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Past, Present, and Future of Periodic Mesoporous Organosilicas—The PMOs

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ABSTRACT
Periodic mesoporous organosilicas (PMOs) represent an exciting new class of organic−inorganic nanocomposites targeted for a broad range of applications such as catalysis and sensing, separations, and microelectronics. Their hallmark is the presence of organic bridging groups incorporated into the channel walls of an ordered nanoporous structure, which represents a useful tool to finely tune the chemical and physical properties of the materials. We discuss the history of the discovery and development of the PMOs emphasizing the most important recent advancements regarding compositions and structures, morphologies, and properties. Furthermore, we present an outlook about the promising future perspectives of PMOs that result from the latest developments in this field.

Introduction

The natural world tends to favor close-packed over porous solid-state structures for thermodynamic reasons. Consequently the character of porous solids, a metastable state of matter, has always fascinated scientists, and it remains a perpetual challenge to drive these materials to their limits.[1] Such materials are not only of high academic interest but also of intense practical value because they exhibit well-defined host−guest chemistry.[2] The specific interactions between host and guest can be used to develop useful materials, products, processes, and devices. For instance, chemical reactions between the solid host and a guest molecule can be used to develop heterogeneous catalysts. Sensors could be created when specific host−guest interactions cause changes in a measurable physical property of the host. Additionally, by exerting precise control over the pore size and shape of the host, as well as over the adsorption strength of the guest, new high efficiency chromatographic devices could be developed.[1,3]

Among porous solids, siliceous compounds have a distinguished position, and their structures traverse a wide range of length scales.[1] Amorphous, porous silicas with large pores and broad pore-size distributions, known as xerogels and aerogels, have found applications as drying agents, adsorbents, and storage systems for organic vapors or liquids. The explosive dynamite, for example, is a xerogel whose pores are filled with nitroglycerin. Microporous crystalline silica-based materials, known as zeolites, on the other hand, have uniform pores ranging from 0.5 to 2 nm and have well-defined crystallographic sites making them very valuable for molecular sieving and in catalysis, especially for raw-oil cracking in the petroleum industry.[4]

Discovery of Periodic Mesoporous Silicas (PMSs)

Much effort has been put into creating zeolite-like materials with ordered and uniform pores larger than 2 nm because this would allow for host−guest chemistry with large molecules and polymers, nanoscale clusters, and wires and enhanced diffusion rates of molecules within the pores. So it was considered a fundamental breakthrough in 1992 when the first periodic mesoporous silicas (PMSs) were discovered.[5] It was shown that through the co-assembly of surfactant micelles and a silica precursor like tetraethyl orthosilicate (TEOS), an ordered nanocomposite forms in which the silica replicates cylindrical

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Geoffrey Ozin received a B.Sc. in chemistry from King's College London in 1965 and a D.Phil. in inorganic chemistry from the University of Oxford in 1967. He was ICI Fellow at the University of Southampton from 1967 to 1969 before joining the University of Toronto in 1969; he became Full Professor in 1977 and University Professor in 2001. Professor Ozin is Honorary Professorial Fellow at The Royal Institution of Great Britain and University College London and is Government of Canada Research Chair in Materials Chemistry. More details are available at the research group's homepage, http://www.chem.toronto.edu/staff/GAO/group.html, Geoffrey Ozin.

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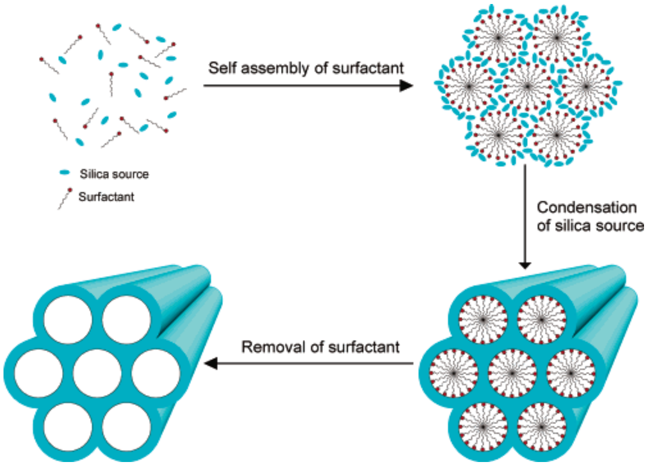

FIGURE 1. Schematic representation of the synthesis of PMSs and PMOs

organic micelles. From this nanocomposite, the surfactant template can be removed leaving the PMS host (Figure 1).

