Mesoporous Materials

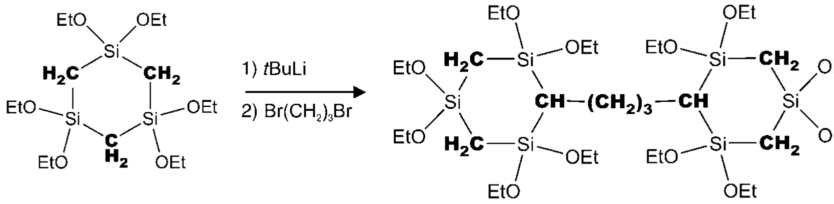
Periodic Mesoporous Organosilicas: Self-Assembly from Bridged Cyclic Silsesquioxane Precursors**

*Kai Landskron and Geoffrey A. Ozin**

Synthetic materials with a hierarchically ordered structure spanning multiple length scales from the molecular up to the macroscopic level, akin to nature's biological systems, are currently of considerable interest for a future nanotechnology that uses "bottom-up" approaches.[1] In this context periodic mesoporous organosilicas (PMOs) are a promising class of compounds.[2–4] They exhibit crystalline mesopores with walls comprising tetrahedrally coordinated silicon[4] centers bridged by oxygen atoms[2] and organic groups (R)[2]. This arrangement represents a fusion of inorganic and organic components at the subnanometer length scale within an ordered nanoscopic material. Because they can be made with powder or film morphologies, their macroscopic shape can also be designed.[5–7] The first PMOs synthesized from silsesquioxanes of the type $(EtO)_3Si\text{-}R\text{-}Si(OEt)_3$ contain one organic bridging group R, such as methene, ethene, or ethylene, bound to each Si atom and consist exclusively of SiO_3R tetrahedra[5–7] leading to an approximate composition of $SiO_{1.5}R_{0.5}$. Recently we have shown that by using cyclic silsesquioxanes of the type $[\{SiR(OEt)_2\}_3]$ a far higher organic load can be achieved in a PMO because each silicon tetrahedral center is bound to two organic bridging groups and an approximate composition of SiOR is reached.[7] We call this class of compounds "high organic group content PMOs". Higher organic content can lead to significantly improved materials properties, such as very low dielectric constants, a high elastic modulus, excellent thermal stability, and hydrophobicity, which make the PMOs interesting as a packaging material for microelectronic applications.[7] Furthermore hierarchical order within the channel walls is achieved owing to the material's exclusive construction from Si_3R_3 3-ring building blocks rather than acyclic building blocks that give a three-dimensional framework with a random distribution of condensed $Si_nO_{n-m}R_m$ rings ($n > 1$; $0 < m < n$).

To drive the complexity and the hierarchical order of the channel walls in high organic group content PMOs to the next level we have aimed to synthesize silsesquioxane precursors in which two cyclic building blocks are bridged by an organic group. Recently we showed that the CH_2 groups of the 3-ring molecule $[\{SiCH_2(OEt)_2\}_3]$ can be lithiated with *t*BuLi and then treated with an electrophile E, such as ethyl iodide, Br_2, or I_2, to yield E-substituted cyclic silsesquioxanes of the type $[\{SiCH_2(OEt)_2\}_2\{SiCHE(OEt)\}]$.[7] This chemistry suggested the use of reagents with two electrophilic ends of the type Hal-R-Hal (Hal = halogen) to achieve ring linkage and then self-assembly of the resulting precursor of the type $[\{[(EtO)_2SiCH_2]_2[(EtO)_2SiCH]\}_2R]$ into a PMO.

We chose 1,2-dibromoethane and 1,3-dibromopropane as electrophiles. While reactions with dibromoethane failed to give the expected ethene-bridged ring silsesquioxane, we successfully obtained the target molecule $[\{[(EtO)_2SiCH_2]_2[(EtO)_2SiCH]\}_2\{(CH_2)_3\}]$ (**1**) with trimethylene-bridged 3-rings (Scheme 1).



1

Scheme 1. Preparation of $[\{[(EtO)_2SiCH_2]_2[(EtO)_2SiCH]\}_2\{(CH_2)_3\}]$ (**1**).

