Periodic Mesoporous Organosilicas with Phenylene Bridging Groups, 1,4-$(CH_2)_nC_6H_4$ ($n = 0-2$)

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Periodic mesoporous organosilicas (PMOs) were prepared by polymerizing phenylene-bridged silsesquioxane precursors containing an incremental increase in methylene spacers [1,4-$(CH_2)_nC_6H_4$ ($n = 0-2$)] in combination with polyoxyethylene(10) cetyl ether (Brij 56) oligomers as structure-directing species under acid catalysis. Surfactant templates were removed from the nanoporous inorganic–organic hybrids using acidified ethanol extractions. Mesoporous organosilicas were characterized by powder X-ray diffraction, nitrogen gas sorption, ^{13}C and ^{29}Si solid-state NMR, scanning and transmission electron microscopy, and thermogravimetric analysis. Organosilica materials formed uniform arrays of 2D-hexagonal mesopores with pore diameters ranging from 2 to 3 nm and corresponding surface areas of 750–1200 m^2g^{-1}. Addition of two methylene groups to the phenylene bridge resulted in a substantial decrease in the pore size, surface area, and pore volume. The thermal stability of the materials decreases in the following order: phenylene > 4-benzyl > *p*-xylene. Aryl–silicon bonded networks display greater thermal stability than methylene–silica covalently bound frameworks. Decomposition of aryl–silica units occurred between 450 and 750 °C, whereas methylene–silica moieties decomposed in the range 300–600 °C. These hybrid mesoporous materials represent the first introduction of precursors with two-structural organic-bridging units as an integral part of the organosilicate-bonded matrix.

Introduction

Engineering porosity in silica materials through the polymerization of precursors cast around a supramolecular template has sparked great interest since the discovery of mesoporous silicas in 1992.[1] This "soft" nanotechnology uses surfactant or block copolymer templates to pattern "hard" inorganic materials. Numerous scientists have extended the compositional range to include non-silica oxides,[2] and terminal organic groups through either a postsynthetic grafting procedure onto surface silanol groups, or co-condensation of monosilanes with tetraethoxysilane.[3] Limited loading of terminal $RSiO_3$ units before structural collapse,[4] congregation at pore openings, and inhomogeneous distributions are restricting factors in the co-condensation method. Nonetheless "meso" materials show promise in a number of applications such as low-k dielectrics, chromatography, and as nano-templates.[5] In 1999, three groups simultaneously reported the formation of a new class of hybrid organic–inorganic materials. Bridged silsesquioxane precursors, where the bridging organic group is covalently bonded within the polysiloxane network, were self-assembled into a mesoporous framework.[6] Termed PMOs, these organosilicate materials were prepared through the surfactant-templated condensation of bridged silsesquioxane precursors, $(R'O)_3SiRSi(OR')_3$. Siloxane linkages provide structural rigidity, while bridge-bonded organic groups allow tailoring of the material properties. Bis-silylated methylene, ethylene, ethene, phenylene and thiophene PMOs were prepared. Acetylene and ferrocene bridges were also integrated, except these materials showed substantial Si–C bond cleavage and synthetic conditions were not optimized.[7] It is clear from these studies that the organic units are structural components of the framework, so material properties (chemical, physical, mechanical, and electrical) can be modulated by the nature and proportion of the bridge-bonded organic moieties in the material. However, the currently synthesized PMOs are limited to short aliphatic chains (methane, ethane, ethene) or rigid and symmetrical aryl bridging groups

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(phenylene, thiophene). Most reports focus on varying morphologies of ethane- and benzene-bridged PMO materials, while the compositional domain remains limited.[8, 9]

Increasing the compositional breadth of PMO materials encounters several roadblocks. Although the ethane-bridged PMO can be prepared under a wide range of conditions (pH, temperature, concentration) increasing the distance between condensable silicon environments requires a more judicial choice of synthesis protocols. In the self-assembly mechanism silicate oligomers form and interact with the micelle surface, transforming the micelles into a hexagonal array through cooperative self-assembly.[10] The process is driven by electrostatic charge density matching between charged surfactant assemblies and inorganic precursors. Increasing the organic content in the bridged silsesquioxanes decreases the charge density on organosilicate species relative to tetraethoxysilane derivatives and hinders the long-range ordering of the material as interfacial interactions between nanobuilding blocks and template become insufficient. In addition, steric constraints imposed by the organic bridges prevent efficient packing. High-organic-content precursors are inherently hydrophobic and either phase separate from the aqueous phase or poorly conform to the micellar template resulting in disordered materials whose pore structures often collapse under the large capillary stresses that develop during drying or surfactant removal. The ability to maintain the framework mesostructure is also a concern with flexible organic-bridges. Furthermore, the flexible Si−O−Si bond can vary between 140 and 180° and therefore easily pack around a cylindrical template retaining the long-range order of the mesostructure. Bridging organic units have more restricted flexibility since the range of conformations in carbon chains is more limited, so bridged silsesquioxanes generally do not form as good replications of the micelle template compared to silicas. Therefore, for longer chain bridged organic groups or larger oligomeric building units, it is necessary to employ a template of sufficient diameter to allow uniform encapsulation by the polymerizing bridge-bonded silsesquioxanes.