Periodic Mesoporous Organosilicas with Terminal Organic Groups

Soon after this discovery, there was much interest in incorporating organic groups into these PMS materials to imbue them with distinct properties. This was accomplished either by grafting organic groups onto the channel walls using the reactivity of the silanol groups in the material or by co-assembling TEOS with an organosiloxane of the type $RSi(OEt)_3$.[6−8] These modifications result in materials with useful properties, such as PMSs with alkanethiol groups in the channels, which can bind toxic heavy metals such as lead and mercury. However, these approaches suffer from some inherent limitations.[9,10] First, both synthesis methods can lead to an inhomogeneous distribution of the organic groups in the pores. Second, silsesquioxane precursors with terminal organic groups must always be co-assembled to some extent with TEOS to form a stable periodic mesoporous structure, thereby limiting the organic content of the material usually to around 25% with respect to the silicon wall sites.

Discovery of Periodic Mesoporous Organosilicas with Bridging Organic Groups—the PMOs

In 1999, our group, as well as those of Stein and Inagaki, independently developed a novel class of organic−inorganic nanocomposites known as “periodic mesoporous organosilicas”, the PMOs.[11−13] In PMOs, the organic groups are located within the channel walls as bridges between Si centers. Such materials can be prepared akin to PMSs, with a high degree of order and uniformity of pores, using a silsesquioxane of the type $(EtO)_3Si{-}R{-}Si(OEt)_3$ as the sole precursor, providing that the group R is sufficiently short and rigid and has favorable condensation kinetics. Because co-assembly with another precursor like TEOS is often not necessary, a homogeneous distribution of the organic groups in the pore walls can be ensured.

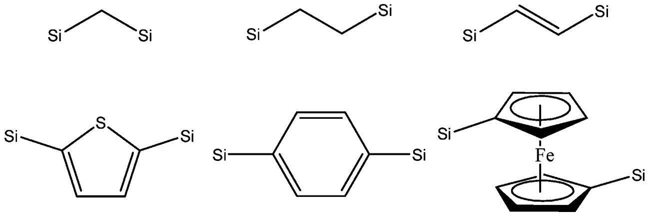

FIGURE 2. Structures of some of the organic bridging groups that were incorporated into the first PMO materials.

Thus, higher organic loading and greater avoidance of pore blockage can be achieved than with terminal organic groups because the material consists entirely of SiO_3RSiO_3 building blocks. Now, a multitude of bridge-bonded organic groups have been incorporated into PMOs,[13] and herein, we highlight some of the most interesting advancements in this field with an emphasis on work that has emerged from our materials chemistry group and outline what we consider to be the most promising future research directions and potential applications.

PMOs with One Organic Bridging Group Bound to Each Silicon Atom

Since their inception, significant work has been done to make PMOs suitable for real world applications. With few exceptions,[14] the pore walls of PMS and PMO materials are amorphous and lack any crystallographically well defined sites. Thus, they lack the diverse shape and size reactivity of their zeolite counterparts, and in areas such as catalysis, we are not aware of any reports indicating that they perform significantly better than the related aerogels or xerogels.

In an effort to make PMO materials more functional, a variety of organic groups have been incorporated, ranging from simple alkane chains[11−13,15] to unsaturated or aromatic groups[16−19] to very large organometallic complexes.[20] The early work in PMOs involved the use of fairly simple precursors, such as those shown in Figure 2, in which limited functionality was present. However some interesting aspects of PMO reactivity were discovered. For instance, in the simplest case of a bridging methene group, some interesting thermal transformations occur. At 350 °C, Si−C bond cleavage begins to occur through a reaction with silanol groups, effectively converting the bridging methene group into a terminal methyl group (Figure 3).[15] This reaction causes important changes in the dielectric constant and hydrophobicity of the material, which will be discussed in the section PMOs as Oriented Thin Films.

Similar thermally induced bond cleavage reactions have been observed for more complicated PMOs such as 1,3,5-tris(triethoxysilyl)benzene.[17] However, in this case controlling the temperature can control the degree of the Si−C bond cleavage without disrupting the ordered mesostructure of the material. When the material is heated to 350 °C, one of the three Si−C bonds in the material can be cleaved so that the material has a doubly bound benzene group. If the sample is heated further to 450 °C, a second Si−C bond can be cleaved, leaving a terminal phenyl group (Figure 4).

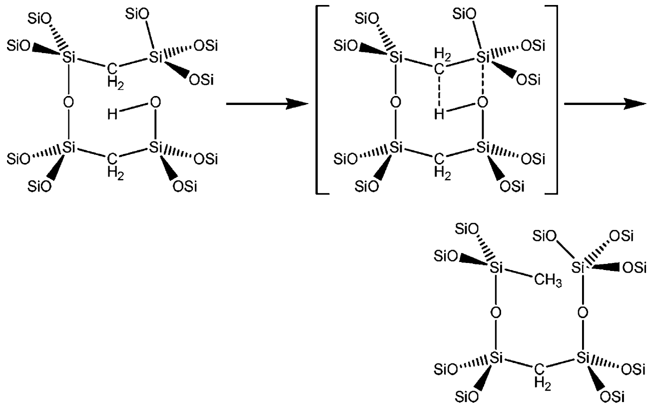

FIGURE 3. Schematic representation of the cleavage of one Si–C bond of a bridging methylene group to form a methyl group that is terminally bound to Si.