After purification by distillation under high vacuum, **1** was obtained in pure form according to ^1H, ^{13}C, and ^{29}Si NMR spectroscopy data as well as electrospray mass spectrometry. In the case of dibromoethane surprisingly we obtained $[\{SiCH_2(OEt)_2\}_2\{SiCHBr(OEt)\}]$ as the main product. The explanation may be that the dibromoethane reacts with the lithiated intermediate through transfer of Br^+ to the ring and elimination of ethene (C_2H_4) and Br^-.

The PMO self-assembled from **1** by using NaCl-assisted acid-catalyzed self-assembly with the tri-block copolyether P123 as templating agent. The as-synthesized material was extracted with a HCl/acetone mixture to remove the template. The resulting PMO showed periodic mesopores with a *d* spacing of 11.5 nm according to powder X-ray diffraction (PXRD) studies (Figure 1 A), a pore diameter of approximately 6 nm, and a channel wall thickness of also approximately 6 nm determined by scanning electron microscopy (SEM; Figure 1 B) and transmission electron microscopy (TEM; Figure 1 D). N_2 adsorption experiments revealed a type IV isotherm with minor hysteresis indicating the existence of highly uniform mesopores (Figure 1 C). A BJH analysis of the adsorption branch showed a narrow pore size distribution with an average pore size of 6.9 nm consistent with the TEM data (Figure 1 C, inset). The BET surface area was determined to be $967\,m^2g^{-1}$. The PMO material displayed excellent thermal stability with no mass loss up to 400 °C in a N_2 atmosphere (determined by thermal gravimetric analysis (TGA)).

^{29}Si magic-angle spinning (MAS) NMR spectroscopy data for both the as-synthesized (Figure 2 A) and the extracted PMO (Figure 2 B) showed a broad signal between $\delta = 0$ and -30 ppm that can be assigned to D sites of the SiC_2O_2

---

[*] Dr. K. Landskron, Prof. G. A. Ozin
Materials Chemistry Research Group
Department of Chemistry
University of Toronto
80 St. George Street, Toronto, Ontario M5S 3H6 (Canada)
Fax: (+1) 416-971-0091
E-mail: gozin@alchemy.chem.utoronto.ca

[**] G.A.O. is Government of Canada Research Chair in Materials Chemistry. He is indebted to the Natural Sciences and Engineering Research Council (NSERC) of Canada for support of this work.

DOI: 10.1002/ange.200462279
© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