The nonionic Brij 56 oligomeric surfactant [$CH_3(CH_2)_{15}(OCH_2CH_2)_{10}OH$] proved more suitable for this study than the shorter chain cetylpyridinium surfactant used to assemble 1,4-bis(triethoxysilyl)benzene derivatives.[9a−e] Nonionic alkyl poly(ethylene oxide) surfactants are nontoxic, biodegradable, display excellent interfacial interactions, and have been used to form mesoporous silica materials.[11] PMOs have been prepared using Brij surfactants with ethane-,[12] ethene-,[13] and benzene-bridged precursors.[14] Moreover, PMOs prepared using nonionic alkylethylene oxide templates were shown to possess better mechanical and hydrothermal stabilities than analogous periodic mesoporous silicas (PMSs).[15] Electrostatic and hydrogen-bonding interactions influence the self-assembly when using nonionic poly(ethylene oxide) surfactants. Employing strongly acidic conditions well below the isoelectronic point of silica (ca. pH = 2) ensures charged protonated organosilanol species are involved and interact preferentially with the PEO blocks promoting cooperative self-assembly into mesophases.

Most bridge-bonded PMO materials are prepared from a single polysilsesquioxane precursor. A recent report by Markowitz and co-workers described the preparation of PMOs through the copolymerization of phenylene and ethylene bridged bis(triethoxysilyl) precursors. The authors were able to tune the properties of the resulting materials, with the mixed PMO materials containing ethane- and benzene-bridges exhibiting the greater adsorption capacity for 4-chlorophenol than either individually condensed PMO. Although the molar ratio of phenylene to ethylene units was similar, the distribution of these organic bridges was presumably random due to mixing, diffusion rates, and differences in hydrolysis and condensation rates of the precursors.[16]

Inagaki and co-workers described the anisotropic organization of 1,4-phenylene and 4,4′-biphenylene units dispersed within a silica matrix forming crystal-like pore walls. Phenyl groups were homogeneously distributed at the molecular level.[9f,g] The synthesis of phenylene bridged PMOs can be aided by $\pi-\pi$ intermolecular interactions between aromatic rings or hydrogen bonding between aromatic ring C−SiOH groups leading to preferential alignment of the organic bridges in the organosilicate network, which may facilitate the self-assembly process into ordered mesostructures.[17] However, this beneficial molecular self-assembly process is inhibited when methylene spacers are added to the bridged silsesquioxane precursors, so new synthetic

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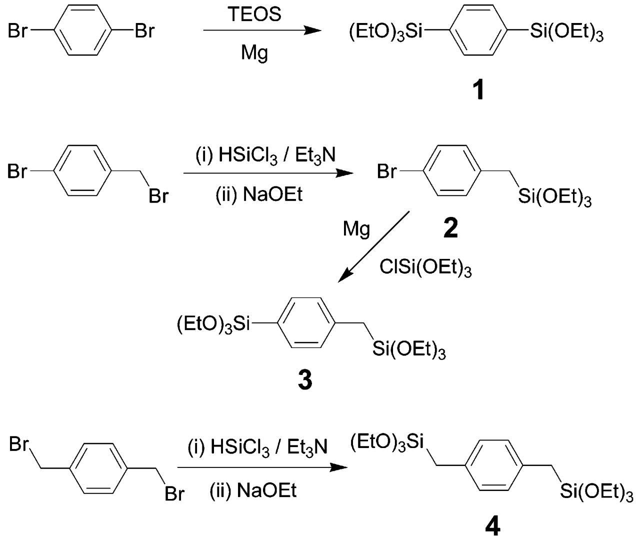
Scheme 1



strategies must be adopted to form well-ordered mesoporous materials.

The bridged silsesquioxane $[1,4\text{-}\{(EtO)_3SiCH_2\}_2C_6H_4]$ was previously used in the formation of xerogel materials.[18] In contrast to the amorphous organosilicate xerogels,[19] PMOs have the prominent features of periodic arrays of mesoscale pores, well-defined pore shapes, narrow pore size distributions on the nanometer scale, insignificant pore blocking, large pore volumes, tunable pore sizes, and high surface areas. Xerogels by contrast, are networks of interconnected, covalently bonded silicas or organosilicas with a random distribution of pore sizes.

In this contribution, we present the preparation of PMOs combining the characteristics of "rigid" aromatic bridges and "flexible" methylene bridges. This new class of aromatic PMOs contains bridge-bonded aryl-methylene units. Well-ordered hexagonal mesoporous structures are formed using alkylethylene oxide surfactant templates.

Results and Discussion

Hybrid PMO precursors were prepared according to Scheme 1. A Grignard type reaction employing tetraethoxysilane, magnesium, and 1,4-dibromobenzene under reflux was used to prepare 1,4-bis(triethoxysilyl)benzene, **1**.[9a] The method of Benkeser involving the reaction of a chlorosilyl anion with benzyl halides was used to synthesize 1,4-(triethoxysilylmethyl)benzene, **4**.[20] Compound **4** was synthesized from trichlorosilane, triethylamine, and $1,4\text{-}C_6H_4(CH_2Br)$ followed by ethanolysis of the Si−Cl bonds. The 4-benzyl-bridged precursor was prepared using a two-step method. Nucleophilic substitution of benzyl−halogen bonds by a trichlorosilyl unit was accomplished using the Benkeser reaction followed by ethanolysis. In the second step, the aryl−halogen bond was exchanged with a triethoxysilyl group using chlorotriethoxysilane under Grignard conditions to yield α, *p*-bis(triethoxysilyl)toluene, **3**. All the precursor molecules were isolated as colorless liquids following multiple distillations in vacuo and were subsequently characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. ^{29}Si resonances for the aryl−silica moiety of **1** occur at −58.1 ppm, whereas the chemical shift of the methylene−silica environments in **4** appear at −50.8 ppm. The 4-benzyl-bridged precursor **3** displays two resonances at −51.6 and −56.6 ppm in the ^{29}Si NMR, attributed to the CH_2Si and ArSi environments, respectively.

