Large-pore mesoporous organosilicas and related polymer nanocomposites

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Large-pore mesoporous organosilicas and related polymer nanocomposites

By

Amanpreet S. Manchanda

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

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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THE CITY UNIVERSITY OF NEW YORK
Abstract

Large-pore mesoporous organosilicas and related polymer nanocomposites

By

Amanpreet S. Manchanda

Advisor: Professor Michal Kruk

The research work in this dissertation covers the synthesis of mesoporous organosilicas and (organo)silica/polymer nanocomposites. The content can be divided into 4 parts (8 chapters).

The first part of the dissertation is the introduction, which covers the background and progress in the field of mesoporous silicas, periodic mesoporous organosilicas and related inorganic/polymer nanocomposites. The second part of the dissertation (Chapter 2-5) involves the synthesis of mesoporous organosilicas from different organosilane precursors at mild acid concentration (0.1 M HCl) and low temperature (0 or 7 °C) using Pluronic F127 (EO106PO70EO106) as a surfactant template. Chapter 2 focused on the synthesis of large-pore periodic mesoporous organosilicas (PMOs) with ethylene bridging groups using 1,2-bis(triethoxysilyl)ethane (BTEE) and 1,2-bis(trimethoxysilyl)ethane (BTME) as well as phenylene-bridged PMOs using 1,4-bis(triethoxysilyl)benzene (BTEB). The use of different micelle swelling agents was also discussed. The resulting PMOs in many cases had face-centered cubic structure with large pore diameters, pore volumes and unit-cell parameters. In Chapter 3, the synthesis of large-pore ethylene (-CH=CH-) bridged PMOs with tunable pore sizes and face-centered cubic structures...
(Fm3m symmetry) using 1,2-bis(triethoxysilyl)ethylene (BTEEn) was discussed. The unit-cell parameters were tuned from 27 to 40 nm and the pore diameters were tuned from 13 to 22 nm by carefully adjusting the amount of swelling agent in the reaction mixture. Chapter 4 covered the synthesis of biphenylene-bridged PMOs using 4,4′-bis(triethoxysilyl)-1,1′-biphenyl (BTEBP) under the above mentioned conditions. The resulting materials had an ordered structure with pore diameters around 8.5 nm. Because of the presence of large aromatic groups in the framework precursor, the materials display a high molecular scale periodicity, which may contribute to the unique sheet type particle morphology. Chapter 5 discussed the synthesis of mesoporous organosilicas with pendant methyl groups using methyltriethoxysilane (MTES) as an organosilica precursor. These organosilicas have one methyl group attached to each silicon atom. The organosilicas have the pore diameters around 10 nm with cylindrical pores arranged in two-dimensional (2-D) hexagonal structure. The mesoporous organosilicas with accessible pores (through framework micropores) were thermally converted to closed-pore mesoporous organosilicas, without any degradation (or with minor degradation) of methyl groups. The closed-pore mesoporous organosilica materials usually have low dielectric constant, and so if a similar pore closing without organic group degradation can be accomplished for materials in a thin-film form, the resulting materials could be very useful in electronics industry.

The third part of the dissertation covers the synthesis of inorganic/polymer nanocomposites. In Chapter 6, poly(N-isopropylacrylamide) (PNIPAAm) brushes were grafted on the surface of large-pore methylene-bridged periodic mesoporous organosilica using surface-initiated activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP). The loading of the polymer can be controlled over a wide range by changing the polymerization time. A high loading of polymer (up to ~35 wt. %) was achieved without the mesopore blocking. This
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The last part of the dissertation (Chapter 8) covers the conclusions from all the chapters.
This is
dedicated to my parents
Amarjit Manchanda and Baljit Manchanda
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<td>OMS</td>
<td>Ordered mesoporous silicas</td>
</tr>
<tr>
<td>PMO</td>
<td>Periodic Mesoporous Organosilicas</td>
</tr>
<tr>
<td>m-PMO</td>
<td>Methylene-bridged Periodic Mesoporous Organosilicas</td>
</tr>
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<td>PEO</td>
<td>Polyethylene Oxide</td>
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<tr>
<td>PPO</td>
<td>Polypropylene Oxide</td>
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<tr>
<td>GPC</td>
<td>Gel Permiation Chromatography</td>
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<tr>
<td>ATRP</td>
<td>Atom Transfer Radical Polymerization</td>
</tr>
<tr>
<td>PNIPAAm</td>
<td>Poly(N-isopropylacrylamide)</td>
</tr>
<tr>
<td>MEO₂MA</td>
<td>2-(2-methoxyethoxy)ethyl methacrylate</td>
</tr>
<tr>
<td>MEO₅MA</td>
<td>Oligo(ethylene glycol)methyl ether methacrylate (Mₙ = 300 g/mol)</td>
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<tr>
<td>LCST</td>
<td>Lower Critical Solution Temperature</td>
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Chapter 1

Introduction
Ordered mesoporous silica (OMS) materials were first reported in 1992 by scientists at Mobil Corporation.\textsuperscript{1,2} The initial inspiration was to develop materials like zeolites for the petroleum cracking. Surfactant micelle-templating (soft templating) approach was used for the synthesis of such materials. OMSs have pore diameters in between 2 - 50 nm range and exhibit periodic nanostructure of well-defined morphologies. Interesting characteristics of these materials have attracted vast interest. Over the past couple of decades, these materials have been explored in different applications, such as adsorption\textsuperscript{3,4}, catalysis\textsuperscript{5}, sensing\textsuperscript{6,7}, energy conversion\textsuperscript{8}, targeted drug delivery\textsuperscript{9,10} and encapsulation of biomolecules\textsuperscript{11,12}.

It was initially hypothesized that OMSs forms through the liquid crystal templating mechanism (Figure 1.1).\textsuperscript{1,2} It was postulated that the surfactant micelles arrange in the form of liquid crystal domains before interacting with the inorganic silicate species (e.g. tetraethylorthosilicate, TEOS and its hydrolysis products), that form an envelope around the micelles. It was later realized that the mechanism is valid only for high concentration surfactant solutions. A more widely accepted mechanism of synthesis of these materials is cooperative self-assembly, which is based on the charge density match between the surfactant and the framework precursor.\textsuperscript{13,14} The mechanism was often valid for low surfactant concentration in solutions. Surfactants initially used for the synthesis of OMSs were ionic alkylammonium surfactants.\textsuperscript{1,2} Because these surfactants have short hydrophobic chains, the maximum pore sizes that can be obtained were typically less than 5 nm.\textsuperscript{1,2,15} It was found that OMSs can be periodically arranged in different pore geometries, such as 2-D hexagonal structures, hexagonal closed packed (3-D hexagonal) structure, body-centered cubic or face centered cubic structures, etc.\textsuperscript{1,2}
One of the developments in this field was the synthesis of mesoporous organosilicas. These materials were initially synthesized mostly by the post-synthesis modification of the ordered mesoporous silicas.\textsuperscript{16,17} This approach has disadvantages, such as usually limited loading of organic groups. One-pot process was also developed for the synthesis of mesoporous silicas with pendant organic groups.\textsuperscript{18} Silicate species, such as tetraethylorthosilicate (TEOS) and organosilane precursor such as methyltriethoxysilane, dimethyldiethoxysilane, triethoxyvinylsilane etc. were co-condensed to form the ordered mesoporous silica materials with pendant organic groups.

In 1999, three different groups separately reported the synthesis of periodic mesoporous organosilicas (PMOs).\textsuperscript{19-21} PMOs are a new class of mesoporous silica analogues in which Si-O-Si linkages are replaced by Si-R-Si linkages, where R can be methylene (\(-\text{CH}_2\)-),\textsuperscript{22,23} ethylene (\(-\text{CH}_2\text{-CH}_2\)-),\textsuperscript{20} ethenylene (\(-\text{CH}=\text{CH}_2\)-),\textsuperscript{19} phenylene (\(-\text{C}_6\text{H}_4\)-),\textsuperscript{24} biphenylene (\(-\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\)-),\textsuperscript{25} thiophene (\(-\text{C}_5\text{H}_4\text{S}\)-),\textsuperscript{26} etc. The bridged organic groups are inherently present in the pore walls. The materials are often synthesized using bridged organosilane precursors only, whereas some PMOs are synthesized via co-condensation of the aforementioned organosilane precursor and

\textbf{Figure 1.1} Mechanism of formation of surfactant-templated ordered mesoporous silicas as proposed by Beck et al.\textsuperscript{1} (adapted from reference 1).
silica precursor or a pendant organosilane precursor.\textsuperscript{27} Functional PMOs with more complicated bridging groups, such as urea,\textsuperscript{28} diurea,\textsuperscript{29} thioether,\textsuperscript{30} disulfide,\textsuperscript{31} etc. have been synthesized for different applications using the co-condensation method. PMOs synthesized exclusively from bridged organosilane precursors typically offer several advantages over post-synthesis modified organosilicas because of the higher content and homogeneity of organic groups throughout the framework.\textsuperscript{19,20} Because of the presence of the organic groups in the framework, various physical and chemical properties of these materials can be tuned easily. The PMOs have an increased surface hydrophobicity (when compared with pure silicas),\textsuperscript{16,18} high hydrothermal stability\textsuperscript{32} and low dielectric constant.\textsuperscript{33,34} Because of their unique properties, they are considered potential candidates for applications in immobilization of various biomolecules,\textsuperscript{35} targeted drug delivery,\textsuperscript{36} low dielectric constant materials in electronics,\textsuperscript{33,34} etc. The PMOs can have different geometries, including 2-dimensional hexagonal,\textsuperscript{20} 3-dimensional hexagonal (P6\textsubscript{3}/mmc symmetry),\textsuperscript{20} cubic (Pm\textsubscript{3}n symmetry),\textsuperscript{37} body centered cubic (Im\textsubscript{3}n symmetry),\textsuperscript{38} face centered cubic (Fm\textsubscript{3}m symmetry),\textsuperscript{39,40} and gyroidal (cubic Ia\textsubscript{3}d symmetry)\textsuperscript{41} (Figure 1.2). The type of the structure formed depends mostly on the type and quantity of surfactant being used, as well as on the framework precursor and other conditions.

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\includegraphics[width=\textwidth]{Lamellar.png}
\caption*{Lamellar}
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\caption*{2-D Hex (p6mm)}
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\includegraphics[width=\textwidth]{Face-centered.png}
\caption*{Face-centered cubic (Fm\textsubscript{3}m)}
\end{subfigure}
\caption{Schemes of structures of ordered mesoporous materials.}
\end{figure}
As discussed previously, alkylammonium surfactants were originally used for the synthesis of mesoporous materials, but typically the pore diameters obtained were rather small (< 5 nm). Large pore PMOs are beneficial in various applications such as catalysis, immobilization and separation of large biomolecules. A major breakthrough in the field of OMS was reported by Zhao et al. where they used commercially available amphiphilic block copolymer surfactant Pluronic P123 (EO20PO70EO20) to synthesize ordered mesoporous silicas with pore diameters of about 10 nm, or even more. The synthesized materials were called SBA-15 and they have pores arranged in a 2-D hexagonal structure. They also have microporosity in the walls related to the wall formation around PEO blocks of the Pluronic surfactant. The use of amphiphilic block copolymers, such as Pluronics, was then explored in the field of PMOs and afforded larger pore sizes, thicker walls and in some cases, narrow pore entrances to the mesopores. Pluronics are poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers and are commercially available with different molecular weights and PEO/PPO weight ratios. Poly(propylene oxide) (PPO) blocks are hydrophobic and it forms a core of the micelles. Poly(ethylene oxide) (PEO) block is hydrophilic and forms a hydrated corona surrounding the core. In 2001, two groups reported first synthesis of ethylene-bridged PMOs using Pluronic P123 as surfactant. The pore sizes obtained were somewhat larger (~7 nm) than those reported earlier and in one case, the mesopores were arranged in a 2-D hexagonal structure. It was seen that the nature of hydrophobic block of the copolymer surfactant has a great effect on the synthesis of well-defined PMO and can lead to PMOs with larger pore sizes. Matos et al. reported synthesis of PMOs using poly(ethylene oxide)-poly(butylene oxide)-poly(ethylene oxide) block copolymer, whose middle block poly(butylene oxide) (PBO), is more hydrophobic than poly(propylene oxide) (PPO) block in Pluronics. The PMOs had a pore size of 10 nm.
Although the pore size obtained was large, PEO-PBO-PEO surfactants are no longer available commercially, which limits the practical significance of this interesting development.

The use of micelle swelling agents (or micelle expanders) was found to be helpful in synthesizing OMS with larger pore sizes.\textsuperscript{15,43} The swelling agent solubilizes inside the micelles resulting in increase in the micelle size, thereby raising the pore sizes of the templated materials (Figure 1.3). Different swelling agents, such as benzene (with trimethylbenzene, TMB being common), alkyl substituted benzenes, linear and cyclic hydrocarbons, etc., were identified as swelling agents. The use of a swelling agent often increases the pore size, but also results in a decrease in the structural ordering or even change in the structure type for pure-silica materials.\textsuperscript{15} The use of swelling agents in the case of PMOs was also found to be helpful, but tuning of the pore sizes was found to be much more challenging than for ordered mesoporous silica counterparts.\textsuperscript{46}
Figure 1.3 The pore size adjustment by using surfactants of different chain length and swelling agents\textsuperscript{15} (Adapted from reference 15).
Reducing the synthesis temperature in addition to the use of swelling agent was found to be very useful in synthesis of OMSs and PMOs with larger pore sizes.\textsuperscript{15,46-48} It was hypothesized that at lower temperatures, there is a higher uptake of swelling agents into the micelles resulting in larger pore sizes.\textsuperscript{48} The conditions (low synthesis temperature and the use of a swelling agent) should be judiciously selected so as to achieve the pore size enlargement without loss of the structural ordering. Initial results show that the use of a swelling agent in combination with the Pluronic surfactant led to PMOs with larger pore sizes, but less well-defined structures.\textsuperscript{49} Various swelling agents such as hexane, benzene, xylene, trimethylbenzene, etc. can be used, but their careful selection is very important. Our group evaluated different swelling agents in the formation of OMS materials, such as large pore SBA-15 with 2-D hexagonal structure of cylindrical mesopores and FDU-12 silicas with face-centered cubic structures of spherical mesopores at low temperature (15 °C).\textsuperscript{47,50} For the surfactant F127 (EO\textsubscript{106}PPO\textsubscript{70}EO\textsubscript{106}) (having 30 wt.% of hydrophobic part), a swelling agent that solubilizes more extensively in the micelles, that is xylene, ethylbenzene or toluene, was selected and resulted in OMS with very large pore sizes, unit-cell parameters and yet with good structural ordering. For Pluronic P123 (70 wt.% hydrophobic part), swelling agent that solubilizes less in the micelles, such as triisopropylbenzene (TIPB) or cyclohexane, gave OMSs with large pore diameters and ordered structures (although cyclohexane was inferior for silicas). By using the strategy based on the swelling agent solubilization in the micelle, our group synthesized large-pore PMOs at low temperatures. Methylene-, ethylene-, ethenylene- and phenylene-bridged PMOs with large pore sizes and 2-D hexagonal symmetry were synthesized at lower temperatures using Pluronic P123 and cyclohexane or TIPB as a swelling agent.\textsuperscript{23} Similarly, for ethylene-bridged PMOs the use of
Pluronic F127 as a surfactant and xylene or toluene as a swelling agent led to the formation of ethylene-bridged PMOs with large pore sizes (up to 16 nm) and a face-centered cubic structure.\textsuperscript{51}

A recent study by Yu et al. showed that a moderate acid concentration (0.05 or 0.10 M HCl) and low temperature (0 or 5 °C) were suitable for the synthesis of ethylene-bridged PMOs with large pores and the face-centered cubic structure.\textsuperscript{52} The synthesized PMOs had the largest pore diameters around 33 nm with unit-cell parameter around 38 nm. The sizes obtained were very high for ethylene-bridged PMOs with Fm3m symmetry, but the values of unit-cell parameters and pore diameters did not seem to be self-consistent (the pore diameter was too high). In a separate study by our group, the synthesis of face-centered cubic ethenylene-bridged PMOs templated by Pluronics was done under mild acid concentration (0.1 M HCl) and low temperature (7 °C).\textsuperscript{53} In this novel material, pore diameters around 13 nm and unit-cell parameters around 31 nm were obtained, which was higher than reported before in case of Fm3m symmetry and unsaturated bridging groups.

As discussed above, large-pore PMOs with 2-D hexagonal symmetry, different bridging groups and controlled pore diameter have been successfully studied, but the work on the synthesis of large-pore PMOs with cubic structures of spherical mesopores was limited.\textsuperscript{46,51,52} Besides, the mesopore volumes of the cubic PMOs were usually low as compared to OMS and PMOs with 2-D hexagonal structure except for the recent report by Hu et al.\textsuperscript{52} that showed the synthesis of ethylene-bridged PMOs with quite large pore volume, but even this material was not quite convenient to synthesize due to the need of costly and inconvenient to handle bis(trimethoxysilyl)ethane (BTME) precursor and the very high values of pore size did not match the unit-cell size. There is an opportunity to extend the development of large-pore large-pore volume face-centered cubic PMOs beyond ethylene-bridged PMOs, studying other bridging
groups. Some of the commercially available bridged organosilane precursors, such as 1,2-Bis(trimethoxysilyl)ethane (BTME) or 1,2-Bis(triethoxysilyl)ethane (BTEE), bis(triethoxysilyl)ethylene (BTEEn), 1,4-Bis(triethoxysilyl)benzene (BTEB), and 4,4’-bis(triethoxysilyl)-1,1’-biphenyl (BTEBp) can be used for the synthesis of PMOs with ethylene, ethenylene, phenylene and biphenylene bridges respectively, under mild acid concentration and low temperatures (Figure 1.4).

Figure 1.4 Representative organosilane precursors for the synthesis of periodic mesoporous organosilicas with different bridging groups.

In the first part of this dissertation, the syntheses of various organosilicas, with either bridging or pendant organic groups under mildly acidic conditions and at low temperature (typically 7 °C) are discussed. In particular, the synthesis of large-pore ethylene-brided PMOs with face-centered
cubic symmetry using BTEE precursor is discussed. Previous studies have used BTME to synthesize ethylene-bridged PMOs, which is a much more costly and less benign precursor compared to BTEE. The synthesis of ethylene-bridged precursor using BTME is also discussed in detail under these conditions. Phenylene-bridged PMOs with face-centered cubic symmetry have been synthesized previously with maximum pore diameter around 10 nm.\textsuperscript{53} Our studies show that the synthesis under these conditions (0.1 M HCl and 7 °C) renders phenylene-bridged PMOs with much large pore diameters (~15 nm) and larger pore volumes, although the materials are not well ordered. The detailed study of the phenylene-bridged organosilicas under these conditions is described in Chapter 2. Also, it is notable that under 2M HCl and higher synthesis temperature, it was seen that for the bridged organosilanes, it was possible to transition from ordered mesoporous structures to single-micelle-templated hollow nanoparticles.\textsuperscript{54} When a similar synthesis was done at 7 °C and 0.1 M HCl for ethylene and phenylene-bridged PMOs, particles with multiple pores template by multiple micelles always formed and there was no evidence of the formation of single-micelle- templated nanoparticles.

While ethylene-bridged PMO is the most common PMO composition and can serve as a testing ground for the development of the synthetic methodology, a number of other PMO compositions are even more appealing. For instance, ethenylene-bridged PMOs have been studied with keen interest primarily because of the unsaturated bridging groups that can be easily modified.\textsuperscript{19,49,53,55,56} Many studies have been conducted on post-modification of these PMOs and various functional groups have been introduced to improve the properties of these PMOs.\textsuperscript{57-59} The application area may be vast for these PMOs, but very limited studies have been conducted on improving the characteristics of ethenylene-bridged PMOs, especially with face-centered cubic structure. According to our literature survey, the largest pore diameters in case of
ethylenylene-bridged PMOs with face-centered cubic structure synthesized were 14 nm.\textsuperscript{53} In Chapter 3 of the dissertation, the synthesis of large-pore ethylenylene-bridged PMOs with face-centered cubic structure and their swelling-agent-based tunability was discussed. The results indicate that the pore sizes can be tuned in a wide range from 13-20 nm by adjusting the amount of swelling agent without the loss in the structural ordering.