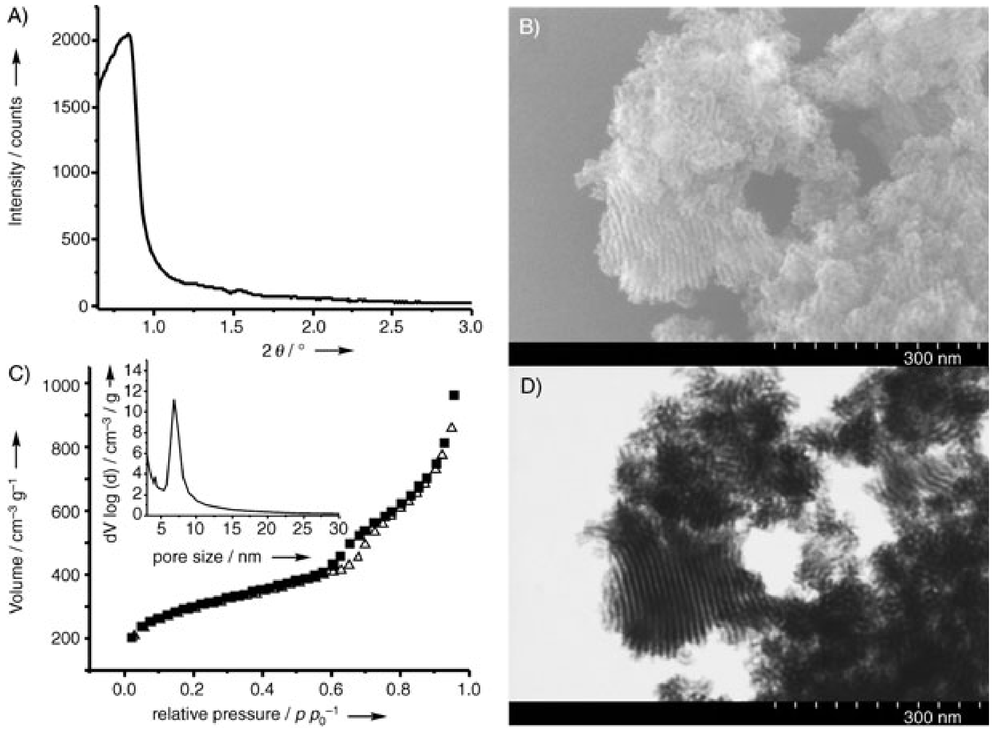


Figure 1. A) PXRD of the extracted PMO, B) SEM image, D) TEM image of the PMO with trimethylene-bridged 3-ring building units, C) N_2 isotherm of the PMO. Inset: pore size distribution.

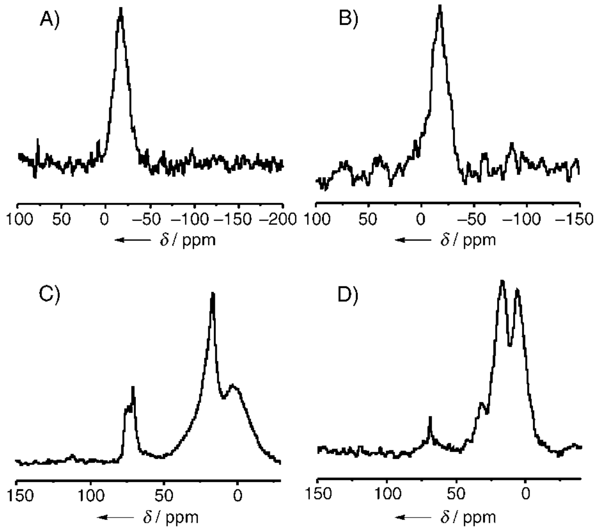


Figure 2. ^{29}Si MAS-NMR spectrum of the as-synthesized PMO (A) and the corresponding spectrum for the extracted PMO (B), the ^{13}C CP-MAS-NMR spectrum of the as-synthesized material (C) and the corresponding spectrum for the extracted PMO (D).

tetrahedra, which correspond well to the chemical shift of the ^{29}Si signals ($\delta = -8.1$ and -9.0 ppm) of the precursor molecule. The presence of the organic groups is confirmed by ^{13}C cross-polarization (CP)-MAS-NMR spectra of the as-synthesized (Figure 2C) and the extracted (Figure 2D) samples. In the spectrum of the extracted material, three overlapping signals around $\delta = 5$, 17, and 32 ppm can be seen, which can be assigned to the trimethylene group as well as the CH and CH_2 groups of the trimethylene-bridged 3-ring units. The peaks correspond well with the ^{13}C signals at $\delta = 36.4$, 23.9 ppm (CH_2 groups of the trimethylene bridge), 14.3, and -1.6 ppm (CH and CH_2 groups of the ring) of the precursor molecule. The weak signal at 69 ppm indicates that small amounts of P123 template remained after the extraction of the material (Figure 2D). In the ^{13}C NMR spectrum of the as-synthesized PMO (Figure 2C) the presence of the P123 template is indicated by intense peaks at $\delta = 70$, 73, and 75 ppm for the carbon atoms bound to oxygen in the polyether. The CH_3 groups of the 1,2-dioxopropene $OCH_2CH(CH_3)O$ groups of P123 that have a chemical shift around $\delta = 20$ ppm overlap with the signals of the organic bridging groups in the channel walls of the PMO which accounts for the difference between the spectra of the as-synthesized and the extracted PMO. The NMR spectroscopic data indicate that practically no Si–C bond cleavage has occurred in the PMO during the self-assembly or the extraction processes. Thus, the integrity of the trimethylene-bridged 3-ring building block is maintained intact in the channel walls of the PMO.

Note that all previous attempts to self-assemble conventional $(EtO)_3SiRSi(OEt)_3$ silsesquioxane precursors that have alkene bridging groups with more than two CH_2 groups between silicon have failed to give PMOs with long range mesostructural order. Hence, the successful self-assembly of the trimethylene-bridged cyclic silsesquioxane precursor **1** to yield the well-ordered trimethylene-bridged 3-ring PMO described herein opens a myriad of opportunities for integrating a far wider range of organic bridging groups into PMOs than previously deemed possible.