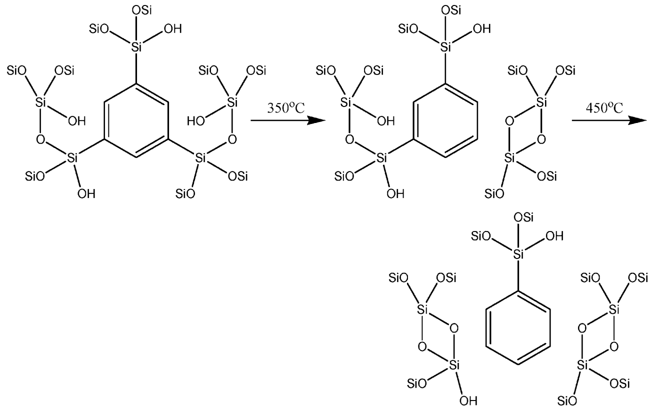

FIGURE 4. Schematic representation of the thermally induced systematic cleavage of the Si–C bonds in 1,3,5-tris(triethoxysilyl)-benzene.

To introduce a chemically reactive group, a methene PMO can be treated with gaseous ammonia at temperatures up to 850 °C to give a material in which Si–N bonds have replaced some of the Si–O and Si–C bonds that make up the framework, effectively incorporating a Lewis basic site within the wall of a previously nonfunctional PMO.[21] This process has been previously accomplished with PMS materials,[22] but the presence of the organic groups seems to make the process more facile and enables a higher loading of the silazane. It is believed this enhancement is because Si–C bonds are significantly weaker than the Si–O bonds, making the incorporation of ammonia easier.[21]

Alternatively, the introduction of a desired functionality can be accomplished through the choice of an appropriate precursor. Several systems have been designed that are able to chelate metal ions with varying degrees of efficiency. One such system is based on the bridging tetrasulfide $(EtO)_3Si(CH_2)_3S{-}S{-}S{-}S(CH_2)_3Si(OEt)_3$.[23] PMOs made from this precursor show a high affinity for Hg^{2+} cations and are able to selectively remove them from an aqueous solution, while showing very low affinities for the related cations Pb^{2+}, Cd^{2+}, Zn^{2+}, or Cu^{2+}. The amount of Hg^{2+} uptake can vary from 627 mg g^{-1} for a material that contains only 2% of the tetrasulfide to 2710 mg g^{-1} for a material that contains a mere 15% of the tetrasulfide.

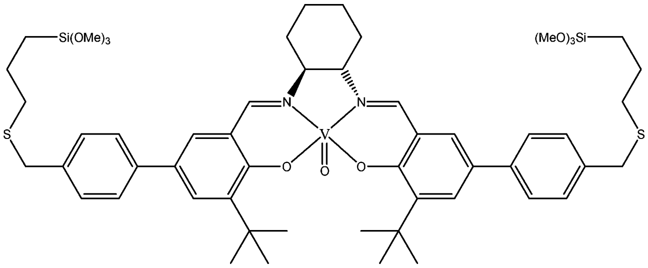

FIGURE 5. PMO precursor for making a chiral catalyst for the cyanosilation of benzaldehyde.

Separate studies have shown that the use of bridging amines[24,25] and cyclam[26–28] moieties are able to bind a variety of transition metal ions. When a PMO is made from *N,N′*-(bis(3-trimethoxysilyl)propyl)ethylenediamine it shows a high affinity for Cu^{2+} ions, while its affinity for Ni^{2+} and Zn^{2+} is comparable to that of a pristine PMS. These materials show absorption of the Cu^{2+} ions until the saturation point is reached,[24] which occurs when only 5–7% of the potential binding sites are occupied. This is typical for most ethylenediamine-functionalized silica systems. A separate study has shown that the binding efficiency of these materials can be increased considerably using molecular imprinting techniques.[25] When the ethylenediamine-functionalized PMO is synthesized in the presence of Cu^{2+} cations, it is possible to create a material in which 85% of the binding sites are occupied, where the binding of the ions is completely reversible.