Biphenylene-bridged PMOs were also synthesized at the low temperature and under mild acid concentration conditions using Pluronic F127 as a surfactant. This PMO composition was first developed successfully by Inagaki et al., and was endowed with the periodic arrangement of the bridging groups in the framework.\textsuperscript{25} Typically, alkylammonium surfactants and basic conditions were used for the synthesis of the PMOs.\textsuperscript{25,60} The pore diameters for the materials were between 2-5 nm. In 2007, Sayari et al. reported the synthesis of biphenylene-bridged PMOs using Pluronic P123 with moderate crystallinity of the pore walls and reduced thermal stability, as compared to the biphenylene- bridged PMOs synthesized previously using alkylammonium surfactants.\textsuperscript{61} Our study described in Chapter 4 involves the synthesis of biphenylene-bridged PMOs using Pluronic F127 at low temperature (0 °C) and mildly acidic conditions (0.1 M HCl). The synthesized PMOs displayed quite large pore sizes ~8.7 nm with ordered structures having maximum interplanar spacing values around 14.5 nm, although we were not able to identify the structure of these materials. These PMOs also show unique morphology of particles in the form of sheets. The biphenylene-bridged PMOs show excellent thermal stability at different calcination temperatures under various environments. Their thermal stability was found to be superior to that of ethylenylene and phenylene-bridged PMOs synthesized under similar conditions.
In addition to PMOs, the synthesis of silicas with pendant organic groups was also explored under the considered conditions, with the hope of generating closed-pore organosilicas through the thermally-induced closing of mesopores. Mesoporous silica materials are considered potentially useful in the electronics industry and are known to have low dielectric constant (low-k) because of their porosity.\(^6^2\) Low-k materials can be especially useful as insulating media on the chips.\(^3^3,^3^4,^6^2\) The synthesis of mesoporous materials using Pluronic block copolymer surfactants (PEO-PPO-PEO) results in formation of micropores in the framework, which are templated by PEO blocks, in addition to mesopores templated by the hydrophobic PPO cores of the surfactant micelles (Figure 1.5). For the purpose of the above mentioned applications, materials with closed pores are desired. The closed-pore structure is not susceptible to contamination from the surrounding gas phase, which could lead to undesirable increase in the dielectric constant and to its inconsistent values. Brinker et al. published several reports on closed-pore silicas and organosilicas synthesized using poly(ethylene oxide)-polystyrene (PEO-PS) as a surfactant template.\(^3^3,^6^3\) Their studies claim that the presence of surfactant leads to the closing of the micropores at higher temperatures. The surfactants used in their study were PEO-PS block copolymers, which are not commercially available. In 2008, our group described a new pathway of closing the mesopores via calcination at sufficiently high temperatures (400 °C or higher).\(^6^4\) The calcination results in shrinkage of silica frameworks and possibly eliminating micropore connections (entrances) to spherical mesopores of FDU-12 silica and other materials. In a different study by our group, SBA-15 silicas with cylindrical mesopores was used and calcination at higher temperatures (~800 °C) resulted in closing of the (micro) pores in the walls of the mesopores, thus making the latter inaccessible.\(^6^5\) PMOs were also tested for pore closing via calcination at higher temperatures, but the treatment resulted in a damage of the organic
groups in the framework.\textsuperscript{65} PMOs or mesoporous organosilicas should have lower dielectric constants than regular OMSs because of the presence of organic groups in the framework.\textsuperscript{33} Results by Brinker et al. showed the possibility of synthesizing mesoporous organosilicas with closed pores using PEO-PS surfactants.\textsuperscript{33,63} In our study, we intended to synthesize closed-pore organosilica materials using the readily available Pluronic surfactants under newly identified conditions discussed above (7 °C and 0.1 M HCl). Also our research aims at studying the mechanism of pore closing and role of surfactant in the closure of mesopores. In Chapter 5, we have studied the formation of closed-pore organosilicas using organosilane precursor with pendant organic group, that is, methyltriethoxysilane. The methyl group is more thermally stable than most of the bridged organosilane groups and our results indicate that the methyl group was intact even after calcination at temperatures that allowed us to close the mesopores.
**Figure 1.5** Mechanism of thermally induced pore closing in ordered mesoporous silicas (adapted from reference 66).  

PMOs with functional groups in the framework are interesting for a wide variety of applications, such as environmental technology, targeted drug delivery, etc. A way for further functionalization of PMOs is the post-synthesis surface modification. PMOs with different functional groups including imine, amine, aldehyde, etc., have been reported in the literature. There have been some studies of surface functionalization of OMSs with polymers. Materials such as SBA-15 and FDU-12 silicas have been grafted with different polymers. The grafting of the polymers on to the surface of nanoporous host can result in improvement of chemical and dimensional stability. Also the polymer/silica nanocomposites would be attractive for variety of...
applications such as drug delivery, chromatographic packings, enzyme encapsulation, stimuli responsive adsorbents, etc. SBA-15 has been previously grafted with polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(N-isopropylacrylamide) (PNIPAAm) and poly(2-(dimethylamino)ethyl methacrylate) (PDAEMA), etc., using a controlled polymerization technique called atom transfer radical polymerization (ATRP). A similar study of grafting the polymers has not been done from surfaces of PMOs. There can be some challenges in the post synthesis modification of PMOs: i) the thermal stability of the organic groups in case of bridged PMOs is not high. So the surface modification of the PMOs should be done in mild conditions and should not result in the cleavage of organic groups or in a structural deformation. ii) PMOs with sufficiently large pore sizes and entrances should be chosen. Smaller size of pore entrances (<5 nm) can result in low loading of polymers and clogging of entrances to mesopores, even if the mesopores are large (>10 nm).

Successful studies on SBA-15 and FDU-12 show, that there are different methods to graft polymers inside the nanopores, such as physical adsorption, “grafting to” (attachment of previously made polymer chain) and “grafting from” approaches (growth of polymer from initiator on the pore surface). Studies show that the “grafting from” approach has shown good results in terms of high polymer loading and appreciable grafting density. Similarly, previous studies demonstrated that the controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP) can be advantageous because of their robustness and the ability to control molecular weight. Activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) is a recent advancement in the ATRP polymerization method, which involves low copper catalyst concentration (< 50 ppm) and the reactions can be done without airtight glassware. Environmentally friendly reducing agents, such
as tin (II) ethylhexanoate or Vitamin C (ascorbic acid) can be used to reduce the Cu(II) in the reaction.\textsuperscript{74,78}

In our work described in Chapter 6, I synthesized a methylene-bridged PMO with large pores of nominal diameter around 28 nm and with high surface area (~ 730 m\(^2\)/g) and large total pore volume (1.49 cm\(^3\)/g) according to the procedure described by Mandal and Kruk\textsuperscript{23} and I studied the grafting of the poly(N-isopropylacrylamide) (PNIPAAm) onto the nanopores of the PMO. Methylene-bridged PMOs are known to be thermally stable\textsuperscript{80} and the pore entrance size in the large-pore PMO was more than 5 nm,\textsuperscript{23} as inferred from the nitrogen adsorption isotherm. PNIPAAm is the thermo-responsive polymer and displays LCST in water around 32 °C, which is very close to the human body temperature.\textsuperscript{81} PNIPAAm has a good biocompatibility and has been studied extensively for drug delivery and other biological applications. In our study, it was seen that the loading of thermo-responsive polymer poly(N-isopropylacrylamide) (PNIPAAm) can be systematically controlled inside the nanopores by adjusting the polymerization time. To the best of our knowledge, this is the first report in which PMOs were grafted with polymers via a controlled radical polymerization.

In the last chapter of the dissertation, we studied the surface functionalization of large-pore SBA-15 materials using poly(oligoethylene glycol) methacrylate brushes of different side chain lengths. The large-pore SBA-15 materials had a 2-D hexagonal structure with cylindrical mesopores and nominal diameter around 29 nm. Different studies show that poly[(oligoethylene glycol) methacrylate] brushes of different oligo(ethylene glycol) chain lengths display different lower critical solution temperature (LCST) in aqueous media. Poly (2-(2’-methoxyethoxy)ethyl methacrylate) (PMEO\(_2\)MA) displays LCST around 26 °C while poly (oligo(ethylene glycol) methacrylate) (M\(_n\)=300 g/mol) (MEO\(_5\)MA) displays LCST around 64 °C.\textsuperscript{82,83} Study by Lutz. al.
shows that a copolymer of MEO$_2$MA and MEO$_5$MA displays LCST in between 26 and 64 °C.\textsuperscript{82,83} Besides this, the polymer offers advantages over PNIPAAm in terms of better hydrophilicity and biocompatibility.\textsuperscript{83} The grafting of poly(oligoethylene glycol) methacrylate brushes has not been studied from the surface of ordered mesoporous materials such as SBA-15. In our study, we used ARGET ATRP as a polymerization technique to graft MEO$_2$MA, MEO$_5$MA their copolymer (MEO$_2$MA-co-MEO$_5$MA). The polymer-silica nanocomposites can have potential applications in stimuli-responsive adsorption, biotechnology, etc. It was also seen that excellent control of polymer loading can be achieved inside the nanopores with low polydispersity index (PDI) of the polymer graft.
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Chapter 2

Facile synthesis of large-pore ethylene- and phenylene-bridged periodic mesoporous organosilicas.

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2.1 Background

The recently developed conditions for the synthesis of large pore PMO’s involves moderate acid concentration (0.1 M HCl instead of previously typically used about 2 M) and low temperatures (below 25 °C) have been proposed for the synthesis of large-pores PMOs.\textsuperscript{1,2} The synthesis at low temperature (\(~15 \, °C\)) previously was found very useful to increase the pore size in case of organosilicas.\textsuperscript{1-4} Moreover in cases of SBA-15 and FDU-12 silicas, swelling agents can be used at lower temperatures to enlarge the pore diameter and unit-cell parameter.\textsuperscript{5,6} These approaches were implemented to form ethylene-bridged PMOs with higher unit cell parameter and pore diameter.\textsuperscript{1,3,4}

While block-copolymer-templated ethylene-bridged PMOs with the face-centered cubic structures have been reported earlier,\textsuperscript{1,3,4} they were prepared using 1,2-bis(trimethoxysilyl)ethane (BTME), which is costly and needs to be handled with caution. Herein, 1,2-bis(triethoxysilyl)ethane (BTEE) is used, which is much less expensive and benign. Herein, we studied the synthesis of ethylene and phenylene-bridged PMO materials at 7 °C using 0.1 M HCl solutions as the synthesis medium. It was observed that the amount of swelling agent can be adjusted to tune the pore sizes and unit-cell parameters of the PMOs. The effects of synthesis temperature and different swelling agents were also studied for the ethylene-bridged PMOs. For the first time, we report the synthesis of ordered face-centered cubic ethylene-bridged PMOs derived from BTEE as a framework precursor. The resulting ethylene-bridged PMOs exhibited large pore diameters up to 23 nm, unit cell parameters up to 44 nm and large pore volumes. Similarly, large-pore ethylene-bridged PMOs were synthesized using 1,2-
bis(trimethoxysilyl)ethane (BTME) as an organosilane framework precursor and xylene as a swelling agent which is similar to previous BTME-based synthesis involving 1,3,5-trimethylbenzene as a swelling agent.\textsuperscript{1} Face-centered cubic or less ordered phenylene-bridged PMOs with pore diameter of ~15.5 nm and unit-cell parameter of 31.5 nm were also obtained. It was identified that the considered conditions (7 °C and 0.1 M HCl) are appropriate for the synthesis of ordered large pore PMOs with large pore volumes, but not suitable for the synthesis of single-micelle templated hollow nanoparticles.

2.2 Experimental Section

2.2.1 Synthesis

Synthesis of ethylene-bridged organosilicas using 1,2-bis(triethoxysilyl)ethane (BTEE)

0.5 g of Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) was dissolved in 30 mL of 0.1 M HCl at 7 °C by stirring for 1 hour. Then 0.5 g (or 1, 4 or 6 g) of xylene isomer mixture (or other swelling agent: ethylbenzene or toluene) and 2.5 g of KCl was added. After 2 hours, a selected volume of BTEE (0.93, 2.17, 2.73, 3.14, or 4.10 mL) was added. The reaction mixture was stirred at 7 °C for 1 day in a covered container. Then the whole solution was transferred to a polypropylene bottle and treated hydrothermally at 100 °C for 1 day. The as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Then the resulting material was calcined at 350 °C under argon for 5 hours (heating ramp 2 °C/min).

Synthesis of ethylene-bridged organosilicas using 1,2-bis(trimethoxysilyl)ethane (BTME)

The synthesis was similar to that reported earlier,\textsuperscript{1} but different temperature and swelling agents were used. 0.5 g of Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) was dissolved in 30 mL of 0.1 M HCl at 7 °C by stirring for 1 hour. Then 0.5 g (or 1, 4 or 6 g) of xylene isomer mixture (or other swelling agent: ethylbenzene or toluene) and 2.5 g of KCl was added. After 2 hours, a selected volume of BTME (0.93, 2.17, 2.73, 3.14, or 4.10 mL) was added. The reaction mixture was stirred at 7 °C for 1 day in a covered container. Then the whole solution was transferred to a polypropylene bottle and treated hydrothermally at 100 °C for 1 day. The as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Then the resulting material was calcined at 350 °C under argon for 5 hours (heating ramp 2 °C/min).
°C for 1 hour. Then 0.5 g (or 1, 2 or 4 g) of xylene isomer mixture (or other swelling agent: ethylbenzene or toluene) and 2.5 g of KCl was added. After 2 hours, a selected volume of BTME (0.42, 0.60, 0.93, 1.10 or 1.86 mL) was added. The reaction mixture was stirred at 7 °C for 1 day in a covered container and then the whole solution was transferred to a polypropylene bottle and treated hydrothermally at 100 °C for 1 day. The as-synthesized material was filtered, washed with deionized water and then dried in a vacuum oven at 60 °C. Finally the material was calcined at 350 °C under argon for 5 hours (heating ramp 2 °C/min).

Synthesis of phenylene-bridged organosilicas using 1,4-bis(triethoxysilyl)benzene (BTEB)

0.5 g of Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$) was dissolved in 30 mL of 0.1 M HCl at 7 °C under stirring for 1 hour. Then 1 g (or 2 or 4.6 g) of xylene isomer mixture and 2.5 g of KCl was added. After 2 hours of stirring, a selected volume of BTEB (0.65, 0.93, 1.10, 1.30 or 1.86 mL) was added to the reaction mixture. Then the mixture was stirred at 7 °C for 1 day. The solution was transferred to a polypropylene bottle and treated hydrothermally for 1 day. The as-synthesized material was filtered, washed with deionized water and dried in a vacuum oven at 60 °C. Finally the material was calcined at 250 °C under air for 5 hours (heating ramp 2 °C/min).

2.2.2 Measurements

Nitrogen adsorption measurements were carried out on Micrometrics ASAP 2020 volumetric adsorption analyzer at -196 °C. The samples were outgassed at 140 °C in the port of the adsorption analyzer before the analysis. Small angle X-ray scattering (SAXS) patterns were recorded on Bruker Nanostar U SAXS/wide angle X-ray scattering (WAXS) instrument equipped with a rotating anode X-ray source and a 2-D detector Vantec 2000. The instrument was in a high flux configuration and the flight path was ~73 cm. Samples were place in the hole
of aluminium sample holder and secured on both sides using a Kapton tape. Transmission electron microscopy (TEM) images were recorded on FEI Tecnai Spirit microscope operated at an accelerating voltage of 120 kV. The samples were first sonicated in ethanol and then deposited on carbon-coated copper grid and the solvent was evaporated under air before the analysis. Cross- polarization magic angle spinning (CP MAS) $^{29}$Si NMR spectra were acquired using Varian INOVA 300 wide bore spectrometer. The operating frequency was 59.6 MHz. Samples were packed into a 5 mm zirconia rotor, loaded into a 5 mm Doty XC-5 CP/MAS probe and spun at 6-8 kHz. Total of 500-1000 scans were acquired based on the sensitivity of the sample. The recycle delay was 5 s, the contact time was 3 ms, and the 90° pulse was 4 ms. The chemical shift reference was 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS).

### 2.2.3 Calculations

The BET surface area ($S_{BET}$) was determined from nitrogen adsorption isotherm in the relative pressure from 0.04-0.20."Total pore volume ($V_i$) was calculated from amount adsorbed at a relative pressure of 0.99." The micropore volume ($V_{\text{mic}}$) was determined using the $\alpha_s$ plot method in the standard reduced adsorption, $\alpha_s$, range from 0.9 to 1.2 using LiChrospher Si-1000 as a reference adsorbent.\(^3\)\(^,\)\(^8\) The sum of the primary mesopore volume ($V_p$) and the micropore volume was evaluated in the $\alpha_s$ range from 2 to 2.5.\(^8\) The mesopore volume was calculated by subtracting $V_{\text{mi}}$ from $V_{\text{mi}} + V_p$ calculated as mentioned above. Pore size distributions (PSDs) were calculated from adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method\(^9\) with KJS correction for cylindrical mesopores\(^10\) and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000.\(^8\) This method underestimates the diameter of spherical mesopores by ~2 nm in the considered pore size range.\(^11\) The pore diameter for most of
the samples was also calculated using a geometrical relation introduced by Ravikovitch and Neimark for materials with face-centered cubic structures of spherical mesopores:\(^\text{12}\):

\[
w_d = a \left( \frac{6}{\pi v} \frac{v_p \rho}{1 + v_p \rho + v_{\text{mic}} \rho} \right)^{1/3}
\]

where \(a\) is the unit-cell parameter calculated from position of (111) peak on the SAXS pattern, \(v\) is the number of spherical mesopores in the unit cell (4 for fcc structure), and \(\rho\) is the framework density. In case of ethylene-bridged PMOs, the framework density was assumed to be 1.52 g cm\(^{-3}\), and 1.42 g cm\(^{-3}\) for phenylene-bridged PMOs, as reported earlier.\(^\text{13}\)

2.3 Results

2.3.1 Synthesis of large-pore ethylene-bridged PMOs using 1,2-bis(triethoxysilyl)ethane (BTEE) as organosilica precursor

Influence of the amount of 1,2-bis(triethoxysilyl)ethane in the reaction mixture

Figure 2.1 shows the SAXS patterns for samples synthesized with different amounts of BTEE as the organosilica precursor. SAXS patterns for samples prepared with BTEE volumes greater than or equal to 2.73 mL show peaks that were clear and correspond to the face-centered cubic structure (Fm3m symmetry). As the amount of the precursor decreased, the SAXS patterns became less resolved. For the lowest amount of organosilica precursor (0.93 mL), the SAXS peak was broader indicating the structural ordering was diminished. The intermediate amount of precursor in the reaction mixture (2.73 mL) gave good structural ordering and large unit-cell
parameters up to 36.8 for the calcined samples and 38.2 nm for the as-synthesized sample (see Table 2.1).

![SAXS pattern for ethylene-bridged PMOs synthesized using 1 g of xylene and different amounts of BTEE (per 0.5 g of Pluronic F127).](image)

**Figure 2.1** SAXS pattern for ethylene-bridged PMOs synthesized using 1 g of xylene and different amounts of BTEE (per 0.5 g of Pluronic F127).

The presence of highly ordered structures was confirmed by TEM images. Samples synthesized with higher volume of organosilane precursor (2.17 mL or higher) show the presence of ordered domains with pores possibly arranged in face-centered cubic structure (Figure 2.2 left). TEM images for the sample synthesized with lowest amount of BTEE (~0.93 mL) show disordered porous structures having domains. The results obtained from TEM are consistent with the SAXS results. Unlike PMOs synthesized at a higher acid concentration (2 M HCl) and temperature (15
°C), the formation of single-micelle templated nanoparticles was not observed, even for very low BTEE/Pluronic F127 ratios (Figure 2.2 right).

![Figure 2.2 TEM images of calcined ethylene-bridged samples prepared using 1 g xylene and (left) 2.73 ml and (right) 0.93 mL of BTEE.](image)

It was seen that as the amount of BTEE decreased, the pore volume increased. However the pore diameter changed little with change in the organosilica precursor volume (Table 2.1). PMO synthesized with 0.93 mL of BTEE had a broad pore size distribution and the highest pore volume of 0.78 cm$^3$/g. A trend of the increase in the pore volume as the amount of BTEE is decreased may occur because lower amount of BTEE yields PMOs with thinner walls and since the pore diameter is almost same, there would be an increase in the total pore volume (lower mass of the walls per pore volume unit). From the nitrogen adsorption isotherms, it was seen that all of these PMOs had the capillary condensation at p/p$_0$ of 0.7-0.9 and the capillary evaporation at relative pressure of 0.48-0.49 (Figure 2.3(a)) which is indicative of the cage like structures having pore entrances less than 5 nm$^{15,16}$ It was seen that when 0.93 mL of BTEE is used in the reaction mixture, the capillary condensation step broadened and thus the pore size distribution
was also broad (Figure 2.3(b)). The SAXS pattern for this sample was also poorly resolved. It was seen that in these mild acid concentration conditions, particles with multiple pores form easily rather than single-micelle templated particles. The results from TEM further confirm this contention (Figure 2.2). With the intermediate volume of BTEE (2.17 and 2.73 mL), the capillary condensation step was steep and occurred at relative pressures of ~0.84 and ~0.86, respectively. The above correspond to narrow pore size distributions and pore diameters of 15.4 and 16.3 nm, respectively. PMOs synthesized with 3.14 mL of BTEE also had a narrow pore size distribution centered at pore diameter of 14.4 nm and unit cell parameter of 33.8 nm, but it had a relatively low pore volume of 0.38 cm$^3$/g.
Figure 2.3 (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcined ethylene-bridged PMOs synthesized using 1 g of xylene and different volumes of BTEE. For clarity the isotherms for the samples prepared using 2.17, 2.73, 3.14 and 4.10 mL BTEE were offset vertically by 300, 500, 700, 800 cm$^3$ STP g$^{-1}$, respectively.
Table 2.1 Structural properties of PMOs synthesized using BTEE under different conditions.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Amount of BTEE (mL)</th>
<th>Temp (°C)</th>
<th>Swelling agent</th>
<th>Amount of swelling agent (g)</th>
<th>( a ) (nm)</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>( V_t ) (cm(^3)/g)</th>
<th>( V_p ) (cm(^3)/g)</th>
<th>( V_{mic} ) (cm(^3)/g)</th>
<th>( w_{KJS} ) (nm)</th>
<th>( w_d ) (nm)</th>
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<td>4.10</td>
<td>7</td>
<td>Xylene</td>
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<td>33.2(35.5)</td>
<td>625</td>
<td>0.54</td>
<td>N/A</td>
<td>0.18</td>
<td>13.1</td>
<td>N/A</td>
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<tr>
<td>3.14</td>
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<td></td>
<td></td>
<td>33.2(36.4)</td>
<td>548</td>
<td>0.38</td>
<td>0.17</td>
<td>0.19</td>
<td>14.5</td>
<td>14.3</td>
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<td>2.73</td>
<td></td>
<td></td>
<td></td>
<td>36.8(38.2)</td>
<td>597</td>
<td>0.48</td>
<td>0.26</td>
<td>0.21</td>
<td>17.1</td>
<td>17.6</td>
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<tr>
<td>2.17</td>
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<td></td>
<td></td>
<td>31.8(35.5)</td>
<td>603</td>
<td>0.54</td>
<td>0.35</td>
<td>0.19</td>
<td>15.3</td>
<td>16.5</td>
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<tr>
<td>0.93</td>
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<td></td>
<td></td>
<td>26.3(28.3)</td>
<td>747</td>
<td>0.78</td>
<td>0.59</td>
<td>0.16</td>
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<td>0.25</td>
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<td></td>
<td></td>
<td></td>
<td>1</td>
<td>36.8(38.2)</td>
<td>597</td>
<td>0.48</td>
<td>0.26</td>
<td>0.21</td>
<td>17</td>
<td>17.6</td>
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<tr>
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<td></td>
<td>4</td>
<td>41.9(44.3)</td>
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<td>0.28</td>
<td>0.18</td>
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<td>6</td>
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<td>0.53</td>
<td>0.31</td>
<td>0.20</td>
<td>23.2</td>
<td>22.3</td>
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<tr>
<td>2.17</td>
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<td>Xylene</td>
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<td>686</td>
<td>0.54</td>
<td>0.30</td>
<td>0.22</td>
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<td>1</td>
<td>31.8(35.5)</td>
<td>603</td>
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<td>0.35</td>
<td>0.19</td>
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<td>16.5</td>
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<td>Xylene</td>
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<td>22.5(23.5)</td>
<td>467</td>
<td>0.31</td>
<td>0.16</td>
<td>0.15</td>
<td>8.3</td>
<td>9.7</td>
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<td>7</td>
<td>36.8(38.2)</td>
<td>597</td>
<td>0.48</td>
<td>0.26</td>
<td>0.21</td>
<td>17</td>
<td>17.6</td>
</tr>
<tr>
<td>2.73</td>
<td>7</td>
<td>Ethylbenzene</td>
<td>1</td>
<td>35.5(38.7)</td>
<td>635</td>
<td>0.50</td>
<td>0.28</td>
<td>0.21</td>
<td>16</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
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<td>33.2(35.5)</td>
<td>382</td>
<td>0.30</td>
<td>0.15</td>
<td>0.13</td>
<td>15.2</td>
<td>14.1</td>
</tr>
<tr>
<td>2.17</td>
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<td>Ethylbenzene</td>
<td>1</td>
<td>31.8(34)</td>
<td>631</td>
<td>0.57</td>
<td>0.34</td>
<td>0.19</td>
<td>14.5</td>
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<td>Toluene</td>
<td></td>
<td>31.8(35.5)</td>
<td>613</td>
<td>0.55</td>
<td>0.36</td>
<td>0.19</td>
<td>15.4</td>
<td>16.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Notation: Temp, Temperature; \( a \), unit-cell parameter for calcined ethylene-bridged organosilicas synthesized with BTEE sample calculated from (111) interplanar spacing (unit-cell parameter for as-synthesized sample is provided in parentheses); \( S_{BET} \), BET specific surface area; \( V_t \), total pore volume; \( V_p \), primary mesopore volume; \( V_{mic} \), micropore volume; \( w_{KJS} \), pore diameter calculated using BJH-KJS method for cylindrical mesopores. \( w_d \), pore diameter calculated using eq 1; N/A, not available with acceptable accuracy.
$^{29}$Si CP MAS NMR result shows that the organic groups were still intact after calcination at 350 °C under argon. NMR spectrum of this ethylene-bridged materials had a peak at -64 ppm, which corresponds to the T$_2$ sites (H$_2$C$_2$-Si(OSi)$_2$(OH)) and there was little or no signal corresponding to Q$_n$ sites (Si(OSi)$_n$(OH)$_{4-n}$), implying the preservation of Si-C bond (Figure 2.4).