Experimental Section

1: $[\{(EtO)_2SiCH_2\}_3]$ (7.5 mmol, 3 g) was dissolved in THF (200 mL; dried over Na/benzophenone) in a 1-l 3-necked flask under nitrogen and cooled to $-78\,°C$ in a dry ice/acetone bath. A 1.7 M solution of *t*BuLi (8.25 mmol, 4.8 mL; Aldrich) was added dropwise and the mixture was stirred for 30 min. Then 1,3-dibromopropane (3.75 mmol, 0.38 mL; Aldrich) was added dropwise. The solution was slowly warmed to room temperature and stirred for 2 days, then the solvent was removed in a rotary evaporator. Pentane (200 mL; anhydrous, 99+ %; Aldrich) was added, and the mixture was filtered. The pentane was evaporated from the filtrate and the residue was distilled under high vacuum. The third fraction gave the desired pure product $[\{[(EtO)_2SiCH_2]_2[(EtO)_2SiCH]\}_2\{(CH_2)_3\}]$ (30 %, b.p. 145 °C at 20 mTorr). ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 58.36$ (s, CH_2), 58.21 (s, CH_2), 58.17 (s, CH_2), 58.13 (s, CH_2), 18.41–18.48 (m, CH_3), 36.44 (s, CH_2), 23.93 (s, CH_2), 14.27 (s, CH), -1.61 ppm (s, CH_2); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.65$–3.85 (24 H, m), 1.45–1.6 (2 H, m), 1.1–1.25 (38 H, m), 0.15–0.3 (2 H, m), 0–0.1 ppm (8 H, m); ^{29}Si NMR (400 MHz, $CDCl_3$): $\delta = -8.1$ (s), -9.0 ppm (s); MS (ESI): *m*/*z*: 832 (100 %).

Synthesis of trimethylene-bridged 3-ring periodic mesoporous organosilica (PMO): NaCl (25.8 mmol, 1.85 g) and Pluronic 123 (0.336 g; BASF) were dissolved in 2 N HCl (8.4 g) and H_2O (155 mmol, 2.8 g). Compound **1** (0.84 mmol, 0.7 g) was added to this solution with vigorous stirring at room temperature. The mixture was stirred at room temperature for 24 h and a white precipitate formed. The mixture was kept under static conditions for another 48 h at 80 °C. After filtration the PMO was obtained as a white powder. The extraction was carried out by stirring the as-synthesized PMOs in a mixture of acetone (250 mL) and 2 N HCl (10 mL) for 2 days.

PXRD patterns were measured with a Siemens D5000 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 154.18$ pm). TEM and SEM images were recorded on a Hitachi S5200 microscope at an accelerating voltage of 30 kV (film fragments on carbon-film-coated Cu grids) at the University of Toronto nanoimaging facilities. All solid-state NMR experiments were performed with a Bruker Avance DSX 400 NMR spectrometer. ^{29}Si MAS-NMR spectra were recorded at a spin rate of 5 kHz and a pulse delay of 5 s. ^{13}C CP-MAS-NMR experiments were performed at a spin rate of 5 kHz, a contact time of 5 ms, and a pulse delay of 3 s. Sorption experiments were performed by a Quantachrome Autosorb-1C machine with N_2 as sorption gas at 77 K starting at a relative pressure $p/p_0 = 10^{-5}$. Seven data points were selected for BET analysis from a relative pressure of 0.1.

Received: October 12, 2004

Published online: March 2, 2005

Keywords: mesoporous materials · organosilica · self-assembly · silicon · soft matter

---

[1] I. W. Hamley, *Angew. Chem.* **2003**, *115*, 1730; *Angew. Chem. Int. Ed.* **2003**, *42*, 1692.
[2] T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867.
[3] B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* **1999**, *11*, 3302.
[4] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **1999**, *121*, 9611.
[5] S. Park, C.-S. Ha, *Chem. Commun.* **2004**, 1986.
[6] O. Dag, C. Yoshina-Ishii, T. Asefa, M. J. MacLachlan, H. Grondey, N. Coombs, G. A. Ozin, *Adv. Funct. Mater.* **2001**, *11*, 213.
[7] K. Landskron, B. D. Hatton, D. D. Perovic, G. A. Ozin, *Science* **2003**, *302*, 266.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim