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Molecularly Ordered Biphenyl-Bridged Mesoporous Organosilica Prepared under Acidic Conditions

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Because of their unique surface properties, periodic mesoporous organosilicas (PMOs) have gained considerable attention since their discovery in 1999.[1] Progress in this field has been the subject of several authoritative reviews.[2] In addition to the long-range-ordered pore system, PMOs, particularly those containing conjugated organic species, exhibit crystal-like pore walls stemming from a layered molecular arrangement of the organic spacers. Such a molecular order was observed directly by X-ray diffraction (XRD) and transmission electron microscopy (TEM).[3] Although there were some hints that limited molecular order in the pore walls of PMOs may occur under acidic conditions,[4] to date, all reported PMOs with clear molecularly ordered pore walls were obtained exclusively under basic conditions in the presence of alkyltrimethyl ammonium surfactants.[3,5] Nevertheless, PMOs prepared under acidic conditions undergo some molecular ordering via postsynthesis hydrothermal treatment in the presence of basic solutions.[6] It should be mentioned that under sol−gel and similar condensation conditions, i.e., without any amphiphile, many organosilsesquioxanes with aromatic spacers give rise to molecularly ordered, lamellar phases with[3c] and without[7] porosity. In the current work, we report the first successful synthesis of molecularly ordered, large-pore biphenyl-bridged organosilica using Pluronic P123 as structure-directing agent under acidic conditions.

Table 1. Structural Properties of Biphenyl-Bridged Organosilica

sample	aging	S_{BET} (m^2/g)	d_{100} (nm)	pore size (nm)	pore volume (cm^3/g)
BPO-1	95 °C, 2 days	773	8.84	5.7	1.10
BPO-2	95 °C, 14 days	667	8.52	5.9	1.30
BPO-3	120 °C, 2 days	611	9.18	6.0	1.20
BPO-4	140 °C, 2 days	710	9.38	5.9	1.15

Since its successful application for the synthesis of the so-called SBA-15 mesoporous silica under acidic conditions,[8] the triblock copolymer Pluronic P123 ($EO_{20}-PO_{70}-EO_{20}$) has been widely used as structure-directing agent for the self-assembly of various mesoporous inorganic and organosilica materials.[9] More recently, different silica mesophases were also synthesized using P123 in the presence of butanol.[10] A similar strategy was adopted here to prepare biphenyl-bridged mesoporous organosilica (BPO-n) using 4,4′-bis(triethoxysilyl)-1,1′-biphenyl-$[(C_2H_5O)_3Si(C_6H_4)_2Si(OC_2H_5)_3]$ in the presence of P123 (MW = 5800) as supramolecular template and *n*-butanol as additive. The molar composition was 1:0.012:1.16:1.22:130 silane:P123:BuOH:HCl:H_2O. In a typical procedure, Pluronic P123 (0.25 g) was first dissolved in 9 g of distilled water and 0.49 g of 35 wt % HCl solution with stirring at 308 K. After complete dissolution, 0.37 g of butanol was added to this clear solution. After 1 h of stirring, 0.80 g of precursor was added and the mixture was left under vigorous stirring at 308 K for 24 h. At this stage, some white precipitate appeared. The mixture was then transferred into a Teflon-lined autoclave and aged at higher temperature under static conditions. The specific aging conditions are listed in Table 1. The materials were thoroughly characterized by XRD, nitrogen adsorption−desorption measurements at 77 K, TEM, ^{29}Si and ^{13}C CP MAS NMR, thermogravimetry, and Raman spectroscopy.

The powder XRD patterns (Figure 1) exhibited a main peak at $2\theta \approx 1°$ (d spacing $\approx$ 9.0 nm), indicating the occurrence of a mesophase. The absence of additional diffraction peaks associated with the pore structure indicates that the latter consists of a disordered wormhole pore system.[11] This is consistent with direct observation by TEM (Figure 2a). Moreover, the XRD profiles exhibited a series of peaks at *d*-spacings 11.5, 5.7, 3.9, 2.9, and 2.3 Å. These peaks were attributed to a lamellar structure with a spacing of 11.5 Å and higher-order harmonics (Figure 2b). Although not as sharp as the peaks exhibited by mesoporous biphenylsilica prepared under basic conditions,[3b] this is the first time that a molecularly ordered mesoporous organosilica was obtained under acidic conditions. Interestingly, high-resolution TEM provided direct evidence of the molecular order within the pore walls (Figure 3). Lattice fringes with ca. 11.5

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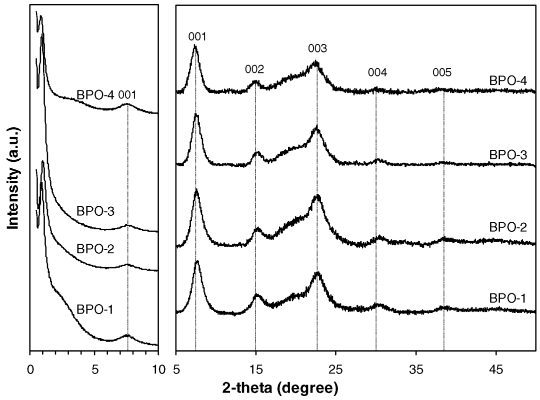

Figure 1. XRD data for BPO-n.