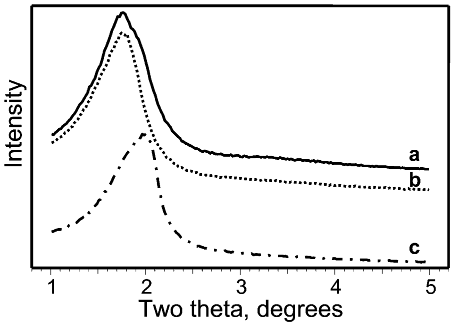


Figure 1. Powder X-ray diffraction patterns of surfactant-extracted PMO materials: (a) phenylene, (b) 4-benzyl, (c) *p*-xylene

PMOs were prepared by condensing the synthesized organosilica precursors around a micellar poly(ethylene oxide) oligomeric template, $C_{16}H_{33}(OCH_2CH_2)_{10}OH$, denoted commercially as Brij 56, in a highly acidic aqueous medium. For a typical PMO synthesis, the Brij-56 surfactant (0.43 g) was dissolved in deionized water (20.9 g) and HCl (1.5 g, 12 M) in a closed polypropylene bottle. The resulting solution was stirred for 1 h at 60 °C, followed by the addition of sodium chloride (2.7 g) and an additional 3 h of stirring. The organosilica precursor 1,4-bis(triethoxysilylmethyl)benzene (1.00 g) was added under vigorous stirring to the clear homogeneous solution. After a few minutes, a white precipitate began to form. The reaction mixture was stirred for 20 h at 60 °C, followed by aging the suspension at 80 °C under static conditions. A compositional molar ratio organosilica/Brij-56/HCl/H_2O/NaCl of 1.0/0.27/6.5/500/20 was used to synthesize the other PMO materials. Templates were removed from the recovered materials by repeated extractions in acidified ethanol (1.5 g HCl to 100 g EtOH for ca. 0.5 g of sample).

Examination of the materials by PXRD revealed an intense low-angle Bragg diffraction peak indicative of an ordered mesostructured material (Figure 1). We tentatively assigned these peaks to the $d(100)$ interplanar spacing of a two-dimensional hexagonal symmetry mesostructure. The d spacing for the phenylene and 4-benzyl precursors appear at 50 Å, corresponding to the 2D-hexagonal unit cell parameter $a_o = 58$ Å. The similar values obtained suggest the steric packing constraints imposed by the bridge-bonded organic group vary little. Increasing the organic bridge to include two methylene units causes a large decrease in the $d(100)$ reflection to 45 Å with a corresponding lattice constant

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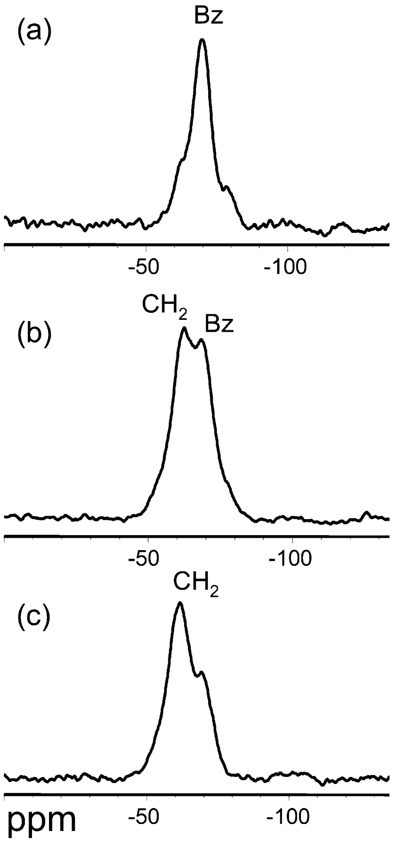

Figure 2. ^{29}Si CP/MAS NMR spectra of the PMO materials: (a) phenylene, (b) 4-benzyl, (c) *p*-xylene.

of 51 Å. This could be a consequence of the increased chain flexibility and hydrophobicity of the organosilane precursor. Typically, scattering peak intensity doubled upon surfactant removal due to enhanced electron contrast, indicating the ordered structures were retained. Unfortunately, the PXRD patterns lack the higher order reflections required to assign symmetry possibly due to the limited long-range order of the materials.

Solid-state ^{29}Si cross-polarization MAS NMR spectra of the surfactant-extracted PMO materials are shown in Figure 2. Resonances appear centered between −60 and −70 ppm representative of T type organosilica species [T_n = $RSi(OSi)_n(OH)_{3-n}$]. A clear absence of Q units [Q_n = $Si(OSi)_n(OH)_{4-n}$] below −100 ppm confirms there is negligible hydrolytic Si−C bond cleavage and the bridge-bonded organic group is maintained intact in the silica framework under the synthetic conditions. Three resonances are resolved for the 1,4-benzene bridged PMO at −63.1, −69.8, and −78.3 ppm, assigned to the T_n (n = 1 to 3) units of a condensed silsesquioxane moiety. The PMO material formed with a *p*-xylene bridge displays an intense resonance for the T_2 [$C-Si(OSi)_2(OH)$] methylene−silica environment at −61.2 ppm. Overall, the $CH_2SiO_{1.5}$ resonances appear about 8 ppm lower than $ArSiO_{1.5}$ chemical shifts. The same trend is reflected in the solution NMR of the triethoxysilane precursors, which show resonances for aryl−silica at −58.1 and −56.6 ppm and methylene−silica chemical shifts of −50.8 and −51.6 ppm. In general, a downfield chemical shift of 5−8 ppm accompanies each subsequent condensation of a terminal ethoxysilyl unit.