![Figure 2.4 $^{29}$Si CP MAS NMR spectrum of the calcined ethylene-bridged organosilica synthesized using 1 g of xylene and 2.73 mL BTEE.](image)

**Pore size tailoring of ethylene-bridged PMOs**

The increase in the relative amount of swelling agent led to a regular trend in increase in the pore diameter as well as the unit cell parameter (see Table 2.1). It can be hypothesized that as the amount of the swelling agent is increased in the synthesis mixture, more and more of the swelling agent is solubilized in the micelles, which results in a larger micelle size and consequently larger pore diameter and unit cell parameters. In an ideal case, the increase takes place without loss of ordering of these PMOs (Scheme 2.1) but typically a deterioration of ordering or its loss, are seen. In the present case, the increase in the pore volume (observed when the relative amount of swelling agent was increased) was rather small, suggesting that the
increase in the uptake of swelling agent by the micelle is not large. The magnitude of the pore volume (compared with the volume of the swelling agent used in the synthesis) suggests that in all cases considered here, excess of the swelling agent was provided.

For the ethylene-bridged PMOs prepared using BTEE as a precursor, the pore diameter can be tailored by adjusting the amount of swelling agent without much change in the structural ordering (see Figure 2.5). When using 2.73 mL of BTEE and xylene, pore diameter was increased by up to ~8 nm (from 15.3 to 23.2 nm) and maximum unit cell parameter reached 44 nm for calcined sample when the amount of xylene from 0.5 g to 6 g in the reaction mixture. Similarly when using 2.17 mL of BTEE and xylene as the swelling agent, the pore diameter was increased by up to 7 nm (from 13.8 to 20.9 nm) and the unit cell parameter was increased by up to ~10 nm (from 30.6 to 40.2 nm) while increasing the mass of xylene in the reaction mixture from 0.5 to 4 g.
Scheme 2.1 The adjustment of the pore diameter using different amount of swelling agent (e.g., xylene) and Pluronic F127 as a surfactant.
When using 2.73 mL BTEE, the relative positions of SAXS peaks corresponded to the face-centered cubic structure (Figure 2.5(a)). The pattern showed four reflections and one shoulder when 0.5 g of xylene was used. The increase in the amount of xylene to 1, 4 and 6 g per 0.5 g of F127 did not lead to any significant loss of ordering, although (331) peak became less resolved. As the amount of xylene was increased from 0.5 to 6 g in the reaction mixture, the unit cell parameter increased from 36.4 nm to 46.3 nm for the as-synthesized sample and 33.2 to 44.3 nm for the calcined samples (Table 2.1). Similar result was in the case of 2.17 mL BTEE, the unit cell parameter appeared to increase from 30.6 nm to 41.9 nm for calcined samples as the amount of xylene was increased from 0.5 to 4 g in the reaction mixture (Figure 2.5(b)). However, in this case the patterns were less resolved. The assumption of the face-centered cubic structure was used in unit-cell size calculations.
Figure 2.5 SAXS pattern for organosilicas prepared using variable amount of xylene and with (a) 2.73 mL of BTEE and (b) 2.17 mL of BTEE.

The ordered structures of the materials were confirmed by TEM, which showed the presence of large ordered domains. The images showed circular lighter spots arranged in a periodic fashion. Although such features can arise from not only spherical pores, but also cylindrical pores aligned parallel to the electron beam, the absence of the images of channels viewed from the side (which looks like series of parallel stripes) suggests that the mesopores are spherical. This is consistent with what can be expected on the basis of SAXS patterns. The increase in the unit-cell parameter was also seen from the TEM images (Figure 2.6).
Figure 2.6 TEM images of calcined organosilica samples prepared using 2.73 ml BTEE and 4 g (left) and 6 g (right) of xylene.

Shown in Figure 2.7(a) are nitrogen adsorption isotherms for calcined ethylene–bridged PMOs synthesized with different amounts of swelling agent (xylene) and 2.73 mL of BTEE. The sample with lower amount of xylene (0.5 g) exhibited a capillary condensation step at a relative pressure of ~0.85. As the amount of xylene increased, capillary condensation pressure changed to higher relative pressure values. When 6 g of xylene was used, the position of capillary condensation step was at relative pressure of ~ 0.91, which corresponds to the substantial increase in the pore size as the amount of the swelling agent was increased. However the position of capillary evaporation steps was about the same (~0.48-0.49) for all of these PMOs because it corresponds to a lower limit of adsorption-desorption hysteresis, which is weakly dependent on the pore size, especially for large mesopores. A similar trend was seen for the lower amount of organosilica precursor (Figure 2.8(a)).
Figure 2.7 (a) Nitrogen adsorption isotherms and (b) pore size distributions of ethylene-bridged PMOs prepared using 2.73 mL BTEE and variable amount of xylene. For clarity the isotherms for the samples prepared using 1, 4 and 6 g were offset vertically by 150, 300 and 450 cm$^3$ STP g$^{-1}$ respectively.

Pore size distributions (PSDs) of the organosilicas prepared with 2.73 mL BTEE showed a trend of increase in the pore diameter as the amount of xylene was increased with little broadening of these distributions (Figure 2.7(b)). The pore size was controlled systematically by adjusting the mass of the swelling agent, and pore diameters in the range between 15.3 and 23.2 nm were synthesized by adjusting the mass of xylene in the reaction mixture (Figures 2.7(b)). In the case when PMOs were obtained with slightly lower amount of BTEE (2.17 mL), PSDs showed narrow peaks and smaller pore diameters when the mass of xylene in the reaction mixture was quite low (0.5 and 1 g). When a larger amount of xylene was used in the reaction mixture, PMOs
with large pore diameter (~20.9 nm) PMOs were synthesized, but it had a broader pore size distribution (Figure 2.8(b)).

**Figure 2.8** (a) Nitrogen adsorption isotherms and (b) pore size distributions of ethylene-bridged PMOs prepared using 2.17 mL of BTEE and variable masses of xylene. For clarity the isotherms for the samples prepared using 1 and 4g xylene were offset vertically by 200 and 400 cm$^3$ STP g$^{-1}$, respectively.

**Effect of temperature**

It was also attempted to carry out the synthesis of ethylene-bridged PMOs at room temperature. PMOs synthesized with xylene at 25 °C exhibited a quite well-resolved SAXS pattern characteristic of the face-centered cubic structure (Fm3m symmetry). The sample synthesized at 7 °C yielded much larger unit-cell parameter of ~37 nm as compared to the sample synthesized at 25 °C, which yields the unit-cell parameter of 25 nm (see SAXS data in Figure 2.9, Table 2.1).
Figure 2.9 SAXS pattern of ethylene-bridged periodic mesoporous organasilicas prepared using 1 g of xylene and 2.73 mL BTEE synthesized at two different temperatures.

Nitrogen adsorption isotherms for these ethylene-bridged PMOs exhibited steep capillary condensation steps at relative pressures of ~ 0.85 and ~0.62 and capillary evaporation steps at relative pressure of ~ 0.48 and 0.47 for the samples synthesized at 7 °C and 25 °C, respectively (Figure 2.10(a)). The isotherm for the sample prepared at 25 °C had a broad hysteresis loop with the desorption at a lower limit of adsorption-desorption hysteresis and thus was similar to the previous isotherms indicating the presence of cage-like pore structures with entrances less than 5 nm.\textsuperscript{15,16} The PMO synthesized at 7 °C exhibited specific surface area of 597 m\textsuperscript{2}g\textsuperscript{-1} and total pore volume of 0.42 cm\textsuperscript{3} g\textsuperscript{-1}, which was high as compared to the surface area of 466 m\textsuperscript{2}g\textsuperscript{-1} and total pore volume of 0.28 cm\textsuperscript{3}g\textsuperscript{-1} for the PMO synthesized at 25 °C (Table 2.1). Pore size
distributions (Figure 2.10(b)) were narrow and centered at ~17 nm for sample prepared at 7 °C and ~8 nm for the sample prepared at 25 °C.

**Figure 2.10** (a) Nitrogen adsorption isotherms and (b) pore size distributions of ethylene-bridged organosilicas prepared using 1 g of xylene and 2.73 mL of BTEE, synthesized at different temperatures.

**Effect of different swelling agents**

Further experiments were done to see the effect of different swelling agents in the considered PMO synthesis. It was observed that very well ordered PMOs with face-centered cubic symmetry can be synthesized using xylene and ethylbenzene as a swelling agent. When 2.73 mL BTEE was used, less structural ordering was seen in samples where toluene was used as a swelling agent (Figure 2.11). Under our normal synthesis conditions using 1 g of swelling agent...
and 2.73 mL of BTEE, unit cell parameters of ~37 nm can be obtained (Figure 2.14(a)). Excellent resolution of the SAXS pattern for the sample prepared in the presence of ethylbenzene is noted. Similar results were obtained when 1 g of swelling agent and 2.17 mL of BTEE was used, but the patterns were much less resolved. (Figure 2.11(b)).

**Figure 2.11** SAXS patterns of ethylene-bridged organosilicas prepared using 1g of different swelling agents and (a) 2.73 mL BTEE and (b) 2.17 mL BTEE.

Nitrogen adsorption isotherms (Figure 2.12 and 2.13) for samples prepared with different swelling agents were similar to those discussed above and were characteristic of PMOs with large spherical mesopores.\textsuperscript{15,16} When 2.73 mL BTEE was used, the capillary condensation was between at a relative pressure of 0.83-0.85 and the capillary evaporation pressure was ~0.48-0.49. The pore diameter was around ~15 nm for all of the samples, but the pore size distribution was quite broad when toluene was used (Figure 2.12(b)). When 2.17 mL BTEE was used, the
isotherms were almost the same and the pore diameter was essentially the same (Figure 2.13(b)). Based on the SAXS and nitrogen adsorption results, it can be concluded that all of these swelling agent work well in forming an ordered cubic structure, but xylene and ethylbenzene work a little better when compared with toluene.

![Graph](image-url)

**Figure 2.12** (a) Nitrogen adsorption isotherms and (b) pore size distributions for ethylene-bridged organosilicas synthesized with 2.73 mL of BTEE and with different swelling agents. For clarity, the isotherms for the samples prepared using xylene and toluene were offset vertically by 150 and 350 cm$^3$ STP g$^{-1}$, respectively.
Figure 2.13 (a) Nitrogen adsorption isotherms and (b) pore size distributions for ethylene-bridged organosilicas synthesized with 2.17 mL BTEE and with different swelling agents. For clarity, the isotherms for the samples prepared using xylene and toluene were offset vertically by 150 and 350 cm³ STP g⁻¹, respectively.

2.3.2 Synthesis of large-pore ethylene-bridged PMOs using 1,2-bis(trimethoxysilyl)ethane (BTME) as organosilica precursor

Influence of the amount of 1,2-bis(trimethoxysilyl)ethane (BTME) in the reaction mixture

A similar behavior was observed in the case of ethylene-bridged PMOs synthesized using BTME, which was the precursor used in the work of Yu et al.¹ In our study, we used 0.1 M HCl and at 7 °C and a judicious selection of the swelling agent, while Yu et al. used 1,3,5-trimethylbenzene (TMB). In our work, PMO with pore diameter of 28 nm was synthesized, which is very high, being much larger than those documented before. Note that Yu et al.¹
reported similar pore sizes, but their reported SAXS patterns suggested a moderate unit-cell size, which is not self-consistent.

SAXS analysis (Figure 2.14) revealed the presence of an ordered structure corresponding to the face-centered cubic structure when a higher volume (~1.86 mL) of BTME was used. It should be noted that 1.86 mL of BTME is equivalent on molar basis to 2.73 mL BTEE. SAXS patterns for samples synthesized with lower volumes of BTME precursor had broad peaks and were less resolved. When 0.60 mL of the precursor was used, the resulting sample had the SAXS pattern that was not resolved at all and the structure was unclear. TEM images for samples synthesized with lower amounts of BTME, shows the presence of smaller particles with some ordering (Figure 2.15). Similar to results obtained in case of BTEE, the lower amounts of BTME did not yield single-micelle-templated nanoparticles.
Figure 2.14 Small-angle X-ray scattering patterns of ethylene-bridged organosilicas prepared with 1 mL of xylene and different amounts of BTME.

Figure 2.15 Transmission electron microscopy images of calcined ethylene-bridged PMOs synthesized with 1 mL xylene and (left) 0.93 mL, (right) 1.10 mL of BTME.
Figure 2.16(a) shows the nitrogen adsorption isotherms for the calcined ethylene-bridged PMOs. The samples exhibited a capillary condensation at a relative pressure of ~0.85-0.87 and capillary evaporation at ~0.49-0.50, the latter being characteristic of pores with entrances less than 5 nm.\textsuperscript{15,16} Pore size distributions were narrow and centered at ~18 nm for samples with BTME volume equal to or larger than 0.93 mL. When the amount of precursor was lowered to 0.60 mL, PMO with very broad pore size distribution was obtained (Figure 2.16(b)). As the amount of the organosilica precursor (BTME) was lowered, the pore volume increased. It is considered that as the amount of BTME was decreased in the reaction mixture, pore walls became thinner and because the pore diameter was almost the same, it resulted in the increase in the pore volume.

**Figure 2.16** (a) Nitrogen adsorption isotherms and (b) pore size distributions of organosilicas prepared with 1 mL of xylene and with different amounts of BTME. For clarity the isotherms for the samples prepared using 1.10, 0.93 and 0.60 mL BTME were offset vertically by 100, 300 and 550 cm\(^3\) STP g\(^{-1}\), respectively.
Table 2.2 Structural properties of PMOs synthesized with BTME under different conditions.\(^b\)

<table>
<thead>
<tr>
<th>Amount of BTME (mL)</th>
<th>Temp (°C)</th>
<th>Swelling agent</th>
<th>Amount of swelling agent (g)</th>
<th>d (nm)</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_t) (cm(^3)/g)</th>
<th>(V_p) (cm(^3)/g)</th>
<th>(V_{\text{mic}}) (cm(^3)/g)</th>
<th>(w_{KJS}) (nm)</th>
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<tr>
<td>1.86</td>
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<td>Xylene</td>
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<td>22.9 (24.8)</td>
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<td>0.45</td>
<td>0.28</td>
<td>0.16</td>
<td>20</td>
</tr>
<tr>
<td>1.10</td>
<td></td>
<td></td>
<td></td>
<td>22.6 (25.2)</td>
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<td>0.58</td>
<td>0.15</td>
<td>21.3</td>
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<tr>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
<td>20 (21.2)</td>
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<td>18.7</td>
</tr>
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</tr>
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<td>7</td>
<td>Xylene</td>
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<td>17.7 (19.2)</td>
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<td>0.57</td>
<td>0.38</td>
<td>0.18</td>
<td>15.9</td>
</tr>
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<td></td>
<td>20 (21.2)</td>
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<td>0.80</td>
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<td>0.14</td>
<td>18.7</td>
</tr>
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<td></td>
<td>20 (21.2)</td>
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<td>24.5 (25.6)</td>
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<td>Ethylbenzene</td>
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<td>18.3 (20.5)</td>
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<td>0.19</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Toluene</td>
<td>16 (16.6)</td>
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<td>0.38</td>
<td>0.22</td>
<td>0.15</td>
<td>12.7</td>
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</tbody>
</table>

\(^b\)Notation: Temp, Temperature for the synthesis; d, interplanar spacing for calcined sample (interplanar spacing for as-synthesized sample is provided in parentheses); \(S_{\text{BET}}\), BET specific surface area; \(V_t\), total pore volume; \(V_p\), primary mesopore volume; \(V_{\text{mic}}\), micropore volume; \(w_{KJS}\), pore diameter calculated using BJH-KJS method for cylindrical mesopores.

\(^{29}\)Si CP MAS NMR for one of the ethylene-bridged PMOs synthesized with BTME showed that the organic groups were intact after calcination at 350 °C under argon. The spectrum had a peak at about -63 ppm which corresponded to the T\(_2\) sites (\(\text{H}_3\text{C}_2\text{-Si(OSi)}_2\text{(OH)}\)) and there were no
clear signals corresponding to $Q_n$ sites ($\text{Si(OSi)}_n\text{(OH)}_{4-n}$), implying the absence of cleavage of Si-C bond (Figure 2.17).

Figure 2.17 $^{29}\text{Si}$ CP MAS NMR spectrum for ethylene-bridged PMO synthesized with BTME and calcined at 350 °C under argon

**Pore size tailoring using swelling agent**

SAXS patterns of the samples prepared with different amounts of the swelling agent are shown in Figure 2.18. As the amount of swelling agent increased in the reaction mixture, the value of d-spacing increased (based on the position of the first peak on the SAXS pattern). However, the SAXS patterns were not sufficiently resolved to assign them to any particular structure. TEM images also showed the enlargement of the pores with the structures resembling mesocellular foams type, when 4 g of xylene was used (Figure 2.19).
Figure 2.18 SAXS patterns for organosilicas prepared using 0.93 mL of BTME and variable amounts of Xylene.

Figure 2.19 TEM image of calcined PMO prepared using 0.93 ml BTME and 4 g of xylene.
As discussed above in case of BTEE, the adjustment of the volume of xylene allowed us to tailor the diameter of the mesopores. It was seen from the nitrogen adsorption isotherms that when lower amount of xylene was used (0.5 g), the capillary condensation step was at a relative pressure of ~0.84 and the capillary evaporation was at relative pressure of ~0.48. The pore diameter was ~15 nm. When the amount of xylene was increased to 1 g, the position of the capillary condensation step changed to the relative pressure of about 0.87 but the position of capillary evaporation remained essentially the same. The average pore diameter increased to ~18 nm. By further increasing the amount of xylene to 2 g and 4 g, the position of capillary condensation step changed to relative pressure of ~0.90 to 0.92 and the pore diameter increased from 20.5 nm and 28 nm respectively, which is higher than those seen before (Figure 2.20). However, the resulting structure does not seem to be ordered.
Figure 2.20 (a) Nitrogen adsorption isotherms and (b) pore size distributions of organosilicas prepared with 0.93 mL BTME and with different amounts of xylene. For clarity the isotherms for the samples prepared using 1, 2 and 4 g xylene were offset vertically by 170, 500 and 850 cm$^3$ STP g$^{-1}$, respectively.

Effect of different swelling agents

Large pore ethylene-bridged PMOs were synthesized in presence of swelling agents such as xylene, ethylbenzene and toluene. From our studies, it was seen that xylene and ethylbenzene worked well providing high pore volume and pore diameter with an ordered structure. The use of toluene as a swelling agent did not render PMOs with high pore volume and pore diameter in comparison to other materials. In the case of PMOs with xylene and ethylbenzene as swelling agent, pore size distributions (Figure 2.21) from the adsorption isotherms were narrow and pore
diameter for these PMOs was around ~18 nm, while when toluene was used as a swelling agent, pore diameter was around 13 nm.