The incorporation of organometallic complexes into the walls of a PMO can turn the material into a heterogeneous catalyst with an large suface area on which reactions can occur.[16] The chiral vanadium oxide catalyst shown in Figure 5 is capable of enantioselectively catalyzing the cyanosilation of benzaldehyde with an enatiomeric excess (ee) of 30% when contained within the wall of a PMO. However, if the same catalyst is grafted onto the pore walls of a PMS, it is able to catalyze the cyanosilation reaction with an ee of 63%.[16] This decrease in enantioselectivity could very well be the result of the steric constraints that are imposed on the catalyst by the surrounding pore wall. When the catalyst is grafted onto the wall of a PMS it is constrained to the confines of the pore, making it less sterically hindered than a catalyst that is contained with the pore wall itself.

If synthesis conditions are chosen carefully, it has been shown that the pore walls of some PMOs can be semicrystalline.[14,18] Through self-assembly of 1,4-bis(triethoxysilyl)benzene around a cationic surfactant under basic conditions, a well ordered mesoporous material can be made that also shows molecular scale periodicity within the pore walls. It is interesting that the xerogels prepared in the same fashion show no such ordering, suggesting that the self-assembly process plays a large part in the ordering of both the pores and the pore walls.[14]

A major drawback of many of the materials mentioned above is that they will not self-assemble into well-ordered structures on their own. All of the above materials that show ion binding capabilities or catalytic properties must be diluted with another silica source, frequently TEOS or

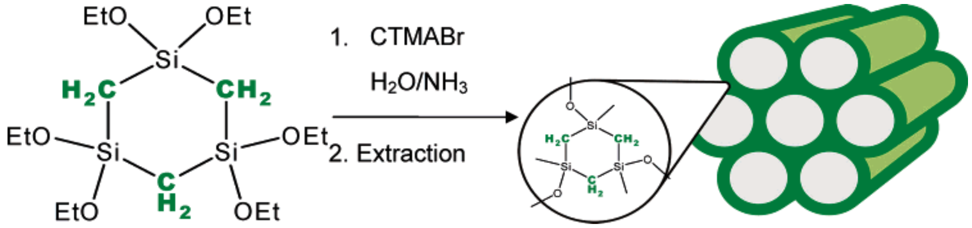

FIGURE 6. Self-assembly of $[SiCH_2(OEt)_2]_3$ with cetyltrimethylammonium bromide as surfactant in an aqueous ammonia solution to make three-ring PMO.

bis(triethoxysilyl)ethane, in order for them to form well-ordered, highly porous materials. This dilution causes several problems that need to be addressed. The first of these problems is the simple fact that the functional groups are at low concentration. In many of their potential applications, it would be desirable to have the concentration of organic be as high as possible. The second problem is the potential for phase separation. If during co-condensation the two precursors phase-separate, it is possible that a well-ordered but nonfunctional silica phase will develop, along with a functional but disordered organosilica phase, and it is very difficult to distinguish the extent to which phase separation may have occurred using standard methods of analysis. But perhaps the most serious problem is the potential inaccessibility of the functional groups. For PMOs to be active, the functional groups must be chemically accessible. It has been shown that relatively small metal cations are able to access the organic groups within the walls of the pores without difficulty; however, when the size of the guest molecule is increased, it becomes less likely that it will be able to access organics within the walls and complications could arise. These types of complications have already been observed in the decrease of enantioselectivity in the aforementioned vanadium catalyst.

High Organic Group Content PMOs with More than One Organic Group Attached to Each Silicon Atom

In PMOs assembled from silsesquioxanes of the type $(EtO)_3SiRSi(OEt)_3$, the number of organic groups is restricted to one organic group attached to each Si atom according to the exclusive presence of SiO_3R building units. Since the organic groups in PMOs are the carrier of the desired property, it is imperative to find pathways that would allow a higher replacement of bridging O atoms by bridging organic groups within the channel walls. This could lead not only to improved physical properties but also to order in the channel walls and new mesostructured topologies or morphologies. Such nanocomposites, which we call "high organic group content PMOs", would consist of SiO_2R_2, $SiOR_3$, or SiR_4 building units. This requires a redesign of the precursor to include these building blocks pre-organized in a molecule that is polymerizable in all three spatial dimensions.

To put these criteria together, rings of the type $[SiR(OEt)_2]_n$ consisting of tetrahedral SiO_2R_2 construction units appear to be a suitable solution. Of these, the cyclic trimer $[SiCH_2(OEt)_2]_3$, originally synthesized by Corriu and coworkers,[29] was chosen as the prototype, which is referred to herein as the three-ring precursor, and successfully self-assembled into a PMO (Figure 6).[30] This PMO has uniform and highly ordered mesopores and a high surface area of around 1700 $m^2\ g^{-1}$. In addition, there are indications from adsorption that it also exhibits micropores in the channel walls, suggesting a hierarchical architecture: submicroporous three-rings condense to larger microporous rings, which are further condensed to give the PMO structure. This PMO also shows excellent thermal stability. No loss of organic groups occurs up to 500 °C in a N_2 atmosphere, and the mesostructure does not change in terms of pore size and order. Interestingly, this PMO undergoes the same distinctive thermal transformation as the methene PMO, transforming CH_2 groups into CH_3 groups through the elimination of silanols between 300 and 500 °C.

