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Synthesis of Periodic Mesoporous Organosilicas with Block Copolymer Templates

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The recent development of mesoporous materials with uniform organic−inorganic frameworks has led to great interest in the properties of these materials.[1−6] These unique periodic mesoporous organosilicas (PMOs) combine the structural properties of ordered mesoporous materials with the chemical properties of both silica and the organic bridging group. The presence of organic functional groups within the matrix gives these materials many of the favorable properties associated with organic polymers, but with improved accessibility to functional sites due to their open pore structure. The silica component of the PMOs gives them both structural rigidity and a degree of hydrophilic character useful for applications in aqueous systems. Although these periodic mesoporous organosilicas have great potential for adsorbent and catalytic applications, they are limited by their relatively small (2−5 nm) pore sizes. Many exciting new applications such as biocatalysis require materials with pores large enough to allow the diffusion of proteins or enzymes throughout their porous matrices. For these reasons, we have created periodic mesoporous organosilicas with larger pore sizes (6−20 nm).

Mesoscopic organosilicas have been synthesized by the acid-catalyzed hydrolysis and condensation of bis(triethoxysilyl)ethane (BTSE) using the triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF) as the structure-directing agent. 1,3,5-Trimethylbenzene (TMB) was added to aqueous copolymer mixtures prior to the addition of the BTSE. After particle synthesis was complete, the triblock copolymer was removed by extraction with ethanol/hydrochloric acid solutions. In a typical synthesis, 2 mL of BTSE was added to a mixture of 1.5 g of Pluronic P123, 0−2.0 g of 1,3,5-trimethylbenzene, 15 mL of 12.2 M HCl, and 75 mL of deionized water under stirring at 55 °C. After the mixture was stirred for 24 h, the resulting gel was cured at 90 °C for an additional 24 h. The composite was then refluxed in ethanol/HCl for 12 h. The extracted material was collected by filtration and air-dried to yield the product. The amount of TMB was varied and its effect on the porous structure of the final products has been examined.

TEM images were taken with a Hitachi H-8100 operating at 200 keV. Samples were prepared by dispersing the particles on holey-carbon-coated copper grids. Nitrogen gas sorption experiments were performed using a Micromeritics ASAP 2010 at 77 K. SAXS experiments were performed on the ORNL 10-m SAXS camera, with a sample−detector distance of 5.119 m using Cu Kα radiation ($\lambda = 1.54$ Å) and a 20×20 cm^2 two-dimensional position-sensitive area detector. The X-ray power was 40 kV and 10 mA.

Block copolymers have been successfully employed as templates for the synthesis of a wide variety of porous metal oxide particles.[7−9] The large pore sizes and ordered pore structures reported for these materials led us to investigate the use of block copolymers for the synthesis of large pore PMO particles. Using supramolecular assembles formed with the triblock copolymer Pluronic P123 as the surfactant template and TMB to expand the surfactant assembly, we produced periodic mesoporous organosilicas (PMOs) with pore diameters of 6−20 nm. Transmission electron micrographs of organosilica materials synthesized with different amounts of TMB are shown in Figure 1. It is interesting to note that an increase in the pore-expanding agent gave not only larger pore sizes but also changes in mesostructure. When no TMB is added (Figure 1a), the resulting organosilicas exhibit a wormhole motif with a pore diameter of approximately 6 nm. The addition of 0.5 g of TMB/1.5 g of P123 (Figure 1b) gives an expanded wormhole structure but with much shorter cylindrical pores or “worms” and a pore size of ≈12 nm. Still larger amounts of the pore expander (2.0 g of TMB/1.5 g of P123, Figure 1c) give hexagonal arrays of spherical pores with diameters of ≈20 nm. This is, to our knowledge, the first reported examples of large pore polysilsesquioxanes with ordered mesostructures.