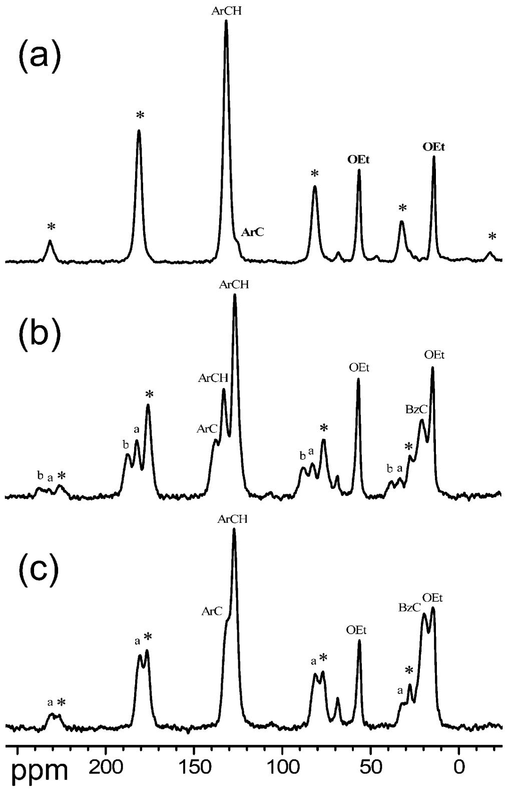

Figure 3. ^{13}C CP/MAS NMR spectra of the PMO materials: (a) phenylene, (b) 4-benzyl, (c) *p*-xylene. (*, a, b) represent spinning sidebands of the parent resonance.

The solid-state ^{29}Si NMR spectrum for the asymmetrically bridged 4-benzyl precursor shows overlapping resonances for organosilica environments coordinated to a phenylene− and methylene−carbon bridge, with the T_2 silica species appearing at −68.3 and −62.5 ppm, respectively. However, we could not distinguish between an −ABBBAA− block copolymer and −ABABAB− preferential head-to-tail alignment of the precursor. Nonetheless, the condensation rates of the different environments do not appear to be significantly different, and a mixture of randomly connected condensed organosilicas likely exists. This leads to formation of a 2D-hexagonal structure instead of a lamellar phase. Regardless, the organic bridge was incorporated in its entirety into the organosilica framework.

The materials were examined by solid-state ^{13}C CP/MAS NMR, and appear in Figure 3. Chemical shifts for the 1,4-benzene bridged PMO is dominated by a single resonance at 133.8 ppm attributed to the aryl carbon atoms with attached hydrogen atoms. The ipso carbon atoms appear as a small shoulder at 131 ppm. Resonances at 16 and 58 ppm are due to residual ethoxy groups from either incomplete condensation or extraction in acidified ethanol converting terminal silanol groups to ethoxysilanes. Remaining peaks are accounted for as spinning sidebands, separated by approximately 5000 Hz from the parent resonance. The 1,4-dimethylbenzene bridged PMO gives intense aryl resonances at 127.3 ppm for the aryl carbons with hydrogen atoms attached, while a peak at 131.2 ppm is attributed to the 1,4-carbon atoms. Methylene silica units display a ^{13}C chemical shift of 19.7 ppm. The 4-benzyl bridged PMO shows three peaks in the aromatic region at 128.6 ppm (2,6-aryl carbons), 134.8 ppm (3,5-aryl carbons), and

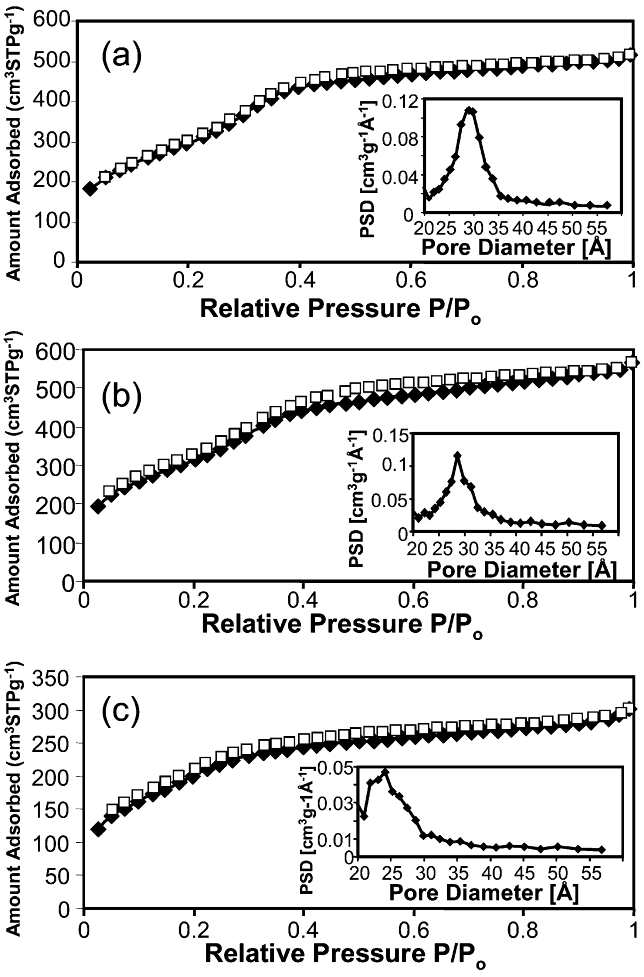

Figure 4. Nitrogen adsorption/desorption isotherms and pore size distributions for the PMO materials: (a) phenylene, (b) 4-benzyl, (c) *p*-xylene.