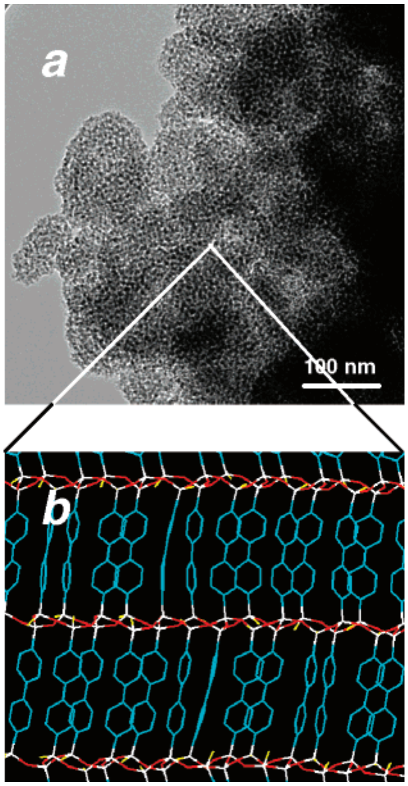

Figure 2. (a) TEM image for BPO-4, (b) schematic of pore wall structure.

Å spacing, similar to the XRD-derived periodic spacing, are clearly observed.

Optimization of the molecular structure of O−Si−(C_6H_4)$_2$−Si−O species using the density functional theory at the B3LYP/6-31G* level and the Gaussian 03 program[12] led to a calculated length of 11.9 Å. This indicates that the biphenyl species are tilted only slightly with respect to the direction perpendicular to the silica layers. In a previous report,[3c] we demonstrated that the occurrence of molecular order within organosilicates is not necessarily associated with an ordered mesopore system. The current work provides a different example from those reported earlier,[3] as the molecular order is associated with a wormhole pore system.

Nitrogen adsorption−desorption isotherms and the corresponding pore size distributions as calculated from the adsorption branch using the KJS (Kruk, Jaroniec, Sayari) method[13] are shown in Figure 4. All isotherms showed a distinct nitrogen condensation step and a hysteresis loop consistent with the occurrence of pores larger than 4 nm.[14,15] Moreover, the hysteresis loop extends to very high relative

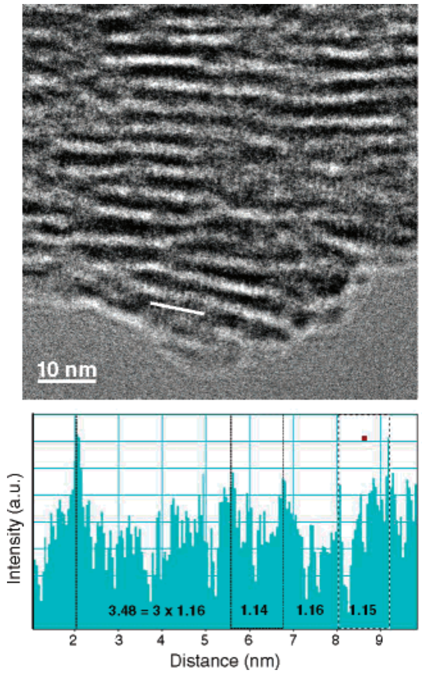

Figure 3. High-resolution TEM image for BPO-1, and intensity across parallel fringes along the white line.

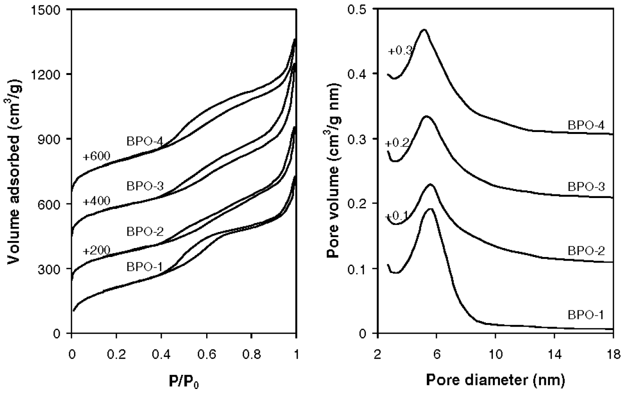

Figure 4. Nitrogen adsorption−desorption isotherms and corresponding pore size distributions for BPO-n.