**Figure 2.21** SAXS patterns of ethylene-bridged organosilicas synthesized with 0.93 mL BTME and with different swelling agents.
Figure 2.22 (a) Nitrogen adsorption isotherms and (b) pore size distributions of ethylene-bridged organosilicas prepared using 0.93 mL of BTEE and with different swelling agents. For clarity the isotherms for the samples prepared using ethylbenzene and xylene were offset vertically by 60 and 250 cm$^3$ STP g$^{-1}$, respectively.

The calcined samples prepared with xylene and ethylbenzene exhibited capillary condensation steps at relative pressures of ~0.87 and capillary evaporation at ~0.48 (Figure 2.22). These isotherms were also characteristic of materials with cage-like pore structures having entrances of diameter less than 5 nm.$^{15,16}$ The sample prepared with toluene as a swelling agent had capillary condensation step at ~0.82 which is lower than that of the other samples. The pore volume of PMOs prepared with xylene and ethylbenzene was 0.80 cm$^3$/g and 0.63 cm$^3$/g, respectively, which is high for block-copolymer-templated PMOs with spherical mesopores. The BET specific surface areas for these PMOs were also high.
2.3.3 Synthesis of large-pore phenylene-bridged PMOs using 1,4-bis(triethoxysilyl)benzene (BTEB) as organosilica precursor

Influence of amount of 1,4-bis(triethoxysilyl)benzene in the reaction mixture

The effect of the ratio of the organosilane precursor to the surfactant was studied in the case of 1,4-bis(triethoxysilyl)benzene (BTEB). SAXS patterns for the highest relative amount (1.86 mL per 0.5 g F127) indicate well-ordered face-centered cubic structure (Figure 2.26). SAXS patterns became less resolved as the amount of the organosilane precursor was decreased to 1.10 mL. Poorly resolved patterns were observed in the case when the volume of BTEB was further decreased to 0.93 and 0.65 mL. In the case when the sample was prepared with 1.10 mL BTEB, TEM images show the presence of small particles with multiple pores (Figure 2.24). In the case when, the similar synthesis was done under 2M HCl, loose aggregates of hollow spherical particles were observed. So, clearly these mild acid concentration conditions (0.1 M HCl) supports the formation of particles with multiple pores, instead of single-micelle template particles.
Figure 2.23 SAXS patterns for phenylene-bridged organosilicas synthesized using different organosilica precursor/surfactant ratios in the presence of xylene. Taken from Ref. 2

Figure 2.24 TEM for calcined phenylene-bridged organosilicas synthesized using 1.10 mL BTEB and 1 g of xylene. Taken from Ref. 2
Figure 2.25(a) shows the nitrogen adsorption isotherms. For the sample synthesized with 1.86 mL BTEB, there was a capillary condensation step at a relative pressure of ~0.77 and capillary evaporation at ~0.48. When a lower amount of BTEB was used (1.10 mL), the sample exhibited additional uptake of nitrogen above the relative pressure of ~0.80, which indicates the presence of mesopores that can be identified as the interparticle pores on the basis of TEM. Similar isotherms with secondary porosity were observed with lower amounts of BTEB (0.93 and 0.65 mL). PSDs calculated from the nitrogen adsorption isotherms were narrow and centered at ~11 nm for the sample synthesized with 1.86 and 1.10 mL BTEB (Figure 2.25(b)). PSDs for the lower amount of BTEB (0.93 mL and 0.65 mL) were broader. The results obtained from the nitrogen adsorption are consistent with SAXS and the TEM results.
Figure 2.25 (a) Nitrogen adsorption isotherms and (b) pore size distributions for phenylene-bridged organosilicas synthesized using different organosilica precursor/surfactant ratios in the presence of xylene. For clarity, isotherms for samples prepared with 1.10, 0.93 and 0.65 mL BTEB were offset vertically by 50, 120 and 190 cm$^3$ STP g$^{-1}$, respectively. Taken from Ref. 2

Pore size tailoring using swelling agent

The adjustment of the relative quantity of the swelling agent yielded phenylene-bridged PMOs with the pore diameter up to 15.3 nm and the unit-cell parameter of 31.8 nm, which are higher than reported before.2 When 1.30 mL BTEB and 1 g of xylene was used, the structure can be identified as a face-centered cubic structure on the basis of SAXS (Figure 2.26). As the amount of xylene was increased from 1 to 2 g, the SAXS pattern become less resolved. TEM images (Figure 2.27) showed the presence of ordered domains. However, weakly ordered structures
were seen on the edges of the particles. The unit cell parameter (calculated under assumption of the face-centered cubic structure) increased from 28.3 nm to ~31 nm (Table 2.3).

Figure 2.26 Small-angle X-ray scattering patterns for calcined phenylene-bridged organosilica samples synthesized using different amounts of xylene as a swelling agent.
Figure 2.27 TEM images of calcined phenylene-bridged organosilicas synthesized with 1.30 mL of BTEB and (left) 1 g and (right) 2 g of xylene.
Table 2.3 Structural properties of PMOs synthesized using BTEB under different conditions$^c$

<table>
<thead>
<tr>
<th>Amount of BTEB (mL)</th>
<th>Temp (°C)</th>
<th>Amount of swelling agent (g)</th>
<th>a (nm)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{mic}$ (cm$^3$/g)</th>
<th>$w_{KJS}$ (nm)</th>
<th>$w_d$ (nm)</th>
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<td>31.8 (33.2)</td>
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<td>0.12</td>
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<td>0.38</td>
<td>0.10</td>
<td>15</td>
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</table>

$^c$Notation: Temp, Temperature; a, unit-cell parameter for calcined phenylene-bridged organosilicas calculated from (111) interplanar spacing (unit-cell parameter for as-synthesized sample is provided in parantheses); $S_{BET}$, BET specific surface area; $V_t$, total pore volume; $V_p$, primary mesopore volume; $V_{mic}$, micropore volume; $w_{KJS}$, pore diameter calculated using BJH-KJS method for cylindrical mesopores. $w_d$, pore diameter calculated using eq 1. $^a$ not calculated due to disordered structure; $^b$ not calculated due to the lack of the sufficient separation between the capillary condensation in primary mesopores and in secondary (interparticle) mesopores.
Nitrogen adsorption isotherms (Figure 2.28(a)) showed that the position of capillary condensation steps changes from ~0.80 to ~0.83, when the amount of xylene was increased to 2 g (or 4.6 g) in the reaction mixture. The position of the capillary evaporation step remained at a relative pressure of ~0.48-49, which was indicative of materials with cage-like pore structures, having pore entrances less than 5 nm. The specific surface area and total pore volume increased from 281 m$^2$/g to 461 m$^2$/g and 0.25 cm$^3$/g to 0.56 cm$^3$/g respectively. Pore size distributions were narrow and centered at 13 nm when 1 g of xylene was used. Pore size distributions became a little wider and were centered at ~15 nm, when amount of xylene was increased in the reaction mixture (Figure 2.28(b)), which is consistent with the SAXS results that suggested the increase in the unit-cell parameter. For the samples prepared with 2 and 4.6 g of the swelling agent, the adsorption branches of the isotherms did not level off after the capillary condensation in the uniform mesopores. This behavior suggested the presence of additional mesopores of diameter above ~20 nm. This conclusion is supported by the TEM images, which showed a rough surface and incomplete consolidation of the material, giving rise to the additional porosity of size larger than the size of the uniform mesopores.

$^{29}$Si CP MAS NMR spectra of the phenylene-bridged organosilica samples calcined at 250 °C under air featured well-resolved peaks corresponding to T sites (at -60,-70 and -80 ppm) with some Q sites peaks at around -100 ppm, which means that a fraction (presumably small) of Si-C bonds got cleaved during the surfactant removal via calcination (Figure 2.29).
Figure 2.28 (a) Nitrogen adsorption isotherms and (b) pore size distributions for phenylene-bridged organosilicas synthesized using different amount of xylene as swelling agent. For clarity, isotherms for samples prepared with 2 and 4.6 g xylene were offset vertically by 50 and 180 cm$^3$ STP g$^{-1}$, respectively.
Inability to form hollow spheres

Unlike in the case of a previously established synthesis in 2 M HCl solution, in 0.1 M HCl, when the relative amounts of BTEE, BTME and BTEB were decreased, there was no evidence of the formation of single-micelle-templated particles. TEM images showed the formation of aggregated structures even at very low relative amounts of BTEE, BTME and BTEB (Figures 2.5, 2.18 and 2.24). The conditions of moderate acid concentration may be unfavorable for the formation of single-micelle-templated nanoparticles, even though the particles with multiple pores form readily under these conditions. One possible reason is the association of PEO blocks with the hydronium ions under more strongly acidic conditions (2 M HCl) that causes stronger repulsion between particles and helps in formation of stable single-micelle-templated nanoparticles. Under the moderately acidic conditions (0.1 M HCl), the protonation of PEO
blocks may be too low, resulting in the lack of repulsive interactions between the particles that would hinder the particle aggregation.

2.4 Summary

Large-pore ethylene and phenylene-bridged periodic mesoporous organosilicas (PMOs) with face-centered cubic structures of spherical mesopores and, in some cases, with less well defined structures were synthesized at moderate acid concentration (0.1 M HCl) and low temperature. This approach was successful for ethylene-bridged PMO precursor BTEE that is less costly and more benign compared to BTME, which is required in hitherto known synthesis. Large pore diameters up to 22 nm and unit-cell parameter up to 44 nm were achieved when BTEE was used as an organosilica precursor. Some PMOs with phenylene-bridged framework had face-centered cubic structures but highest pore diameter of 15 nm and unit-cell parameter of 32 nm were achieved for materials with lower degree of structural ordering. Further lowering in temperature and judicious selection of a swelling agent and its content may yield even larger pore diameters and unit-cell parameters and/or higher degree of structural ordering.
References:


(7) Sing, K. S. Pure and applied chemistry 1985, 57, 603.


Chapter 3

Synthesis of Large-Pore Periodic Mesoporous Organosilicas with Unsaturated Bridging Groups

The work demonstrated in this chapter has been submitted to Microporous and Mesoporous Materials for publication.
3.1 Background

Periodic mesoporous organosilicas (PMOs) are a special class of ordered mesoporous silicas having organic moieties in the pore walls. The large surface areas, tunable pore sizes, well-defined structures and the presence of different organic groups makes them very attractive materials for various applications. Over the past few years, PMOs with different bridging groups such as methane, ethane, ethylene, phenylene, biphenylene, thiophene, etc., with different structures such as 2-dimensional hexagonal, 3-dimensional hexagonal (P6\textsubscript{3}mmc), cubic (Pm3n), body centered cubic (Im3n), face centered cubic (Fm3m), gyroidal structure, etc., have been synthesized. The presence of different organic groups presents an opportunity to facilely tailor various physical and chemical properties. Up to now, these materials have been studied for various potential applications, including low dielectric-constant materials, catalysis, light harvesting, drug delivery, environmental technology, etc.

Among the above mentioned PMOs, ethylene-bridged PMOs have been studied with keen interest primarily because of the unsaturated bridging groups (-Si-CH=CH-Si), that can be modified easily. Various studies have been conducted on the post-synthesis chemical modification of these PMOs and different functional groups have been introduced to improve their properties. Some of the potential applications of the ethylene-bridged periodic mesoporous organosilicas include their use as catalysts and adsorbents. Although the application area may be vast for these PMOs, limited studies have been conducted to synthesize large-pore ethylene-bridged PMOs. Some studies have been done on ethylene-bridged PMOs with cylindrical pores, but there are very few reports on ethylene-bridged PMOs with spherical mesopores.
A new strategy has been developed recently to synthesize large-pore periodic mesoporous organosilicas by decreasing both the synthesis temperature and acidic concentration.\textsuperscript{26,34} In particular, our research group used this strategy to synthesize large-pore ethylene-bridged PMOs with face-centered cubic structure at low temperature (7°C) and mild acid concentration (0.1 M HCl).\textsuperscript{26} Notably, this was the only published report of the ethylene-bridged PMOs with well-ordered face-centered cubic structure. The maximum pore sizes obtained were around 14 nm and unit-cell parameters were around 30 nm.

Herein, we report an easy method to further increase the pore size of ethylene-bridged PMO with face-centered cubic structure by adjusting the amount of the swelling agent in the reaction mixture. In the obtained materials, pore diameters can be tuned from 13 to 21 nm by adjustment of relative amount of the swelling agent, without the loss in the structural ordering. These findings are surprising, because the previous work on PMOs synthesized under more acidic conditions (2M HCl) showed little or no pore size increase with increase (doubling) of the quantity of the swelling agent in the synthesis mixture.

3.2 Experimental Section

3.2.1 Synthesis

The synthesis was similar to that described in Ref.,\textsuperscript{26} but instead of a single mass of the swelling agent, different masses were used in different trials. 0.5 g of Pluronic F127 (BASF) was dissolved in 30 mL of 0.1 M aqueous HCl solution at 7 °C under magnetic stirring until the whole polymer dissolved. Then 0.25 g (or 0.5, 1, 2, 4, 6 or 7 g) of xylene isomer mixture (Aldrich) and 2.5 g of KCl was added. After 2 hours, 1.73 mL of bis(triethoxysilyl)ethylene, BTEEn (Gelest) was added. The reaction mixture was stirred at 7 °C for 1 day in a covered
container. Then the whole solution was transferred to a polypropylene bottle and treated hydrothermally at 100 °C (or 130 °C) for 1 day. The resulting as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Finally, the material was either calcined at 350 °C under argon for 5 hours (heating ramp 2 °C/min) or extracted using 60 mL ethanol and 5 mL HCl to remove the surfactant.

### 3.2.2 Measurements

Nitrogen adsorption measurements were carried out on Micrometrics ASAP 2020 volumetric adsorption analyzer at -196 °C. The samples were outgassed at 140 °C in the port of the adsorption analyzer before the analysis. Small angle X-ray scattering (SAXS) patterns were recorded on Bruker Nanostar U SAXS/wide angle X-ray scattering (WAXS) instrument equipped with a rotating anode X-ray source and a 2-D detector Vantec 2000. The instrument was in a high flux configuration and the flight path was ~73 cm. Samples were placed in the hole of aluminium sample holder and secured on both sides using Kapton tape. Transmission electron microscopy (TEM) images were recorded on FEI Tecnai spirit microscope operated at an accelerating voltage of 120 kV. The samples were first sonicated in acetone and then deposited on a carbon-coated copper grid and the solvent was dried under air before the imaging.

$^{29}\text{Si}$ magic angle spinning (MAS) and cross-polarization (CP) MAS NMR experiments were carried out on a Varian INOVA 300 wide bore spectrometer. The operating frequency was 59.6 MHz. Samples were packed into a 5 mm zirconia rotor, loaded into a 5 mm Doty XC-5 CP/MAS probe and spun at 6-8 kHz. Total of 500-1000 scans were acquired based on the sensitivity of the sample. The recycle delay was 5 s, the contact time was 3 ms, and the 90° pulse was 4 ms. The chemical shift reference was 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS).
3.2.3 Calculations

The BET surface area ($S_{BET}$) was determined from nitrogen adsorption isotherm in the relative pressure range from 0.04 to 0.20. Total pore volume ($V_t$) was calculated from amount adsorbed at a relative pressure of 0.99. The micropore volume ($V_{mic}$) was determined using the $\alpha_s$ plot method in the standard reduced adsorption, $\alpha_s$, range from 0.9 to 1.2 using LiChrospher Si-1000 as a reference adsorbent. The sum of the primary mesopore volume ($V_p$) and the micropore volume was evaluated in the $\alpha_s$ range from 2 to 2.5. The mesopore volume was calculated by subtracting $V_{mi}$ from $V_{mi} + V_p$ calculated as mentioned above. Pore size distributions (PSDs) were calculated from adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method with KJS correction for cylindrical mesopores and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000. This method underestimates the diameter of spherical mesopores by ~2 nm in the considered pore size range. The pore diameter for most of the samples was also calculated using a geometrical relation introduced by Ravikovitch and Neimark for materials with face-centered cubic structures of spherical mesopores:

$$w_d = a \left( \frac{6}{\pi \nu} \frac{V_p \rho}{1 + V_p \rho + V_{mic} \rho} \right)^{1/3}$$ (1)

where $a$ is the unit-cell parameter calculated from position of (311) peak on the SAXS pattern, $\nu$ is the number of spherical mesopores in the unit cell (4 for fcc structure), and $\rho$ is the framework density. The framework density for ethylene-bridged PMOs was assumed to be 1.52 g cm$^{-3}$. 

"Chapter 3"
3.3 Results

Synthesis of large-pore ethylene-bridged PMOs

Ethenylene-bridged PMOs with variable amounts of xylene exhibited well-resolved SAXS patterns characteristics of the face-centered cubic structure (Figure 3.1). In the case of calcined samples, the unit-cell parameters can be increased from 27 to 40 nm, as the amount of xylene is increased from 0.25 to 4 g in the reaction mixture (Table 3.1). In this case, even when a higher mass of xylene was used (≤ 4 g), the structure was still very well-resolved with clear four peaks corresponding to the face-centered cubic structure. The hydrothermal treatment was also done at a higher temperature (130 °C), which resulted in a slight increase in the size of unit-cell parameter (Figure 3.1(b), Table 3.1). The unit cell parameter of as-synthesized materials was as large as 40.7 nm when 4 g of xylene was used. The unit-cell sizes obtained for the ethylene-bridged PMOs were much larger than those reported before in the literature. These results are unique because normally the use of higher amounts of a swelling agent results in larger pore sizes, but at the same time the structural ordering decreases considerably and in some cases, the pore geometry changes as well.

TEM images of the samples prepared with different quantities of the swelling agent are shown in Figure 3.2. In all cases, well-ordered structures were observed. Figure 3.2(b) and (d), as well as the lower right part of Figure 3.2(c) can be identified as [110] projections of the face-centered cubic (fcc) structure. Figure 3.2(f) appears to show [110] projection of the fcc structure with stacking faults characteristic of stacking sequences of 3-D hexagonal structure. Figure 3.2(e) and a top part of Figure 3.2(c) can be identified as [100] projections of the fcc structure. However, some parts of the samples appeared disordered (see for instance top of Figure 3.2(a)), which was minor for the samples prepared with higher quantities of xylene (2 g or more), but
more visible in the sample prepared using its lower quantity (1 g). The TEM images confirm that
the ordering has been preserved, or perhaps even enhanced, when larger quantities of the
swelling agent were present in the synthesis mixture. Also, some areas imaged by TEM (see
Figure 3.2(a), (b), (d) and (e)) were dark and no nanoscale structure could be discerned therein,
especially when a lower quantity of xylene was used, but mesopore structures were often
observed on the edges of the particles. The observation of disordered domains, which are quite
prominent in TEM images for the sample prepared with a lower quantity of the swelling agent (1
g), can be reconciled with a very well resolved SAXS pattern if one envisions that many large
ordered domains may be too thick to allow electrons to pass through them and be identified and
thus would render dark areas on TEM images 26

Figure 3.1 SAXS pattern for calcined ethylene-bridged PMOs synthesized using different
amounts of xylene hydrothermally treated at (a) 100 °C and (b) 130 °C.
Figure 3.2 TEM images of calcined ethylene-bridged PMOs synthesized using (a) 1, (b) 2, (c) 4, (d,e) 6 and (f) 7 g of xylene. The samples were hydrothermally treated at 100 °C.
Table 3.1 Structural properties of calcined ethylene-bridged PMOs synthesized using bis(triethoxysilyl)ethylene as a framework precursor under different conditions.\(^a\)

<table>
<thead>
<tr>
<th>Mass of xylene (g)</th>
<th>Hydrothermal treatment temperature (°C)</th>
<th>(a) (nm)</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_t) (cm(^3)/g)</th>
<th>(V_p) (cm(^3)/g)</th>
<th>(V_{\text{mic}}) (cm(^3)/g)</th>
<th>(w_{\text{KJS}}) (nm)</th>
<th>(w_d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>100</td>
<td>27.7 (30.6)</td>
<td>396</td>
<td>0.35</td>
<td>0.18</td>
<td>0.13</td>
<td>11.4</td>
<td>13.1</td>
</tr>
<tr>
<td>0.5</td>
<td>100</td>
<td>31.3 (33.2)</td>
<td>403</td>
<td>0.37</td>
<td>0.25</td>
<td>0.12</td>
<td>14</td>
<td>15.1</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>32.7 (36.3)</td>
<td>402</td>
<td>0.39</td>
<td>0.25</td>
<td>0.11</td>
<td>15</td>
<td>16.3</td>
</tr>
<tr>
<td>1</td>
<td>130</td>
<td>34.0 (37.0)</td>
<td>442</td>
<td>0.46</td>
<td>0.33</td>
<td>0.12</td>
<td>16.6</td>
<td>17.7</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>37.0 (40.8)</td>
<td>410</td>
<td>0.43</td>
<td>0.31</td>
<td>0.11</td>
<td>18</td>
<td>19.1</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>38.0 (42.7)</td>
<td>444</td>
<td>0.46</td>
<td>0.33</td>
<td>0.12</td>
<td>19.6</td>
<td>20.4</td>
</tr>
<tr>
<td>4</td>
<td>130</td>
<td>40.0 (42.4)</td>
<td>404</td>
<td>0.49</td>
<td>0.38</td>
<td>0.09</td>
<td>20.2</td>
<td>21.9</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>37.3 (41.8)</td>
<td>372</td>
<td>0.40</td>
<td>0.29</td>
<td>0.10</td>
<td>19.6</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>130</td>
<td>38.5 (42.7)</td>
<td>463</td>
<td>0.52</td>
<td>0.36</td>
<td>0.14</td>
<td>21.2</td>
<td>20.5</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>37.3 (42.4)</td>
<td>453</td>
<td>0.48</td>
<td>0.34</td>
<td>0.12</td>
<td>20.6</td>
<td>19.7</td>
</tr>
<tr>
<td>7</td>
<td>130</td>
<td>38.5 (43.7)</td>
<td>426</td>
<td>0.49</td>
<td>0.35</td>
<td>0.11</td>
<td>21.2</td>
<td>20.6</td>
</tr>
</tbody>
</table>

\(^a\) Notation: \(a\), unit-cell parameter for calcined ethylene-bridged sample calculated from (311) interplanar spacing (unit-cell parameter for as-synthesized sample is provided in parentheses); \(S_{\text{BET}}\), BET specific surface area; \(V_t\), total pore volume; \(V_p\), primary mesopore volume; \(V_{\text{mic}}\), micropore volume; \(w_{\text{KJS}}\), pore diameter calculated using BJH-KJS method for cylindrical mesopores. \(w_d\), pore diameter calculated using eq 1.
From the nitrogen adsorption isotherms, it was seen that all of these PMOs had the capillary condensation at a relative pressure ($p/p_o$) within 0.75-0.90 range and capillary evaporation at a relative pressure of 0.48-0.49, which is characteristics of large cage-like pores having entrances less than 5 nm (Figure 3.3(a)). It was seen that when 0.25 g of xylene was used, the sample exhibited a steep capillary condensation steps at a relative pressure of ~0.78. The position of capillary condensation step moved to higher relative pressures, as the swelling agent amount was increased from 0.25 to 4 g in the reaction mixture. The shift in the position of capillary condensation step corresponds to the increase in the sizes of the pores. A further increase in the amount of xylene above 4 g did not cause any major shift in the capillary condensation step, which is consistent with the SAXS data. A similar trend was seen when the samples were hydrothermally treated at 130 °C (Figure 3.4(a)). The hydrothermal treatment at a higher temperature resulted in a slight shift in the position of capillary condensation step to higher relative pressures. The specific surface area, total pore volume, primary mesopore volume and micropore volume derived from the adsorption isotherms are listed in Table 3.1. Also, it can be seen that there was a slight increase in the pore volume as the amount of xylene was increased (Table 3.1).