Table 1. Structural Properties of the PMO Materials

sample	d^a (Å)	BET surface area^b (m^2/g)	total pore volume^c (cm^3/g)	pore size^d (Å)	wall thickness^e (Å)
phenylene	50	1073	0.80	29	29
4-benzyl	50	1134	0.87	29	29
p-xylene	45	743	0.47	24	28

[a] $d(100)$ spacing of the extracted materials from PXRD. [b] Multipoint BET calculated over the relative pressure P/P_o range 0.05–0.15. [c] Determined from the amount adsorbed at 0.99 P/P_o. [d] Calculated using the BdB–FHH method from the adsorption branch of the isotherm. [e] Estimated from a_o-pore size; where $a_o = (2d(100)/\sqrt{3})$ is the unit cell parameter for a hexagonal lattice.

139.6 ppm (4-aryl carbon), and a chemical shift of 22.2 ppm is observed for the methylene group. Clearly, the carbon moieties are retained and the C–Si covalent bond is stable under the synthetic conditions. A small peak at approximately 70 ppm is likely due to Brij-56 trapped in closed pores that are inaccessible by the solvent.

Nitrogen adsorption/desorption analysis revealed the typical 2-step type IV isotherms indicative of mesoporous materials. Isotherms of the solvent-extracted PMO materials and corresponding pore size distributions are shown in Figure 4. Structural parameters of the organosilica PMOs are listed in Table 1. Adsorption isotherms exhibited steep increases in adsorption at a relative pressure range of 0.1 to 0.3 P/P_o due to capillary condensation of nitrogen in the mesopores. Nitrogen adsorption measurements for the phenylene bridged PMO show a uniform pore size distribution with an average diameter of 29 Å estimated by the BdB–FHH method (Broekhoff-de Boer, Frenkel-Halsey-Hill) using the adsorption branch.[21] A large surface area of 1073 m^{2}g^{-1} was calculated using the multipoint BET method (Barrett-Emmett-Teller) using data points over a relative pressure range of 0.05 to 0.15 P/P_o. The total pore volume of the material was 0.80 cm^{3}g^{-1} from the amount adsorbed at a relative pressure of 0.99 P/P_o. The wall thickness was calculated as 29 Å from the $d(100)$ lattice spacing and pore size assuming a 2D-hexagonal structure. In comparison to similar materials prepared in the absence of salt, the wall thickness is considerably larger, and the average pore diameter is smaller, but the surface area is larger.[14,15] The BdB–FHH pore diameter, BET surface area, total pore volume, and wall thickness for the 4-benzyl-bridged PMO were estimated to be 29 Å, 1134 m^{2}g^{-1}, 0.80 cm^{3}g^{-1}, and 29 Å, respectively. Overall, the PMO materials assembled with phenylene and 4-benzyl bridged units exhibit similar physical characteristics suggesting the packing constraints and hydrophobicity of the precursors are not significantly different. Measurements on the *p*-xylene PMO resulted in large decreases in pore size, surface area, and total pore volume to 24 Å, 743 m^{2}g^{-1}, and 0.40 cm^{3}g^{-1}. The wall thickness remains almost constant though, decreasing by only 3%. Reductions in both d spacing and pore size (ca. 5 Å) suggest partial penetration of the precursor into the palisade layer of the surfactant micelle or contraction of the template. Protic polar cosolvents such as ethanol and methanol are known to cause contraction of mesoporous silicas prepared with cetyltrimethylammonium bromide surfactants.[22] The amphiphilic nature of the charged organosilica precursor containing hydrophilic SiO_3 terminal groups and hydrophobic organic bridges may have an analogous effect on the template. In general, the xerogel materials reported in the literature using 1,4-dimethylbenzene bridged precursors exhibited substantially lower BET surface areas attributed to their macroporous nature, with no discernible pore size distributions.

Analysis of the PMO materials by electron microscopy provided direct structural evidence that the materials are organized into ordered arrays of two-dimensional hexagonal mesopores. Electron microscopy images of the phenylene-bridged PMO viewed perpendicular to the pore axis (SEM) and viewed parallel to the channels (TEM), reveal well-ordered arrangements of mesoscopically ordered pores with hexagonal symmetry (Figure 5). High-resolution SEM images of the 4-benzyl and *p*-xylene-bridged PMOs viewed perpendicular to the pore axis confirm the existence of a 2D-hexagonal mesostructure (Figure 6).

Thermogravimetric analysis of the products was carried out under an air and nitrogen atmosphere to examine the relative thermal stability of the materials (Figure 7). A weight loss of less than 5% was generally observed below 120 °C caused by desorption of phys-