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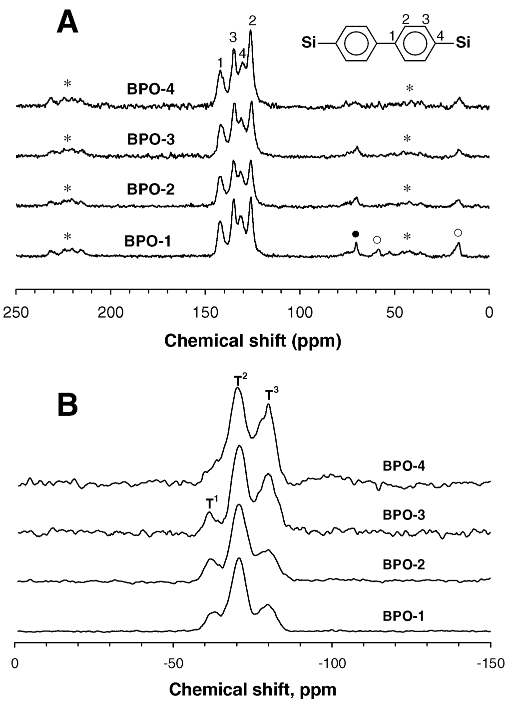

Figure 5. (A) ^{13}C CP-MAS NMR and (B) ^{29}Si MAS NMR spectra of extracted biphenyl-bridged organosilica. (○) $-OC_2H_5$, (*) side bands, (●) P123 template.

pressures associated with interparticle porosity. The average mesopore size for all samples was ca. 5.9 nm. This is actually the first successful synthesis of large-pore mesoporous biphenylsilica. Other structural properties of the materials are collected in Table 1. As seen, increased aging time or temperature did not affect such properties.

TGA analysis of selected organosilica samples (see Figure S1 in the Supporting Information) showed that the material is stable under nitrogen until 300 °C. The somewhat lower stability compared to mesoporous biphenylsilica prepared under basic conditions[3b] is to be associated with the lower degree of condensation (vide infra). The total weight loss was 60%, in excellent agreement with the 59.4% weight loss calculated on the basis of the formula $O_{1.5}Si(C_6H_4)_2SiO_{1.5}$.

Solid-state ^{13}C CP MAS NMR spectra exhibited four peaks at 125.5, 131.4, 135.0, and 141.2 ppm (Figure 5), attributable to the four different carbon atoms of the biphenyl species in the $O_{1.5}Si-(C_6H_4)_2-SiO_{1.5}$ network. Two additional small signals at 16.2 and 58.0 ppm were assigned to nonhydrolyzed ethoxy groups. The signal at 71 ppm is associated with some remaining P123 template. Solid-state ^{29}Si MAS NMR spectra (Figure 5B) featured typically three signals at -63.5, -72, and -86 ppm, which were attributed to T^1 [C***Si***(OSi)(OH)$_2$], T^2 [C***Si***(OSi)$_2$OH] and T^3 [C***Si***(OSi)$_3$] silicon resonances, respectively.[1,15] Moreover, no Q^n [***Si***(OSi)$_n$(OH)$_{4-n}$] species were detected in the range -90 to -110 ppm, indicating that no separate silica phase occurred, and all the Si$-$C bonds were preserved during the material synthesis and template removal. In comparison to the biphenyl-bridged organosilica prepared under basic conditions at the same temperature, i.e., 95 °C, the current material (BPO-1) prepared under acidic conditions showed T^2 to be the dominant silicon species instead of T^3. To increase the relative content of T^3 species, i.e., improve the degree of condensation, we extended the aging period to 14 days (BPO-2) at the same temperature (95 °C), but no significant changes in the T^n relative amounts occurred. However, using higher aging temperature (120 or 140 °C) for 2 days (BPO-3 and BPO-4) brought about a significant increase in T^3 species at the expense of T^1 and T^2 (see Table S1 in the Supporting Information), indicating further condensation of the organosilica framework.

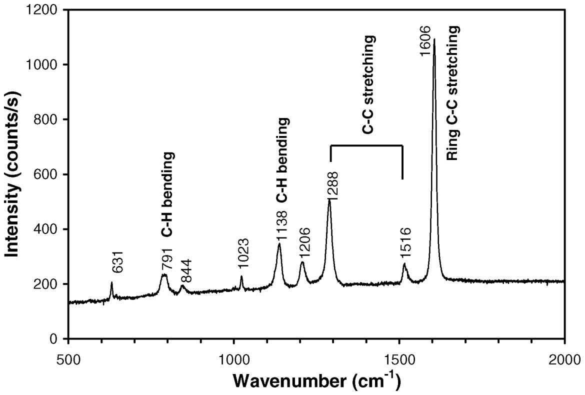

Figure 6. Raman spectrum for BPO-1.

Additional evidence for the occurrence of biphenylsilica species was obtained by Raman spectroscopy, as shown in Figure 6. Although this technique does not provide conclusive evidence for the Si$-$C bond,[16] all peaks can be associated with the biphenyl spacer (see Table S2 in the Supporting Information).[16a,17]

In summary, wormhole large-pore, molecularly ordered biphenyl-bridged mesoporous organosilica was successfully synthesized under acidic conditions using triblock copolymer P123 as structure-directing agent and butanol as additive. Characterization results clearly indicate that these materials have a wormhole mesoporous structure combined with molecular-scale order of biphenyl species into a layered structure within the material pore walls. In addition to their high surface area, these mesoporous organosilicas have larger pores and pore volume than the corresponding materials prepared under basic conditions.

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Supporting Information Available: Thermogravimetry analysis data, relative content of silicon T^n species, and Raman peak assignment (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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