In addition, the three-ring precursor $[SiCH_2(OEt)_2]_3$ can be chemically modified by abstracting a proton from a CH_2 group of the three-ring with *t*-BuLi. The lithiated ring can then be reacted with various electrophiles such as I_2, Br_2, and EtI. These substituted rings can also be self-assembled into PMOs with high structural order, and practically all side groups remain after removing the template from the PMO. The substitution by EtI verifies that a C−C carbon bond formation between the ring and side groups is possible, suggesting that a great variety of side groups can be introduced in this way. The successful introduction of iodo and bromo groups not only demonstrates that heteroatoms can be attached to the ring but further provides PMOs with the potential to react with nucleophiles, which we currently are investigating.

Presently a myriad of possibilities for high organic group content PMOs can be envisioned. The presence of three CH_2 groups in the three-ring building block suggests that multifunctional PMOs, in which the different kinds of functionality are integrated in a single building block, are possible. It should be possible to carry out the lithiation and electrophilic substitution reaction three times with different electrophiles to give a three-ring PMO precursor with three different side groups representing three different functionalities (Figure 7a). The use of bi-electrophiles could also allow rings to be linked leading to even more complex building blocks and functionalities (Figure 7b). Because the ring has more connecting points than a conventional PMO precursor, this may also be a promising pathway for PMOs with long bridging chains, since self-assembly is difficult when such bridging groups are between simple $Si(OEt)_3$ units. Additionally the organic

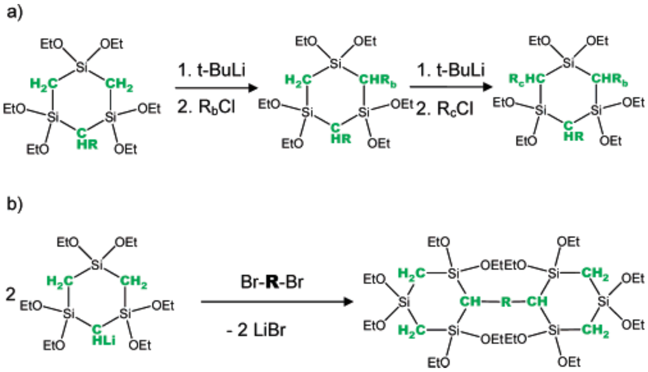

FIGURE 7. Potential synthesis of (a) a PMO precursor with three different functionalities R by stepwise lithiation and (b) interlinked PMO precursor rings with a bifunctional electrophile Br–R–Br.

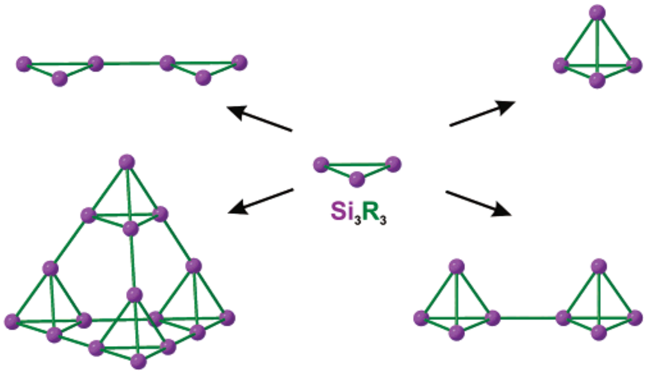

FIGURE 8. Formal condensation of three-rings [(EtO)$_2$SiR]$_3$ leads to condensed rings and cages under formal elimination of EtO groups for ultrahigh organic group content PMOs with SiOR$_3$ and SiR$_4$ building units. Purple balls represent the Si tetrahedral centers. Green lines symbolize the bridging groups R; the ethoxy groups are omitted for clarity.

bridging groups are not limited to CH$_2$ groups or substituted CH$_2$ groups, but also many others can be incorporated by similar synthetic methods giving rings of well-defined size, shape, and composition.

PMOs built of larger rings of the type [SiR]$_n$, $n > 3$, with various R groups could be used as building blocks to give PMOs with channel walls having discrete micropore sizes leading to high binding selectivities toward guest molecules, which would be very interesting for catalysis, sensing, separation, or chemical storage and controlled release applications.

Condensing rings leads to cages, and this concept points toward building blocks for ultrahigh organic group content PMOs with more than two bridging organic groups bound to each Si atom (Figure 8). For example, an adamantane-like cage would provide a PMO precursor with exclusively three organic groups around each Si atom. Linking such cages makes the synthesis of PMOs with SiR$_4$ units with an even higher organic content a realistic opportunity.