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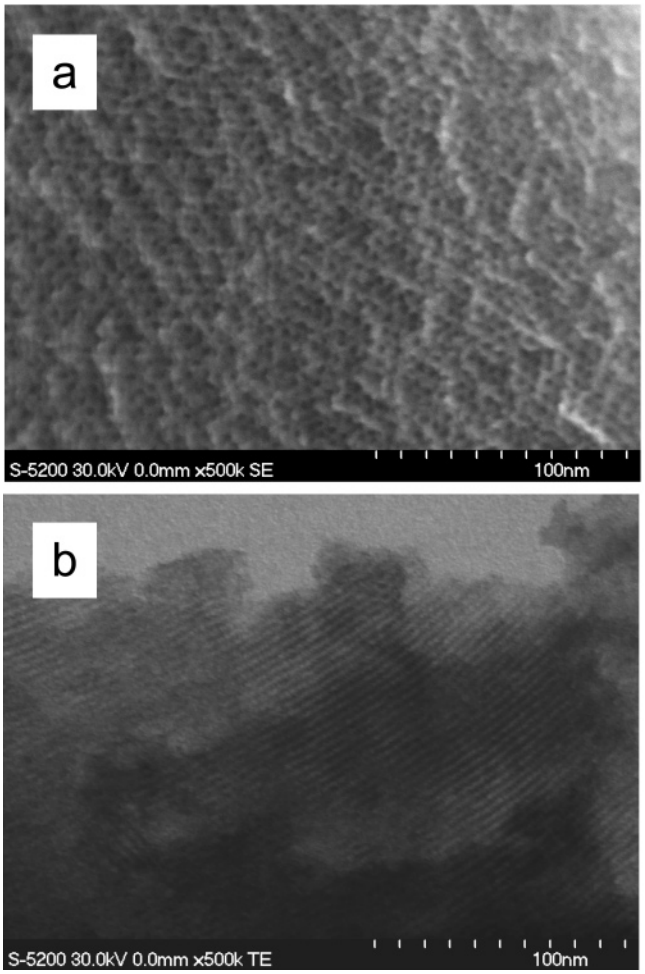

Figure 5. Electron microscopy images of the phenylene-bridged PMO: (a) SEM perpendicular to the channel axis, (b) TEM parallel to the channel axis.

isorbed and chemisorbed water and ethanol. Small weight losses between 200 and 300 °C are probably associated with the removal of trapped trace surfactant within closed pores or to partial dehydroxylation and condensation of surface silanol units. Under nitrogen, aromatic Si−C bonds of the phenylene bridged PMO begin to fragment above 450 °C. Thermal degradation of the organosilicate framework involving Si−C and C−C bond cleavage occurs over the range 450−750 °C. Breakdown of the methylene−silica bonds of the *p*-xylene PMO occurs above 320 °C and decomposes over the range 320−600 °C. The 4-benzyl bridged PMO shows a multiple-step TGA graph attributed to decomposition of $SiCH_2$ and ArSi moieties with onset temperatures of 320 and 450 °C. In air, framework decomposition begins above 400 °C for methylene-bridged aromatics and above 600 °C for the 1,4-benzene-bridged PMO. The PMOs display relative thermal stabilities in the order phenylene > 4-benzyl > *p*-xylene.

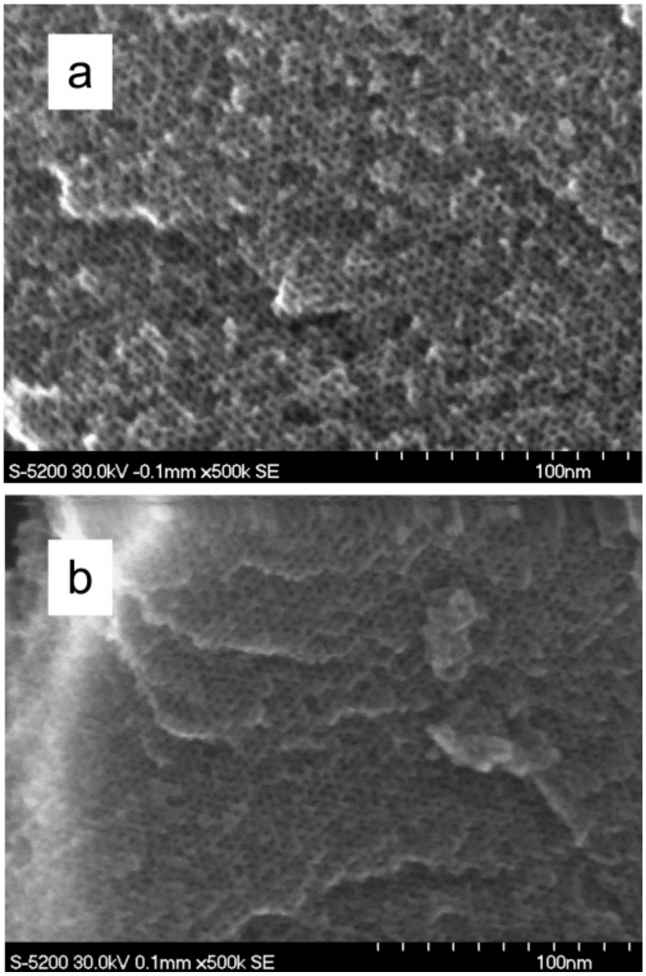

Figure 6. Scanning electron microscopy images of the methylene−phenylene-bridged PMOs: (a) 4-benzyl, (b) *p*-xylene.

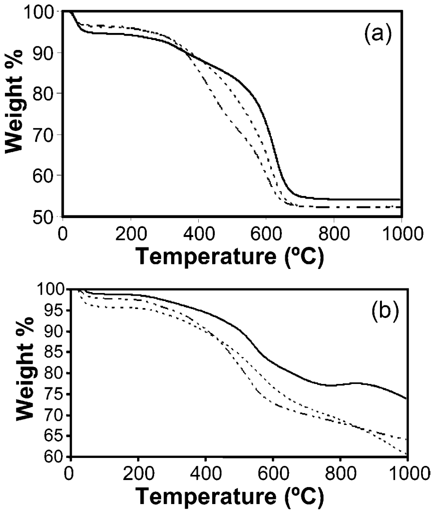

Figure 7. Thermogravimetric analysis plot of the PMO materials: (a) air atmosphere, (b) nitrogen atmosphere (−, 1,4-benzene; ···, 4-benzyl; ··−··, 1,4-dimethylbenzene)