Pore size distributions (PSDs) derived from adsorption isotherms were narrow for all of these PMOs (Figure 3.3(b)). When 0.25 g xylene was used, the pore size was around 11 nm (as calculated using eq 1, the nominal BJH-KJS pore diameter was 13 nm) The increase in the amount of xylene in the reaction mixture results in a rise in the pore diameter, without much broadening of the pore size distribution peaks. The pore diameter can be tuned between 13 and 21 nm by adjusting the mass of xylene from 0.25 to 4 g. There was only a slight change in the pore diameter, as the amount of the swelling agent was increased beyond 4 g. PSDs for the
samples hydrothermally treated at 130 °C were also similar and showed an increase in the pore diameter as the mass of xylene increased from 1 to 4 g (Figure 3.4(b)). The results obtained from adsorption isotherms were consistent with the SAXS and TEM results.

As seen from the results, the increase in the amount of the swelling agent leads to the formation of PMOs with larger unit-cell sizes and pore sizes. It can be hypothesized that the uptake of the swelling agent by the micelles increases, as the amount of swelling agent is increased in the reaction mixture, leading to larger pore sizes and unit-cell parameters. When the concentration of the swelling agent was increased up to a certain level, a further increase becomes negligible. It should be noted that the increase in the pore volume (observed when the relative amount of swelling agent was increased) was rather small, suggesting that the increase in the uptake of the swelling agent by the micelle is not large. The magnitude of the pore volume (compared with the volume of the swelling agent used in the synthesis) suggests that in all cases considered here, an excess of the swelling agent was provided.
Figure 3.3 (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcined ethylene-bridged PMOs synthesized using different amounts of xylene and hydrothermally treated at 100 °C. For clarity, in (a), the isotherms were offset vertically by 150, 320, 475, 650, 850, and 975 cm$^3$ STP g$^{-1}$ for materials synthesized using 0.5, 1, 2, 4, 6, and 7 g of xylene, respectively.
Figure 3.4 (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcined ethylene-bridged PMOs prepared using 1.73 mL BTEEn and variable amount of xylene. The samples were hydrothermally treated at 130 °C. For clarity, in (a), the isotherms were offset vertically by 250, 450, and 700 cm$^3$ STP g$^{-1}$ for materials synthesized using 4, 6, and 7 g of xylene, respectively.

$^{29}$Si CP MAS NMR results for the samples calcined at 350 °C under argon display peaks around -65 and -80 ppm corresponding to the T$^2$ (C-Si(OSi)$_2$(OH)) and T$^3$ (C-Si(OSi)$_3$) sites. The spectra also had peaks corresponding to Q$^n$ sites (Si(OSi)$_n$(OH)$_{4-n}$) between 100 and 120 ppm, corresponding to Si-C bond cleavage (Figure 3.5). Alternatively, the extraction using 2M HCl and ethanol was done to remove the surfactant, which preserved the integrity of ethylene-bridging groups. In this case, peaks corresponding to T$^2$ and T$^3$ sites only were seen and there were little or no peaks corresponding to Q$^n$ sites (Figure 3.5). It is known from the previous studies the extraction may result in accessible mesopores and in preserving the integrity of the organic groups, but may not be effective for the complete removal of surfactant.
Figure 3.5 $^{29}\text{Si}$ CP MAS NMR spectrum for ethylene-bridged PMO synthesized using 7 g xylene and 1.73 mL BTEEn followed by calcination at 350 °C under argon. The sample was hydrothermally treated at 130 °C.

3.4 Summary

Ethenylene-bridged PMOs with very well ordered face-centered cubic structures were synthesized at moderate acid concentration (0.1 M HCl) and low temperature (7 °C). It was seen that the use of the swelling agent allows one to expand the pore diameter of the spherical mesopores, without the loss in the structural ordering. The role of the swelling agent in synthesis of ethylene-bridged PMOs has not been studied and this approach demonstrates a facile pathway of getting a range of pore sizes via adjustment of the swelling agent, without loss in structural ordering. The obtained results demonstrate a simple pathway to synthesize large-pore unsaturated-bridged PMOs, which may be extended to other PMOs prepared under similar conditions.
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Chapter 4

Synthesis of biphenylene-bridged periodic mesoporous organosilicas with high molecular-scale crystallinity and unique particle morphology.
4.1 Background

Ordered mesoporous silicas (OMS), first synthesized in 1992, have gathered great attention in the past couple of decades due to their exceptional properties.\(^1\) Over the few years, one of the major developments in this field was the synthesis of periodic mesoporous organosilicas (PMOs) which have organic group as the part of the pore walls.\(^2,3\) The progress in this field has led to synthesis of PMOs having various bridging groups, such as methylene,\(^4\) ethylene,\(^3,5\) ethenylene,\(^2,6\) phenylene,\(^7\) xyylene,\(^8\) biphenylene,\(^9\) thiophene\(^7.\) Many applications have been shown in the literature, including their use in catalysis,\(^10\) electronics,\(^11\) biotechnology,\(^12\) adsorption\(^13\) etc.

For the first time in 2002, Inagaki et al. reported a synthesis of phenylene-bridged PMO with crystal-like pore walls, that is, with periodic arrangement of organic bridging groups in the framework.\(^14\) Later the same research group also showed the synthesis of biphenylene-bridged PMOs with crystallinity in the pore walls.\(^9\) The research over the past decade has led to identification of other PMOs such as ethylene,\(^15\) naphthalene,\(^16\) divinylbenzene,\(^17,18\) divinylpyridine\(^19\) bridged materials with crystalline pore walls. These materials are attractive and have unique optical and electronic properties as well.\(^16,20,21\) It was initially hypothesized that basic conditions were required to achieve high degree of framework condensation and mostly alkylammonium surfactants were used for synthesis of these PMOs.\(^20\) A limitation of using short-chain alkylammonium surfactant is that the pore diameter of the templated materials is rather small (< 4 nm). Recently, there has been some success in the synthesis of the PMOs with crystalline pore walls under acidic conditions using amphiphilic block copolymer surfactants.\(^22,23\) Jaroniec et al. synthesized phenylene-bridged PMOs having moderate molecular scale crystallinity and large pore diameters (~8.7 nm) using Pluronic F127 surfactant under acidic...
Sayari et al. demonstrated the successful synthesis of biphenylene-bridged PMOs with moderately large pore sizes (~6 nm) using Pluronic P123 under acidic conditions. These PMOs had moderate molecular scale crystallinity and relatively low thermal stability as compared to biphenylene-bridged PMOs synthesized using alkylammonium surfactant. The reason of difficulty in achieving high degree of ordering may be that the hydrophilic block of the surfactant (PEO) may disrupt the atomic scale ordering based on periodic arrangements of the large aromatic bridging groups. It should be noted that typically the periodicity in these PMOs does not arise from π-π stacking of the aromatic bridging groups, but from these groups acting as spacers between the silica layers. Consequently, the repeating distance in the framework increases with distance between silicon atoms in the bis-silyl precursor.

Recently, low temperature and moderate acid concentration conditions were effectively used to demonstrate the synthesis of large-pore PMOs with different bridging groups. In our study, we have chosen these conditions to show the synthesis of large-pore biphenylene-bridged PMOs having high molecular scale crystallinity. The synthesized PMO displayed large pore sizes (8.7 nm) with periodic pore structures having the interplanar spacing around 14 nm. The PMOs also showed unique particle morphology arranged in the form of sheets, as verified by SEM and TEM. It should be noted that in the case of phenylene-bridged organosilane precursors, similar conditions did not render PMOs with high molecular scale crystallinity. The biphenylene-bridged PMOs showed excellent thermal stability at different calcination temperatures under various environments. Their thermal stability was found to be superior than that of ethenylene and phenylene-bridged PMOs synthesized under similar conditions.
4.2 Experimental Section:

4.2.1 Synthesis

The synthesis was carried out by dissolving 0.5 g of Pluronic F127 in 30 mL of 0.1 M HCl followed by magnetic stirring in a water/ice bath maintained at 0 °C. Then, 1 g of toluene or xylene (Aldrich) and 2.5 g of KCl were added. After 2 hours, 0.93 mL of 4,4′-bis(trithoxysilyl)-1,1′-biphenyl (BTEBP) (Aldrich) was added. For some of the reactions, the volume of BTEBP was varied from 0.58 to 1.50 mL, keeping all other conditions the same. The reaction mixture was stirred for 1 day in a covered container. Then, the whole solution was transferred to a polypropylene bottle and treated hydrothermally at 100 °C for 1 day. The resulting as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Finally, the material was calcined at 250 °C under air (or 350 °C under argon, or 300 °C under nitrogen) for 5 hours (heating ramp 2 °C/min) to remove the surfactant.

4.2.2 Measurements

Nitrogen adsorption measurements were carried out on Micrometrics ASAP 2020 volumetric adsorption analyzer at -196°C. The samples were outgassed at 140°C in the port of the adsorption analyzer before the analysis. Small angle X-ray scattering (SAXS) patterns were recorded on Bruker Nanostar U SAXS/wide angle X-ray scattering (WAXS) instrument equipped with a rotating anode X-ray source and a 2-D detector Vantec 2000. The instrument was in a high flux configuration and the flight path was ~73 cm. Samples were place in the hole of aluminum sample holder and secured on both sides using Kapton tape. Wide-angle XRD was recorded on a Rigaku MiniFlex II instrument with Cu Kα radiation. Transmission electron microscopy (TEM) images were recorded on FEI Tecnai G2 Twin microscope operated at an
accelerating voltage of 120 kV. The samples were first sonicated in ethanol and then deposited on carbon coated copper grid and subsequently the solvent was evaporated under air before the analysis. Cross- polarization magic angle spinning $^{29}$Si NMR spectra (CP MAS) were acquired using Varian INOVA 300 wide bore spectrometer. The operating frequency was 59.6 MHz. Samples were packed into a 5 mm zirconia rotor, loaded into a 5 mm Doty XC-5 CP/MAS probe and spun at 6–8 kHz. 1000-2000 scans were acquired based on the sensitivity of the sample. The chemical shift reference was 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS).

4.2.3 Calculations

The BET specific surface area ($S_{BET}$) was determined from a nitrogen adsorption isotherm in the relative pressure from 0.04 to 0.20. The total pore volume ($V_t$) was calculated from the amount adsorbed at a relative pressure of 0.99. The micropore volume ($V_{mic}$) was determined using the $\alpha_s$ plot method in the standard reduced adsorption, $\alpha_s$, range from 0.9 to 1.2 using LiChrospher Si-1000 as a reference adsorbent. Pore size distribution (PSD) was calculated from the adsorption branch of the nitrogen adsorption isotherm using the Barrett-Joyner-Halenda (BJH) algorithm with KJS correction for cylindrical mesopores and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000.

4.3 Results

Synthesis of biphenylene-bridged PMOs

WAXS pattern for the sample synthesized with 0.93 mL of BTEBP displayed five strong peaks at $\theta$ values of 7.4, 14.4, 22.3, 28 and 40.6° corresponding to the $d$-spacing values of 1.19, 0.60, 0.40, 0.32 and 0.22 nm (Figure 4.1). The values suggest a type of framework ordering reported earlier for PMOs with crystalline pore walls, that is, a sequence of silica layers separated by the
organic bridging groups with a d-spacing value of 1.19 nm. A similar WAXS pattern with distinct peaks was observed when the BTEBP volume was different from 0.93 mL (Figure 4.1). The WAXS pattern and the values observed here are very similar to the data reported by Inagaki et al.\textsuperscript{9}, in the case of biphenylene-bridged PMOs synthesized using alkylammonium surfactants. Methylene, ethylene and ethenylene-bridged PMOs reported under similar conditions do not show crystallinity in the pore walls, while phenylene-bridged PMO shows some broad peaks in WAXS pattern and thus a low to moderate crystallinity. A possible reason considered before is that the PEO (poly(ethylene oxide)) block of the amphiphilic block copolymer surfactant can interfere with the periodic arrangement of the aromatic bridging groups and thus disrupt the molecular scale periodicity in the structure. Due to the possibility of the presence of two separate phases: a mesoscopically ordered phase and a framework-ordered phase, such a conclusion may be premature, in our case.
Figure 4.1 WAXS patterns for calcined biphenylene-bridged organosilicas prepared using different volumes of BTEBP (per 0.5 g of F127) and 1 g of toluene.

SAXS patterns of biphenylene-bridged PMOs showed a peak at a much lower 2θ values corresponding to the mesoscale periodicity (Figure 4.2). As there was only peak in SAXS pattern, it is difficult to assign any structure. The d-spacing values calculated from SAXS were in the range 13.8-14.5 nm (Table 4.1) and were higher than the reported values in case of biphenelyene-bridged PMOs synthesized using alkylammonium and Pluronic P123 surfactant.14,23 TEM images showed the presence of mesopores, but the arrangement of mesopores was not clear and it is difficult to assign any particular structure (Figure 4.3). Interestingly, it was observed in TEM that the particles were very well-defined sheets. A further investigation of this by SEM also shows the presence of unique particle morphology in the form of sheets (Figure 4.4). The reason could be the presence of large biphenylene bridging groups in the pore walls and its capacity to form periodic wall structures readily, thus stimulating to
formation of well-defined particles with unique morphology. The interactions between the biphenylene-bridged precursor and the Pluronic F127 surfactant could also play a role in formation of such morphology, as this kind of arrangement was not seen in previous studies when the biphenylene-bridged PMOs were synthesized using ionic alkylammonium surfactants.\textsuperscript{14,23}

Figure 4.2 SAXS patterns for calcined biphenylene-bridged organosilicas prepared using different volumes of BTEBP (per 0.5 g of F127) and 1 g of toluene.
Figure 4.3 TEM images of calcined biphenylene-bridged organosilicas prepared using 0.93 mL BTEBP and 1 g of toluene (left) and 1 g of xylene (right).

Figure 4.4 SEM images of (left) as-synthesized and (right) calcined biphenylene-bridged organosilicas prepared using 0.93 mL BTEBP and 1 g of toluene.

Nitrogen adsorption isotherms of the calcined biphenylene-bridged samples synthesized using different volumes of BTEBP are shown in Figure 4.5(a). For all of the samples, there was a capillary condensation step at a relative pressure of ~0.68-0.71 and capillary evaporation at a
relative pressure of ~0.47. The capillary evaporation at a lower limit of adsorption-desorption hysteresis means that some entrances to the mesopores are below 5 nm. Pore size distributions (PSDs) of these organosilicas were narrow and pore sizes (at the maximum) were in between 8.1-8.8 nm (Figure 4.5 (b)). PMO prepared under similar conditions, but with a different swelling agent, (e.g. xylene) also showed a similar adsorption isotherm with a capillary condensation at a relative pressure of ~ 0.70 and the pore diameter around 8 nm (Table 4.1). It was seen that as the amount of BTEBP was decreased in the reaction mixture, there is a slight increase in the pore volume (Table 4.1). The pore volume and the specific surface area were not so high, which may be due to the large biphenylene-bridging groups and their ability to form thick walls. The other reason may be the interaction of the framework precursor with the micelles during the synthesis, which resulted in a limited volume of the micelle core in which the framework precursor did not condense. Alternatively, there might be some domains of non-surfactant-templated (and thus low-surface-area) organosilica in addition to surfactant-micelle-templated-domains.
Table 4.1. Structural properties of PMOs synthesized using BTEBp under different conditions\textsuperscript{a}

<table>
<thead>
<tr>
<th>Amount of BTEBp (mL)</th>
<th>Temp (°C)</th>
<th>Swelling agent</th>
<th>Amount of swelling agent (g)</th>
<th>d (nm)</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_t) (cm(^3)/g)</th>
<th>(V_p) (cm(^3)/g)</th>
<th>(V_{\text{mic}}) (cm(^3)/g)</th>
<th>(w_{\text{KJS}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>0</td>
<td>Toluene</td>
<td>1</td>
<td>13.8</td>
<td>200</td>
<td>0.14</td>
<td>0.09</td>
<td>0.05</td>
<td>8.2</td>
</tr>
<tr>
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<td>Toluene</td>
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<td>13.4</td>
<td>202.7</td>
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<td>0.11</td>
<td>0.05</td>
<td>8.8</td>
</tr>
<tr>
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<td>Toluene</td>
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<td>14.5</td>
<td>217.1</td>
<td>0.18</td>
<td>0.13</td>
<td>0.05</td>
<td>8.6</td>
</tr>
<tr>
<td>0.58</td>
<td>0</td>
<td>Xylene</td>
<td>1</td>
<td>14</td>
<td>246</td>
<td>0.19</td>
<td>0.14</td>
<td>0.05</td>
<td>8.2</td>
</tr>
<tr>
<td>0.93</td>
<td>0</td>
<td>Xylene</td>
<td>1</td>
<td>13.6</td>
<td>121</td>
<td>0.11</td>
<td>0.08</td>
<td>0.03</td>
<td>8.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Notation: Temp, Temperature; d, interplanar spacing for calcined at 250 °C under air or 350 °C under argon ethylene-bridged organosilicas synthesized with BTEBP; \(S_{\text{BET}}\), BET specific surface area; \(V_t\), total pore volume; \(V_p\), primary mesopore volume; \(V_{\text{mic}}\), micropore volume; \(w_{\text{KJS}}\), pore diameter calculated using BJH-KJS method for cylindrical mesopores.
Figure 4.5 (a) Nitrogen adsorption isotherms and (b) pore size distributions for calcined biphenylene-bridged organosilicas prepared using different volumes of BTEBP. For clarity, the isotherms for samples prepared using 1.30, 0.93 and 0.58 mL BTEBP were offset vertically by 20, 50 and 70 cm³ STP g⁻¹ respectively.
$^{29}$Si CP MAS NMR for biphenylene-bridged PMO samples calcined under different atmospheres and/or temperatures are shown in Figure 4.6. All the samples displayed peaks around -70 and -80 ppm corresponding to $T_2$ and $T_3$ sites, respectively. It was also seen that there were little or no peaks between -100 to -120 ppm ($Q_n$ sites) which suggests the absence of Si-C bond cleavage. One of the disadvantages of PMOs is their thermal stability, and their structure often is compromised during calcination at high temperatures. Calcined ethylene- and phenylene-bridged PMOs synthesized under similar conditions display major population of $Q_n$ sites (Figure 4.7), suggesting that biphenylene bridging groups are more thermally stable. Such PMOs with a higher thermal stability can be useful in different areas where high thermal stability is required, including the formation of closed-pore PMOs. The thermal stability in our case seems to be higher than that reported by Sayari et al. (where Pluronic P123 was used) and was comparable to what was seen in case of alkylammonium surfactants used as templates.

![Figure 4.6 $^{29}$Si CP MAS NMR spectra of biphenylene-bridged organosilicas synthesized using 0.93 mL BTEBP and calcined at different temperatures and environments.](image-url)
Figure 4.7 $^{29}$Si CP MAS NMR spectrum for ethylene (top) and phenylene (bottom) PMOs synthesized under similar conditions and calcined at either 250 °C under air or 350 °C under argon.