Nitrogen gas adsorption analyses were used to characterize the porous organosilicas. The utility of the TMB is clearly illustrated by the nitrogen adsorption isotherms in Figure 2. The organosilica synthesized with 2.0 g of TMB adsorbs more than twice as much nitrogen as the sample made without TMB. The structural parameters of the organosilicas are listed in Table 1. Pore volumes were calculated from nitrogen gas sorption analysis. Pore diameters and lattice parameters were determined by TEM. Each of these properties increase with increasing TMB concentration. A small-angle X-ray scattering (SAXS) plot of the organosilica synthesized

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(1) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.

(2) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.

(3) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867.

(4) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.

(5) MacLachlan, M. J.; Asefa, T.; Ozin, G. A. *Chem. Eur. J.* **2000**, *6*, 2507.

(6) Kruk, M.; Jaroniec, M.; Guan, S.; Inagaki, S. *J. Phys. Chem. B* **2001**, *105*, 681.

(7) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(8) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813.

(9) Schmidt-Winkel, P.; Lukens, W. W.; Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121*, 254.

10.1021/cm010852d CCC: $20.00

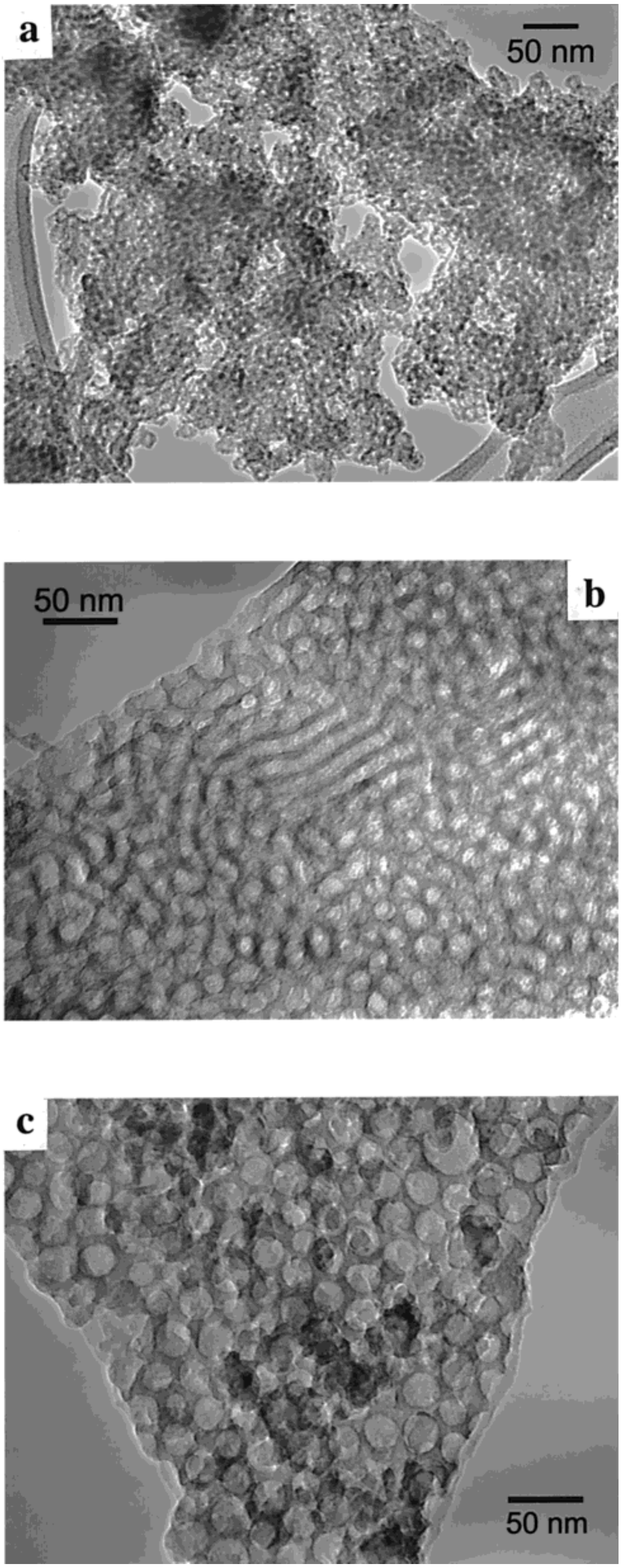

Figure 1. Transmission electron micrographs of organosilicas synthesized with 0 g (a), 0.5 g (b), and 2.0 g (c) of TMB/1.5 g of triblock copolymer.