Inorganic salts have been introduced in the self-assembly of silicates with ethylene oxide surfactants to increase the hydrothermal stability, control morphology, and broaden the synthesis conditions for the self-assembly of mesoporous silicas.[23] Addition of sodium chloride to the PEO−PPO−PEO triblock copolymer P123 was found to increase the structural order in an ethane bridged PMO.[24] Synthesis of nonionic ethylene oxide templates proceeds through a $(S^0H^+)(X^-I^+)$ pathway, with X^- playing a crucial role in the electrostatic interface. The mechanism is mediated through a combination of electrostatic and hydrogen-bonded interactions. Furthermore, sodium ion coordination to the PEO blocks results in dehydration of the hydrophilic ethylene oxide chains of the surfactant thereby decreasing solubility in the aqueous phase and favoring micelle formation. However, the result is a lower hydrodynamic volume for the micellar aggregate, so self-assembly is expected to yield smaller pore dimensions. In addition, microporosity decreases with salt addition as the more tightly packed PEO chains are less likely to protrude into the growing organosilica walls. Moreover, the increased ionic strength of the aqueous media may increase the partition of charged oligomeric nanobuilding blocks between the aqueous and surfactant phases increasing the interaction between the template and charged silicate species and facilitate formation of an ordered mesophase.

Conclusion

We have described the formation of periodic mesoporous organosilicas (PMOs) with aryl−methylene bridge-bonded organic units. Materials were prepared by the hydrolysis and condensation of bridged silsesquioxane precursors around a polyoxyethylene(10) cetyl ether (Brij 56) template. Highly ordered mesoporous organosilicas were prepared under acidic conditions with sodium chloride added to assist the assembly process. This is the first report of the incorporation of "rigid" phenylene and "flexible" methylene units integrated together into homogeneous PMOs.

Experimental Section

Reagents. The chemicals trichlorosilane, 4-bromobenzyl bromide, α,α′-dibromo-*p*-xylene, 1,4-dibromobenzene, triethylamine, tetraethoxysilane, and Brij 56 were purchased from Aldrich. Chlorotriethoxysilane was prepared via the literature method, with repeated fractional distillations yielding the pure product.[25] 1,4-Bis(triethoxysilyl)benzene was prepared following the reported synthesis.[9a−e] Dry solvents (THF, diethyl ether, and hexanes) were distilled over Na/benzophenone prior to use.

Characterization. Powder X-ray diffraction patterns were collected on a D5000 Siemens diffractometer equipped with a high-power long-focus Cu Kα source operating at 50 kV/35 mA. The secondary beam was monochromatized by a Kevex Si/Li solid state detector. The experimental patterns were collected on a step scan mode. The obtained diffraction data were processed with DiffracPlus Eva 8.0 software. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained using a Hitachi S-5200 microscope with an accelerating voltage of 30 kV/10 μA. Samples were prepared by depositing solids onto carbon-coated Cu grids. Nitrogen adsorption measurements were recorded on a Quantachrome Autosorb-1C with N_2 as adsorbate at 77 K. Materials were outgassed at 120 °C for 20 h prior to sample measurement. Solid-state ^{13}C (100.6 MHz) and ^{29}Si (79.5 MHz) cross-polarization magic-angle spinning NMR were recorded on a Bruker DSX 400 NMR spectrometer. The following experimental parameters were used: ^{13}C CP-MAS NMR experiments (5 kHz spin rate, 3 s recycle delay, 5 ms contact time, $\pi/2$ pulse width of 6.5 μs, 5000−8000 scans) and ^{29}Si CP-MAS NMR experiments (5 kHz spin rate, 3 s pulse delay, 5 ms contact time, $\pi/2$ pulse width of 5.0 μs, 12 000−18 000 scans). Spectra were referenced to the external standards adamantane (major peak at 38.5 ppm relative to TMS) for ^{13}C and $Si[Si(CH_3)_3]_4$ (major peak at −9.98 ppm vs TMS) for ^{29}Si. TGA spectra were recorded on a Perkin-Elmer TGA7 instrument with a heating rate of 10 °C min^{-1} under nitrogen. Solution phase ^{1}H and ^{13}C NMR were measured using a Varian VXR 300 MHz spectrometer and referenced to the residual protons of the deuterated solvents. A Varian 400 MHz spectrometer was used to measure ^{29}Si NMR spectra.

Monomer Syntheses. *p-Bromobenzyltriethoxysilane.* A solution of 4-bromobenzyl bromide (50.00 g, 0.20 mol) trichlorosilane (30.3 mL, 0.30 mol) dissolved in 300 mL of anhydrous ether was added dropwise to a solution of triethylamine (41.6 mL, 0.30 mol), and ether (200 mL) at 0 °C under N_2. Following addition, the reaction mixture was slowly warmed to room temperature and stirred for 3 days. The mixture was filtered, and volatile reagents and solvents were removed by vacuum distillation. A white solid was obtained and added in small portions to a solution of ethanol under a strong flow of nitrogen to remove HCl. The mixture was filtered, and the solvent was removed. A colorless liquid was obtained by vacuum distillation (110 °C, 0.050 mmHg). Yield: 30.0 g, 45%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, 9H, $SiOCH_2\mathit{CH_3}$, ^3J = 7.0 Hz), 2.18 (s, 2H, $ArCH_2$), 3.80 (q, 6H, $SiO\mathit{CH_2}CH_3$, ^3J = 7.0 Hz), 7.08 (d, 2H, ArH, ^3J = 8.5 Hz), 7.36 (d, 2H, ArH, ^3J = 8.4 Hz). ^{13}C (75.48 MHz, $CDCl_3$) δ 18.53 ($SiO\mathit{CH_2}CH_3$), 21.01 ($ArCH_2$), 58.79 ($SiO\mathit{CH_2}CH_3$), 118.47 (ipso-CBr), 130.82 (ArHSi), 131.32 (ArHBr), 136.85 (ipso-CSi).