4.4 Summary

Biphenylene-bridged PMOs were synthesized using Pluronic F127 and toluene as a swelling agent under moderately acidic conditions and low temperatures. The resulting PMOs displayed high framework ordering and some meso scale periodicity similar to what was observed in case of alkylammonium surfactants. The PMOs had quite large pore diameters of 8.8 nm and d-spacing values of 14 nm. The PMOs also displayed higher thermal stabilities than the corresponding ethylene and phenylene-bridged PMOs synthesized under similar conditions.
References


Chapter 5

Synthesis of closed-pore mesoporous organosilicas by thermally induced pore closing.
5.1 Background

Since the discovery of ordered mesoporous silicas (OMSs) in 1992, they have been considered intriguing because of their unique properties.\textsuperscript{1,2} The progress in this field led to the development in the synthesis of mesoporous silicas modified with organic groups, also known as mesoporous organosilicas.\textsuperscript{3-6} Mesoporous organosilicas can be of two types: the so-called periodic mesoporous organosilicas (PMOs) having organic moieties as the bridging groups in the silica-like framework or the mesoporous silicas with pendant organic groups.\textsuperscript{3-6} For the latter, organosilicas prepared via one-pot synthesis method that involves mixing of silica and organosilica precursors may have some advantages in comparison to mesoporous silicas with organic groups introduced via post-synthesis modification because the former may have higher uniformity and higher loading of organic groups.\textsuperscript{7,8} Mesoporous organosilicas have an edge over ordered mesoporous silicas in many respects because of their higher surface hydrophobicity,\textsuperscript{8,9} hydrothermal stability,\textsuperscript{10,11} mechanical stability \textsuperscript{10,11} and lower dielectric constant.\textsuperscript{12} Because of their excellent properties, they have been evaluated in various applications such as environmental technology,\textsuperscript{13,14} catalysis,\textsuperscript{15} light harvesting\textsuperscript{16} and electronics.\textsuperscript{12}

Organosilicas with closed mesopores can be potential candidates as low dielectric constant materials and can have a lot of applications in electronics industry.\textsuperscript{12,17,18} Recently it was shown that in some cases, calcination can be used to transform mesoporous silica with cage-like mesopores having narrow entrances to silicas with closed mesopores, which involves closing (or narrowing) the connections between the mesopores.\textsuperscript{19,20} The thermally induced pore closing is applicable to silicas with spherical mesopores, and even with cylindrical mesopores. However, there was no success in thermally-induced closing the mesopores of bridged organosilicas without the degradation of the organic groups.\textsuperscript{19}
Herein, moderate-acid concentration and low-temperature conditions were used to synthesize mesoporous organosilicas using methyltriethoxysilane (CH$_3$-Si-(OC$_2$H$_5$)$_3$), (MTES). This precursor does not have a bridging organic group like ((R’O)$_3$Si-R-Si(OR’)$_3$ (where R’ is an alkyl, such as methyl or ethyl; R is the organic bridging group) type silanes, but it has a pendant methyl group. MTES has only three hydrolyzable groups that could participate in condensation of this precursor, whereas common alkoxy silanes of formula Si(OR’)$_4$, can form up to 4 crosslinks and bridged organosilanes can form up to 6 cross-links. R”-Si(OR’)$_3$ precursors (R” is the organic pendant group) are usually mixed with Si(OR’)$_4$ or ((R’O)$_3$Si-R-Si(OR’)$_3$) precursors to facilitate the formation of 3-D crosslinked frameworks.$^{21-23}$ It is rarely recognized that CH$_3$-Si(OR’)$_3$ precursors are actually capable of forming 3-D cross-linked frameworks on their own,$^{12}$ if conditions are appropriately selected. For this study, we have chosen MTES because of that and additionally because the pendant methyl groups are thermally stable.

Organosilicas with closed spherical mesopores templated by poly(ethylene oxide)-polystyrene (PEO-PS) block copolymers were reported earlier$^{12,24-26}$ and the shrinkage of PS block of the surfactant was claimed to be responsible for closing of the mesopores at higher temperature.$^{12}$ The methyl-functionalized silica that we synthesized had cylindrical mesopores that closed after the removal of surfactant, which indicates that the role of surfactant in closing the mesopores is not direct and the actual reason for closing the mesopores is the shrinkage of the structure at higher calcination temperature.
5.2 Experimental Section

5.2.1 Synthesis

0.5 g of Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) was dissolved in 30 mL of 0.1 M HCl at 7 °C under stirring for 1 hour. Then 1 g of xylene (isomer mixture), 2.5 g of KCl and 0.027 g of NH\textsubscript{4}F was added. After 2 hours, a selected volume of methyltriethoxysilane (MTES) (1, 1.25, 1.50 or 2 mL) was added. The reaction mixture was stirred at 7 °C for 1 day in a closed container. Then the whole solution was transferred to polypropylene bottle and treated hydrothermally at 100 °C for 1 day. The as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Then the resulting material was calcined at different temperatures (300, 350, 400 °C) under air or argon for 5 hours (heating ramp 2 °C/min).

5.2.2 Characterization

Small-angle X-ray scattering (SAXS) patterns were acquired on a Bruker Nanostar U SAXS/wide-angle X-ray scattering instrument with a 2-D detector Vantec-2000 and a rotating anode X-ray source. Samples were placed in a hole of a sample holder and secured from both sides with a Kapton tape. Transmission electron microscope (TEM) images were acquired on a Hitachi H-7500 operated at 120 kV at Institute for Basic Research in Development Disabilities (IBR), Staten Island and JEOL 2000FX instrument operated at 200 kV at Lehigh University, PA. Before imaging, samples were dispersed in ethanol under sonication and deposited on a carbon-coated copper grid. Nitrogen adsorption measurements at -196 °C were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the measurements, samples were outgassed at 140 °C under vacuum in a port of the analyzer. \textsuperscript{29}Si and \textsuperscript{13}C cross-polarization (CP) magic-angle spinning (MAS) NMR experiments were carried out on a Varian INOVA 300
wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 Tesla. The operating frequency for $^{29}$Si measurements was 59.6 MHz and it was 75.4 MHz for $^{13}$C measurements. The samples were packed into a 5 mm zirconia rotor and loaded into a 5 mm Doty XC-5 CP/MAS probe and spun at 6–8 kHz. A total of 300-1100 scans were acquired depending on the sensitivity of a given sample. The recycle delay was 3 s, the contact time was 3 ms for $^{13}$C and 2.3 ms for $^{29}$Si NMR measurements, and the 90° pulse was 4 ms. The chemical shift reference was 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS).

5.2.3 Calculations

The BET surface area ($S_{BET}$) was determined from nitrogen adsorption isotherm in the relative pressure from 0.04-0.20. The total pore volume ($V_t$) was calculated from amount adsorbed at a relative pressure of 0.99. The micropore volume ($V_{mic}$) was determined using the $\alpha_s$ plot method in the standard reduced adsorption, $\alpha_s$, range from 0.9 to 1.2 using LiChrospher Si-1000 as a reference adsorbent. The sum of the primary mesopore volume ($V_p$) and the micropore volume was evaluated in the $\alpha_s$ range from 2 to 2.5. The mesopore volume was calculated by subtracting $V_{mi}$ from $V_{mic} + V_p$ calculated as mentioned above. Pore size distributions (PSDs) were calculated from adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method with KJS correction for cylindrical mesopores and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000.

5.3 Results

Synthesis of methyl-functionalized silica using methyltriethoxysilane as precursor

Figure 5.1 shows SAXS patterns of organosilicas synthesized with different volumes of methyltriethoxysilane (MTES). The presence of one strong peak in the SAXS pattern suggested
the presence of an ordered structure, except for the lowest quantity of MTES (1 mL). The structure was the most ordered when the volume of the precursor used was 1.50 mL. Since the SAXS pattern had only one peak, it is difficult to assign the pore structure just based on it. The interplanar spacing (d) calculated from the first peak in the SAXS pattern is around 15 nm for the calcined samples and 16-17.3 nm for the as-synthesized samples (Table 5.1). TEM images for sample prepared with 1.50 mL of MTES and calcined at 300 °C under air showed the presence of channel-like structure, which suggests cylindrical mesopores arranged in a 2-D hexagonal structure (Figure 5.2).

**Figure 5.1** SAXS patterns for organosilicas prepared using different volumes of MTES precursor. The samples were calcined at 300 °C under air.
Nitrogen adsorption analysis showed the formation of a mesoporous structure with quite narrow pore size distribution (Figure 5.3). When the amount of MTES used is 1 mL, there was no pore accessibility, or the porous structure had not formed, as seen from the low adsorption capacity and featureless SAXS pattern. When the amount of MTES was increased to 1.25 mL, the capillary condensation was observed at a relative pressure of ~0.80. As the amount of precursor was further increased to 1.50 mL, the capillary condensation step was also observed. When using 2 mL of MTES, the height of capillary condensation step decreased, which corresponds to a decrease in the accessible pore volume while the pressure of capillary condensation remained essentially the same (Figure 5.3(a)). For all the samples, low pressure hysteresis was observed below the relative pressure of 0.40, which suggests that either nitrogen molecules had difficulty with diffusing into some mesopores (because the diffusion was slow) or the framework underwent a distortion during the adsorption process, or both. Higher amounts of MTES used in the reaction mixture (1.25-2 mL) resulted in narrow pore size distribution with pore diameter in
the range of 9.5-10.5 nm (Figure 5.3(b)). The specific surface areas ($S_{\text{BET}}$) of the calcined organosilicas were 48-142 m$^2$ g$^{-1}$, total pore volumes ($V_t$) were between 0.05-0.14 cm$^3$ g$^{-1}$, and the primary mesopore volume ($V_p$) were 0.03-0.11 cm$^3$ g$^{-1}$. 

Table 5.1 Structural parameters of mesoporous organosilicas synthesized with methyltriethoxysilane (MTES) at different conditions.$^a$

<table>
<thead>
<tr>
<th>Amount of MTES (mL)</th>
<th>Calcination conditions</th>
<th>d (nm)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{mic}$ (cm$^3$/g)</th>
<th>$w_{KJS}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>300 °C Air</td>
<td>15.6 (17.3)</td>
<td>71</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>10.3</td>
</tr>
<tr>
<td>1.50</td>
<td>15 (16)</td>
<td>142</td>
<td>0.14</td>
<td>0.11</td>
<td>0.03</td>
<td>9.6</td>
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</tr>
<tr>
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<td>15.2 (16.2)</td>
<td>109</td>
<td>0.11</td>
<td>0.08</td>
<td>0.02</td>
<td>10.6</td>
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<tr>
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<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>300 °C Air</td>
<td>15(16)</td>
<td>142</td>
<td>0.14</td>
<td>0.11</td>
<td>0.03</td>
<td>9.6</td>
</tr>
<tr>
<td>400 °C Argon</td>
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<td>246</td>
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<td>0.21</td>
<td>0.05</td>
<td>11.2</td>
<td></td>
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<tr>
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<tr>
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<td>18</td>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>300 °C Air +</td>
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<td>14</td>
<td>-</td>
<td>-</td>
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<tr>
<td>400 °C Argon</td>
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</tbody>
</table>

$^a$Notation: d, interplanar spacing for calcined methyl-functionalized organosilicas (interplanar spacing for as-synthesized sample is provided in parantheses); $S_{BET}$, BET specific surface area; $V_t$, total pore volume; $V_p$, primary mesopore volume; $V_{mic}$, micropore volume; $w_{KJS}$, pore diameter calculated using BJH-KJS method for cylindrical mesopores.
Figure 5.3 (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcined organosilicas using different amounts of MTES as an organosilica precursor. The samples were calcined at 300 °C under air.

**Thermally-induced mesopore closing**

For the purpose of making the mesopores inaccessible (closed mesopores), the sample synthesized with 1.50 mL MTES was chosen. This sample was then subjected to calcination at different temperatures under different environments. Figure 5.4 shows the nitrogen adsorption isotherms and pore size distributions of these samples. For the sample calcined at 400 °C under argon, the position of capillary condensation was at a relative pressure of ~0.76 and this sample had the highest total pore volume ($V_t$) of 0.26 cm$^3$g$^{-1}$ and specific surface area ($S_{BET}$) of 246 m$^2$ g$^{-1}$ (Table 5.1). The pore diameter of this sample was 11.2 nm, which was slightly higher than that of other samples, which may be due to the effective removal of surfactant under these conditions (Figure 5.4(b)). When the sample was calcined at 300 °C under air, the capillary
Chapter 5

condensation pressure was almost the same (relative pressure of ~0.79), but the total pore volume ($V_t$) was 0.14 cm$^3$/g and the specific surface area ($S_{BET}$) was 142 m$^2$/g. The pore diameter was slightly lower (~9.6 nm) (Figure 5.4(b)). When the sample was calcined at 350 °C under air, the position of the capillary condensation step remained almost the same, but the height of the capillary condensation steps decreased considerably. The total pore volume and the specific surface area also decreased (see Table 5.1). This could mean that the mesopores started to become inaccessible at the higher temperatures. To further evaluate this, the as-synthesized materials were calcined at even higher temperatures. When the same sample was calcined at 400 °C under air, there was no nitrogen uptake (as seen on the adsorption isotherms in Figure 5.4). Similar result was observed when the sample was first calcined at 300 °C under air followed by calcination at 400 °C under argon (Figure 5.4(a)). These results indicate possibly two things: either the closing of the pore entrances (micropores) in the framework or the collapse of the structures at higher temperatures.

TEM images for the sample calcined at 300 °C under air (Figure 5.1) and 400 °C under argon (Figure 5.5(a)) clearly showed the pattern of parallel stripes, which confirmed the presence of mesopores, presumably cylindrical and arranged in 2-D hexagonal structure. TEM images for the sample calcined at 300 °C under air followed by calcination at 400 °C under argon also shows the presence of ordered structures with channel-like domains, which confirms that the structure was still intact while the mesopores have been closed (Figure 5.5(b)).

SAXS patterns (Figure 5.6) of these samples showed that the mesoporous organosilicas calcined at 300 °C under air or 400 °C under argon had presumably ordered structures with d-spacing around 15 nm. When the sample was calcined at 300 °C under air followed by calcination at 400 °C under argon, there was shrinkage in the unit-cell, as d-spacing value decreased from 15.3 nm
to 13.5 nm. In the case when the as-synthesized sample was calcined at 400 °C under air, the d-spacing value was reduced to 12.5 nm. In all of these cases, there was one peak on the SAXS pattern, which suggests that the structure did not collapse. Combining all the results, it can be concluded that the calcination at a higher temperature did not result in the collapse of the structure, but it caused the shrinkage of the structure, which resulted in closing of the pore entrances (micropores in the framework) or reduction in their size below the size of N₂ molecule (see Scheme 5.1).

**Figure 5.4** (a) Nitrogen adsorption isotherms and (b) pore size distributions of methyl-functionalized organosilicas synthesized using 1.5 mL of MTES and calcined at different temperatures.
Figure 5.5 Transmission electron microscopy images of organosilicas prepared using 1.5 mL MTES and calcined at 400 °C under argon (a) and 300 °C under air followed by 400 °C under argon (b).

Figure 5.6 Small-angle X-ray scattering patterns of methyl-functionalized organosilicas synthesized using 1.5 mL of MTES and calcined at different temperatures.
Scheme 5.1 Mechanism of thermally-induced pore closing in ordered mesoporous organosilicas.

Figure 5.7 $^{29}$Si CP MAS NMR spectra of methyl-functionalized organosilicas synthesized using 1.5 mL of MTES and calcined under different conditions.

$^{29}$Si CP MAS NMR studies revealed that samples calcined at 300 °C, 350 °C under air or 400 °C under argon have $T_3$ sites ($H_3C-Si(OSi)_3$) and there are no peaks corresponding to the $Q_n$ sites.
(Si(OSi)\textsubscript{n}(OH)\textsubscript{4-n}), where n=0-4, which would reveal the Si-C bond cleavage (Figure 5.7). For the sample calcined at 300 °C air followed by calcination at 400 °C under argon, there are T\textsubscript{3} sites, but no Q\textsubscript{4} sites, which combined with the pore inaccessibility determined above suggests a successful synthesis of closed-pore organosilica with intact organic groups. However, for the sample calcined at 400 °C under air, there were T\textsubscript{3} sites along with a small fraction of Q\textsubscript{4} sites (Si(OSi)\textsubscript{4}) which suggests that some Si-C bonds have been cleaved during calcination. 13C CP MAS NMR spectra of all of these samples had one sharp peak around -3.7 ppm, corresponding to the carbon atoms for methyl groups attached to Si atom (Figure 5.8). This indicates that the organic group (-CH\textsubscript{3}) is either present or absent, that is, it did not undergo any chemical conversion while remaining in the material.

**Figure 5.8** 13C CP MAS NMR spectrum of methyl-functionalized organosilica synthesized using 1.5 mL of MTES and calcined at 300 °C under air.

**5.4 Summary**

Novel organosilicas with pendant methyl groups were facilely synthesized at moderate acid concentration (0.10 M HCl) and low temperature (7 °C). The organosilicas had good structural
ordering of parallel cylindrical mesopores. The pore diameters of the organosilicas were 9-11 nm. Thermally-induced mesopore closing was achieved by calcining the samples at higher temperatures. More importantly, a selection of a proper mode of calcination (300 °C air, 400 °C argon) did not result in the cleavage of the organic groups, and thus the integrity of the organic groups was preserved during the pore closure process.
References


Chapter 6

Grafting of poly(N-isopropylacrylamide) brushes on the surface of cylindrical mesopores of periodic mesoporous organosilica via atom transfer radical polymerization
6.1 Background

Surfactant-templated nanoporous silica materials are considered alluring since their discovery in 1992.\textsuperscript{1,2} The materials have high surface areas, large pore volumes and diameters tunable in the mesopore range.\textsuperscript{3} They have been studied for various applications in targeted drug delivery,\textsuperscript{4} encapsulation of biomolecules,\textsuperscript{5} environmental technology,\textsuperscript{6,7} catalysis\textsuperscript{8,9} etc. Among the different nanoporous materials, periodic mesoporous organosilicas (PMOs) are particularly attractive because organic groups are present as the part of the pore walls (-Si-R-Si-).\textsuperscript{10,11} The presence of organic moieties in the pore walls allows for adjustment of physical and chemical properties. These materials have higher surface hydrophobicity,\textsuperscript{12} higher hydrothermal stability\textsuperscript{13} and lower dielectric constant\textsuperscript{14} as compared to ordered mesoporous silica (OMS) materials. Up to now, PMOs have been explored in different avenues and they also have diverse potential applications in areas including light harvesting,\textsuperscript{15} biotechnology,\textsuperscript{16} and electronic materials.\textsuperscript{17}

The pore surface of the surfactant-templated silicas, such as SBA-15 and FDU-1, have been successfully grafted with different polymers of high loading.\textsuperscript{18,19} Polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(N-isopropylacrylamide) (PNIPAAm) and poly(2-(dimethylamino)ethyl methacrylate) (PDAEMA), etc., have been grafted on these silica materials.\textsuperscript{18,20} The grafting of polymers inside the nanopores can foster their applications and improve the stability of the materials.\textsuperscript{20} To the best of our knowledge, similar studies on periodic mesoporous organosilicas (PMOs) have not been conducted so far. There are several parameters that can be critical for this study: 1) the pore diameter should be large, preferably well above 10 nm; 2) the size of the entrances to the mesopores (or pore windows) should be large enough so that the mesopores will not get blocked easily; 3) The stability of the bridging organic groups should be maintained during the grafting process; and 4) the PMO surface should be susceptible
to the modification with the initiator and should not scavenge copper species (crucial component of ATRP catalyst) or radicals.

In our study, we chose methylene-bridged PMO for the surface-initiated atom transfer radical polymerization via activators regenerated by electron transfer (ARGET ATRP). Methylene-bridged PMOs are known to have high thermal stability and additionally their chemical and dimensional stability can be enhanced by grafting different polymers. Our group recently reported the synthesis of large-pore methylene-bridged PMOs with adjustable pore entrances, which may be critical for grafting the macromolecules inside the nanopores. ARGET ATRP technique was chosen because of its advantage, including the low concentration of copper catalyst (<50 ppm) and no need for airtight glassware, in contrast to conventional ATRP. Different polymers can be chosen for grafting polymers from the surface of PMOs. In our study, we chose PNIPAAm because it is the most studied thermo-responsive polymer and it displays LCST in water around 32 °C, which is very close to the human body temperature. PNIPAAm has good biocompatibility and has been studied extensively for drug delivery and other biological applications.

6.2 Experimental section

6.2.1 Materials

Methylene-bridged organosilica was synthesized according to the earlier work. 1.2 g of Pluronic P123 was dissolved in 42 mL of 1.3 M HCl. After the surfactant dissolved, the reaction mixture was moved to a refrigerated water bath set at 15 °C. Then after 2 hours, 6.5 mL of cyclohexane and 3.43 mL of 1,2-bis(triethoxysilyl)methane (BTEM) was added. The reaction mixture was stirred for one day and then the whole solution was transferred to a Teflon-coated
autoclave and heated at 150° C for 2 days. The resulting as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Finally, the material was calcined at 300 °C under air for 5 hours (heating ramp 2 °C/min). N-(isopropylacrylamide) was purified by passing through a column filled with basic alumina. The ligand tris[(2-pyridyl)methyl]amine (TPMA) was acquired from ATRP Solutions, Inc. and was used as received. The initiator, 3-(chlorodimethylsilyl)propyl 2-bromo(isobutyrate (BiB), was synthesized and grafted to the surface of the organosilica, followed by the surface modification with trimethylchlorosilane according to the procedure discussed elsewhere. Copper (II) chloride and tin (II) ethylhexanoate (Sn(EH)₂) were used as received.