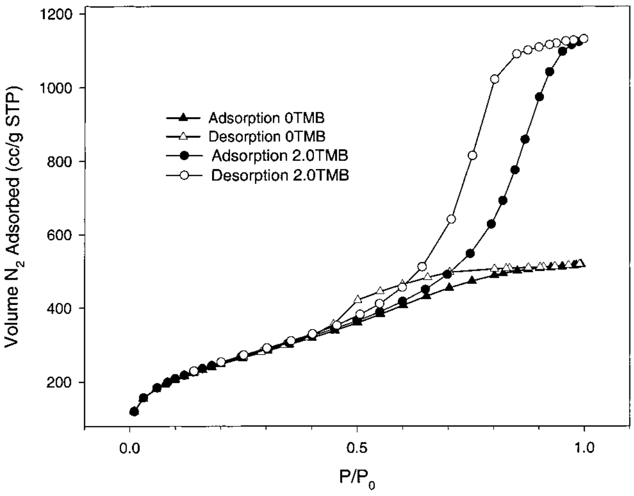

Figure 2. Nitrogen adsorption isotherms.

Table 1. Structural Parameters of Large Pore Periodic Organosilicas[a]

sample	S_{BET} (m^2/g)	V_t (cm^3/g)	a_0 (nm)	D_{TEM} (nm)
0 TMB	910	0.85	12	6
0.25 TMB	951	1.11	14	8
0.5 TMB	864	1.23	18	12
1.0 TMB	937	1.59	22	16
2.0 TMB	928	1.80	25	20

[a] S_{BET} = BET surface area; V_t = total pore volume; a_0 = lattice parameter estimated by TEM; D_{TEM} = pore diameter estimated by TEM.

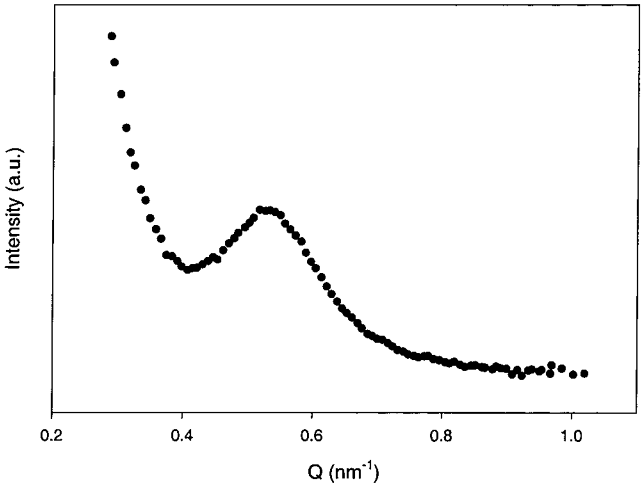

Figure 3. SAXS plot of organosilica formed without TMB.

without TMB is shown in Figure 3. The Q_{max} of 0.51 nm^{-1} corresponds to a *d* spacing of 12 nm, which agrees well with the value (11 nm) estimated by TEM.

In conclusion, we report the first examples of large pore periodic mesoporous organosilica particles synthesized with triblock copolymer templates under acidic conditions. PMOs with pore sizes from 6 to 20 nm have been characterized. Organosilicas synthesized without TMB as a pore-swelling agent exhibit a wormhole motif. Moderate addition of TMB gives expanded wormhole structures. Relatively large amounts of TMB give periodic mesoporous organosilicas with hexagonal arrays of spherical pores. Further work is in progress to immobilize biomolecules on the internal surfaces of these large pore organosilicas.

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