthesis conditions in order to obtain desired useful materials.

Nagarajan\textsuperscript{87} et al. studied different types of solubilizates, hydrocarbons in particular, in the solubilization in Pluronic surfactants. Using direct gas chromatography measurement, it was found that the extent of solubilization is higher for the aromatic hydrocarbons (solubilization decreases with increasing number of carbon substituents on the aromatic ring) than aliphatic hydrocarbon (solubilization decreases with long alkyl chain length). The result was consistent with the calculation of Flory-Huggins interaction parameter computed in terms of Hildebrand-Scatchard solubility parameters.\textsuperscript{87} The Flory-Huggins interaction parameter pertains to the mixing of different components in a polymer solution. While the mixing of two different molecules is entropically favorable, the mixing occurs if the increase in entropy in Gibbs free energy of mixing for such reaction exceeds the enthalpy gain. A small value for Flory-Huggins interaction parameter, in which the positive enthalpic effect is small, suggests a large degree of solubilization for those components in the mixture, because the entropy of mixing would
overcome such small enthalpic contribution. The Hildebrand-Scatchard solubility parameters for hydrocarbons decrease with increasing number of carbon substituents on the benzene ring for aromatic series and with decreasing chain length for aliphatic series.\textsuperscript{87} An increase in the difference in the Hildebrand-Scatchard solubility parameter between the two components in the mixture would decrease the solubilization interaction for the two components.\textsuperscript{87} Nagarajan\textsuperscript{88} published a detailed computational modeling of this process in 1999. Nagarajan\textsuperscript{88} also reported the extent of solubility of the solubilizates can induce the transition in micelle shape from spheres to cylinders and then to lamellae, which was found to be controlled by the free energy of mixing of the solubilizates with the PPO core and compensated by the stretching or the deformation of the corona, leading to cylindrical or lamellae micelle shapes.

Earlier work used alcohols (butanol, pentanol, hexanol)\textsuperscript{43,44}, aliphatic hydrocarbons (pentane, hexane, heptane, octane, etc)\textsuperscript{44,46,68,89}, and aromatic hydrocarbons (1,3,5-triisopropylbenzene)\textsuperscript{45} as swelling agents to enlarge the pore diameter in the block-copolymer-templated 2-D hexagonal structures of cylindrical pores up to 15 nm, with (100) interplanar spacing up to 17 nm (which corresponds to the unit-cell parameter, that is the distance between adjacent pore centers, of up to 19 nm). In recent work, Sörensen et al.\textsuperscript{90} have used PPO homopolymer to swell Pluronic F127 micelles and obtained SBA-15 silicas with pore diameters up to 13 nm (determined using the BJH method which overestimates pore diameter for cylindrical pores in this size range).\textsuperscript{89} Our work involving TIPB as a swelling agent and Pluronic P123 as a surfactant afforded SBA-15 with (100) interplanar spacing up to 26 nm and pore diameter up to about 26 nm.\textsuperscript{50} While this work was a major progress in the synthesis of large-pore SBA-15, the originally reported materials began to exhibit lower degree of structural ordering and small ordered domain once the (100) interplanar spacing exceeded about 22 nm,
and in particular, the ordering of the largest pore silicas was quite low. While the decrease in the structure ordering could be mitigated by appropriate optimization of TIPB/P123 ratio, an identification of other powerful, perhaps superior swelling agents, for SBA-15 synthesis, would be highly desirable.

Ideally, one can envision that a moderate swelling of the micelles with any appropriate swelling agent can lead to uniform pore size expansion in the SBA-15 synthesis. The nature of the swelling agent and its solubilization within the surfactant micelles will determine the extent of pore size increase in the mesoporous structure of the resulting material. As mentioned before, it was known from the literature that the extent of solubilization of alkyl-substituted aromatic hydrocarbons in surfactants, including Pluronic block copolymers used in SBA-15 synthesis, decreases as a number and/or size of alkyl substituents increases. TMB is known to swell Pluronic P123 micelles in an excessive manner, as seen from the tendency to form mesocellular foams instead of SBA-15, unless the relative amount of TMB used is low. Therefore, 1,3,5-triethylbenzene (TEB) was evaluated by us as a somewhat milder swelling agent in comparison to TMB, but TEB appeared to produce excessively strong swelling and poorly ordered silica products. Therefore, one can hypothesize that a swelling agent that solubilizes similarly to TIPB (perhaps somewhat more strongly) in Pluronic P123 surfactant would be a suitable, perhaps superior, swelling agent candidate for SBA-15 synthesis. As is described in this Dissertation, it was possible to identify such a swelling agent.
1.1.4. Characterization of Structures of Mesoporous Materials

For highly ordered mesoporous materials, small angle X-ray scattering (SAXS) or X-ray diffraction (XRD) patterns show several well-resolved reflections that reflect the structural ordering of the materials. For 2-D hexagonal materials (Scheme 9, left), such as SBA-15 silicas, which are the main subject of this Dissertation, the ratio of the angular positions of a given peak to the angular position of the main (first) peak is: $\sqrt{h^2 + hk + k^2}$ to 1 for a peak with an index $(hk0)$. Note that one can consider angular positions of peaks instead of the corresponding interplanar spacings, because the peaks are present at very low angles and $\sin(\theta)$ is proportional to $\theta$, thus latter being inversely proportional to the interplanar spacing. Given that $h$ and $k$ are integers and are greater than or equal to 0, the expected peak ratios for 2-D hexagonal structure are: 1: $\sqrt{3}$ : $\sqrt{4}$ : $\sqrt{7}$ : $\sqrt{12}$ : $\sqrt{13}$… for (100), (110), (200), (210), (300), (220), and (310) peaks, respectively. As for face-center-cubic structure (Scheme 9, right), one should expect a strong (111) reflection, followed by (200) (usually not separated from (111) peak), (220), (311), (400), (331), (420), (422), (531), (553), etc. This corresponds to a peak ratio of: $1: \sqrt[3]{\frac{4}{3}} : \sqrt[3]{\frac{8}{3}} : \sqrt[3]{\frac{11}{3}} : \sqrt[3]{\frac{16}{3}} : \sqrt[3]{\frac{19}{3}} : \sqrt[3]{\frac{20}{3}} : \sqrt[3]{\frac{24}{3}} : \sqrt[3]{\frac{24}{3}} : \sqrt[3]{\frac{35}{3}} : \sqrt[3]{\frac{53}{3}}$… It should be noted that for both structures, not all peaks may appear on a pattern of any particular material (see Figure 1 for illustrative SAXS scattering patterns), because some of them may not be sufficiently intense.
Scheme 9. Schematic drawing of 2-D hexagonal structure (left) and face-centered-cubic structure (right).

Figure 1. SAXS patterns for 2-D hexagonal SBA-15 silica (SBA-15, left) and face-center-cubic silica (right).

High specific surface area (200 – 800 m²/g) and narrow pore size distribution are often inferred from nitrogen adsorption for ordered mesoporous materials. Adsorption isotherms often level off after the capillary condensation in the primary (ordered) mesopores is completed (see Figure 2 for adsorption/desorption isotherm for an SBA-15 silica sample). For materials with well accessible cylindrical mesopores, a narrow adsorption/desorption hysteresis loop with parallel branches is typically seen,⁷,⁵⁰ which is referred to as H1 type hysteresis loop (Figure 2 and 3).¹,⁹¹ By International Union of Pure and Applied Chemistry (IUPAC) definition, H1-type
hysteresis loop possesses nearly vertical and parallel capillary condensation (adsorption) and evaporation (desorption) branches, which is interpreted as an evidence of well accessible mesopores. On the other hand, H2-type hysteresis loop is expected for pores with narrow parts leading to wide sections (typically referred to as ink-bottle pores or as cage-like pores); and features an inclining adsorption branch and nearly vertical desorption branch (see Figure 3). More recent work showed that in such a case, the adsorption branch can also be very steep, whereas the desorption branch does not have to be very steep.\textsuperscript{15,86} H3 and H4-type hysteresis loops are associated with slit-shaped pores of aggregates of plate-like particles and pores of narrower size, respectively. H4-type hysteresis loops may appear for particles with quite narrow pores, which additionally have larger inner voids spaces in them.\textsuperscript{92} Normally, the adsorption-desorption hysteresis is not observed below a certain pressure limit, which is referred to as the lower limit of adsorption-desorption hysteresis. This limit for nitrogen at 77 K is at relative pressures of 0.4 – 0.5.\textsuperscript{92} Therefore, the capillary condensation in mesopores at relative pressure below 0.4 is not accompanied by hysteresis. Low pressure hysteresis is another feature that maybe seen in adsorption isotherms, in which the hysteresis loop may be observable down to a very low relative pressure, well below lower limit of adsorption-desorption hysteresis (the dashed curves in the hysteresis loops shown in Figure 3). This may result from a slow diffusion to/from some mesopores, the swelling of non-rigid pores, or with the irreversible uptake of molecules in pores of sizes that are similar to the size of adsorptive molecules.\textsuperscript{93} This phenomenon is frequently observed for microporous adsorbents, particularly for active carbon.\textsuperscript{94}
Figure 2. Nitrogen adsorption isotherm for SBA-15 silica features narrow adsorption/desorption hysteresis loop with parallel branches and adsorption isotherm that leveled off as the capillary condensation is completed. The behavior is characteristic of uniform, large cylindrical mesopores without constrictions.

Figure 3. IUPAC classification of hysteresis loops.\textsuperscript{90}
TEM images allow one to visualize the ordered pore arrangements (Figure 4) and estimate the interplanar spacing. While TEM can be used to identify the ordered structure type, it is typically better to combine this identification method with SAXS/XRD in the case of ordered mesoporous materials. Scanning electron microscope (SEM) can map out the morphology of the surface of OMS, if sufficiently high resolution can be achieved. It also allows one to see the shape of particles of the material. \(^7^0\)

Figure 4. TEM image of SBA-15 silica features honeycombs (transparent arrow) and striped patterns (solid arrow).
1.2. Synthesis of Large Pore SBA-15 Silica with Two-dimensional Hexagonal Structure

SBA-15 silica with two-dimensional hexagonal arrays of cylindrical mesopores (typically with connections among adjacent pores, which are much narrower than the main cylindrical mesopores)\(^8,38,79\) introduced by Zhao et al.\(^6,7\) in 1998 has attracted significant attention in the scientific and engineering community as these materials have beneficial properties that are useful in many applications. The synthesis is reproducible and involves commercially available Pluronic surfactants (manufactured by BASF) under acidic conditions with an appropriate selection of the initial synthesis temperature (typically \(\sim 35\,^\circ\text{C}\)), as well as a kind and relative amount of the silica precursor.

1.2.1. Pluronic Surfactants

Pluronic triblock copolymer surfactant names start with a letter followed by two or three numbers. The letter describes the appearance of the polymer: F (flake), P (paste), or L (liquid). The first one (if there are two) or two (if there are three) numbers multiplied by 300 indicates the molecular weight of the hydrophobic PPO block and the last number multiplied by 10 \(\%\) gives the hydrophilic PEO weight percent.\(^95\) In the case of Pluronic P123 (chemical formula is shown in Figure 5), this surfactant is a paste with \(12 \times 300\,\text{g/mol} = \sim 3600\,\text{g/mol}\) PPO and 30 wt. \(\%\) PEO. On the other hand, Pluronic F127 consists of solid flakes with the same molar mass of PPO, but with 70 wt. \(\%\) PEO in the polymer. The differences in the content of hydrophobic domains and in the molecular weight of the surfactant give rise to the variation of micellar structures that these surfactants form\(^96\) and consequently to the diversity of pore structures.
observed in the mesoporous materials templated by Pluronics. For instance, Pluronic F127 is used primarily for synthesizing spherical mesopores in a body-centered cubic structure,\(^7\) or face-centered cubic structure,\(^{11}\) while Pluronic P123 is used for hexagonally ordered cylindrical pores,\(^7\) as well as gyroidal (cubic Ia3d) structure.\(^{9,10}\) However, there are some cases in which Pluronic F127 can be used to template a 2-D hexagonal arrays of mesopores in carbons (FDU-15, developed at Fudan University) synthesized using different synthesis methods,\(^{97-100}\) and silicas (SBA-15).\(^{43,44}\)

![Chemical formula for Pluronic P123](image)

Figure 5. Chemical formula for Pluronic P123 composed of 20 hydrophilic ethylene oxide units on each side of the middle block composed of 70 propylene oxide units.

### 1.2.2. Silica Precursors

Silicon alkoxides are most commonly used as silica precursors in the synthesis of copolymer-templated mesoporous silicas.\(^6,7\) Soluble silicates were also used as precursors in SBA-15 synthesis.\(^{39,101}\) It should be noted that in the case of MCM-41 and related materials, soluble silicates are often employed,\(^3\) while they are usable, but less common for SBA-15 and other copolymer-templated materials.\(^{39}\) In the present study, tetraethyl orthosilicate (TEOS) (Figure 6) is solely used. Tetramethyl orthosilicate (TMOS), which has smaller alkoxy groups in comparison to TEOS, has been used successfully by others\(^{45,102,103}\) in the synthesis of SBA-15 materials. TMOS has the ability to hydrolyze faster than TEOS in comparable acidic conditions.
However, it was noticed that slower hydrolysis rate of the silica precursor also bear its advantage in the pore size tailoring of the mesoporous materials.\textsuperscript{102} Although the exact mechanism is not clear, perhaps, the use of a slower hydrolyzing precursor allows more time for the uniform incorporation of the swelling agent under conditions in which the hydrolysis and condensation are already accelerated by the addition of NH\textsubscript{4}F catalyst. Silica alkoxides with longer alkyl chains had also been used to promote different morphologies of particles of SBA-15 materials, such as spherical and fiber-like. Because of the fact that the silica precursor before hydrolysis is quite hydrophobic, there has been a notion that the silica precursor can participate in the swelling of the micelles,\textsuperscript{70,102,104} as also suggested by some work described in a subsequent section in this Dissertation. Upon the hydrolysis, in which partially hydrolyzed TEOS becomes hydrophilic, TEOS enters the hydrophilic PEO corona of the micelles. Alternatively, TEOS can be significantly hydrolyzed before reacting with the surfactant, thus, deposits directly onto the corona of the micelles. The exact mechanism cannot be concluded exclusively as there may be numerous pathways in which TEOS is incorporated and there are many factors that may affect the micellar system.
Figure 6. Chemical structure of tetraethyl orthosilicate (TEOS) and its formation of a silica network. Note: The structure is truncated and schematic, in which the size of the rings or scheme does not reflect the actual size and population of the rings; each silicon is bonded to four oxygen atoms, while each oxygen is bonded to two silicon atoms or one silicon and one hydrogen atom.

1.2.3. Swelling Agents

Table 2 provides a summary of swelling agents that were used in the synthesis of SBA-15 silica. As mentioned earlier, there are a few criteria for the appropriate choice of a swelling agent in the synthesis of ordered mesoporous materials, including SBA-15 silica.