6.2.2 Synthetic Procedures

Surface-initiated ARGET ATRP of NIPAAm was carried out in a similar procedure mentioned elsewhere. Initiator-modified organosilica (30 mg, with 0.013 mmol initiator), NIPAAm monomer (160 mg, 1.41 mmol), a premixed solution of CuCl₂ (0.048 mg, 0.00036 mmol) and tris[(2-pyridyl)methyl]amine (0.96 mg, 0.0033mmol) in anisole (0.24 mL) and anisole (3.30 mL) were added into a ~5 mL glass vial. The vial was closed with a rubber septum and the mixture was stirred for 20 min before injecting a solution of the reducing agent, Sn(EH)₂ (51 mg, 0.126 mmol) in anisole (0.3 mL). The molar ratio of the components in the mixture was as follows: initiator : Cu(II) : TPMA : NIPAAm = 1 : 0.028 : 0.25 : 108. The mixture for polymerization of NIPAAm was heated in an oil bath at 40 °C. The polymerization was terminated by opening the vial and exposing the copper catalyst to oxygen from the air. The polymer/organosilica composite was recovered by filtration, washed with tetrahydrofuran (THF), acetone and methanol, and finally dried in a vacuum oven.
6.2.3 Characterization

Small-angle X-ray scattering (SAXS) patterns were acquired on a Bruker Nanostar U SAXS/wide-angle X-ray scattering instrument with a 2-D detector Vantec-2000 and a rotating anode X-ray source. Samples were placed in a hole of a sample holder and secured from both sides with a Kapton tape. Nitrogen adsorption measurements at -196 °C were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the measurements, samples were outgassed at 80 °C under vacuum in a port of the analyzer. Thermogravimetric analysis (TGA) was done under air with 10 °C min\(^{-1}\) ramping rate to 800 °C on Hi-Res 2950 thermogravimetric analyzer from TA Instruments. Molecular weight distributions were determined by gel permeation chromatography (GPC) on Tosoh EcoSEC HLC-8320GPC with refractive index detector and polystyrene standards. The cleavage of polymers from nanoporous organosilica was done using HF as mentioned elsewhere.\textsuperscript{18}

6.3 Results

Methylene-bridged periodic mesoporous organosilica (m-PMO) with large pore diameter and 2-D hexagonal structure was used as supports to graft the temperature- responsive polymer poly(N-isopropylacrylamide). The surface of the PMO was first modified with ATRP initiator, that is, 3-(2-bromoisobutyryloxy)propyltrimethylsilyl (BiB) groups and then with trimethylsilyl (TMS) groups. The obtained initiator modified PMO (m-PMO-BiB-TMS) was placed in glass vial to which monomer (N-isopropylacrylamide), copper (II) chloride, ligand (tris (2-pyridylmethyl)amine) (TPMA) and solvent (anisole) were added (Scheme 6.1).

The successful grafting of the initiator was confirmed by thermogravimetry analysis (TGA), that showed weight loss around 14 wt. % which was much higher than the weight loss of the
unmodified PMO (Figure 6.1). Also, there was a peak on FTIR spectrum around 1720 cm\(^{-1}\) corresponding to the C=O stretching in the initiator (BiB) (Figure 6.2). Moreover, it was seen from the nitrogen adsorption that the specific surface area as well as the pore volume decreased when the BiB and TMS groups were attached. From SAXS, peaks corresponding to 2-D hexagonal structure were seen (Figure 6.3).

Table 6.1 Structural parameters of materials.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization Time</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_t) (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-PMO</td>
<td>-</td>
<td>734</td>
<td>1.49</td>
<td>27.5</td>
</tr>
<tr>
<td>m-PMO-BiB-TMS</td>
<td>-</td>
<td>479</td>
<td>1.08</td>
<td>27.4</td>
</tr>
<tr>
<td>m-PMO-PNIPAAm 12%</td>
<td>3</td>
<td>245</td>
<td>0.64</td>
<td>25.2</td>
</tr>
<tr>
<td>m-PMO-PNIPAAm 16%</td>
<td>4</td>
<td>232</td>
<td>0.59</td>
<td>24.9</td>
</tr>
<tr>
<td>m-PMO-PNIPAAm 19%</td>
<td>7</td>
<td>221</td>
<td>0.52</td>
<td>22.5</td>
</tr>
<tr>
<td>m-PMO-PNIPAAm 35%</td>
<td>14</td>
<td>71</td>
<td>0.22</td>
<td>22.2</td>
</tr>
</tbody>
</table>

\(^a\)Notation; \(S_{\text{BET}}\), BET specific surface area; \(V_t\), total pore volume; pore diameter was calculated using BJH-KJS method for cylindrical mesopores, which is known to lead to an overestimation of the pore diameter.
Scheme 6.1 Grafting of poly(N-isopropylacrylamide) in the cylindrical mesopores of methylene-bridged organosilica using activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP).
**Figure 6.1** Weight change patterns under air for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).

**Figure 6.2** FTIR spectra for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composite is indicated in wt.%).
Figure 6.3 SAXS patterns for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).

Nitrogen adsorption isotherms (Figure 6.4) showed that as the polymer loading inside the nanopores increased, the specific surface area and pore volume decreased systematically (Table 6.1). For instance, the BET specific surface area decreased from 479 m$^2$/g, in the case of initiator-modified periodic mesoporous organosilica (m-PMO-BiB-TMS) to ~ 71 m$^2$/g, in the case where the polymer loading was 35%. Similarly, the pore volume decreased from ~1 cm$^3$/g (m-PMO-BiB-TMS) to 0.22 cm$^3$/g (m-PMO-PNIPAAm 35%). In all cases, even when the polymer loading was very high (~35 wt %), the mesopores were still accessible. Pore size distributions (PSDs) show that the pore diameter also decreased quite systematically, when the polymer loading was increased (Figure 6.5). The thicknesses of the polymer layer estimated from
the pore diameter decrease were 1.1, 1.2, 2.4, 2.6 nm for 12, 16, 19 and 35 wt.% PNIPAAm, respectively.

The successful grafting of the PNIPAAm was confirmed by FTIR spectroscopy. The FTIR spectra of m-PMO PNIPAAm 35 % show peaks around 1540 and 1640 cm$^{-1}$ corresponding to the amide I (C=O) and amide II (N-H) from PNIPAAm polymer$^{20}$ (Figure 6.2). Similarly, as observed in SBA-15/PNIPAAM composites reported earlier, two bands corresponding to the isopropyl groups at 1385 and 1370 cm$^{-1}$ were observed and strong features corresponding to C-H bending absorption bands of CH$_2$ were observed at 1460 cm$^{-1}$. 
**Figure 6.4** Nitrogen adsorption isotherms for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).

**Figure 6.5** Pore size distributions for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of n-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).
$^{13}$C CP MAS NMR of m-PMO had a peak around 0 ppm corresponding to the methylene carbons. For the m-PMO-PNIPAAm composite, in addition to peak at 0 ppm, there were peaks at 22 and 42 ppm, which correspond, respectively, to the methyl carbons and the carbons attached to the nitrogen in the isopropyl groups of PNIPAAm\(^{20}\) (Figure 6.6), which further confirms the successful grafting of PNIPAAm on the surface of PMO. $^{29}$Si CP MAS NMR spectrum of the methylene-bridged PMO showed peaks around -61 and -69 ppm corresponding to the $T_2[\text{SiC(OH)(OSi)}_2]$ and $T_3[\text{SiC(OSi)}_3]$ sites. No peaks corresponding to Q sites were observed, implying the absence of Si-C bond cleavage. Similarly, after the modification with the ATRP initiator (BiB-TMS) groups and PNIPAAm, peaks corresponding to $T_3$ sites were observed and there were little or no peaks corresponding to Q sites (Figure 6.7).

![Figure 6.6](image)

**Figure 6.6** $^{13}$C CP MAS NMR spectra for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).
Figure 6.7 $^{29}$Si CP MAS NMR spectra for methylene-bridged periodic mesoporous organosilicas before and after attachment of initiation sites and polymerization of N-isopropylacrylamide (loading of PNIPAAm in the composites is indicated in wt.%).

Figure 6.8 TEM image for methylene-bridged periodic mesoporous organosilicas grafted with poly(N-isopropylacrylamide) (loading of 35 wt.% PNIPAAm).
SAXS patterns show that the structure was intact after the polymerization. SAXS patterns of the m-PMO-PNIPAAm composites exhibited (100) peak and a broad feature related to unresolved (110) and (200) peaks corresponding to ordered 2-D hexagonal structure (Figure 6.3). The positions of the peaks did not change much when compared to m-PMO and m-PMO-BiB-TMS. It was seen that (110), (200) feature got slightly broader with grafting of PNIPAAm polymer. TEM image of m-PMO- PNIPAAM composite shows the presence of an ordered structure with channel like domains, which suggests the pores arranged in 2-D hexagonal structure. The results obtained from TEM also confirm that the pore structure was still intact after the polymerization.

Table 6.2 Structural parameters of PMOs grafted with PNIPAAm.b

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Time (hrs)</th>
<th>Polymer loading (%)</th>
<th>( M_n )</th>
<th>PDI</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-PMO-PNIPAAm 19%</td>
<td>7</td>
<td>19</td>
<td>3173</td>
<td>1.27</td>
<td>28</td>
</tr>
<tr>
<td>m-PMP-PNIPAAm 35%</td>
<td>14</td>
<td>35</td>
<td>4263</td>
<td>1.48</td>
<td>37</td>
</tr>
</tbody>
</table>

bNotation: \( M_n \), number average molecular weight of the polymer; PDI, polydispersity index; DP, degree of polymerization.

In the case of m-PMO PNIPAAm 19% and m-PMO-PNIPAAm 35%, the polymers were cleaved from the surface using HF and then were characterized by GPC (Figure 6.9). The molecular weights obtained were 3173 and 4263 g/mol for the loading of 19% and 35 wt.% respectively. The degree of the polymerization (DP) achieved inside the nanopores was also significant. The increase in the molecular weight with the increase in polymerization time is a proof of the
controlled growth of the polymer inside the nanopores. Polydispersity indexes (PDIs) were 1.27 and 1.48 when the polymer loading was 19% and 35%, respectively (Table 6.2). PDI obtained was higher as compared to the normal ATRP, but in line with those observed in ARGET ATRP in the mesopores of ordered silicas. This report is the first example where the controlled growth of a polymer was achieved in the nanopores of a PMO.

![Graph showing normalized intensity vs retention time for m-PMO-PNIPAAm 19% and m-PMO-PNIPAAm 35%](image)

**Figure 6.9** Gel permeation chromatography (GPC) molecular weight distributions for PNIPAAm cleaved from the surface of m-PMO/PNIPAAm composites.

### 6.4 Summary

ARGET ATRP, an eco-friendly approach, was successfully used to graft thermo-responsive poly(N-isopropylacrylamide) inside the nanopores of methylene-bridged periodic mesoporous organosilicas. The loading of the polymer can be controlled systematically by adjusting the polymerization times. Quite high molecular weights of the polymers (~ 4263 g/mol) with
significant degree of polymerization (~37) was achieved without blocking of the nanopores. The study demonstrates that ATRP in general and ARGET ATRP in particular is a facile and powerful tool for grafting polymers on the surface of the PMOs.
References.


(18) Cao, L.; Kruk, M. Polymer Chemistry 2010, 1, 97.


(23) Jochum, F. D.; Theato, P. Chemical Society Reviews 2013, 42, 7468.


Chapter 7

Grafting of poly[(oligoethylene glycol) methacrylate] brushes on the surface of cylindrical mesopores of ordered silica via atom transfer radical polymerization with activators regenerated by electron transfer
7.1 Background

Nanoporous materials, such as ordered mesoporous silicas, have been studied extensively because of their interesting characteristics. The excellent features of these materials include high surface areas and tunable pore sizes with good dimensional stability. Some of the well-studied mesoporous silica materials include MCM-41, MCM-48, SBA-15, FDU-12, and KIT-6 type materials. SBA-15 is a good example of mesoporous silica material in which the pore volume, surface area and pore diameter can be tuned facilely. Also, the mesoporous silica materials have the pore connectivity (or pore window) size tunable in a wide range, which helps in the encapsulation of nanoparticles and biomolecules.

Surface functionalization of mesoporous silica materials is often beneficial in applications in different areas, such as environmental technology, catalysis, targeted drug delivery, encapsulation of various biomolecules, etc. The silica surface can be grafted with various polymers that can improve its chemical stability, adsorption and catalytic properties. Besides this, stimuli-responsive polymers can be introduced in the mesopores, which can be used in various applications, such as biotechnology chromatography packing columns, enzyme encapsulation, etc.

There are different methods to graft polymers, such as physical adsorption, as well as “grafting to” and “grafting from” approaches. Grafting of polymers on concave surfaces of mesoporous hosts can be challenging as the entrances to the mesopores can be less than 10 nm in size and can get blocked by the polymer graft. The physical adsorption of polymer may result in poor polymer loading and also does not prevent the leaching of the polymer. “Grafting to” method, in which the preformed polymer is attached to the surface, can be a good approach to load polymers, but can also offer limitations, such as low grafting density due to the steric
hindrance between the polymer chains.\textsuperscript{32-34} Surface-initiated ‘grafting from’ approach is often a more suitable method to attach polymers onto the concave surface of nanopores with high polymer loading and higher graft density.

Different polymerization techniques can be used for polymerization via ‘grafting from’ approach.\textsuperscript{25,28,29,35,36} In particular, controlled radical polymerization techniques such as surface-initiated atom transfer radical polymerization (ATRP) can be advantageous because of its robustness and the ability to control the molecular weight of the polymer.\textsuperscript{36} Some studies indicate their successful use in grafting polymers inside the mesoporous silica.\textsuperscript{36} One disadvantage of this technique is that the end products may be contaminated with copper catalyst, and this may cause further problem especially if the products are to be used in biological applications. Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) is a recent advancement in ATRP, in which the excess amount of reducing agent is used in the reaction to constantly regenerate Cu\textsuperscript{I} species (ATRP activator) from Cu\textsuperscript{II} species, otherwise formed irreversibly during the termination process or action of residual oxygen. Therefore, the copper catalyst concentration is usually below 50 ppm in ARGET ATRP and the reactions can be done without airtight glassware. Environmentally friendly chemicals, such as tin (II) ethylhexanoate and ascorbic acid can be used as reducing agents in the reaction.

Recently, our group used SBA-15 materials to graft different polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(N-isopropylacrylamide) (PNIPAAm) and poly(2-(dimethylamino)ethyl methacrylate) (PDAEMA) via surface-initiated ARGET ATRP method.\textsuperscript{28,29} The results showed a good control of the molecular weight of polymers with quite low polydispersity index grafted on the surface of nanopores. However, the grafting of the
temperature-responsive polymers, such as poly[(oligoethyleneglycol) methacrylate] on the surface of nanoporous silica has not been studied, even though its shorter side-chain variant poly [di(ethylene glycol) methyl ether methacrylate] (PMEO₂MA) was studied in surface-initiated polymerization in the mesopores (L.Huang, PhD. Dissertation, CUNY GC, 2013). Poly[(oligoethyleneglycol) methacrylate]-based polymers are considered advantageous because they are known to be biocompatible, and their hydrophilicity and lower critical solution temperature (LCST) can be tuned by adjusting oligo(ethyleneglycol) chain length.³⁷,³⁸ In our study, we wanted to explore controlled/living polymerization technique, that is ARGET ATRP, for controlled grafting of poly[(oligoethyleneglycol) methacrylate] brushes of different chain lengths such as poly [di(ethylene glycol) methyl ether methacrylate] (PMEO₂MA), poly [oligo(ethyleneglycol)methyl ether methacrylate] (PMEO₅MA), and copolymers of MEO₂MA-co-MEO₅MA di(ethylene glycol) methyl ether methacrylate (MEO₂MA) and oligo(ethyleneglycol)methylether methacrylate (MEO₅MA) (P(MEO₂MA-co-MEO₅MA), that are known to be temperature responsive in solution.

7.2 Experimental section

7.2.1 Materials

SBA-15 mesoporous silica was synthesized according to the earlier work.⁷ 2.4 g of Pluronic P123 was dissolved in 84 mL 1.3 M HCl. After the surfactant dissolved, the mixture was moved to water bath at 13 °C. Then 2 g of triisopropylbenzene (TIPB) and 5.5 mL of tetraethyl orthosilicate (TEOS) was added. The reaction mixture was stirred for one day and then hydrothermally treated at 130 °C for another day. The resulting as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Finally, the
material was calcined at 550 °C under air for 5 hours (heating ramp 2 °C/min). Di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA) (Aldrich) and oligo(ethylene glycol)methyl ether methacrylate (MEO$_5$MA, $M_n=300$ g/mol) was purified by passing through a column filled with basic alumina. The ligand tris[(2-pyridyl)methyl]amine (TPMA) was acquired from ATRP Solutions, Inc. and was used as received. The initiator, 3-(chlorodimethylsilyl)propyl 2-bromoisobutyrate (BiB), was synthesized and grafted to the surface of silica, followed by the surface modification with trimethylchlorosilane, according to the procedure reported earlier.$^{39}$ Copper (II) chloride and tin (II) ethylhexanoate (Sn(EH)$_2$) were used as received.

### 7.2.2 Synthetic Procedures

ARGET ATRP of di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA) initiated from the surface was carried out as follows. Initiator modified silica (30 mg, with 0.017 mmol initiator), MEO$_2$MA monomer (265.4 mg, 1.41 mmol), a premixed solution of CuCl$_2$ (0.048 mg, 0.00023 mmol) and tris[(2-pyridyl)methyl]amine (0.96 mg, 0.0033 mmol) in anisole (0.24 mL) and anisole (3.30 mL) were added into a ~5 mL glass vial. The vial was closed with rubber septum and mixture was stirred for 20 min before injecting a solution of reducing agent, Sn(EH)$_2$ (51 mg, 0.126 mmol) in anisole (0.3 mL). The molar ratio of the components in the mixture was as follows: initiator: Cu(II):TPMA: MEO$_2$MA= 1: 0.013: 0.19: 80. The mixture for polymerization of MEO$_2$MA was heated in an oil bath at 40 °C. The polymerization was terminated by opening the vial and exposing the copper catalyst to oxygen from the air. The polymer/silica composite was recovered by filtration, washed with tetrahydrofuran (THF), acetone and methanol, and finally dried in a vacuum oven. In the case of surface initiated polymerization of oligo(ethylene glycol)methyl ether methacrylate (MEO$_5$MA), similar conditions were applied with the following ratio of reactants: Initiator:Cu(II):TPMA:MEO$_5$MA=1:0.013:0.19:68. Also, in
the case of surface initiated polymerization of poly (MEO₂MA-co-MEO₅MA), the same conditions were applied with the following ratios of reactants: Initiator:Cu(II):TPMA:MEO₂MA:MEO₅MA=1:0.013:0.19:39:39. The solvent was anisole and the reaction temperature was 40 °C.

![Figure 7.1](image)

**Figure 7.1** The structures of (a) di(ethylene glycol) methyl ether methacrylate (MEO₂MA) and (b) oligo(ethylene glycol) methacrylate (MEO₅MA) Mₙ=300 g/mol.

### 7.2.3 Characterization

Small-angle X-ray scattering (SAXS) patterns were acquired on a Bruker Nanostar U SAXS/wide-angle X-ray scattering instrument with a 2-D detector Vantec-2000 and a rotating anode X-ray source. Samples were placed in a hole of a sample holder and secured from both sides with a Kapton tape. Nitrogen adsorption measurements at -196 °C were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the measurements, samples were outgassed under vacuum in a port of the analyzer at 140 °C for silicas and at 80 °C for the modified silica samples. Thermogravimetric analysis (TGA) was done under nitrogen with 5 °C min⁻¹ ramping rate to 800 °C on Hi-Res 2950 thermogravimetric analyzer from TA Instruments.
Molecular weight distributions were determined by gel permeation chromatography (GPC) on Tosoh EcoSEC HLC-8320GPC with refractive index detector and polystyrene standards. The cleavage of polymers from nanoporous silica was done using 48% HF, as described elsewhere.  

7.3 Results

ARGE ATRP of di(ethylene glycol) methyl ether methacrylate (MEO\textsubscript{2}MA) inside the nanopores of SBA-15

Ordered nanoporous silica SBA-15 with 2-D hexagonal structure and BJH-KJS pore diameter around 30 nm (which is an overestimation) was chosen for grafting of the polymer inside the nanopores. The selected SBA-15 had BET specific surface area of 357 m\textsuperscript{2}/g and pore volume of 1.07 cm\textsuperscript{3}/g. The first step in grafting the polymer is the surface modification of silica with 3-(2-bromoisobutyryloxy) propyltrimethylsilyl groups (BiB, ATRP initiator) and trimethylsilyl (TMS) groups (Scheme 7.1). The amount of the initiator loaded (BiB-TMS) from TGA was estimated around 14 wt.% (Figure 7.2). It was seen that from the nitrogen adsorption analysis that the BET specific surface area decreased ~32.5% to 241 m\textsuperscript{2}/g and pore volume decreased ~14% to 0.92 cm\textsuperscript{3}/g, as compared to unmodified SBA-15. Also it was seen from pore size distributions (PSDs) that the pore diameter decreased around 2.8 nm as the BiB-TMS groups are attached to SBA-15 (Figure 7.3, Table 7.1). Pore diameters calculated from the adsorption isotherms using BJH-KJS method overestimate the sizes of cylindrical mesopores with pore diameters above 10 nm.\textsuperscript{40,41} SAXS patterns before and after immobilization of the initiator corresponded to the 2-D hexagonal structure with cylindrical mesopores (Figure 7.4). The d-spacing (d\textsubscript{100}) value calculated from the first peak in SAXS pattern was ~22.6 nm, for the unmodified SBA-15 as well as modified SBA-15 materials. The successful immobilization of the BiB-TMS groups was
also confirmed by the FTIR spectra (Figure 7.5), in which new peaks appeared around 1720 cm\(^{-1}\), corresponding to the C=O bond in BiB (Scheme 7.1).

![Weight change patterns recorded under nitrogen for SBA-15, before and after attachment of the initiation sites and polymerization of di(ethylene glycol) methyl ether methacrylate (the loading of PMEO\(_2\)MA in the composites is indicated in wt.%).](image)

**Figure 7.2** Weight change patterns recorded under nitrogen for SBA-15, before and after attachment of the initiation sites and polymerization of di(ethylene glycol) methyl ether methacrylate (the loading of PMEO\(_2\)MA in the composites is indicated in wt.%).
Figure 7.3 (a) Nitrogen adsorption isotherms and (b) pore size distributions, before and after attachment of initiation sites and polymerization of di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA) (loading of PMEO$_2$MA in the composites is indicated in wt.%).
Figure 7.4 SAXS patterns of SBA-15 before and after attachment of initiation sites and polymerization of di(ethylene glycol) methyl ether methacrylate (loading of PMEO\textsubscript{2}MA in the composites is indicated in wt.%)
Table 7.1 Structural parameters of materials.a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization time</th>
<th>$S_{BET}$ ($\text{m}^2/\text{g}$)</th>
<th>$V_t$ ($\text{cm}^3/\text{g}$)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
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<td>SBA-15</td>
<td>-</td>
<td>357</td>
<td>1.07</td>
<td>30.5</td>
</tr>
<tr>
<td>SBA-15 BiB-TMS</td>
<td>-</td>
<td>241</td>
<td>0.92</td>
<td>27.8</td>
</tr>
<tr>
<td>SBA-15 PMEO$_2$MA 17%</td>
<td>1.5</td>
<td>110</td>
<td>0.47</td>
<td>27.2</td>
</tr>
<tr>
<td>SBA-15 PMEO$_2$MA 20%</td>
<td>2</td>
<td>56</td>
<td>0.19</td>
<td>25.6</td>
</tr>
<tr>
<td>SBA-15 PMEO$_2$MA 31%</td>
<td>2.5</td>
<td>33</td>
<td>0.10</td>
<td>24.4</td>
</tr>
</tbody>
</table>

*aNotation: $S_{BET}$, BET specific surface area; $V_t$, total pore volume; pore diameter, calculated using BJH-KJS method for cylindrical mesopores.

Figure 7.5 FTIR spectra before and after attachment of initiation sites and polymerization of (di(ethylene glycol) methyl ether methacrylate (PMEO$_2$MA 31%), oligo(ethylene glycol) methacrylate (PMEO$_5$MA 34%), as well as copolymerization of di(ethylene glycol) methyl ether methacrylate and oligo(ethylene glycol) methacrylate (PMEO$_2$MA-co-PMEO$_5$MA 31%).
Scheme 7.1 Grafting of poly(di(ethylene glycol) methyl ether methacrylate) (PMEO$_2$MA), poly(oligo(ethylene glycol) methacrylate) (PMEO$_5$MA) and poly(di(ethylene glycol) methyl ether methacrylate copolymerized oligo(ethylene glycol) methacrylate) (PMEO$_2$MA-co-PMEO$_5$MA) in the cylindrical mesopores of SBA-15 silica using activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP).

For the polymerization, initiator immobilized on SBA-15 was placed in the glass vial to which monomer di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA), copper (II) chloride, tris[(2-pyridyl)methyl]amine (TPMA) ligand and anisole (solvent) was added. The vial was then sealed with rubber septum and a reducing agent Sn(EH)$_2$ was added. The polymerization was performed
at 40 °C. The polymerization time was varied for three different experiments between 1.5 to 3 hours (Scheme 7.1).

Products after 1.5, 2 and 3 hours of polymerization were analyzed by thermogravimetry (Figure 7.1). TGA results under nitrogen indicate that the organic group content in SBA-15/poly(MEO₂MA) composites increased to 29, 32 and 41 wt.% with polymerization times of 1.5, 2 and 3 hours, respectively. The corresponding percentages of polymer moieties were 17, 20, and 31 wt.% respectively. From the nitrogen adsorption isotherms, it was seen that when the polymer loading increased, the BET specific surface area and total pore volume decreased (Figure 7.3(a)). For the polymer loading of 31 wt.%, the mesopores were still accessible although their BET specific surface area was 33 m²/g and total pore volume was 0.10 cm³/g (Table 7.1). Pore size distributions (Figure 7.3(b)) also exhibited a quite systematic decrease in the pore diameter as the polymer loading increased. The thickness of polymer layer corresponding to the pore diameter decrease can be estimated as 0.3, 1.1 and 1.7 nm (which appears to be underestimated) for 13, 17 and 31 wt.% respectively of PMEO₂MA loading. SAXS patterns of SBA-15/P(MEO₂MA) composites suggested that 2-D hexagonal structure was still intact even when the polymer loading was high as 31%. It was also seen that as the polymer loading increased, (100) became less intense (Figure 7.4). At first it may seem that (110) peak become broader, but actually the (200) peak might have emerged, even if it was not well resolved. FTIR spectra of the SBA-15-PMEO₂MA show that as the polymer loading increases, the peak at 1720 cm⁻¹ corresponding to the stretching of carbonyl group, became stronger, as expected from the fact that the initiator carries C=O moiety and the incorporation of the polymer increases its abundance. Also, peaks around 2940 cm⁻¹ were seen, which can correspond to the C-H stretch modes from the aliphatic carbons of the polymer (Figure 7.5).
ARGET ATRP of oligo(ethylene glycol)methyl ether methacrylate inside the nanopores of SBA-15

Similarly, the polymerization of oligo(ethylene glycol) methacrylate ($M_n=300$ g/mol, MEO<sub>5</sub>MA) was performed in the pores of ordered mesoporous silica SBA-15 via ARGET ATRP. A different batch of SBA-15 was used in the polymerization, which had a similar KJS-BJH diameter of about 29 nm. The BET specific surface area ($S_{BET}$) was 411 m<sup>2</sup>/g and total pore volume was 1.37 cm<sup>3</sup>/g.

The polymerizations of MEO<sub>5</sub>MA were performed similarly in anisole at 40 °C with polymerization time ranging from 1.5 to 2.5 hours (Scheme 7.1). TGA results under nitrogen show that the organic content in SBA-15/P(MEO<sub>5</sub>MA) composites increased to 25, 35, 41, and 43 wt.% with polymerization times of 1.5, 1.75, 2, and 2.5 hours respectively. The corresponding percentages of polymer moieties were 13, 24, 31 and 34 wt.% respectively (Figure 7.6).

In this case also, nitrogen adsorption analysis provided an insight into the polymer grafting process. The BET specific surface area and the total pore volume decreased as the polymer loading increased. The surface area decreased to 73 m<sup>2</sup>/g and pore volume decreased to 0.27 cm<sup>3</sup>/g, when the polymer loading increased to 34 wt.% (Figure 7.7, Table 7.2). In this case also, it was seen from the pore size distributions (PSDs) that the pore diameter decreased systematically as the polymer loading increased. The thickness of the polymer layer estimated from the change in the pore diameter was around 0.1, 0.6, 1 and 1.75 nm for 13, 24, 31 and 34 wt.% of PMEO<sub>5</sub>MA loading, respectively. Of course, these numbers are not fully accurate, as they may be subject to some random errors related to the determination of the capillary condensation pressure, a systematic error related to change in surface properties and its influence.
on the capillary condensation, and so on. Especially the polymer layer thickness of 0.1 nm seems to be severely underestimated. Samples show SAXS patterns corresponding to a 2-D hexagonal structure (Figure 7.8). (200) peak become better visible with a higher polymer loading. Overall, even with higher polymer loadings, the structure remains intact. In this case also FTIR spectra for P(MEO₅MA) showed a strong peak at 1720 cm⁻¹ and peaks around 2940 cm⁻¹ corresponding to stretching of additional carbonyl bonds present in the polymer, and C-H stretch modes from the aliphatic carbons of the polymer, respectively.

![Figure 7.6 Weight change patterns for SBA-15 under nitrogen, before and after attachment of initiation sites and polymerization of oligo(ethylene glycol) methacrylate (Mₙ=300 g/mol, MEO₅MA) (loading of PMEO₅MA in the composites is indicated in wt.%).](image-url)
Figure 7.7 (a) Nitrogen adsorption isotherms and (b) pore size distributions for SBA-15 before and after attachment of initiation sites and polymerization of oligo(ethylene glycol) methacrylate (Mₙ=300 g/mol, MEO₅MA) (loading of PMEO₅MA in the composites is indicated in wt.%).
Figure 7.8 SAXS patterns before and after attachment of initiation sites and polymerization of oligo(ethylene glycol) methacrylate ($M_n=300$ g/mol, MEO$_5$MA) (loading of PEO$_5$MA in the composites is indicated in wt.%).
### Table 7.2 Structural parameters of materials.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization time</th>
<th>BET specific surface area (m(^2)/g)</th>
<th>Total pore volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>-</td>
<td>411</td>
<td>1.37</td>
<td>29</td>
</tr>
<tr>
<td>SBA-15 BiB-TMS</td>
<td>-</td>
<td>225</td>
<td>0.96</td>
<td>27.3</td>
</tr>
<tr>
<td>SBA-15 PMEO(_5)MA 13%</td>
<td>1.50</td>
<td>177</td>
<td>0.70</td>
<td>27.1</td>
</tr>
<tr>
<td>SBA-15 PMEO(_5)MA 24%</td>
<td>1.75</td>
<td>132</td>
<td>0.62</td>
<td>26.1</td>
</tr>
<tr>
<td>SBA-15 PMEO(_5)MA 31%</td>
<td>2</td>
<td>82</td>
<td>0.33</td>
<td>25.3</td>
</tr>
<tr>
<td>SBA-15 PMEO(_5)MA 34%</td>
<td>2.5</td>
<td>73</td>
<td>0.27</td>
<td>23.8</td>
</tr>
<tr>
<td>SBA-15 P(MEO(_2)MA-co-PMEO(_5)MA) 16%</td>
<td>1</td>
<td>112</td>
<td>0.46</td>
<td>26</td>
</tr>
<tr>
<td>SBA-15 P(MEO(_2)MA-co-PMEO(_5)MA) 23%</td>
<td>2</td>
<td>116</td>
<td>0.46</td>
<td>24.2</td>
</tr>
<tr>
<td>SBA-15 P(MEO(_2)MA-co-PMEO(_5)MA) 31%</td>
<td>2.50</td>
<td>86</td>
<td>0.37</td>
<td>23.2</td>
</tr>
</tbody>
</table>

\(^{a}\)Notation: S\(_{\text{BET}}\), BET specific surface area; V\(_t\), total pore volume; pore diameter calculated using BJH-KJS method for cylindrical mesopores.
ARGEAT ATRP of copolymer of di(ethylene glycol) methyl ether methacrylate (MEO2MA) and oligo(ethylene glycol)methyl ether methacrylate (MEO5MA) inside the nanopores of SBA-15

To graft the copolymers inside the nanopores of SBA-15, monomers di(ethylene glycol) methyl ether methacrylate (MEO2MA) and oligo(ethylene glycol)methyl ether methacrylate (MEO5MA) were used and ARGET ATRP was performed from the initiator-modified SBA-15. The polymerizations were done in a similar manner as for homopolymers using anisole as a solvent with polymerization times ranging from 1.5 to 2.5 hours (Scheme 7.1). The resulting SBA-15/polymer nanocomposites were characterized by thermogravimetry (Figure 7.9). TGA results under nitrogen indicate that the organic content in SBA-15/P(MEO2MA-co-MEO5MA) composites increased to 27, 35 and 41 wt.% with polymerization times of 1.5, 2 and 2.5 hours respectively. The corresponding percentages of polymer moieties were 16, 23, and 31 wt.%, respectively.

Nitrogen adsorption analysis shows the successful grafting of P(MEO2MA-co-MEO5MA) copolymer, because the pore volume and BET specific surface area decreased systematically as the copolymer loading increased. When the copolymer loading was 16 wt.%, the BET specific surface area was 112 m²/g and the pore volume was 0.46 cm³/g (Table 2). As the polymer loading increased to 31 wt.%, the BET surface area decreased to 70 m²/g and pore volume decreased to 0.36 cm³/g. Similarly the BJH-KJS pore diameter decreased from ~ 29 nm (in the case of unmodified SBA-15) to 23 nm (in case of copolymer loading of 31 wt.% (Figure 7.10). SAXS patterns show the retention of the periodic structure after grafting (Figure 7.11). (200) peak, originally essentially invisible, become more intense when the polymer loading was very high. Clearly, the structure still remained intact even when the copolymer loading was very high.
Similarly in this case, FTIR spectra show peaks around 1720 cm$^{-1}$ corresponding to carbonyl group stretching in the initiator and copolymer. Also, peaks around 2940 cm$^{-1}$ were observed from the C-H stretching modes from the aliphatic carbons of the polymer (Figure 7.5).

**Figure 7.9** Weight change patterns for SBA-15 under nitrogen, before and after attachment of initiation sites and copolymerization of di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA) and oligo(ethylene glycol) methacrylate (M$_n$=300 g/mol, MEO$_5$MA) (loading of PMEO$_2$MA-co-PMEO$_5$MA in the composites is indicated in wt.%).
Figure 7.10 (a) Nitrogen adsorption isotherms and (b) pore size distributions for SBA-15, before and after attachment of initiation sites and copolymerization of di(ethylene glycol) methyl ether methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (Mₙ=300 g/mol, MEO₅MA) (loading of PMEO₂MA-co-PMEO₅MA in the composites is indicated in wt.%).
Figure 7.11 SAXS pattern for SBA-15, before and after attachment of initiation sites and polymerization of di(ethylene glycol) methyl ether methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (M₅O₅MA) (loading of PMEO₂MA-co-PMEO₅MA in the composites is indicated in wt.%).

In the cases of SBA-15-PMEO₂MA 31%, PMEO₅MA 34% and P(MEO₂MA-co-MEO₅MA) 31%, the grafted polymers was first cleaved by HF and then was characterized by GPC. The molecular weights obtained were in the range of 5932-6946 g mol⁻¹ (Figure 7.12). Polydispersity index (PDI) in all the three cases was 1.26-1.37. Combining the TGA, nitrogen adsorption and GPC results, the grafting density for SBA-15 PMEO₂MA 31% was calculated to be 0.13 chains/nm². The grafting density for SBA-15 PMEO₅MA was calculated to be 0.15 chains/nm² and ~0.11 chains/nm² for the copolymer SBA-15 PMEO₂MA-co-PMEO₅MA (Table 7.4).
Table 7.3 Characteristics of SBA-15 grafted with polymers.\textsuperscript{b}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymerization time (hrs)</th>
<th>Polymer loading (%)</th>
<th>M\textsubscript{n}</th>
<th>PDI</th>
<th>DP</th>
<th>Grafting density (chains/nm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEO\textsubscript{2}MA</td>
<td>3</td>
<td>31</td>
<td>6718</td>
<td>1.34</td>
<td>36</td>
<td>0.13</td>
</tr>
<tr>
<td>MEO\textsubscript{2}MA</td>
<td>2.5</td>
<td>34</td>
<td>5932</td>
<td>1.28</td>
<td>20</td>
<td>0.15</td>
</tr>
<tr>
<td>MEO\textsubscript{2}MA-co-MEO\textsubscript{5}MA</td>
<td>2.5</td>
<td>31</td>
<td>6946</td>
<td>1.37</td>
<td>-</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\textsuperscript{b}Notation: M\textsubscript{n}, number average molecular weight of the polymer; PDI, polydispersity index; DP, degree of polymerization.

Figure 7.12 Gel permeation chromatography (GPC) molecular weight distributions for poly(di(ethylene glycol) methyl ether methacrylate) (P-MEO\textsubscript{2}MA 31\%), poly(oligo(ethylene glycol) methacrylate) (P-MEO\textsubscript{5}MA 34\%), poly (di(ethylene glycol) methyl ether methacrylate (MEO\textsubscript{2}MA) and oligo(ethylene glycol) methacrylate) (P-MEO\textsubscript{2}MA-co-MEO\textsubscript{5}MA 31\%).
7.4 Summary

An environmentally friendly polymerization technique, atom transfer radical polymerization with activators regenerated by electron transfer (ARGET ATRP) was successfully employed to synthesize poly (2-(2’-methoxyethoxy)ethyl methacrylate) (PMEO₂MA), poly (oligo(ethylene glycol) methacrylate) (PMEO₅MA) and copolymer P(MEO₂MA-co-MEO₅MA) brushes inside the high surface area SBA-15 nanoporous host. For all of these polymers, it was seen that their grafting can be systematically controlled inside the mesopores. Polymers and copolymers with quite high molecular weight (from ~6000 to ~7000 g/mol) and low polydispersity index (from 1.28 to 1.37) were obtained inside the nanopores without mesopore blocking.
References


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Chapter 8

Conclusions
In the first part of the dissertation, conditions of low temperature (0 or 7 °C) and moderate acid concentration (0.1 M HCl) were explored to synthesize large-pore periodic mesoporous organosilicas (PMOs) templated by Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) combined with appropriate swelling agents, for instance xylene. PMOs with different bridging groups were developed with large pore diameters and typically with large pore volumes. Most of the PMOs exhibited face-centered cubic structures of spherical mesopores. The conditions involving moderate acid concentration and low temperature are favorable for the synthesis of PMOs with many organic bridging groups. The conditions were also suitable for the synthesis of mesoporous silicas with each silicon atom modified with an organic (methyl) group. Such highly organic-functionalized mesoporous materials are otherwise difficult to synthesize.

Ethylene-bridged PMOs were synthesized at low temperature (7 °C) and mildly acidic conditions (0.1 M HCl) using Pluronic F127 copolymer surfactant. 1,2-bis(triethoxysilyl)ethane (BTEE), a more benign and economical alternative to typically used 1,2-bis(trimethoxysilyl)ethane (BTME), was used to synthesize ethylene-bridged PMO with face-centered-cubic PMOs with pore sizes up to 22 nm and unit-cell parameters up to 45 nm. The pore diameter increased systematically with the relative amount of the swelling agent. The total pore volume of the PMOs was up to 0.60 cm\textsuperscript{3}/g. Xylene and ethylbenzene worked best in the synthesis of these large-pore PMOs. Ethylene-bridged PMOs were also synthesized using 1,2-bis(trimethoxysilylethane) (BTME), which also rendered seemingly disordered materials with high pore diameter (up to 29 nm) and large total pore volumes up to 1 cm\textsuperscript{3}/g. Unlike in the case of the organosilica synthesis under more highly acidic conditions (2 M HCl), the reduction of the BTEE (or BTME)/Pluronic F127 ratio did not lead to the formation of single-micelle-templated hollow nanospheres.
Phenylene-bridged PMOs were also synthesized using 1,4-bis(trithoxysilyl)benzene (BTEB) and the role of a swelling agent was evaluated under the above mentioned conditions (7 °C and 0.1 M HCl). Face-centered cubic phenylene-bridged PMO with rather large pore diameter around 14 nm and unit-cell parameter around 28 nm was synthesized. A larger amount of the swelling agent rendered materials with even larger pore diameters but also resulted in a decrease in the structural ordering. The decrease in the framework-precursor/surfactant ratio at a typically used swelling agent/surfactant ratio led to a decrease in the particle size, but did not lead to the emergence of individual single-micelle templated nanoparticles.

Using Pluronic F127 surfactant and xylene as a swelling agent, ethylene-bridged PMOs with well-ordered face-centered cubic structure were also synthesized under the considered conditions. The pore sizes of the PMOs can be adjusted from 13 to 22 nm simply by changing the relative amount of the swelling agent. The unit-cell parameters were in the range of 27-38 nm. The highest total pore volumes were around 0.50 cm³/g. The unique observation for these PMOs was that larger amounts of the swelling agent did not decrease the structural ordering, allowing us to obtain highly ordered large-PMOs.

Using a similar synthesis procedure, a biphenylene-bridged PMO was obtained at 0 °C under moderate acidic concentration (0.1 M HCl). The PMOs had a pore diameter of about ~ 8 nm and unique sheet-type morphology. These biphenylene-bridged PMOs had high molecular scale crystallinity and high thermal stability, being comparable to the PMOs synthesized using alkylammonium surfactants. However, it has not been ascertained if the molecular-level crystallinity is characteristic of the walls of the uniform mesopores or appears in an impurity phase.
Since the above reaction conditions worked so well for the bridged organosilicas, the synthesis of mesoporous silicas with pendant organic groups under these new conditions (7 °C and 0.1 M HCl) was attempted. Methyltriethoxysilane was used as an organosilane precursor and Pluronic F127 was used as a surfactant. Organosilicas with pendant methyl groups, pore sizes around 10 nm, and good structural ordering (most likely 2-D hexagonal symmetry) was synthesized. These unique materials exhibited one methyl group covalently bonded to each silicon atom, which is a highly uncommon structural feature for materials with porosity. The thermal treatment at higher temperatures resulted in shrinkage or closing of the mesopores and thereby forming closed-pore mesoporous organosilicas. Presumably, micropores in the framework shrink or sinter upon heating, thus hindering access to the mesopore interiors. $^{29}$Si CPMAS NMR confirm that the methyl groups were intact even after the thermal treatment at higher temperatures.

In the second part of the dissertation, syntheses of polymer-grafted silicas and organosilicas were discussed in detail. The nanoporous hosts with high surface areas, pore volumes and pore diameters were functionalized using stimuli-responsive polymers. Methylene-bridged PMOs and large pore SBA-15 silicas were selected as hosts, and were grafted with different polymers.

Methylene-bridged PMO was successfully functionalized with poly (N-isopropylacrylamide) using surface-initiated activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP). The growth of the polymer inside the nanopores of the PMO can be systematically controlled by adjusting the polymerization time. The molecular weight up to ~4263 g/mol and the degree of polymerization around 37 was achieved without blocking of the nanopores. This report is the first study in which the mesopores of the PMOs were successfully grafted with the surface-bound polymer. The findings of the study can be used to
synthesize other PMO/polymer composites with potential applications. The ability to incorporate
the framework organic moiety and a sophisticated polymer graft on the surface is remarkable.

A pure silica large-pore SBA-15 support was used to explore the grafting of another polymer
known for its stimuli-responsive properties, that is poly(oligo ethylene glycol) methacrylate.
Brushes, of poly (2-(2’-methoxyethoxy)ethyl methacrylate) (PMEO₂MA) and poly
(oligo(ethylene glycol) methacrylate) (Mₙ=300 g/mol) (PMEO₅MA) were successfully grafted
using ARGET ATRP. Also a random copolymer based on MEO₂MA and MEO₅MA was grafted
from the surface of nanopores. The synthesized silica/polymer nanocomposites had high polymer
loadings (~34 wt.%). The molecular weights of the grafted polymers were in the range of 5000-
6000 g/mol with quite low PDI. It was seen that the loading of the homopolymers and the
copolymer inside the nanopores can be adjusted by adjusting the polymerization time.