α-p-Bis(triethoxysilyl)toluene. p-Bromobenzyltriethoxysilane (25.00 g, 75.0 mmol) was dissolved in THF (100 mL) and added dropwise to a solution of iodine-activated Mg (3.65 g, 150.0 mmol), chlorotriethoxysilane (16.40 g, 82.5 mmol), and THF (100 mL) at 60 °C. The reaction mixture was refluxed for 48 h, filtered, and the solvent was removed under vacuum. The yellow residue was rinsed with hexanes (3 × 100 mL), and filtered to remove magnesium salts. Subsequently, the solvent was removed from the filtrate to yield a straw-colored oil. A colorless liquid was obtained by vacuum distillation (130 °C, 0.050 mmHg). Yield: 11.6, 37%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, 9H, $CH_2SiOCH_2\mathit{CH_3}$, ^3J = 7.0 Hz), 1.26 (t, 9H, $ArSiOCH_2\mathit{CH_3}$, ^3J = 7.0 Hz), 2.25 (s, 2H, $ArCH_2$), 3.77 (q, 6H, $CH_2SiO\mathit{CH_2}CH_3$, ^3J = 7.0 Hz), 3.88 (q, 6H, $ArSiO\mathit{CH_2}CH_3$, ^3J = 7.0 Hz), 7.23 (d, 2H, ArH, ^3J = 7.9 Hz), 7.56 (d, 2H, ArH, ^3J = 7.9 Hz). ^{13}C (75.48 MHz, $CDCl_3$) δ 18.33 ($SiO\mathit{CH_2}CH_3$), 18.40 ($SiO\mathit{CH_2}CH_3$), 20.98 ($ArCH_2$), 58.83 ($SiO\mathit{CH_2}CH_3$), 58.88 ($SiO\mathit{CH_2}CH_3$), 126.36 (ipso-$ArHCH_2$), 128.69 (ArHSi), 135.00 ($ArHCH_2$), 140.44 (ipso-CSi).^{29}Si (79.42 MHz, $CDCl_3$) δ −51.55 (CH_2Si), −56.63 (ArSi). Mass spectrum [EI; *m*/*e* (relative intensity)] 416.2050 (13.5%), calcd. for $C_{19}H_{36}O_6Si_2$: 416.2050.

1,4-Bis(triethoxylsilylmethyl)benzene. A solution of α,α′-dibromoxylene (15.00 g, 56.8 mmol), trichlorosilane (17.2 mL, 0.170 mol), and THF (300 mL) was added dropwise to a solution of triethylamine (23.6 mL, 0.170 mol), and THF (200 mL) at 0 °C under N_2. The reaction mixture was slowly warmed to room temperature and stirred for 48 h. The mixture was filtered and THF and volatile reagents were removed by vacuum distillation. A white solid was obtained and added in small portions to a solution of ethanol under a steady flow of nitrogen. The mixture was filtered, and the solvent was removed. A colorless liquid was obtained by vacuum distillation (160 °C, 0.050 mmHg). Yield: 7.6 g, 31%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, 18H, $SiOCH_2\mathit{CH_3}$, ^3J = 7.0 Hz), 2.15 (s, 4H, $ArCH_2$), 3.73 (q, 12H, $SiO\mathit{CH_2}CH_3$, ^3J = 7.0 Hz), 7.03 (s, 4H, ArH). ^{13}C (75.48 MHz, $CDCl_3$) δ 18.34 ($SiO\mathit{CH_2}CH_3$), 19.79 ($ArCH_2$), 58.78 ($SiO\mathit{CH_2}CH_3$), 128.91 (ArH). 133.53 (ipso-C). ^{29}Si (79.42 MHz, $CDCl_3$) δ −50.81.

PMO Syntheses. Brij 56 (0.46 g, 0.67 mmol) was dissolved in deionized water (22.34 g, 1.24 mol) and HCl (1.59 g 12 M, 16.1 mmol) in a closed polypropylene bottle at 50 °C. The resulting solution was stirred for 1 h, followed by the addition of sodium chloride (2.90 g, 49.6 mmol), and stirred for 3 h. 1,4-Bis(triethoxysilyl)benzene (1.00 g, 2.48 mmol) was added under vigorous stirring to the clear homogeneous solution.

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After a few minutes a white precipitate began to form. Mixing was continued for 16 h at 60 °C, followed by aging the suspension at 80 °C under static conditions for 24 h. A fine white powder was collected by filtration, and washed with water, methanol, and acetone. Surfactant templates were removed from the mesoporous organosilicas through a solvent-extraction procedure. Approximately 0.5 g of the as-synthesized product was mixed in acidified ethanol (1.5 g of concentrated HCl to 100 g of EtOH) at 60 °C for 12 h, and repeated twice. Extracted PMOs were filtered, washed with ethanol and acetone, and dried at 80 °C for 24 h. A yield of about 0.3−0.35 g was typically recovered. A similar procedure was employed for the other PMO materials using a molar ratio of organosilica/Brij-56/HCl/H_2O/NaCl of 1.0/0.27/6.5/500/20.

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Supporting Information Available: ^{29}Si solution NMR of the precursors (a) 1,4-bis(triethoxysilyl)benzene, (b) α, *p*-bis-(triethoxysilyl)toluene, and (c) 1,4-(triethoxysilylmethyl)benzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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