Aromatic hydrocarbons that exhibit moderate extent of solubilization in Pluronic surfactants (primarily in the hydrophobic PPO core) are the main focus of this Dissertation. In an aqueous solution of surfactant micelle in water, swelling agent is partitioned in to the compatible hydrophobic part of the micelles. The swelling agent can interact with PPO blocks via induced dipole/induced dipole attraction. The polarity of PPO units may also induce dipole moments in the hydrophobic hydrocarbon swelling agent, and thus lead to some attraction by van der Waals force of dipole/induced dipole interaction. The interaction of the swelling agent with the corona PEO parts of the surfactant or with solvent water is likely to be insignificant due to the lack of
significant miscibility and thus lead to spatial separation. If any interactions exist, they would be van der Waals weak attractive forces.

As discussed previously, TMB possesses too strong swelling ability in the synthesis of SBA-15 using Pluronic P123 surfactant, because of which mesocellular foam (MCF) materials typically form beyond the mesopore diameter of 12 nm. Therefore, “weaker” swelling agents were investigated in our early work. 1,3,5-TIPB works very well as a swelling agent in the synthesis of SBA-15 materials.\textsuperscript{50,51} (100) interplanar spacings, $d_{100}$, up to 26 nm and pore diameters of up to 26 nm (nominal BJH pore diameter up to 34 nm) were achieved.\textsuperscript{50} However, the degree of structural ordering tended to decrease for larger interplanar spacing values, especially for $d_{100}$ above 22 nm. While the adjustment of the molar ratio of the swelling agent to the surfactant (TIPB/P123) allows one to improve the structure to an extent that $d_{100} = 28$ nm (or perhaps even a little bit larger) can be achieved, the degree of ordering diminishes for the highest achievable interplanar spacings.\textsuperscript{50,51} This was suggested by the decrease in resolution from SAXS patterns (Figure 7), and less organized features seen in TEM images (Figure 8) with decreasing initial synthesis temperature.

It is also known that the use of swelling agents that solubilize in Pluronics to a small extent (linear hydrocarbons, cyclohexane) is a powerful way to obtain highly ordered SBA-15 silicas with $d_{100}$ up to ~15 nm. It is clear that the use of swelling agents that exhibit moderate extent of solubilization is the most beneficial. However, there is a need to identify swelling agents that would be more potent than linear hydrocarbons, cyclohexane, or even TIPB.
Figure 7. SAXS patterns (top left), adsorption isotherms (top right), and pore size distributions (bottom) for SBA-15 silicas synthesized with Pluronic P123, TIPB, TEOS, in the presence of NH₄F. Reprinted with permission from Cao, L.; Man, T.; Kruk, M. Chemistry of Materials 2009, 21, 1144. Copyright 2009 American Chemical Society.
Figure 8. TEM images for SBA-15 silicas synthesized with Pluronic P123, TIPB, TEOS, in the presence of NH$_4$F. Reprinted with permission from Cao, L.; Man, T.; Kruk, M. Chemistry of Materials 2009, 21, 1144. Copyright 2009 American Chemical Society.
Table 2. Swelling agents used in the reported syntheses of SBA-15 silicas.

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Structure</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycloalkane</td>
<td>Cyclohexane</td>
<td><img src="cyclohexane.png" alt="Image" /></td>
<td>Afforded well-ordered SBA-15 with pore diameter up to 13 nm. However, highly suitable for the synthesis of periodic mesopores organosilicas with very large pores.</td>
<td>50</td>
</tr>
<tr>
<td>Aliphatic hydrocarbon</td>
<td>Pentane-hexadecane</td>
<td><img src="pentane-hexadecane.png" alt="Image" /></td>
<td>The pore size increases with decreasing alkane chain length, which follows the order of the extent of solubilization of these hydrocarbons in Pluronic surfactant micelles in aqueous solutions. Pore diameters of up to ~15 nm have been reported ((d_{100}) up to 14.6 nm). The uptake of these swelling agents in Pluronic surfactants appears to be small</td>
<td>46,68,89</td>
</tr>
<tr>
<td>Aromatic hydrocarbon</td>
<td>Trimethyl-benzene (TMB)</td>
<td><img src="trimethyl-benzene.png" alt="Image" /></td>
<td>Initially, it appeared that TMB allows one to obtain SBA-15 with pore diameter up to 30 nm; later it was reported that SBA-15 with pore diameters of up to 12 nm has been achieved, but pore diameter beyond 12 nm was for mesocellular foam (MCF) with spherical pores. Apparently, TMB has found to swell the micelles too strongly.</td>
<td>6,7,40</td>
</tr>
<tr>
<td></td>
<td>Triethyl-benzene (TEB)</td>
<td><img src="triethyl-benzene.png" alt="Image" /></td>
<td>Not successful in allowing to achieve an ordered structure, but clearly a powerful swelling agent</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1,3,5-triisopropyl-benzene (1,3,5-TIPB)</td>
<td><img src="1,3,5-triisopropyl-benzene.png" alt="Image" /></td>
<td>(d_{100}) of up to 28 nm were achieved; Pore diameters up to 28 nm were achieved (for less ordered silicas, as seen from SAXS, (d_{100}) was up to 30 nm).</td>
<td>45,50,51</td>
</tr>
</tbody>
</table>
1.2.4. Formation of SBA-15 Materials

In the formation of SBA-15 materials under most common conditions (~35 °C, Pluronic P123 surfactant, and no swelling agent), it is believed that spherical micelles are present in the solution prior to the addition of the silica precursor. After the addition of the silica source, the elongation of the silica-decorated micelles takes place and the elongated composite micelles arrange themselves in a hexagonal pattern. Alfredsson’s group\textsuperscript{106,107} and Goldfarb’s group\textsuperscript{108,109} carried out studies of the formation of SBA-15 silicas. Alfredsson et al.\textsuperscript{106,107} suggested that the micelle aggregation is initiated by a micelle–micelle attraction as the oligomeric/polymeric silica that adsorbs onto the PEO domain of the micelles continues to condense, forming the silica network with adjacent micelles. Similarly, Goldfarb et al.\textsuperscript{108} concluded that the initial spheroidal micelles fuse into threadlike micelles that become longer and straighter as time evolves as evident by cryo-TEM study. Goldfarb\textsuperscript{108} claimed that the elongation of the micelles is a consequence of a reduction in polarity and water content within the micelles as silicates adsorb and polymerize. Based on the study, Goldfarb summed up the following sequence of events in the formation of SBA-15 silicas: (i) silicate adsorption on globular micelles possibly accompanied with some aggregate growth, (ii) the association of these globular micelles into flocs, (iii) the precipitation of these flocs, and (iv) micelle–micelle coalescence generating (semi)infinite cylinders that form the two-dimensional hexagonally ordered arrays.\textsuperscript{108}
1.2.5. Hydrothermal Treatment

Because of the fact that the properties of Pluronic P123 surfactant are temperature dependent, it can be expected that a hydrothermal treatment, in other words, the heating of the reaction mixture of temperature higher than that at which the material formed, can further fine-tune some features of the resulting SBA-15 material, such as the pore size, pore wall thickness, micropore volume, and specific surface area.

After the formation of the 2-dimensional hexagonal structure, the PEO chains are enclosed in the silica network\textsuperscript{8,38,78} and they are the source for the micropores in the final product (Scheme 8).\textsuperscript{8,38} When the temperature is elevated, the hydrophilicity of the PEO chains decreases and thus the PEO chains aggregate in the silica wall and/or even retract from the silica wall and join the more hydrophobic core of the micelles.\textsuperscript{8} This results in a slight increase in the pore size and a reduction in the microporosity and specific surface area. Moreover, the hydrothermal treatment decreases the shrinkage of the silica walls upon calcination (See Figure 9).\textsuperscript{7,8}

The hydrothermal treatment temperature for SBA-15 in a normal synthesis ranges from 80 °C to 130 °C. At the higher end of this temperature range, the microporosity is minimized and the specific surface area is decreased. The unit cell parameter, however, stays nearly constant for uncalcined samples. It is believed that during the hydrothermal treatment, which causes the increase of in the mesopore size, the wall thickness decreases and the wall becomes denser in a sense that the microporosity is reduced.\textsuperscript{8,110,111}
1.2.6. Removal of Surfactant Template

In order to obtain materials with fully accessible mesopores in the micelle-templating process, the removal of templates from as-synthesized inorganic-organic (silica/surfactant) composites must be employed. There are many different methods for surfactant removal, including calcination, extraction, removal via treatment in a microwave reaction system (microwave digestion), and irradiation using high energy ultraviolet lamp. Each of these methods has its advantages and disadvantages. Among them all, calcination is the most common template removal method due to the easy operation and complete elimination of the shrinkage.
organic components.\textsuperscript{112,113} The organic surfactant can be totally decomposed or oxidized and volatilized under air or nitrogen atmosphere. To ensure the liberation of porosity, the calcination temperature should be below the collapse temperature of mesoporous materials (about 1000 °C for silicas\textsuperscript{38}), but above ~300 °C under air to burn out the PEO-PPO-PEO type surfactants. The heating rate may need to be low enough to avoid local overheating resulting in a structural collapse (especially significant in framework-modified (doped) silicas or non-silica compositions). At first, a two-step calcination was adopted by Mobil scientists in the early times, in which the first one hour under nitrogen allows the decomposition of the surfactant followed by five hours under air or oxygen to burn it out completely.\textsuperscript{112} To simplify the procedure, Zhao et al.\textsuperscript{112} later found that heating under air at a slow rate and keeping the final temperature constant for four to six hours can substitute the heating in nitrogen atmosphere in the first hour, as confirmed by the FT-IR spectra and elemental analysis, which shows that such an adjustment completely removes the triblock copolymer template. In fact, the heating rate can be up to at least 20 °C/min for SBA-15.\textsuperscript{51}

Upon calcination, the shrinkage of the framework takes place, thus the decrease in the size of the mesopores is observed. It is believed that at approximately 300 °C, in which water has evaporated and the polymer surfactant has been oxidized, the materials experience the condensation of the framework (that is, the condensation of silanol groups forming siloxane bridges with the release of water).\textsuperscript{114} To ensure the stability of the SBA-15 silicas during storage, it is recommended to calcine the material to a higher temperature (~550 °C), which would reduce the chance for water adsorption, rehydroxylation, and structural collapse, although the latter is unlikely to occur for block-copolymer-templated silicas that have thick walls. Even
SBA-15 calcined at 400 °C can be stored for many years with a retention of the structural ordering and with only a moderate decrease of specific surface area and total pore volume.⁵¹
## 2.

**Conditions for the Synthesis of Large-Pore SBA-15 Silica with Two-Dimensional Hexagonal Structure of Cylindrical Mesopores and Characterization Methods**
2.1. Materials

PEO-PPO-PEO Pluronic triblock copolymers P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}), P103 (EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}), P104 (EO\textsubscript{27}PO\textsubscript{61}EO\textsubscript{27}), L92 (EO\textsubscript{8}PO\textsubscript{47}EO\textsubscript{8}), and P84 (EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}) were provided by BASF and were used as received. The synthesis of SBA-15 silicas was attempted using aromatic hydrocarbons as micelle expanders, including 1,3-di-tert-butylbenzene (1,3-DTBB), 1,4-di-tert-butylbenzene (1,4-DTBB), 1,3,5-triisopropylbenzene (TIPB), 1,4-diisopropylbenzene (1,4-DIPB), and 1,3,5-tri-tert-butylbenzene (1,3,5-TTBB). These compounds were used as received. The synthesis procedures were similar to those developed earlier in the case of TIPB, but they needed to be carefully modified by selecting appropriate temperature, swelling agent/P123 ratio, and sequence of addition of swelling agent and TEOS.\textsuperscript{50,70} The molar composition of the synthesis mixture typically was: TEOS : Pluronic surfactant : micelle expander : NH\textsubscript{4}F : HCl : H\textsubscript{2}O = 1 : 0.0168 : x : 0 or 0.0295 : 4.42 : 186.

Low temperature synthesis. A typical synthesis procedure was as follows: 2.4 g of Pluronic P123 (and 0.027 g NH\textsubscript{4}F, if selected) was dissolved under mechanical stirring in 84.0 mL of 1.30 M aqueous HCl solution in a water bath (nominal temperature accuracy of 0.01 °C) set at selected initial synthesis temperature. After at least one hour, a selected amount of swelling agent was added followed by the addition of 5.5 ml of TEOS (within a few minutes). The solution continued to be stirred for 24 hours at the set temperature in an open polypropylene bottle. Then, the product was either isolated by filtration or subjected to hydrothermal treatment at different temperatures (from 100 to 130 °C) in a closed container for periods of time from 1 to 2 days. The heating at 100 °C was performed in polypropylene bottles, whereas the heating at
higher temperatures was carried out in Teflon-lined autoclaves. The resulting products were isolated by using sintered glass filter, washed with water and dried at ~60 °C in a vacuum oven. At last, the products were calcined under air at 550 °C for 5 hours (heating ramp 2 °C min\(^{-1}\)).

**Room temperature synthesis.** A procedure similar to that described above was used, except water bath without temperature control, or no water bath was used. A polypropylene bottle with the solution mixture was placed (in a bath, where applicable) over a magnetic stirring plate, and the reaction mixture was stirred magnetically (or mechanically). Surfactants other than Pluronic P123 (mostly P103) were used in many cases. The remaining parts of the synthesis were carried out as described above.

**Synthesis above room temperature.** A mineral oil bath placed over a hot plate was used to control the temperature above 25 °C and stirring was either magnetic or mechanical. The bottle containing the mixture was partially covered with parafilm to prevent excessive evaporation of components of the synthesis mixture. The remaining parts of the synthesis were carried out as described above.

### 2.2. Characterizations

**Small-angle X-ray Scattering (SAXS).** SAXS patterns were measured using Bruker Nanostar U SAXS/wide-angle X-ray scattering (WAXS) system with a rotating anode X-ray source and Vantec-2000 2-dimensional detector. The Nanostar U system had a sample-to-detector distance of about 72 cm and was in high-flux configuration. The powder samples were placed in a hole in a sample holder and secured from both sides using a Kapton tape.
**Nitrogen Adsorption Measurements.** Nitrogen adsorption isotherms were measured at -196 °C on Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the adsorption analysis, calcined samples were outgassed under vacuum at 200 °C in the port of the adsorption analyzer.

**Transmission electron microscopy (TEM).** TEM images were recorded on FEI Tecnai Spirit microscope operated at 120 kV. Before imaging, the samples were dispersed in ethanol by sonication and subsequently deposited on a carbon-coated copper grid.

### 2.3. Calculations

The specific surface area, $S_{\text{BET}}$, was calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method. The total pore volume, $V_t$, was determined from the amount adsorbed at a relative pressure of 0.99. Pore size distributions (PSDs) were determined from adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method with the Kelvin equation for hemispherical meniscus and the statistical film thickness curve for macroporous silica. The BJH pore diameter, $w_{\text{BJH}}$, is defined as the position of the peak maximum on the pore size distribution.
3.

Results and Discussion
3.1. Selection of Swelling Agents

3.1.1. Optimization Approach

Based on our knowledge of the synthesis of surfactant-templated large pore SBA-15 silicas using swelling agents to achieve the pore enlargement, we have selected a few swelling agents to investigate their effectiveness. In the aromatic hydrocarbons series, it was hypothesized that the most suitable swelling agent for the synthesis of SBA-15 using Pluronic P123 surfactant might be found between TMB and 1,3,5-TIPB in the extrapolated sequence of the extent of solubilization of the aromatic hydrocarbons in Pluronics (see Figure 10).\(^{50,85,86}\) As was already discussed, 1,3,5-TIPB\(^{50,51}\) is the most suitable and successful swelling agent reported so far for the synthesis of large-pore SBA-15 involving Pluronic P123, which provided efficient swelling ability and afforded very-large-pore SBA-15 silicas.\(^{50,51}\) However, it was observed that the quality of the SBA-15 silicas decreased when the pore sizes approached their upper limits (pore diameter and \(d_{100}\) of 26 nm) using 1,3,5-TIPB to synthesize SBA-15 silicas.\(^{50}\) Further optimization of TIPB/P123 molar ratios allowed one to reach some improvement (so that two peaks and one shoulder can be seen for silicas with \(d_{100}\) up to 28 nm)\(^{51}\), but still the issue of decreasing degree of structural ordering and eventual loss of ordering with the increase in the unit-cell size remained. In addition, it is known the combination of Pluronic P123 and TMB readily leads to excessive swelling and the formation of mesocellular foams.\(^{40}\) Earlier studies suggested that this relation is relevant to the synthesis of porous materials using aromatic swelling agents.\(^{85,86}\) Moreover, there were indications that alkylbenzene with the same total number of carbon atoms in alkyl substituents work similarly well as swelling agents no matter what actual size, number and position of the alkyl substituents is.\(^{74}\) The extent of solubilization of aromatics hydrocarbons in the Pluronic surfactants increases with decrease in number of/and
size of alkyl substituents.\textsuperscript{88} It would be beneficial to identify a swelling agent for SBA-15 synthesis that swells more strongly than TIPB and yet in a controlled manner, unlike in the case of TMB. Hence, we have attempted to use swelling agents from the aromatic hydrocarbon series that contain between 4 and 8 carbon atoms in the substituents on the benzene ring (that is, a higher number than in the case of TMB and lower than in the case of TIPB) to enhance the swelling action in a controlled manner with the goal to obtain even larger cylindrical pores and/or higher degree of structural ordering. Another goal was to improve our understanding of criteria of the selection of swelling agents so that they can be more easily identified for a target synthesis.

There is evidence that the number of carbon atoms in alkyl substituents is the most important factor, while the structure of substituents plays a secondary role.\textsuperscript{74} Since TMB has 3 carbon atoms in alkyl substituents and swells too much, while TIPB has 3x3=9 carbon atoms in the substituents and works well, triethylbenzene (TEB) with 3x2=6 carbon atoms in the substituents on the benzene ring was evaluated, but seemed to swell excessively in the case of Pluronic P123. Thus, we have attempted to use di-tert-butyl benzene (DTBB) (2x4=8 carbon atoms) as a swelling agent candidate for SBA-15 synthesis, which would possibly be more potent than TIPB and at the same time, would not swell excessively (like TMB). As will be discussed later, 1,3-DTBB was found to be an excellent swelling agent in the synthesis of highly ordered very-large-pore SBA-15 materials, in which (100) interplanar spacings above 25 nm and up to 29 nm were achievable with unprecedented quality. We also made some progress in the use of a swelling agent with 6 carbon atoms in the substituents (1,4-diisopropylbenzene, 1,4-DIPB), nonetheless, we found it inferior to TIPB.
Figure 10. Aromatic hydrocarbons as swelling agents for SBA-15 synthesis using Pluronic P123 surfactant in the order from left to right describing the extent of solubilization in Pluronic surfactants, in which moderate swelling of the micelles can result in SBA-15 materials and excessive swelling leads to mesocellular foams (MCFs).

Surprisingly, we found that there might be a dramatic difference in the suitability of isomers of alkyl aromatics as swelling agents. However, the difference is not unexpected if physical properties of the isomers are significantly different. 1,4-di-tert-butylbenzene (1,4-
DTBB) has significantly higher melting point than 1,3-di-tert-butylbenzene (1,3-DTBB). The differences are likely to arise from appreciably stronger intermolecular interactions in 1,4-DTBB in comparison to 1,3-DTBB. In aromatic molecules without polar substituents, the intermolecular interactions are expected to be stronger if the molecules can effectively pi-stack. Therefore, 1,4-DTBB with substituents at para position is likely to exhibit more effective (closer) pi-stacking than 1,3-DTBB of substituent at meta position. When 1,3-DTBB molecules are pi-stacked, the steric hindrance of the substituents would make pi-stacking less effective, as one of the substituents of the second 1,3-DTBB molecule has to be placed between the substituents of the first molecule or placed in the opposite direction, but at the same distance. Either way, the steric hindrance for effective pi-stacking may be significant. 1,4-DTBB can possibly pi-stack with the substituents of one molecule rotated by 90° with respect to those of the second molecule. The latter is likely to be less sterically hindered. Therefore, 1,3-DTBB is a liquid and 1,4-DTBB is a solid at room temperature.

Although pi-stacking is not likely once the swelling agent is added to the synthesis mixture. During its initial evaluation, 1,4-DTBB appeared to precipitate out from the solution even if it was dissolved in silica precursor prior to the addition. The synthesis temperature may simply be too low for 1,4-DTBB to work efficiently in these conditions. Or perhaps, 1,4-DTBB is more favorable in solubilizing in TEOS than PPO, rendering its swelling action in the PPO region. So we continued the work with 1,3-DTBB only. However, we evaluated the mixtures of 1,4-DTBB with TIPB. As discussed later, no detrimental effect and perhaps same beneficial effects of 1,4-DTBB were seen. 1,3,5-tri-tert-butylbenzene (1,3,5-TTBB) was also evaluated with expectation of its insufficiently strong swelling action, but its low solubility in water and solid state at room temperature made it a poor swelling agent that was difficult to fully evaluate.
Good quality SBA-15 materials have been synthesized with 1,3-DTBB. The refinement of the quality of these materials has been investigated, namely, the adjustment of the amount of swelling agent and modification of the amount of the silica precursor. Although these adjustments did not significantly change the pore size and uniformity for SBA-15 silicas prepared at 14.5 °C and above, they led to a major improvement at lower temperatures, allowing us to obtain SBA-15 with uncommonly large unit-cell parameters and with significant or even unprecedented degree of structural ordering.

The attempts to synthesize OMS at room temperature involved Pluronic P103 (EO_{17}PO_{66}EO_{17}), Pluronic P104 (EO_{27}PO_{61}EO_{27}), Pluronic L92 (EO_{8}PO_{47}EO_{8}), and Pluronic P84 (EO_{19}PO_{43}EO_{19}). Although these attempts were planned specifically for the syntheses of SBA-15 materials, the use of Pluronic P104 and P84 surprisingly led to the formation of a different structure of interest, the face-center-cubic ordered mesoporous silica (Chapter 3.5).

The selection of an appropriate Pluronic surfactant is essential for the synthesis of SBA-15 silicas. As mentioned earlier, the hydrophilic and hydrophobic components in the Pluronic surfactant give rise to the different micellar structures that can template ordered mesoporous materials.

As shown earlier (Yingyu Li and Michal Kruk, unpublished work) for silicas with spherical pores and is shown hereafter in the present work for SBA-15 with cylindrical mesopores, the initial synthesis temperature can be selected based on the critical micelle temperature of the Pluronic surfactants in water. Further temperature adjustment is to be investigated to determine the lowest temperature at which good quality large-pore materials still persist, while good quality of smaller-pore materials may be achieved at higher temperatures.
3.1.2. Initial Evaluation of Swelling Agents

Based on the discussion presented above, swelling agents in the aromatic hydrocarbons series containing 4 to 8 carbon atoms in the substituents on the benzene rings are potential candidates in the synthesis of large-pore SBA-15 silicas. Earlier work on 1,3,5-triethylbenzene (1,3,5-TEB) (6 carbon atoms in alkyl substituents) indicated that it is a powerful swelling agent, but there was no success in using it to obtain a large-pore SBA-15. Herein, 1,4-diisopropylbenzene (1,4-DIPB) (6 carbon atoms in alkyl substituents) was evaluated, but did not yield promising results (SAXS patterns, adsorption isotherms, and pore size distributions are shown in Figure 11 and 12 for samples prepared using 1,4-DIPB and 1,3,5-TEB, respectively). Although the SAXS pattern indicated SBA-15 material was formed, the background intensity was quite high, suggesting secondary porosity, and \( d_{100} \) was 12.8 nm at the initial synthesis temperature of 15 °C, which is significantly lower than what was observed for the synthesis of SBA-15 using TIPB as the swelling agent. Therefore, our attention was directed to a swelling agent with a higher number of carbon atoms in the alkyl substituents: di-tert-butylbenzene (DTBB) with 8 carbon atoms in the substituents. DTBB has two isomers that are commercially available: 1,3-DTBB and 1,4-DTBB. The latter is cheaper, so it was first evaluated. However, 1,4-DTBB is a solid at room temperature and seemed to precipitate out of the synthesis mixture even after dissolving it in TEOS prior to its addition. While 1,4-DTBB and 1,4-DIPB were not found useful for the synthesis of large-pore SBA-15 when they were used as single swelling agents, they were found appropriate as components of swelling agent mixtures. In particular, the use of TIPB mixed with 1,4-DTBB or 1,4-DIPB or 1,3-DTBB (which will be discussed in depth later) afforded highly ordered SBA-15 with \( d_{100} \) of \( \sim 16 \) nm and KJS pore diameters of 19 – 20 nm at the initial synthesis temperature of 15 °C. The lowering of the temperature to 14 °C
allowed us to increase $d_{100}$ to ~18 nm in the synthesis using a mixture of 1.2 mL of TIPB and 0.2 mL of 1,3-DTBB as the swelling agent (Figure 13). Clearly, the swelling agent mixtures did not lead to the structural heterogeneity, but rather to high quality SBA-15 silicas (Figure 13 – 15; see Table 3 for structural parameters). However, the scope of their usefulness was not fully evaluated, because of the emergence of a superior single swelling agent, 1,3-DTBB, which is a liquid at room temperature (unlike 1,4-DTBB) and immediately afforded promising results. Finally, it should be noted that 1,3,5-tri-tert-butylbenzene (1,3,5-TTBB), which has 3 more carbon atoms in the substituents ($3 \times 4 = 12$) than 1,3,5-TIPB, was evaluated. While it was a solid at room temperature, its use afforded a silica with moderate pore size. This is consistent with our expectation that 1,3,5-TTBB would be a weaker swelling agent than TIPB. 1,3,5-TTBB was not evaluated further.
Figure 11. SAXS pattern (top), nitrogen adsorption isotherm (bottom left), and pore size distribution (bottom right) for SBA-15 silica synthesized with Pluronic P123, 0.6 ml 1,4-DIPB as a swelling agent, 5.5 ml TEOS, in the absence of NH₄F at initial synthesis temperature of 15 °C.
Figure 12. SAXS pattern (top), nitrogen adsorption isotherm (bottom left), and pore size distribution (bottom right) for silica synthesized with Pluronic P123, 1,3,5-TEB as a swelling agent, TEOS, in the presence of NH₄F at initial synthesis temperature of 17 °C. Adapted from Cao, L.; Man, T.; Kruk, M. Chemistry of Materials 2009, 21, 1144.
Figure 13. SAXS pattern (top left), nitrogen adsorption isotherms (top right), and pore size distributions (bottom) for SBA-15 silicas synthesized with Pluronic P123, mixture of 1.2 mL 1,3,5-TIPB and 0.2 mL 1,3-DTBB as swelling agents, 5.5 mL TEOS, in the presence of NH₄F at the initial synthesis temperature of 14 – 15 °C.
Figure 14. SAXS patterns (top left), nitrogen adsorption isotherms (top right), and pore size distributions (bottom) for SBA-15 silica synthesized with Pluronic P123, mixture of 1.0 mL 1,3,5-TIPB and 0.2 mL 1,4-DIPB as swelling agents, 5.5 mL TEOS, in the presence of NH₄F at the initial synthesis temperature of 14 – 15 °C.
Figure 15. SAXS pattern (top left), nitrogen adsorption isotherm (top right), and pore size distribution (bottom) for SBA-15 silica synthesized with Pluronic P123, mixture of 0.1 g 1,4-DTBB dissolved in 1.2 mL 1,3,5-TIPB as swelling agents, 5.5 mL TEOS, in the presence of NH₄F at the initial synthesis temperature of 15 °C.
Table 3. SBA-15 silicas synthesized with Pluronic P123 using mixtures of swelling agents and 5.5 mL TEOS in the presence of ammonium fluoride. The samples were hydrothermally treated at 130 °C for 1 day, and finally calcined.

<table>
<thead>
<tr>
<th>Initial Syn. Temp.</th>
<th>Swelling Agent Mixture</th>
<th>(d_{100}) as (nm)</th>
<th>(d_{100}) cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.2ml TIPB 0.2ml 1,3-DTBB</td>
<td>17.2</td>
<td>16.5</td>
<td>425</td>
<td>1.52</td>
<td>20.1</td>
<td>3.5</td>
</tr>
<tr>
<td>14</td>
<td>1.2ml TIPB 0.2ml 1,3-DTBB</td>
<td>18.6</td>
<td>18.0</td>
<td>318</td>
<td>1.38</td>
<td>20.1</td>
<td>2.8</td>
</tr>
<tr>
<td>15</td>
<td>1.0ml TIPB 0.2ml 1,4-DIPB</td>
<td>16.2</td>
<td>15.8</td>
<td>427</td>
<td>1.57</td>
<td>19.1</td>
<td>2.4</td>
</tr>
<tr>
<td>14</td>
<td>1.0ml TIPB 0.2ml 1,4-DIPB</td>
<td>18.8</td>
<td>17.8</td>
<td>300</td>
<td>1.13</td>
<td>21.4</td>
<td>3.4</td>
</tr>
<tr>
<td>15</td>
<td>0.1g 1,4-DTBB dissolved in 1.2 ml TIPB</td>
<td>16.8</td>
<td>16.2</td>
<td>422</td>
<td>1.42</td>
<td>19.1</td>
<td>2.8</td>
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</table>

Note: \(d_{100}\) as and \(d_{100}\) cal, (100) interplanar spacing for uncalcined (or as synthesized) sample (as) and calcined sample (cal); BET Surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total Pore Volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width at ½ height is determined from pore size distribution.

3.1.3. Identification of 1,3-di-tert-butylbenzene as excellent swelling agent for ultra-large-pore-SBA-15

As will be discussed hereafter, exceptionally well ordered SBA-15 materials with 2-D hexagonal structure of very large cylindrical pores were successfully synthesized using 1,3-
DTBB as the swelling agent. Their structural ordering, as seen from SAXS and TEM was, in many cases, better than that achieved with TIPB. It is notable that the synthesis using TIPB was extensively optimized over the time period of several years, whereas the synthesis with 1,3-DTBB was developed over a shorter period of time and its optimization was limited to some extent by a limited supply of costly 1,3-DTBB available for the study. 1,3-DTBB is expected to be a more powerful swelling agent than 1,3,5-TIPB due to its predicted higher solubilization within the Pluronic surfactant micelles.

In the case of 1,3-DTBB, SAXS patterns (Figure 16) for “standard” synthesis with ammonium fluoride (NH$_4$F) (analogous to that developed earlier$^{50}$ for 1,3,5-TIPB) were well-resolved and characteristic of highly ordered 2-D hexagonal SBA-15 for initial synthesis temperatures of 14 °C and 15 °C. At 13 °C, (100) interplanar spacing of 21.5 nm was achieved with retention of 2-D hexagonal structure, which is larger than that documented for any swelling agent except for TIPB. However, the (100) peak appeared on a high background, which was similar to results obtained earlier$^{50}$ for TIPB in the case of TIPB/P123 mass ratio of 1 : 2.4 at low initial synthesis temperatures and was indicative of somewhat lower quality. While the nitrogen adsorption isotherm (Figure 17) for this sample exhibited a steep capillary condensation step at quite high relative pressures, thus showing a narrow distribution of large mesopores, the isotherm also featured an additional hysteresis loop closing at a relative pressure of ~0.50, which indicated a fraction of disorganized pores. This result was similar to that observed earlier in TIPB-based synthesis.$^{50}$ The aforementioned undesirable feature (Figure 17) became more prominent when the initial synthesis temperature was decreased to 12.50 °C, while the ordering was essentially lost (Figure 16). In the case of the synthesis with TIPB, this additional disordered porosity could be eliminated by increasing the TIPB/P123 mass ratio to a certain optimal value.
However, for 1,3-DTBB based synthesis, this adjustment led to further deterioration of the structure. Therefore, a different strategy was needed in order to overcome this issue.

The synthesis without the use of NH₄F was explored, which is similar to the synthesis recently developed for TIPB at an initial synthesis temperature of 17 °C. In the latter case, the material exhibited larger (100) interplanar spacing compared to the counterpart prepared in the presence of NH₄F. At the same time, the material was highly ordered. In the case of 1,3-DTBB studied herein, SAXS patterns (Figure 16) for the sample prepared at 15 °C had better resolved peaks than in the case where NH₄F was used. As the temperature was gradually lowered to 13.50 °C, d₁₀₀ up to 27 nm was achieved with the retention of good structural ordering. However, at 13 °C, the SAXS pattern was featureless. In the present work, the initial synthesis temperature has been the main variable in tailoring the pore size for SBA-15 materials prepared with 1,3-DTBB below room temperature, as was the case for 1,3,5-TIPB. Honeycomb structures and channel-like mesopores of SBA-15 were clearly visible in TEM images (Figure 18) for the sample prepared at 15 °C. With decreasing initial synthesis temperature, the pore diameter of the resulting materials increased (Figure 19). Nonetheless, the uniformity of the pore diameter, and the periodicity of the 2-D hexagonal structure (as seen from SAXS, Figure 16) decreased as the initial synthesis temperature was lowered and the formation of the SBA-15 material was eventually not observed. From SAXS results, one can observe that the main (100) peak shifted to lower 2θ angles with the decrease in temperature, which shows an increase in the interplanar spacing. However, this peak became less resolved (as seen by lower intensity and/or broadening), which suggests that the uniformity decreased as the temperature decreased. Lastly, the relative position of the peaks was characteristic of 2-D hexagonal structure. Namely, 1ˢᵗ peak
and 2\textsuperscript{nd} peaks on SAXS patterns exhibited the position ratio of close to $1: \sqrt{3}$ for the considered samples. (100) interplanar spacings and other structural parameters for these samples are summarized in Table 4.

Figure 16. SAXS patterns of silicas synthesized using 1,3-di-tert-butylbenzene as micelle expander added after the addition of TEOS, with NH$_4$F (left) and without NH$_4$F (right). 5.5 ml TEOS was used as the silica source at different initial synthesis temperature, and the samples were subjected to hydrothermal treatment at 130 °C for 1 day, and finally calcined.
Figure 17. Nitrogen adsorption isotherms of SBA-15 silicas (or other structure) prepared with 5.5 ml TEOS (added before adding 1,3-DTBB), and 1.2 ml 1,3-DTBB at different initial synthesis temperature in the presence of NH₄F (left) and in the absence of NH₄F (right).
Figure 18. TEM images of SBA-15 silica prepared at 15 °C in the absence of ammonium fluoride, using 5.5 ml TEOS (added before the addition of 1,3-DTBB), and 1.2 ml 1,3-DTBB. The sample was hydrothermally treated at 130 °C for 1 day, and finally calcined.
Figure 19. Pore size distributions of SBA-15 silicas (or other structure) prepared with 5.5 ml TEOS (added before adding 1,3-DTBB), 1.2 ml 1,3-DTBB at different initial synthesis temperature in the presence of NH$_4$F (left) and in the absence of NH$_4$F (right); Insert in the figure on the right magnifies the region denoted with a dotted arrow.
Table 4. SBA-15 silica synthesized with 1,3-DTBB as the swelling agent added before addition of TEOS (except for sample denoted with #) and 5.5 mL TEOS in the presence or absence (denoted with *) of ammonium fluoride, hydrothermally treated at 130 °C for 1 day, and finally calcined.

<table>
<thead>
<tr>
<th>Initial Synthesis Temp.</th>
<th>d$_{100}$ as (nm)</th>
<th>d$_{100}$ cal (nm)</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
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<tr>
<td>12.5</td>
<td>no peak</td>
<td>no peak</td>
<td>276</td>
<td>0.95</td>
<td>48.8</td>
<td>24.1</td>
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<tr>
<td>13</td>
<td>22.7</td>
<td>21.5</td>
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<td>1.24</td>
<td>20.6</td>
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<tr>
<td>15</td>
<td>17.0</td>
<td>16.4</td>
<td>340</td>
<td>1.22</td>
<td>19.6</td>
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</tr>
<tr>
<td>13*</td>
<td>a</td>
<td>a</td>
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<td>b</td>
<td>b</td>
</tr>
<tr>
<td>13.5*</td>
<td>26.8</td>
<td>27.2</td>
<td>352</td>
<td>1.11</td>
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<td>21.8</td>
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<td>1.45</td>
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<td>19.2</td>
<td>334</td>
<td>1.18</td>
<td>20.4</td>
<td>3.3</td>
</tr>
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</table>

Note: d$_{100}$ as and d$_{100}$ cal, (100) interplanar spacing for uncalcined (as-synthesized) sample (as) and calcined sample (cal); BET Surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total Pore Volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width at ½ height is determined from pore size distribution. a: No peak on SAXS pattern. b: Shoulder seen on pore size distributions.
As far as nitrogen adsorption isotherms (Figure 17) are concerned, the midpoints of the capillary condensation steps systematically shifted to higher relative pressures (from 0.90 to 0.96) with the decrease in the initial synthesis temperature, signifying that the lowering of the temperature increases the pore diameter. Pore size distributions (Figure 19) calculated from the isotherms showed that the pore diameter increased with the decrease in the initial temperature, but the pore size distribution peak broadened significantly at the lowest considered temperatures, leading to a conclusion that the pores were less uniform in these cases. Interestingly, when comparing pore size distributions (Figure 19) for the syntheses with and without NH₄F at initial synthesis temperature at 15 °C, the pore diameters were very similar, and at the same time, pore size distributions were both quite narrow. When the initial temperature is lowered to 14 °C, in the synthesis without the use of NH₄F, the pore size increased significantly, while maintaining narrow pore size distribution, even though a modest pore size increase was seen for the synthesis with NH₄F. Finally, in the synthesis at 13 °C without NH₄F, the SBA-15 structure did not form (based on SAXS, Figure 16), or perhaps, a different structure formed which would need further investigation to be determined, which is different from the synthesis with NH₄F, which still afforded a well-ordered material when the same initial temperature was used. It should be noted that the pore size distributions shown herein overestimate the pore diameter, which is expected to be close to d₁₀₀ listed in Table 4.

When the synthesis temperature decreased below 14 °C, an additional porosity of smaller size was evident from the pore size distributions (Figure 19, right) and the problem became more significant as the temperature decreased and the interplanar spacing increased. The origin of additional porosity was not identified so far, but it may possibly be related to the partially
collapsed layered structure, because this porosity develops on the expense of the volume of the ordered mesopores and overall pore volume.

The first attempt to overcome the issue with the additional porosity was the change in the sequence of the addition of the swelling agent and TEOS. At first, all syntheses were done by adding TEOS before adding the swelling agent two minutes later. We discovered that this sequence worked well at the higher end of the initial synthesis temperature range considered here (14.5-17 °C). However, at 14 °C or below, the additional porosity gradually became more and more prominent. Hence, the addition sequence was changed, particularly the swelling agent and TEOS were mixed together prior to adding to the reaction mixture, which is a procedure typically used in our earlier work,\textsuperscript{50} and was found in the present study to work quite well in the synthesis with 1,3-DTBB. Nonetheless, adding swelling agent before TEOS is the sequence that was utilized in most of the syntheses with 1,3-DTBB, since the formation of additional smaller pores at ~10 nm was suppressed to a considerable extent in this case (see Figure 20).

The procedure involving the addition of 1,3-DTBB a few minute before the addition of TEOS afforded a series of SBA-15 materials whose nitrogen adsorption isotherms, pore size distributions, and SAXS patterns are shown in Figure 21, 20, and 22, respectively. The structural information derived from adsorption data and SAXS is listed in Table 5. These SBA-15 materials had (100) interplanar spacings ranging from 17 to 27 nm, and well-resolved SAXS patterns characteristic of 2-D hexagonal structure. The strong (100) peak visible at relatively low background is particularly noteworthy for samples prepared at 13.5 °C– 14 °C, whose $d_{100}$ was 23 - 27 nm. Our previous work with TIPB normally resulted in ultra-large-pore SBA-15 silicas with (100) peaks much weaker and less separated from the background\textsuperscript{50,51}, suggesting either
smaller ordered domain sizes or the presence of some disordered structures scattering at very low angles.

However, the drawback of the synthesis with 1,3-DTBB added before the addition of TEOS (5.5 ml) was that the trend in the unit-cell size and pore size increase with the initial synthesis temperature decrease was not strictly followed at 13.75 – 14 °C (see Figure 20 and 22; and Table 5). Moreover, the additional smaller (disorganized) mesopores (~10 nm in diameter) were still observed (although were not prominent) for temperature of 13.75 °C or lower.

![Figure 20. Pore size distributions for calcined samples of SBA-15 silicas prepared at initial synthesis temperatures between 13.5 °C and 17 °C with 1.2 mL 1,3-DTBB (added before the addition of TEOS) and 5.5 mL TEOS in the absence of NH₄F. The samples were subjected to hydrothermal treatment at 130 °C for 2 days.](image)
Figure 21. Nitrogen adsorption isotherm for calcined samples of SBA-15 silicas prepared at the initial temperature between 13.5 °C and 17 °C with 1.2 mL 1,3-DTBB (added before the addition of TEOS) and 5.5 mL TEOS in the absence of NH₄F. The samples were hydrothermally treated at 130 °C for 2 days.
Figure 22. SAXS patterns for calcined samples of SBA-15 silica prepared between 13.5 °C and 17 °C with 1.2 mL 1,3-DTBB (added before the addition of TEOS) and 5.5 mL TEOS in the absence of NH₄F after hydrothermal treatment at 130 °C for 2 days. *Hydrothermal treatment at 130 °C for 1 day.
Table 5. SBA-15 synthesized with 1.2 mL 1,3-DTBB as the swelling agent (added before the addition of TEOS) and 5.5 mL TEOS in the absence of ammonium fluoride.

<table>
<thead>
<tr>
<th>Synthesis Temp</th>
<th>$d_{100}$AS</th>
<th>$d_{100}$cal</th>
<th>BET(m$^2$/g)</th>
<th>Pore Volume(cm$^3$/g)</th>
<th>Pore Diameter(nm)</th>
<th>Width of PSD at ½ Height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17C</td>
<td>17.8</td>
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<td>15C</td>
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<td>362</td>
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<td>5.2</td>
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<td>1.32</td>
<td>23.0</td>
<td>5.9</td>
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<td>311</td>
<td>1.12</td>
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<td>367</td>
<td>1.29</td>
<td>42.9</td>
<td>19.6</td>
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</table>

Note: $d_{100}$ as and $d_{100}$ cal, (100) interplanar spacing for uncalcined (as-synthesized) sample (as) and calcined sample (cal); BET Surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total Pore Volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width at ½ height is determined from pore size distribution.

In order to further improve the quality of ultra-large-pore SBA-15 materials, additional optimization of synthesis conditions was attempted. Previously, the increase in the amount of TEOS in the synthesis of SBA-15 with 1,3,5-TIPB as the swelling agent led to an increase in the pore size, which provided a method to improve ordering of SBA-15 with the largest unit-cell sizes achievable using that method (as is discussed in Chapter 3.2). In the synthesis using 1,3-DTBB as the swelling agent, such a change in composition of the synthesis mixture did not benefit the resulting materials, but instead it led to a marked decrease in ordering (although this
issue was not studied in depth). Therefore, the effect of the decrease in the amount of TEOS was investigated. Through this approach, the problem of additional porosity was eliminated (or at least minimized). As the volume of TEOS was decreased from 5.5 ml to 4.5 ml at 13.5 °C (Figure 23), it is evident that the additional porosity around 7 nm was greatly diminished by using a smaller amount of TEOS, and by changing the sequence of addition of TEOS and 1,3-DTBB (that is, by adding 1,3-DTBB a few minutes prior to the addition of TEOS). TEM images (Figure 24 and 25) provided evidence of the formation of high quality materials for samples prepared with 4.5 ml of TEOS at the initial synthesis temperature between 13.5 °C and 14 °C. Moreover, employing lower amounts of TEOS than in our original synthesis (down to as low as 3.4 mL per 2.4 g P123) led to the formation of well-ordered SBA-15 materials (as suggested by TEM images-Figure 25, SAXS-Figure 26, N₂ adsorption isotherms and BJH pore size distributions-Figure 27). A material prepared using 1,3-DTBB as the swelling agent at 13 °C under these conditions had featureless SAXS pattern and pore size distribution (Figure 28 and 29) when the larger amount of TEOS (5.5 mL per 2.4 g P123) was used. The decrease in the amount of TEOS (from 4.5 mL to 3.4 mL) in the syntheses at 13 °C decreased the pore diameter of the resulting materials, while slightly narrowing the pore size distributions (Figure 29). Better structural ordering of SBA-15 silica samples synthesized with lower amount of TEOS (4.5 mL or less) is evident from the well-resolved SAXS patterns shown in Figure 28. Data obtained from SAXS and gas adsorption analysis are summarized in Table 6.
Figure 23. BJH pore size distributions for SBA-15 samples prepare at 13.50 °C. By lowering the amount of TEOS and switching the addition sequence of 1,3-DTBB and TEOS, the additional porosity ~7 nm is greatly reduced.
Figure 24. TEM images for SBA-15 silicas prepared with Pluronic P123, 1.2 mL 1,3-DTBB (added before the addition of TEOS), 4.5 mL TEOS, no ammonium fluoride, at an initial temperature of 13.5 – 14 °C.
Figure 25. TEM images for SBA-15 silicas prepared at 13 °C with Pluronic P123, 1.2 mL of 1,3-DTBB (added before the addition of TEOS), no NH₄F, and different amounts of TEOS (per 2.4 g TIPB).
Figure 26. SAXS patterns for calcined SBA-15 prepared with Pluronic P123, 1.2 mL 1,3-DTBB (added before the addition of TEOS), no NH$_4$F, and 4.5 mL TEOS at the initial synthesis temperature between 13 °C and 14 °C. The samples were hydrothermally treated at 130 °C for 2 day, except for the sample denoted *, which was hydrothermally treated at 130 °C for 1 day.
Figure 27. N\textsubscript{2} adsorption isotherms (top) and pore size distributions (bottom) for SBA-15 prepared with Pluronic P123, 1.2 mL 1,3-DTBB (added before the addition of TEOS), no NH\textsubscript{4}F, and 4.5 mL TEOS at the initial synthesis temperature between 13 °C and 14 °C. The samples were hydrothermally treated at 130 °C for 2 day, except for the sample prepared at 13.5 °C, which was hydrothermally treated at 130 °C for 1 day.
Figure 28. SAXS patterns for SBA-15 silicas prepared at 13 °C using 1,3-DTBB (added before the addition of TEOS), different amount of TEOS (3.4 mL to 5.5 mL), hydrothermally treated for 130 °C for 2 day *samples were hydrothermally treated for 130 °C for 1 day. $ TEOS was added before 1,3-DTBB.
Figure 29. Pore size distributions for SBA-15 silicas prepared at 13 °C using 1,3-DTBB (added before the addition of TEOS), with different amounts of TEOS (from 3.4 mL to 5.5 mL). The samples were hydrothermally treated for 130 °C for 2 day, except for the sample prepared with 4.1 ml and 5.5 ml of TEOS, which was hydrothermally treated for 130 °C for 1 day and TEOS was added before 1,3-DTBB for sample prepared with 5.5 ml of TEOS.
Table 6. SBA-15 silicas synthesized with 1.2 mL 1,3-DTBB as the swelling agent (added before the addition of TEOS) and different amounts of TEOS (between 3.4 mL – 5.0 mL) in the absence of NH₄F. The samples were hydrothermally treated at 130 °C for 2 days.

<table>
<thead>
<tr>
<th>Synthesis Temperature</th>
<th>TEOS (mL)</th>
<th>d₁₀₀ as (nm)</th>
<th>d₁₀₀ cal (nm)</th>
<th>BET (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ Height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14C</td>
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<td>21.3</td>
<td>20.1</td>
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<td>1.33</td>
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<tr>
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</tr>
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<td>29.0</td>
<td>29.0</td>
<td>337</td>
<td>1.21</td>
<td>43.9</td>
<td>11.4</td>
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<tr>
<td>13C</td>
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Note: d₁₀₀ as and d₁₀₀ cal, (100) interplanar spacing for uncalcined (or as synthesized) sample (as) and calcined sample (cal); BET Surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total Pore Volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width of PSD at ½ height is determined from pore size distribution. a: No peak on SAXS pattern. b: Only shoulder was observed on pore size distribution, the peak was very broad.
The selection of a suitable sequence of addition of 1,3-DTBB and TEOS, combined with
the optimization of 1,3-DTBB ratio led to SBA-15 silicas with exceptionally high (100)
interplanar spacings (up to 29 nm), and large sizes of 2-D hexagonal ordered domains (as seen
from TEM and additionally suggested by low background of very low 2θ angles on SAXS
patterns). Based on TEM, the ordering of these materials is superior to that seen for the
synthesis of ultra-large-pore-SBA-15 with TIPB,\textsuperscript{50,51} which was extensively optimized over
many years of its development. It is thus clear that 1,3-DTBB is the second documented swelling
agent for the synthesis of ultra-large-pore SBA-15 with $d_{100}$ approaching 30 nm, and it tends to
be the best one as far as the degree of structural ordering is concerned. It is likely that 1,3-DTBB
would be suitable for the synthesis of highly ordered large-pore periodic mesoporous
organosilicas, for which TIPB and cyclohexene are the best known swelling agents.\textsuperscript{105}

The adjustment of the amount of 1,3-DTBB was also investigated. At 17 °C, lowering the
amount of swelling agent by 50% (from 1.2 mL to 0.6 mL) led to a decrease in the pore size by 5
nm with narrowing of the pore size distribution and resulting in sharper, more intense SAXS
peaks (Figure 30). The increase in the volume of swelling agent by 50% (from 1.2 mL to 1.8
mL) certainly increased the pore diameter; however, a broad peak on the pore size distribution
and a less resolved SAXS pattern indicated that overall structure was less ordered. It should be
noted that the latter sample does not seem to be fully representative for our synthesis, but the
trend in pore size increase appears to be genuine. Interestingly enough, the use of the volume of
1,3-DTBB other than 1.2 mL at 13.50 °C did not seem to be beneficial as evident from nitrogen
adsorption (broad PSD) and SAXS (less resolved patterns, see Figure 31). Based on these
outcomes, the adjustment of 1,3-DTBB/Pluronic P123 ratio appears to be a useful method for
pore size adjustment at higher initial synthesis temperatures (17 °C), but is not beneficial at the lower end of the temperature range studied.
Figure 30. SAXS patterns (top), adsorption isotherm (bottom left), and BJH pore size distributions (bottom right) for SBA-15 silicas prepared at 17 °C with different amounts of 1,3-DTBB (added before the addition of TEOS).
Figure 31. SAXS patterns (top), adsorption isotherm (bottom left), and BJH pore size distributions (bottom right) for SBA-15 silicas prepared at initial temperature of 13.50 °C with different amounts of 1,3-DTBB (added before the addition of TEOS), 5.5 mL TEOS, in the absence of ammonium fluoride. The samples were subjected to hydrothermal treatment at 130 °C for 2 days.
3.2 Unit-Cell Size Tailoring for Large-Pore SBA-15 through Adjustment of Tetraethyl-orthosilicate : Surfactant Ratio

In an earlier section, we discussed that the decrease in the amount of TEOS was necessary in the synthesis of SBA-15 silicas using Pluronic P123 surfactant and 1,3-DTBB as the swelling agent at ~13 °C in order to obtain the best quality materials. This successful optimization actually evolved from our earlier study on the beneficial effects of the increase in the amount of TEOS in the synthesis of SBA-15 silicas using Pluronic P123 and TIPB. At first, TEOS was accidentally added in an excessive amount and resulted in somewhat larger unit-cell size of SBA-15 silicas in comparison to the standard synthesis, while a high degree of ordering was maintained. The ability to tune the unit-cell size through the adjustment of TEOS/P123 ratio was studied at different temperatures (T. Man, L. Cao, B. Adewale, M. Kruk, unpublished work). Here, its use for ultra-large-pore SBA-15 is discussed. In the synthesis of SBA-15 silica using Pluronic P123 surfactant and TIPB as the swelling agent, as the amount of TEOS increased at the initial synthesis temperature of 12.75 °C, the unit-cell size and pore size tended to increase. SAXS patterns (Figure 32) showed that the (100) peak shifted to the lower 2θ values indicating that the (100) interplanar spacing increased to some extent with increasing the relative amount of TEOS used. At 12.75 °C, one can observe that as the amount of TEOS increased, the SAXS patterns became less resolved. Yet, the resolution of SAXS patterns for samples with similar d_{100} was similar or even better than that for the corresponding samples whose interplanar spacing was enlarged through the temperature decrease with concomitant TIPB/P123 ratio adjustment.50,51
Nitrogen adsorption isotherms (Figure 33, left) showed that the relative pressure of the capillary condensation shifted to the higher values with increasing the relative amount of TEOS. The BJH pore size distributions derived from the adsorption data (Figure 33, right) shifted to larger pore sizes with the increase of the relative amount of TEOS. Nevertheless, the uniformity of the mesopores was decreased, as seen from the broader peaks on the pore size distributions, which is consistent with the less resolved SAXS patterns. The increase in the pore diameter with the increase of the relative amount of TEOS is surprising, as an opposite trend related to the pore wall thickening can be envisioned for increased silica/surfactant ratios. The trend observed herein suggests that the increase in the relative amount of TEOS may promote the uptake of the swelling agent by the surfactant micelles, or that TEOS may itself contribute to the swelling of the micelles under these conditions. The sample prepared with 6.5 ml of TEOS was particularly interesting as it had $d_{100}$ of 27.6 nm and it appears to be much better ordered than the corresponding sample that we reported earlier. The present results are noteworthy, as they demonstrate the synthesis of highly ordered ultra-large-pore SBA-15 with $d_{100} = \sim 27$ nm, which can only be rivalled by the reported optimized synthesis based on Pluronic P123 and carefully optimized proportion of TIPB, and P123/1,3-DTBB based synthesis described in Chapter 3.1. TEM images in Figure 34 showed the features (channel-like mesopores and honeycomb arrangements of mesopores) pertinent to SBA-15 materials. Table 7 summarizes the structural parameters derived from SAXS and gas adsorption for a series of sample prepared at 12.75 °C using 5.5 ml - 7.5 ml of TEOS.
Figure 32. SAXS patterns for SBA-15 silicas synthesized at 12.75 °C using Pluronic P123, 2.4 ml TIPB, NH₄F, and different volumes of TEOS per 2.4 g of Pluronic P123.
Figure 33. Nitrogen adsorption isotherms (left) and pore size distributions (right) for SBA-15 silicas synthesized at 12.75 °C using Pluronic P123, 2.4 ml TIPB, NH₄F, and different volumes of TEOS per 2.4 g of Pluronic P123.
Figure 34. TEM images for SBA-15 silica prepared with Pluronic P123 at the initial synthesis temperature of 12.75 °C, with 6.5 ml TEOS (added before the addition of 2.4 ml TIPB), in the presence of NH$_4$F. The sample was hydrothermally treated at 130 °C for 1 day, and then calcined.
Table 7. Structural parameters for SBA-15 silicas synthesized at 12.75 °C using Pluronic P123, 2.4 ml TIPB, NH₄F, and different amounts of TEOS.

<table>
<thead>
<tr>
<th>Amount of TEOS (mL)</th>
<th>d₁₀₀ as (nm)</th>
<th>d₁₀₀ cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
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</table>

Note: d₁₀₀ as and d₁₀₀ cal, (100) interplanar spacing for uncalcined (or as synthesized) sample (as) and calcined sample (cal); BET Surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total Pore Volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width of PSD at ½ height is determined from pore size distribution. a: Estimated from the position of a shoulder on SAXS pattern.
3.3 Room-Temperature Synthesis of Large-Pore SBA-15

3.3.1 Room Temperature Synthesis of SBA-15

In contrast to the low-temperature syntheses of very-large-pore SBA-15 discussed above, there is little evidence in the scientific literature that the synthesis of SBA-15 silica with very large pores can be reproducibly accomplished at room temperature (~25 °C or above it) using commercially available and convenient Pluronic block copolymers. The initial report on the synthesis of SBA-15 with pores up to 30 nm by using Pluronic P123 swollen by TMB\(^6,7\) was followed by a report indicating that such a synthesis affords SBA-15 with pores of diameter only up to 12 nm, while the larger-pore materials are primarily mesocellular foams (MCFs).\(^40\) Later studies have not invalidated the latter conclusion. The well-documented syntheses of SBA-15 at or above room temperature using Pluronics afforded \(d_{100}\) up to 17 nm and pore diameters up to ~12 nm (in the case of Pluronic F127 combined with alkanes and alcohols)\(^43,44\) or \(d_{100}\) up to 13 nm (using Pluronic P123/octane combination)\(^68\) and pore diameters up to ~13 nm.\(^46\) Due to the importance of large-pore SBA-15 silicas, the development of their room-temperature Pluronic-based synthesis is an important aim.

The recent work involving Pluronics with a high fraction of PEO blocks confirmed the hypothesis that the temperature range in which the pore diameters increase with the temperature decrease for Pluronic/swelling-agent templates is related to critical micelle temperature (CMT) (Li, Y., Kruk, M., manuscript in preparation).\(^118\) Namely, the higher CMT, the higher the temperatures at which a strong increase in pore size with temperature decrease were observed. We expected that the same is true for Pluronics with a large fraction of PPO. Therefore, it was
hypothesized that the selection of a Pluronic block copolymer with similar PPO fraction as that in P123, but with a higher CMT may allow us to shift the temperature window for large-pore SBA-15 synthesis to room temperature. The motivation was to synthesize large-pore SBA-15 silicas near room temperature, where temperature control is easier or even not needed. An additional goal was to further confirm the hypothesis that for surfactant/swelling agent pairs used as templates, a significant dependence of unit-cell size on temperature is observed at temperatures related to CMT.

First, it should be noted that at 25 °C, the synthesis of SBA-15 silica with Pluronic P123 and in the absence of NH₄F rendered a good quality material with d₁₀₀ of 12.0 nm when 0.6 ml of TIPB was added as a swelling agent. However, as the amount of the swelling agent was increased, which is a standard approach to obtain a larger pore size, the homogeneity of the material became an issue. SAXS results (Figure 35) for SBA-15 silica prepared at 25 °C using Pluronic P123 and 1.2 ml of TIPB as swelling agent showed that the material is a 2-D hexagonal structure, but the background intensity at low angles was enhanced relative to the (100) peak, indicating that there may be a prominent secondary mesoporosity, which is consistent with gas adsorption results (Figure 36). Notably, even though the (100) interplanar spacing increased slightly with the increase in the amount of swelling agent used, the pore diameter did not increase (see Table 8). Further increase in the relative amount of the swelling agent was even more detrimental. The ratio of positions of the SAXS peaks for samples prepared with 1.8 ml and 2.4 ml was about 1:2, indicating that these might be layered materials (perhaps onions¹¹⁹), which were observed in the case of P123 and TIPB as the phase succeeding SBA-15 when the amount of TIPB was increased under certain conditions. It was observed that the hysteresis loops were no longer narrow and with parallel adsorption/desorption branches often seen for uniform and
accessible cylindrical mesopores. The increase in uptake of nitrogen continued to very high relative pressure, so secondary porosity was evident (Figure 36). BJH pore diameters for these samples are listed in Table 8. These results indicated that the synthesis of large-pore SBA-15 at or above room temperature using Pluronics is not a trivial matter, because the addition of the swelling agent may induce formation of a different phase, even if one can achieve the enlargement of the pore size and pore volume. This is consistent with conclusions of Lettow et al. for Pluronic P123/TMB pair, although in the present case of Pluronic P123/TIPB, mesocellular foams do not seem to form and onions are a more likely product.119

Figure 35. SAXS patterns for silicas prepared at initial temperature of 25 °C with Pluronic P123, TIPB, TEOS, (no NH₄F), after hydrothermal treatment at 120 °C for 1 day and calcination.
Figure 36. Adsorption isotherms (left) and pore size distributions (right) for silicas prepared at initial temperature of 25 °C with Pluronic P123, TIPB, TEOS, (no NH₄F), after hydrothermal treatment at 120 °C for 1 day and calcination.
Table 8. Structural parameters for SBA-15 silicas synthesized at initial temperature of 25 °C with Pluronic P123, various amount of 1,3,5-TIPB as the swelling agent (added before the addition of TEOS), and 5.5 mL of TEOS, in the absence of ammonium fluoride. Hydrothermal treatment was carried out at 120 °C for 1 day.

<table>
<thead>
<tr>
<th>Amount of TIPB (mL)</th>
<th>d_{100} as (nm)</th>
<th>d_{100} cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>12.4</td>
<td>12.0</td>
<td>569</td>
<td>0.97</td>
<td>15.0</td>
<td>2.4</td>
</tr>
<tr>
<td>1.2</td>
<td>12.9</td>
<td>12.2</td>
<td>552</td>
<td>0.91</td>
<td>13.7</td>
<td>1.1</td>
</tr>
<tr>
<td>1.8</td>
<td>15.1</td>
<td>14.2</td>
<td>607</td>
<td>1.36</td>
<td>17.8</td>
<td>a</td>
</tr>
<tr>
<td>2.4</td>
<td>15.6</td>
<td>15.8</td>
<td>582</td>
<td>1.62</td>
<td>19.8</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Notes: d_{100} as and d_{100} cal, (100) interplanar spacing for uncalcined (as-synthesized) sample (as) and calcined sample (cal); BET surface area is calculated based on nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer-Emmett-Teller (BET) method; Total pore volume is determined from the amount adsorbed at a relative pressure of 0.99; Pore diameter is obtained from as a maximum on the BJH pore size distribution; Width of PSD at ½ height is determined from pore size distribution. a: Difficult to determine without ambiguity due to a broad peak.

Pluronics P103, P104, P105, L92, and P84 (Figure 37) have smaller hydrophobic PPO block, but quite similar hydrophilic PEO to hydrophobic PPO mass ratio as Pluronic P123. The CMTs of these Pluronic surfactants are (or are expected to be) above that of Pluronic P123. Therefore, these Pluronic surfactants were selected for the evaluation of the feasibility of the synthesis of large-pore SBA-15 silica around room temperature. Table 9 listed the estimated
CMTs of these Pluronic surfactants in water at Pluronic concentrations relevant for mesoporous silica synthesis.\textsuperscript{56}

Figure 37. Structures of Pluronic triblock copolymer surfactants that we re-evaluated herein for the synthesis of SBA-15 silicas near room temperature.
Table 9. Estimated CMTs for ~3 % Pluronic solutions (as used in SBA-15 synthesis) in water based on Reference 56.

<table>
<thead>
<tr>
<th>Pluronic triblock copolymer</th>
<th>CMT for ~3 % solution (as used in SBA-15 synthesis) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P123</td>
<td>14</td>
</tr>
<tr>
<td>P103</td>
<td>&lt;19.5</td>
</tr>
<tr>
<td>P104</td>
<td>19</td>
</tr>
<tr>
<td>P105</td>
<td>19</td>
</tr>
<tr>
<td>P84</td>
<td>25</td>
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</table>

3.3.1.1 Use of Pluronic P103/1,3,5-Triisopropylbenzene Pair in Large-Pore SBA-15 Synthesis.

Pluronic P103 surfactant is composed of 30 wt. % PEO blocks and 70 wt. % PPO blocks. The first attempt to use Pluronic P103 involved an initial temperature of 25 °C and TIPB as the swelling agent in the absence of NH₄F. The NH₄F-free conditions⁷⁰ were selected because they afford somewhat larger unit-cell sizes and pore diameters for SBA-15 templated by Pluronic P123 at 17 °C (when compared to the synthesis⁵⁰ involving NH₄F) and it was expected that a similar behavior would be seen around room temperature as long as the synthesis affords SBA-15 under these conditions. The quality of SBA-15 silicas synthesized with Pluronic P103 surpassed that of silicas synthesized with Pluronic P123 at 25 °C. SAXS data (Figure 38) showed low background, intense and well-resolved peaks for materials prepared with P103 and TIPB, the latter in the volume ranging from 0.6 ml to 2.4 ml per 2.4 g P103. As expected, (100) interplanar spacing tended to increase with increasing the amount of TIPB added under these synthesis conditions (note that 1.8 mL of TIPB was somewhat out of sequence). (100) interplanar spacings ranged from 11.3 to 14.5 nm for calcined samples, surpassing the value of 13 nm previously
well-documented for room temperature of SBA-15 with Pluronic P123 and octane.\textsuperscript{68} This is additionally noteworthy, because P123 surfactant used by others\textsuperscript{68} has a larger molecular weight and the octane/P123 volume ratio was much higher than TIPB/P103 volume ratio. The relative positions of the SAXS peaks provided clear evidence that these materials obtained in our study were SBA-15 silicas. Adsorption isotherms (Figure 39) for this series of samples suggested that accessible cylindrical mesopores were present, as seen by narrow hysteresis loops with parallel adsorption-desorption branches. The adsorption isotherms leveling off after the capillary condensation step suggested large sizes of ordered domains in the material. In addition, pore size distributions did not show any additional porosity. TEM images (Figure 40 and 41) showed honeycomb (two-dimension hexagonal feature) and series of stripes (the channel-like pores seen from the side). Table 10 summarized data obtained from SAXS and gas adsorption analysis for this series of samples.
Figure 38. SAXS results for SBA-15 silicas prepared with Pluronic P103, various amounts of TIPB (added before the addition of TEOS) per 2.4 g P123, 5.5 mL of TEOS, in the absence of NH₄F, by using the hydrothermal treatment at 120 °C for 1 day, followed by calcination.
Figure 39. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for SBA-15 silicas prepared with Pluronic P103, various amounts of TIPB (0.6 mL – 3.0 mL, added before adding TEOS) per 2.4 g P123, and 5.5 mL of TEOS, in the absence of NH₄F. The samples were subjected to the hydrothermal treatment at 120 °C for 1 day, and calcined. * Denotes hydrothermal treatment at 130 °C for 1 day.
Figure 40. TEM images for SBA-15 silicas prepared with Pluronic P103 at initial synthesis temperature of 25 °C, 1.2 ml TIPB, and 5.5 mL TEOS, in the absence of NH₄F. The samples were subjected to the hydrothermal treatment at 100 °C for 2 days, and calcined.
Figure 41. TEM images for SBA-15 silicas prepared with Pluronic P103 at initial synthesis temperature of 25 °C, 2.4 ml TIPB, and 5.5 mL TEOS, in the absence of NH₄F. The samples were subject to the hydrothermal treatment at 100 °C for 2 days, and calcined.
Table 10. SBA-15 silicas synthesized at 25 °C with Pluronic P103, with various amounts of 1,3,5-TIPB (0.6 mL – 3.0 mL per 2.4 g P123, added before the addition of TEOS), and 5.5 mL of TEOS, in the absence of ammonium fluoride. The samples were subjected to the hydrothermal treatment at 120 °C for 1 day (∗ denotes 100 °C for 2 day), and calcined.

<table>
<thead>
<tr>
<th>Volume of TIPB (mL)</th>
<th>d&lt;sub&gt;100&lt;/sub&gt; as (nm)</th>
<th>d&lt;sub&gt;100&lt;/sub&gt; cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>11.9</td>
<td>11.2</td>
<td>748</td>
<td>0.93</td>
<td>11.3</td>
<td>1.6</td>
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<tr>
<td></td>
<td>11.8*</td>
<td>11.3*</td>
<td>330*</td>
<td>0.61*</td>
<td>13.6*</td>
<td>1.9*</td>
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<tr>
<td>1.2</td>
<td>13.5</td>
<td>12.9</td>
<td>873</td>
<td>1.40</td>
<td>13.9</td>
<td>1.5</td>
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<td></td>
<td>13.3*</td>
<td>12.8*</td>
<td>541*</td>
<td>1.36*</td>
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<td>2.3*</td>
</tr>
<tr>
<td>1.8</td>
<td>14.9</td>
<td>14.1</td>
<td>714</td>
<td>1.09</td>
<td>15.2</td>
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<td></td>
<td>15.0*</td>
<td>14.5*</td>
<td>461*</td>
<td>1.16*</td>
<td>18.5*</td>
<td>6.7*</td>
</tr>
<tr>
<td>2.4</td>
<td>14.4</td>
<td>13.6</td>
<td>676</td>
<td>1.10</td>
<td>14.7</td>
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<td>1.29*</td>
<td>19.0*</td>
<td>3.5*</td>
</tr>
<tr>
<td>3.0</td>
<td>15.0</td>
<td>14.5</td>
<td>627</td>
<td>1.01</td>
<td>16.0</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>14.6*</td>
<td>14.5*</td>
<td>572*</td>
<td>1.12*</td>
<td>17.1*</td>
<td>4.3*</td>
</tr>
</tbody>
</table>
As the initial synthesis temperature decreased, one can expect an increase in the unit-cell parameter and pore size. Indeed, (100) peaks were shifted to lower 2θ angles, which implies an increase in the interplanar spacing. However, at 20 °C, the SAXS pattern became difficult to interpret (Figure 42). Adsorption isotherms (Figure 43) exhibited broader and broader hysteresis loops as the initial synthesis temperature decreased. A lower quality of the material was reflected in the pore size distribution that showed a broad peak for the material formed at 20 °C. Table 11 summarized the data obtained for this series of samples.

Figure 42. SAXS patterns for SBA-15 silica synthesized with Pluronic P103, 1.8 ml of TIPB, TEOS, no NH₄F, at the initial synthesis temperature of 20 °C – 24 °C, after hydrothermal treatment at 120 °C for 1 day, and calcination.
Figure 43. Nitrogen adsorption isotherms (left) and pore size distributions (right) for SBA-15 silicas synthesized with Pluronic P103, 1.8 ml of TIPB, TEOS, no NH₄F, at initial synthesis temperature of 20 °C – 24 °C, after hydrothermal treatment at 120 °C for 1 day, and calcination.

Table 11. Structural parameters for SBA-15 silicas synthesized with Pluronic P103, 1.8 mL of 1,3,5-TIPB as the swelling agent, added before the addition of 5.5 ml TEOS, in the absence of ammonium fluoride at the initial synthesis temperature 20 °C – 24 °C, with hydrothermal treatment at 120 °C for 1 day, and calcined.

<table>
<thead>
<tr>
<th>Initial synthesis temp. (°C)</th>
<th>d₁₀₀ as (nm)</th>
<th>d₁₀₀ cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
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<tbody>
<tr>
<td>20</td>
<td>19.6</td>
<td>18.4</td>
<td>642</td>
<td>1.20</td>
<td>17.5</td>
<td>Broad</td>
</tr>
<tr>
<td>22</td>
<td>14.8</td>
<td>14.2</td>
<td>560</td>
<td>1.22</td>
<td>17.6</td>
<td>5.0</td>
</tr>
<tr>
<td>24</td>
<td>13.9</td>
<td>13.6</td>
<td>488</td>
<td>1.31</td>
<td>17.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>
While the synthesis of large-pore SBA-15 silica using Pluronic P103 around room temperature seems to be better than that involving Pluronic P123, it became a challenge as the initial synthesis temperature decreased and less uniform materials with large interplanar spacing formed (as discussed above). Although using NH₄F-free conditions in the synthesis in SBA-15 silica was expected to give us the advantage to obtain larger pores (as discussed above), NH₄F has proven its effectiveness by facilitating the condensation of silica at a faster rate to produce good-quality materials. In the case of Pluronic P103 at 20 °C, highly ordered SBA-15 silica was successfully synthesized when NH₄F was added. SAXS data, gas adsorption, and pore size distribution (Figure 44) results suggested that SBA-15 silica with d₁₀₀ of 13.4 nm and BJH pore diameter of 17.4 nm was synthesized (when hydrothermal treatment at 100 °C for 2 days was employed), while in the absence of NH₄F, the poorly ordered material formed (as discussed above). TEM images (Figure 45) showed the channel-like pores of the SBA-15 silica that was synthesized at 20 °C in the presence of NH₄F. Very well-ordered SBA-15 with quite large (100) interplanar spacing of 12.1 nm and BJH pore diameter of 15.4 nm formed also at 25 °C.
Figure 44. SAXS pattern (top left), adsorption isotherm (bottom left) and pore size distribution (bottom right) for SBA-15 silica prepared with Pluronic P103, 1.2ml TIPB, TEOS, 27 mg NH₄F, at 20 °C and 25 °C, after hydrothermal treatment at 100 °C for 2 days, and calcined.
Figure 45. TEM image for SBA-15 silica synthesized at 20 °C using Pluronic P103, 1.2 ml TIPB, 5.5 mL of TEOS, in the presence of NH$_4$F, with hydrothermal treatment at 100 °C for 2 days, and calcination.

While the temperature control in the large-pore SBA-15 synthesis is very important, we were able to synthesize SBA-15 silica at room temperature (in a water bath to reduce possible temperature fluctuations) without a temperature control when NH$_4$F was used. At room temperature, such a modification afforded exceptional quality SBA-15 silica that is comparable to those synthesized with the temperature control. Figure 46 shows a comparison of adsorption
isotherms and pore size distributions of two samples prepared similarly, one with temperature-controlled water bath of 24 °C and one without temperature control (temperature of the water bath used to moderate temperature fluctuations was ~21 °C). Both samples exhibited narrow hysteresis loops and very narrow pore size distributions. SAXS patterns (Figure 46 bottom) indicated that very highly ordered SBA-15 silica was synthesized without the temperature. SAXS patterns for both samples were very similar, but the pattern for the sample prepared with no temperature control was slightly better resolved. In the absence of NH₄F in the syntheses without the temperature control, adsorption isotherms showed broader hysteresis loops (in some cases with branches not being parallel), while SAXS data suggested that they were SBA-15 silicas, although the peaks were less resolved and some samples had an additional feature (small shoulder) at the left side of the (100) peak suggesting a possible contamination of SBA-15 with some other structure. Table 12 listed the data obtained from SAXS and gas adsorption analysis for these two SBA-15 silica samples.
Figure 46. Nitrogen adsorption isotherms (top left), pore size distributions (top right), and SAXS patterns (bottom) for SBA-15 silicas synthesized around room temperature using a water bath with temperature control (24 °C) and without temperature control (water bath temperature was ~21 °C). Samples were synthesized with 2.4 g P103, 1.8 ml TIPB, 5.5 ml TEOS, subjected to hydrothermal treatment at 120 °C for 1 day, and were calcined.
Table 12. Structural parameters for SBA-15 silica synthesized around room temperature using a water bath with temperature control (24 °C, denoted by *) and without temperature control (water bath temperature at ~21 °C). Samples were synthesized with 2.4 g P103, 1.8 ml TIPB, 5.5 ml TEOS, subjected to hydrothermal treatment at 120 °C for 1 day.

<table>
<thead>
<tr>
<th>Initial synthesis temp. (°C)</th>
<th>d$_{100}$ as (nm)</th>
<th>d$_{100}$ cal (nm)</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
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<td>13.5</td>
<td>495</td>
<td>1.42</td>
<td>16.2</td>
<td>1.1</td>
</tr>
<tr>
<td>24 *</td>
<td>13.9</td>
<td>13.6</td>
<td>488</td>
<td>1.31</td>
<td>17.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The results for the synthesis of SBA-15 silica with Pluronic P103 surfactant and TIPB are very promising. The convenience at room temperature, even without the use of a temperature control in the presence of NH$_4$F, afforded high quality SBA-15 silicas with d$_{100}$ of ~14 nm, which is large. Furthermore, the presence of NH$_4$F in the synthesis of SBA-15 silicas opened the opportunity to shorten the synthesis process to as little as six hours, which had already included the hydrothermal treatment step, and the quality of the resulting sample was excellent. This development will be discussed in section 3.4.

### 3.3.1.2 Pluronic P103/1,4-Diisopropylbenzene Pair for SBA-15 Synthesis

The swelling agent 1,4-diisopropylbenzene (1,4-DIPB) contains six carbon atoms on the benzene substituent and based on the discussion presented above, it should possess a stronger swelling ability than TIPB or 1,3-DTBB. For the synthesis around room temperature, Pluronic P103 surfactant and 1,4-DIPB combination afforded well-ordered SBA-15, but with a limited
unit-cell size. The highest $d_{100}$ obtained for this combination was 11.40 nm, which is smaller than what observed for Pluronic P103 and TIPB combination and within the range attainable without selling agents using Pluronic P123.\textsuperscript{101} However, in the successful synthesis with 1,4-DIPB, only 0.6 ml of the swelling agent per 2.4 g P103 was added, which is lower than 1.2 – 2.4 ml TIPB used in the syntheses discussed earlier. Even 0.9 ml of 1,4-DIPB seemed to provide excessive swelling for the synthesis. In Figure 47, SAXS pattern showed a stronger background relative to the (100) main peak, which probably was due to the fact that secondary (disordered) mesoporosity was very prominent. The (100) interplanar spacing was 12.10 nm. The adsorption isotherm (Figure 47 bottom left) showcased a continuous increase in the uptake of nitrogen until the relative pressure approached saturation vapor pressure. The pore size distribution for this sample (Figure 47 bottom right) was quite broad and “noisy”. In a series of SBA-15 silicas synthesized using Pluronic P103 and 0.6 ml of 1,4-DIPB at different initial synthesis temperatures, adsorption isotherms (Figure 49, left) had quite narrow hysteresis loops with nearly parallel adsorption and desorption branches, suggesting well-accessible mesopores. The uptake of nitrogen seemed to increase slightly after the capillary condensation in ordered mesopores was completed for samples prepared at 24 °C, suggesting a moderate particle size leading to inter particle mesopores or some other kind of secondary mesoporosity. Such a feature seemed to be minimized with decreasing initial synthesis temperature to 23 °C or lower. The pore size distributions (Figure 48, top right) showed narrow peaks and pore diameter reached 12.70 nm for the synthesis at 23 °C. Although the BJH pore diameter did not follow the trend in which decreasing initial synthesis temperature increases the pore size (as was observed in many other cases discussed herein, which might also have been caused by the lowered hydrothermal treatment temperature for this particular sample), SAXS data (Figure 48 bottom) suggested that
the (100) interplanar spacing shifted slightly to lower 2θ angle (and thus d_{100} increased) with decreasing in the initial synthesis temperature to 20 °C. The resolution of SAXS patterns and the relative position of the peaks demonstrated excellent ordering of SBA-15 structures obtained under these synthesis conditions. These results showed that P103/1,4-DIPB pair can afford highly ordered SBA-15 around room temperature, even though the unit-cell sizes and pore diameters of these materials are not particularly large. TEM images in Figure 49 and 50 confirmed the formation of SBA-15 structured material featuring channel-like mesopores with two-dimensional hexagonal arrangement. Table 13 summarizes the data obtained from SAXS and gas adsorption for this series of sample.
Figure 47. SAXS pattern (top), nitrogen adsorption isotherm (bottom left), and pore size distribution (bottom right) for SBA-15 silica prepared using Pluronic P103 at 24 °C (temperature controlled water bath), 0.9 ml DIPB as a swelling agent, 5.5 ml TEOS (in the absence of NH₄F), and the hydrothermal treatment at 130 °C for 1 day, followed by calcination.
Figure 48. Nitrogen adsorption isotherms (top left), pore size distributions (top right) and SAXS patterns (bottom) for SBA-15 silica synthesized with Pluronic P103, 0.6 ml 1,4-DIPB, TEOS, no NH₄F, and hydrothermal treatment at 130 °C for 1 day (* indicates treatment at 100 °C for 2 days), followed by calcination.
Figure 49. TEM for SBA-15 silicas synthesized with Pluronic P103, 0.6 ml 1,4-DIPB, TEOS, no NH₄F at 20 °C. The samples were hydrothermally treated at 130 °C for 1 day, and finally calcined. Images feature channel-like pores viewed from the side and projections through 2-D hexagonal arrangements in the SBA-15 structure.
Figure 50. TEM for SBA-15 silicas synthesized with Pluronic P103, 0.6 ml 1,4-DIPB, TEOS, no NH₄F at 24 °C. The samples were hydrothermally treated at 130 °C for 1 day, and finally calcined. Images feature channel-like pores viewed from the side and projections through 2-D hexagonal arrangements in the SBA-15 structure.
Table 13. Structural parameters for SBA-15 silica synthesized with Pluronic P103, 0.6 ml 1,4-DIPB, TEOS, no NH₄F. The samples were hydrothermally treated at 130 °C for 1 day (* indicates hydrothermal treatment at 100 °C for 2 days).

<table>
<thead>
<tr>
<th>Synthesis Temperature (°C)</th>
<th>d₁₀₀ as (nm)</th>
<th>d₁₀₀ cal (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
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<tr>
<td>20*</td>
<td>11.9</td>
<td>11.4</td>
<td>715</td>
<td>0.94</td>
<td>12.2</td>
<td>2.0</td>
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<td>11.3</td>
<td>11.2</td>
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<td>11.2</td>
<td>532</td>
<td>1.01</td>
<td>11.8</td>
<td>1.8</td>
</tr>
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</table>

3.3.1.3 Unsuccessful Attempt to Use Pluronic L92 and P105 Block Copolymers

Pluronic L92 (EO₉PO₄₇EO₉) and P105 (EO₃₇PO₅₆EO₃₇) were used in the investigation of the synthesis of SBA-15 silicas around room temperature. However, these two Pluronic surfactants were not found suitable for the intended purpose. For materials prepared with Pluronic L92 and 0.6 ml or 1.2 ml of TIPB as swelling agent, SAXS patterns (Figure 51 top) showed high background intensity relative to the main peak intensity, suggesting a considerable secondary mesoporosity. Although the main peaks were quite well-resolved, the subsequent peaks were not easily identifiable. Adsorption isotherms (Figure 51 bottom left) revealed a continuous increase in nitrogen uptake, confirming SAXS indication of secondary mesoporosity. The pore size distributions for these materials were quite broad, as shown in Figure 51. While these results are not good, it is noteworthy that the main SAXS peaks for these samples were at quite low angles (as for such a small block copolymer surfactant) and the peak position significantly shifted to lower angles as the amount of the swelling agent was increased. These
results are encouraging. It is possible that we just did not identify appropriate conditions to make use of this surfactant as a template.

Pluronic P105 did not produce SBA-15 silica as seen in TEM images in Figure 52. There are visible porous regions, but these mesopores are not organized in any specific arrangement. SAXS patterns (Figure 53 top) displayed a quite strong background relative to the main peak, indicating a prominent secondary mesoporosity. Although there is a second peak on the SAXS pattern, the relative positive to the first peak (ratio of 1:1.62) did not suggest the formation of SBA-15 material. The adsorption isotherm (Figure 53 bottom left) was consistent with the SAXS results, and showed a steep increase in the uptake of nitrogen after the capillary condensation step, revealing the existence of some secondary mesopores. The pore size distribution (Figure 53 bottom right) for this sample was broad. Further studies would be required to more fully evaluate the suitability of P105 as a template, but the current results are unsatisfactory.
Figure 51. SAXS patterns (top), nitrogen adsorption isotherms (bottom left), and pore size distributions (bottom right) for silicas prepared using Pluronic L92 at initial temperature of 25 °C, TIPB as a swelling agent (0.6 and 1.2 ml), and 5.5 ml TEOS (in the absence of NH₄F). The samples were hydrothermally treated at 120 °C for 1 day, and then calcined.
Figure 52. TEM images for silica prepared using Pluronic P105, 1.8 ml TIPB as a swelling agent, and 5.5 ml TEOS (in the absence of NH4F). The sample was hydrothermally treated at 120 °C for 1 day, and then calcined.
Figure 53. SAXS pattern (top), nitrogen adsorption isotherm (bottom left), and pore size distribution (bottom right) results for silica prepared using Pluronic P105 at initial temperature of 25 °C (temperature controlled water bath), 1.8 ml TIPB as a swelling agent, and 5.5 ml TEOS (in the absence of NH4F). The sample was hydrothermally treated at 120 °C for 1 day, and then calcined.
3.4 Short Synthesis of SBA-15 Silicas

Another remarkable implication of the use of NH₄F in the synthesis of large-pore SBA-15 silica is that the synthesis process can be shortened from two - three days to as little as several hours. As mentioned earlier, NH₄F has the ability to accelerate the condensation and hydrolysis of the silica precursors. Therefore, in the presence of NH₄F, the formation of the materials can be achieved with shorter stirring time. Higher temperature (160 - 170 °C) for hydrothermal treatment can also be employed. The sample can be treated for as little as 3 hours at 150 – 170 °C to obtain similar result as those for hydrothermal treatment at 120 °C for one day. Cao and Kruk described such a method using Pluronic P123 surfactant. Herein, the synthesis using Pluronic P123/TIPB and 6.5 ml of TEOS, SAXS patterns (Figure 54) showed that well-ordered SBA-15 silicas were synthesized via both normal synthesis and the short synthesis method. The SAXS pattern for the sample from the short synthesis highly resembled that for the normal synthesis, suggesting the time shortening did not compromise the quality of the resulting material.
Figure 54. SAXS patterns for traditional (initial synthesis temperature at 12.75 °C) and short synthesis of SBA-15 silica prepared with Pluronic P123, 2.4 ml TIPB, 6.5 ml TEOS, in the presence of NH$_4$F, with hydrothermal treatment at 130 °C for 1 day (traditional) and 170 °C for 3 hours (short synthesis), and subsequent calcination.

When the short synthesis was implemented for SBA-15 templated by Pluronic P103 surfactant, the resulting materials showed good reproducibility, and they were comparable to the materials obtained via the traditional synthesis. The adsorption isotherm (Figure 55, left) featured a narrow hysteresis loop with parallel adsorption and desorption branches, which is an indication of well accessible pores. A similar isotherm was seen for a sample obtained via normal (longer) synthesis procedure. Pore size distributions (Figure 55, right) for the samples from both methods were narrow and the pore diameter for the sample from the short synthesis was slightly larger than that for the sample from the normal synthesis. It has been seen that this time-saving synthesis method did not compromise the quality of the material. SAXS pattern was very well resolved for SBA-15 silica prepared via the short synthesis method, and it was very similar to what was
observed for the normal synthesis (see Figure 55 bottom). TEM images (Figure 56) showed the well-ordered channel-like features of SBA-15 silicas from the short synthesis.
Figure 55. Nitrogen adsorption isotherms (left), pore size distributions (right), and SAXS patterns (bottom) for traditional and short synthesis (initial synthesis temperature of 24 °C) of SBA-15 silica prepared with Pluronic P103, 1.8 ml TIPB, TEOS, in the presence of NH₄F, hydrothermally treated at 120 °C for 1 day (traditional) and 160 °C for 3 hours (short), and subsequently calcined.
Figure 56. TEM images for the short synthesis of SBA-15 silica prepared with Pluronic P103, 1.8 ml TIPB, TEOS, in the presence of NH$_4$F, which was hydrothermally treated at 160 °C for 3 hours, and then calcined.
3.5. Face-Centered-Cubic Structure Formation Using Pluronic P104/Triisopropylbenzene and P84/Triisopropylbenzene Pairs

In the attempt to synthesize SBA-15 silicas at room temperature, a few Pluronic surfactants with smaller size of PPO block (in comparison to P123) and thus with higher CMT in water were investigated, as discussed above. Pluronic P104 and P84 did not produce SBA-15 silicas as expected, but they led to the formation of silica with face-centered-cubic (FCC) structure, as indicated by SAXS and TEM. These results are fascinating as one would not expect to obtain FCC materials with these Pluronic surfactants and furthermore, adsorption results reveal that the pore volumes of these materials are higher than those of the FCC materials that are typically synthesized with Pluronic F127 surfactant in the presence of appropriate swelling agents.

3.5.1. Use of Pluronic P104/1,3,5-Triisopropylbenzene Pair in the Ordered Mesoporous Silica Synthesis

In comparison to Pluronic P103 (EO_{17}PO_{60}EO_{17}), Pluronic P104 (EO_{27}PO_{61}EO_{27}) has a similar size hydrophobic poly(propylene oxide) block and somewhat larger hydrophilic poly(ethylene oxide) block. At the initial synthesis temperature of 25 °C, the combination of Pluronic P104 and 1.8 ml of TIPB in our usual synthesis procedure (but without NH_{4}F) led to the unexpected formation of silica with the face-centered cubic structure (Fm3m symmetry).

Adsorption isotherms (Figure 57, left) featured hysteresis loops that were quite broad, even after the hydrothermal treatment at 120 °C for 1 day, suggesting the presence of cage-like pores in the
material. Pore size distributions (Figure 57, right) showed single, strong, narrow peaks. It should be pointed out that the hysteresis loop for the sample hydrothermally treated at 120 °C for 1 day was closer to narrow hysteresis loops with parallel adsorption/desorption branches that are usually observed for SBA-15 materials. Nonetheless, SAXS results (Figure 58) indicated that these are silicas with face-centered-cubic structures. It can be concluded that SAXS patterns featured one strong (111) refraction, (or possibly a superposition of (111) and (200) peaks), followed by a small (220) peak and a stronger (311) peak, and then (331) refraction. TEM images showed large ordered domains and features that can be identified as (111) and (110) projections of FCC structure (Figure 59). Table 14 contains data entries taken from earlier reports for comparison with the current FCC material prepared with Pluronic P104 and P84 (the latter to be discussed in the next section). Clearly, the mesopore volumes for samples described herein are significantly higher than those synthesized with F127 surfactant, even though the unit-cell parameter and pore diameter were smaller for samples prepared with either P104 or P84.
Figure 57. Nitrogen adsorption isotherms (left) and pore size distributions (right) for face-centered cubic silicas prepared with Pluronic P104, 1.8 ml TIPB, 5.5 ml TEOS, in the absence of NH₄F. The samples were hydrothermally treated at 100 °C for 2 days or 120 °C for 1 day, and then calcined. The isotherm for the sample hydrothermally treated at 120 °C is offset vertically by 450 cm³ STP g⁻¹.
Figure 58. SAXS patterns for face-centered cubic silicas prepared with Pluronic P104, 1.8 ml TIPB, 5.5 ml TEOS, in the absence of NH₄F. The samples were hydrothermally treated at 100 °C for 2 days or 120 °C for 1 day, and then calcined.
Figure 59. TEM images for face-centered cubic silicas prepared with Pluronic P104, 1.8 ml TIPB, 5.5 ml TEOS, in the absence of NH₄F, featuring (111) (top right region and bottom image) and (110) (top left region) projections. The sample was hydrothermally treated at 100 °C for 2 days, and then calcined,
Table 14. Structural parameters of face-centered cubic silicas prepared with Pluronics P104, P84, and F127, for samples subjected to hydrothermal treatment at 100 °C for 2 days.

<table>
<thead>
<tr>
<th>Synthesis temperature (°C)</th>
<th>Pluronic Surfactant</th>
<th>a_{uc} (nm)</th>
<th>a (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>Width of PSD at ½ height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>P104</td>
<td>23.4</td>
<td>21.5</td>
<td>770</td>
<td>1.07</td>
<td>12.0</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.0^</td>
<td>22.0^</td>
<td>585^</td>
<td>1.11^</td>
<td>12.8^</td>
<td>1.7^</td>
</tr>
<tr>
<td>40</td>
<td>P84</td>
<td>19.1</td>
<td>18.1</td>
<td>817</td>
<td>1.06</td>
<td>9.4</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.1^</td>
<td>18.2^</td>
<td>679^</td>
<td>1.17^</td>
<td>10.2^</td>
<td>2.6^</td>
</tr>
<tr>
<td>14 $</td>
<td>F127</td>
<td>55.2</td>
<td>45.3</td>
<td>130</td>
<td>0.24</td>
<td>23.5^{KJS}</td>
<td>#</td>
</tr>
<tr>
<td>15 *</td>
<td>F127</td>
<td>37.0</td>
<td>31.2</td>
<td>334</td>
<td>0.36</td>
<td>16.98</td>
<td>#</td>
</tr>
</tbody>
</table>

Notations: ^ samples were hydrothermally treated for 120 °C for 1 day; $ data entries taken from Reference 87 for a sample synthesized with 4.5 g of xylene. * denotes data entries taken from reference 121. Pore diameter calculating using KJS method. # data not available. Column a_{uc} is defined the unit-cell parameter for as-synthesized (uncalcined) sample and equal to d_{111} x \sqrt{3}; a is the unit-cell parameter for calcined sample.

3.5.2. Use of Pluronic P84/1,3,5-Triisopropylbenzene Pair in the Ordered Mesoporous Silica Synthesis

Similarly, Pluronic P84 surfactant was first used to evaluate its suitability for templating SBA-15 silica around room temperature. However, this surfactant has higher CMT than Pluronic P103 or P104^{56}, so the initial temperature for the synthesis with Pluronic P84 in successful trial was 40 °C. After a few experiments and characterization, the results were similar to those obtained for the Pluronic P104 and TIPB combination, which was discussed above. The
adsorption isotherm for the sample hydrothermally treated at 100 °C (Figure 60, left) revealed a hysteresis loop similar to those seen for materials with cage-like mesopores. The hysteresis loop for the sample hydrothermally treated at 120 °C for one day featured quite parallel capillary condensation/evaporation steps and was much more narrow (in comparison to that for the sample treated at 100 °C for 2 days). The pore size distributions (Figure 60, right) indicated that these materials had somewhat smaller pore sizes than those in the samples synthesized with Pluronic P104, but the pore size distribution peaks were strong and narrow. SAXS patterns (Figure 61) showed characteristics that pertain to FCC structure, as discussed in the previous section for P104 and TIPB pair used in the synthesis. TEM images shown in Figure 62 have been acquired for a sample prepared at 40 °C and hydrothermally treated at 100 °C for two days. They exhibited (100) projection (left region in the upper image) and presumably (110) projection of FCC structure with stacking faults related to 3-D hexagonal stacking sequences (ABABAB instead of ABCABC) in the close-packed structure.14 Our development of syntheses of FCC silicas templated with Pluronic P104 and P84 casts some light on the syntheses recently developed by others121-124 with Pluronic PE9400 surfactant (EO21PO47EO21) and TMB as a swelling agent. Based on our work, it is likely that some of their samples are face-centered cubic and similarly to our materials, are examples of FCC silicas with high pore volume.
Figure 60. Nitrogen adsorption isotherms (left) and pore size distributions (right) for face-centered cubic silicas prepared with Pluronic P84, 1.2 ml TIPB, 5.5 ml TEOS, in the absence of NH₄F. The samples were hydrothermally treated at 100 °C for 2 days or 120 °C for 1 day, and then calcined. The isotherm for the sample hydrothermally treated at 120 °C was offset vertically by 380 cm³ STP g⁻¹.
Figure 61. SAXS patterns for face-centered cubic structured silicas prepared with Pluronic P84, 1.2 ml TIPB, 5.5 ml TEOS, in the absence of NH₄F. The samples were hydrothermally treated at 100 °C for 2 days or 120 °C for 1 day, and then calcined.
Figure 62. TEM images for face-centered cubic silicas prepared with Pluronic P84 and 1.2 ml TIPB, synthesized at 40 °C and hydrothermally treated at 100 °C for 2 days, and then calcined.
4.

Conclusions
The incorporation of a swelling agent in the synthesis of SBA-15 silicas using Pluronic P123 surfactant remains the most powerful method for the increase in the pore size of these very popular porous materials from commonly obtained 5 – 12 nm to about 30 nm. While 1,3,5-triisopropylbenzene (TIPB) was reported by us to be an excellent swelling agent, the quality of the material was compromised as the pore size exceeded ~20 nm and especially when it approached its upper limit (26 – 28 nm). It was the hypothesis in the present work that a powerful, perhaps the most potent swelling agent for the synthesis of SBA-15 silica using Pluronic P123 surfactant should be an alkyl-substituted benzene with the number of carbon atoms in alkyl-substituents between that for trimethylbenzene (TMB) (3 carbons) that is well-known to afford excessive swelling, and Triisopropylbenzene (TIPB) (9 carbons). Mixtures of TIPB and potentially more powerful swelling agent (with fewer carbon atoms on the benzene ring than TIPB, and thus with higher expected extent of solubilization in Pluronics) were investigated. Mixtures of TIPB and small amount (up to 17 % by volume) of 1,3-di-tert-butylbenzene (1,3-DTBB), 1,4-di-tert-butylbenzene (1,4-DTBB), and 1,4-diisopropylbenzene (1,4-DIPB) afforded highly ordered SBA-15 silicas with \( d_{100} \) up to ~18 nm at initial synthesis temperature of 14 – 15 ℃. However, the potential of these swelling agent mixtures was not fully investigated.

When 1,3-DTBB was used alone as a swelling agent in the presence of ammonium fluoride, \( d_{100} \) reached 21.5 nm at initial synthesis temperature of 13 ℃. The 2-D hexagonal structure and narrow pore size distribution was confirmed by SAXS, gas adsorption and TEM. While these results were encouraging, they were not as good as the best results reported with TIPB as a swelling agent. To further advance out work, we took advantage of ammonium fluoride-free synthesis, which in previous study involving TIPB showed promise in obtaining
highly ordered materials with large pore sizes. Using the latter modification, $d_{100}$ of 26.8 nm, which is very large, was achieved with materials synthesized at 13.5 °C. We further optimized this synthesis by adjusting the amount of the silica source (TEOS), and changing the addition sequence of the swelling agent and TEOS. As the volume of TEOS was decreased to 4.10 mL per 2.4 g of P123 in the absence of ammonium fluoride at synthesis temperature of 13.25 °C, ordered SBA-15 silica with $d_{100} = 29$ nm was achieved. The increase of the amount of 1,3-DTBB to enlarge the pore size was found to be unsuitable, unless the initial synthesis temperature was relatively high.

An increase in the relative amount of TEOS was beneficial in the synthesis of very-large-pore SBA-15 silica templated by Pluronic P123 surfactant using TIPB as the swelling agent. At 12.75 °C, ordered SBA-15 with $d_{100}$ up to 27 nm (and perhaps even 31 nm) was achieved as the amount of TEOS was increased by 18 – 36 %. Well-resolved SAXS patterns, nitrogen adsorption isotherms with narrow hysteresis loops, narrow pore size distributions, and TEM images featuring channel-like structures and two-dimensional hexagonal pore arrangements, provided evidence that SBA-15 silicas were produced. In addition, the comparison of results suggested that better quality of ultra-large-pore SBA-15 may be achieved via the increase in the relative amount of TEOS, rather than by decreasing the initial synthesis temperature.

In the synthesis of SBA-15 silica, it was confirmed herein that one can shorten the synthesis procedure to as little as six hours. This method essentially relies on the presence of ammonium fluoride as it is known to be the silica condensation catalyst. Thus, the formation of silica network can be facilitated at a faster rate. Such a modification may require the hydrothermal treatment at a high temperature (160 °C) for at least 3 hours. Based on SAXS, gas
adsorption, and TEM, it was confirmed that the shortening of the synthesis can be accomplished for the synthesis of ultra-large-pore SBA-15 with TEOS/surfactant ratio adjustment and also for the room temperature synthesis discussed below. Such a modification was reproducible and the resulting materials were highly comparable to the “traditional” (long) synthesis, which is several times longer.

The synthesis of SBA-15 silica at room temperature using Pluronic P123 surfactant and 1,3,5-TIPB swelling agent was not promising. Although highly ordered SBA-15 silica with \(d_{100}\) of 12.0 nm was obtained at 25 °C using small amount (0.6 ml) of TIPB as swelling agent in the absence of \(\text{NH}_4\text{F}\), the further optimization by increasing the amount of the swelling agent in the synthesis was not beneficial, and instead produced less uniform or even disorganized materials, as suggested by SAXS and nitrogen adsorption. It is believed that the critical micelle temperature (CMT) was too low for this surfactant, leading to less than optimal interactions with a swelling agent at room temperature. Therefore, a few Pluronic surfactants (P103, L92, P105, P104, and P84) with higher CMT (in comparison to that of P123) were explored as better template candidates for the room temperature synthesis of SBA-15.

Pluronic P103 surfactant with TIPB as swelling agent gave very promising results in the synthesis of SBA-15 silica around room temperature. At 25 °C, when the volume of TIPB was increased in the absence of \(\text{NH}_4\text{F}\), the resulting materials reached \(d_{100}\) of 14.5 nm with good structural ordering and uniformity. However, the decrease in the initial synthesis temperature did not increase the range of achievable (100) interplanar spacings for good-quality SBA-15, in part because the products appeared to be contaminated by unidentified impurity with large interplanar spacing. Nonetheless, in the synthesis at 20 °C, the incorporation of \(\text{NH}_4\text{F}\) allowed for the formation of highly ordered SBA-15 with \(d_{100}\) of 13.4 nm and BJH pore diameter of 15.4 nm,
and this synthesis variant also holds some promise from room-temperature synthesis, which requires further exploration.

The control of the initial synthesis temperature at a constant level was a critical factor in a successful large-pore SBA-15 synthesis with Pluronics. Temperature governed the resulting micelle size (and thus the pore size). However, we have effectively eliminated the need for use of a temperature control in the case of the synthesis of SBA-15 with $d_{100} = 13$ nm. The key is to include NH$_4$F in such a synthesis. Hence, the formation of the silica network can occur rapidly in such a way that the fluctuation of the temperature would not influence the resulting material. SAXS and nitrogen adsorption results highly resembled those from synthesis carried out with the temperature control.

Pluronic P103 and 1,4-diisopropylbenzene (1,4-DIPB) pair produced SBA-15 silica around room temperature. Although 1,4-DIPB, based on our prediction, is expected to be a more powerful swelling agent than TIPB, the largest (100) interplanar spacing obtained with it was 11.4 nm using a small relative amount of 1,4-DIPB as the swelling agent, which is close to $d_{100}$ for SBA-15 silicas synthesized without the use of any swelling agent. We found that using somewhat larger volume of 1,4-DIPB led to excessive swelling, as suggested by SAXS and nitrogen adsorption.

We were not able to identify conditions in which Pluronic L92 and P105 would be useful in the synthesis of SBA-15 around room temperature. SAXS, nitrogen adsorption, and TEM results showed that SBA-15 material was not formed using these Pluronic surfactants. However, the interplanar spacing of the currently unidentified product of L92-based synthesis exhibited a strong dependence on the amount of swelling agent in the synthesis mixture.
Surprisingly, Pluronic P104 and P84 surfactants with about 40 wt. % of PEO domains led to the formation of face-centered cubic (FCC) silicas. Adsorption isotherms of these materials featured hysteresis loops that were quite broad and resembled the ones observed for porous materials with cage-like pores. SAXS patterns featured peaks that can be identified as (111) refraction (with some contribution from (200) peak), followed by a small (220) peak and a stronger (311) peak, and then (331) refraction, which are usually seen for FCC materials. TEM images featured some characteristic projections for the FCC structure. These FCC materials templated by P104 and P84 are interesting as their mesopore volumes are higher than those of previously reported FCC silicas templated by Pluronic F127 surfactant.
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