PMOs as Oriented Thin Films

Most PMOs developed to date have been powders precipitated and filtered from solution without any control of morphology. A thin film morphology, which can be patterned lithographically, is important and necessary for many applications such as sensors, membranes, biomedical or functional nanocomposite coatings, thin film chromatography, and microelectromechanical systems (MEMs).

One immediate application for PMO films is for low dielectric constant (k) layers in microelectronic systems. The increasing density of devices and interconnects demands insulating dielectric materials with k sufficiently low to prevent cross-talk and limit the signal delays caused by intra- and interlayer capacitance.[31,32] A new generation of low-k materials must be less than silica ($k \approx 3.8$), and ultimately, ultralow k layers ($k < 2.0$) are required soon as device feature sizes approach 100 nm and smaller.[33]

There are three important ways to achieve a low k value. The first is to incorporate a large porous volume fraction, since $k_{\mathrm{air}} \approx 1.0$, though very highly porous or disordered networks (i.e., aerogels) can become mechanically fragile. The second is to reduce the atomic weight and polarizability of the matrix network. For silica-based materials, there are many examples incorporating terminal organic groups in place of Si–O–Si bridges as organosilicas. However, many of these sacrifice mechanical stability by disrupting the network connectivity of siloxane bridges with terminal organic groups.[34] Finally, the material must resist moisture adsorption, so surface silanol groups are generally capped using hexamethyldisilazane (HMDS) or trimethylsilyl chloride (TMSC).[34,35]

Supported films of PMS can be deposited by dip-coating or spin-coating.[36,37] Ogawa[36] first reported spin-coated hexagonal films using an acidic silicate/surfactant solution. Lu et al.[37] introduced the principle of “evaporation-induced self-assembly” (EISA), associated with the rapid formation of mesostructured thin films and aerosol-generated particles. In EISA, an excess of volatile solvent keeps the surfactant below the critical micelle concentration until it is spread upon a substrate, when rapid solvent evaporation allows self-assembly of the silica/surfactant micelles. EISA is very useful for controlling morphology because the hydrolyzed solution can be applied to patterning by soft lithography moulds (i.e., micromolding in capillaries (MIMIC)),[38] ink-jet printing,[39] or growing within the channels of porous alumina,[40] in addition to conventional photolithography.[41]

Dag et al.[42] first reported PMO films synthesized by casting thick films of alkyl-, 2,5-thiophene-, and 1,4-phenylene-bridged silsesquioxanes. A nonionic surfactant was used in a lyotropic liquid-crystal templating method. However, the resulting order of the films was not very high, and this method requires careful control over the vacuum-assisted removal of the ethanol produced through hydrolysis, which can destroy the mesostructure. Lu et al.[43] demonstrated the application of the EISA method for PMO thin films. Thin films of bridged ethene–silica were prepared using cationic, nonionic, and anionic surfactants. Films were prepared with an increasing ratio of precursor/TEOS, calcined, and then treated with HMDS to remove surface silanols. There was a decrease in dielectric constant with increasing organic content to values of $k = 1.98$ and increasing elastic modulus and hardness values

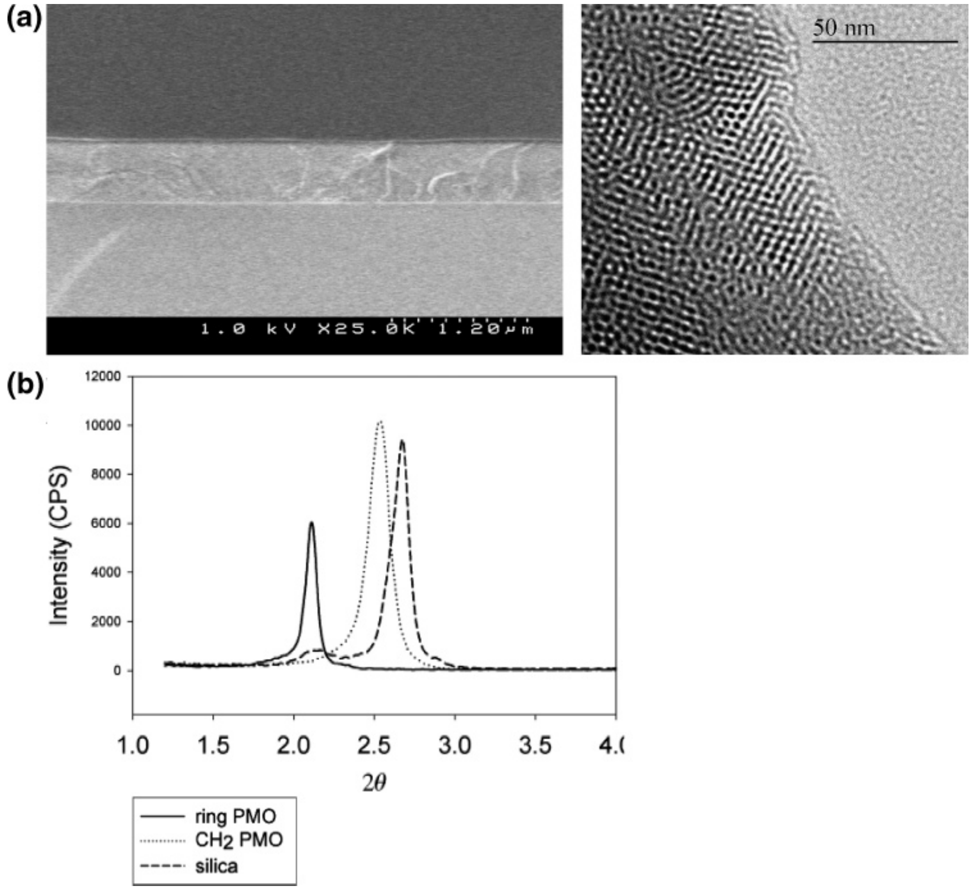

FIGURE 9. (a) An SEM image of the cross-section (left) and a TEM image of the hexagonal mesostructure (right) of a methenesilica PMO thin film and (b) PXRD spectra of PMS, methenesilica PMO, and three-ring PMO films after calcination at 300 °C.

corresponding to the replacement of Si−O−Si with Si−$(CH_2)_2$−Si bridges.

The most recent examples of PMO thin films come from our own work on the application of EISA methods. We have developed a generalized procedure applicable for a wide range of bridged silsesquioxane precursors (i.e., methene, ethene, ethylene, 1,4-phenylene, and 1,3,5-phenylene) and the three-ring PMO.[30,43] Briefly, silsesquioxane precursors (such as $[(EtO)_2Si(CH_2)]_3$), HCl/H_2O, surfactant and ethanol are stirred in solution and spin-coated onto glass or silicon. The ∼500 nm thick films are calcined in nitrogen or solvent-extracted in MeOH/HCl without cracking or loss of mesostructure. Figure 9a illustrates a methenesilica film in cross-section with a corresponding TEM image of the 2D hexagonal mesostructure. Figure 9b shows powder X-ray diffraction (PXRD) spectra of methene and three-ring PMO films, which indicate an interesting difference in *d* spacing with chemical structure. ^{29}Si MAS NMR on powder scratched from films confirmed that Si−C bonds were not cleaved during the film deposition or calcination.

Films with varying organic content can be synthesized using appropriate mixtures of the silica (tetramethyl orthosilicate, TMOS) and the PMO precursors. As result, three-ring PMO films were produced with molar fractions of the Si sites $f_R = D/(D + Q) = 0, 0.25, 0.5, 0.75$, and 1,[30] where D is an SiO_2R_2 unit, and Q is an SiO_4 unit. Similarly, methene PMO films were produced for $f_M = T/(T + Q)$, where T is an SiO_3R unit, with the same ratios.[44] A linear dependency of the (100) *d* spacing on the organic molar fraction *f* was observed for both materials, indicating their compositional homogeneity according to the Vegard law (Figure 10).

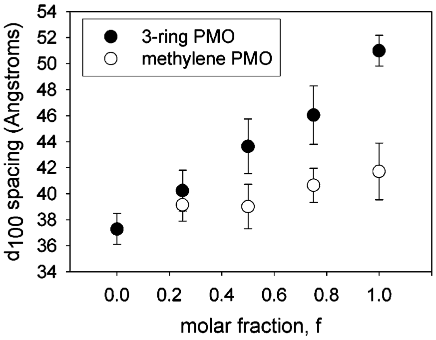

FIGURE 10. The linear change in the (100) *d* spacing for the methenesilica and three-ring PMO films as a function of the organic content, as measured by the molar fraction *f*.

Parallel-plate capacitance measurements at 1 MHz were used to calculate *k* for the calcined films. Both materials showed *k* decreasing with increasing organic group content to values $k \approx 2.5$ for films made entirely from the organic precursors (i.e., $f = 1.0$) (Figure 11). However, an interesting result was achieved by taking advantage of the silanol-eliminating transformation from bridging methene to terminal methyl groups discussed

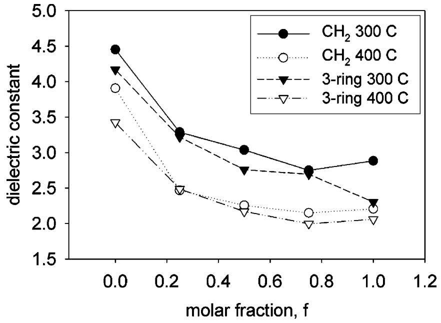

FIGURE 11. The change in dielectric constant for the methenesilica and three-ring PMO films as a function of the organic content. Results are shown for the normal calcined materials (Si–C bonds intact) and those treated at 400 °C (bridge–terminal transformation).

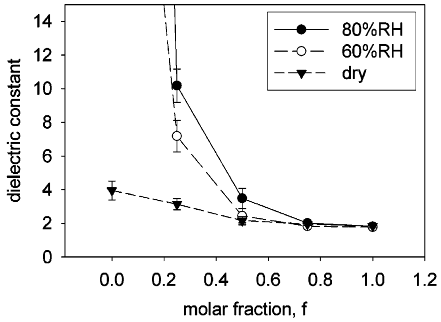

FIGURE 12. The change in dielectric constant after exposure to 60% and 80% relative humidity environments for the methenesilica PMO after 500 °C heat treatment as a function of the organic content.

above. We heated the *same* samples to 400–500 °C (under N_2), which caused a partial D to T site conversion in the three-ring PMO and a partial T to Q conversion in the methene PMO. As a result, k decreased further, to values as low as 1.9 and 1.8 for the three-ring and methene films having $f = 1.0$. We are currently optimizing these values further through control of porosity and structural phase. Furthermore, preliminary tests indicate that k for the 500 °C-treated methene PMO increased from 1.8 to only 1.9 after 5 days exposure to 80% relative humidity (Figure 12), unlike those compositions with $f < 0.75$. The significance is that a postsynthesis surface modification (using HMDS or TMSC, for example) is not necessary for moisture resistance, just a thermal treatment to induce what we term “self-hydrophobization”. Nanoindentation measurements of the PMO films indicate mechanical properties similar to mesoporous silica (i.e., $E \approx 10$ GPa). Therefore, it seems that PMO films may have an ideal combination of dielectric, mechanical, and moisture-resistance properties for next generation low-k microelectronic applications.

PMOs Future Perspectives—Matter that Matters

The greatest appeal of the PMOs is their ability to fuse the strength of two of the central chemistry disciplines, namely, organic and inorganic chemistry, with the power of the solid-state, colloid, liquid crystal, and sol–gel sciences. The result of this union is a new world of nanocomposites in which organic groups can be integrated, by design, into an inorganic material with crystalline mesoporosity. The exciting research results for PMOs that have been reported by many groups around the world since their announcement in 1999 bode well for the future science and technology of this new class of hybrid materials.

A pertinent question five years after the discovery of PMOs is what next? Beyond the obvious extensions already outlined in the previous chapters, one of the new frontiers will likely involve higher levels of complexity in the form of hierarchical architectures that have structural features spanning nanometer to micrometer and larger dimensions, in which some attribute of the PMOs will play a central role in terms of materials structure–property–function relations and ultimately utility. This is a “global” way of thinking about PMOs, where, for example, PMO precursors and PMOs with a particular form can be self-assembled with other nanomaterials such as clusters, colloids, wires, rods, spirals, rings, and sheets through specific chemical bonding and interfacial interactions to create purposeful constructs.

To illustrate, with a judicious choice of organic, a PMO-based colloidal crystal film or colloidal crystal capillary column could function as separator and optical Bragg detector in micro-total analysis and nano-analytical systems in the still emerging field of proteonomics. Similarly, with an acidic organic group and designed mechanical properties, a PMO could enable an alternative to Nafion as the proton exchange membrane for a H_2–O_2 fuel cell or new heterogeneous catalysts. A PMO film having an organic functionalized with an alkane sidearm could serve as the matrix for organizing an array of ligand-capped semiconductor quantum dots for use as the active component in a new generation of light-emitting diodes. With appropriate organics, PMOs could be made into flexible patches for the controlled release of pharmaceuticals due to distinct adsorption–desorption properties that a PMO could have toward drugs. PMOs with intentionally designed solvatochromic or fluorescent molecular recognition bridging organics within the channel walls could be made into fibers by the method of electrospinning to make a smart PMO cloth that senses, through an optical absorption or emission change, chemical or biological warfare agents. It would be fascinating to co-assemble PMO precursors and polyelectrolytes with block copolymer templates to form a new generation of hybrids with novel properties emerging from pore walls comprised of organosilica and polymer moieties. Lessons learned from the PMOs suggest that the utilization of building blocks other than silsesquioxanes could lead to mesostructured materials of the next kind incorporating inorganic rings and cages such as borazines, thiazenes, phosphazenes, boranes, and carboranes functionalized with alkoxysilanes. These are just a few glimpses of the prospects for the next higher level of PMO research beyond the obvious in the not too distant future.

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