

Ordered Mesoporous Ceramics Stable up to 1500 °C from Diblock Copolymer Mesophases

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The synthesis of mesoporous silica-type ceramic materials through co-assembly of silica sources with organic structure-directing agents has been the focus of intense research activities over the past decade. The field was pioneered by a seminal research paper from scientists of the Mobil Corp. in 1992 about low-molecular-weight ionic surfactant-templated synthetic procedures.¹ In the second half of the 1990s, macromolecular nonionic surfactants were used for the first time to structure-direct orthosilicates^{2,3} and organically modified silica precursors⁴ from aqueous solutions and organic solvents, respectively, extending the accessible pore sizes of the resulting mesoporous materials to hundreds of angstroms. Shortly afterward, this approach was generalized to other metal oxides.⁵ Despite these advances, nanostructuring of high-temperature non-oxide ceramics such as silicon carbonitrides (SiCN) or silicon carbides (SiC) has remained a major challenge. In 2003, we reported an amphiphilic poly(isoprene-*block*-ethylene oxide) diblock copolymer (PI-*b*-PEO) as a structure-directing agent for a polysilazane pre-ceramic polymer commercially known as Ceraset.⁶ This work paved the way toward the preparation of various high-temperature SiCN-type ceramic mesostructures.⁷ Further unpublished studies in our laboratories showed, however, that this approach failed to produce porous high-temperature ceramics. In the present contribution we show the preparation of mesoporous ceramic materials stable up to 1500 °C based on a related approach using poly(isoprene-*block*-dimethylamino ethyl methacrylate) (PI-*b*-PDMAEMA) as the structure-directing agent for Ceraset (see Figure 1). Deviation from PEO as the hydrophilic block is motivated by limited PEO/Ceraset miscibility and PEO crystallization in polymer/Ceraset composites (both PI and PDMAEMA are amorphous polymers).

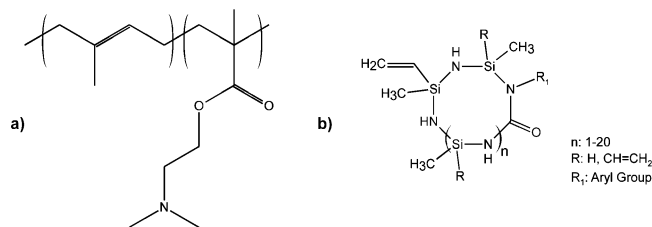


Figure 1. Chemical structures of (a) poly(isoprene-*block*-dimethylamino ethyl methacrylate) and (b) Ceraset, a polyureamethylvinylsilazane.

The block copolymer PI-*b*-PDMAEMA was synthesized using anionic polymerization as described elsewhere.⁸ The physical characteristics of the polymer **MK1** studied here were determined by gel-permeation chromatography (GPC) and ¹H NMR. The resulting polymer had a molecular weight of 20 100 g/mol and 26 wt % PDMAEMA with polydispersity index below 1.2. Ceraset (KION Corp.) and the radical initiator, dicumyl peroxide (Aldrich), were used as received. The chemical structures of block copolymer and Ceraset are shown in Figure 1. In a typical synthesis, a 5 wt % block copolymer solution in tetrahydrofuran (THF) was mixed with

the radical initiator (1–0.5 wt % with respect to the mass of Ceraset added) and the silazane precursor and stirred for 1 h. The solution was poured into a Petri dish and a film cast by solvent evaporation on a hot plate at 50 °C for 3 h. The film was then annealed in a vacuum oven for 24 h at 50 °C and subsequently ramped up to 120 °C for 1 h to cross-link the silazane. Here we will discuss a composite **MK1/1** with a polymer-to-Ceraset weight ratio of 1/2. After structure analysis, the composite was heat-treated using 1 °C/min ramps under nitrogen up to temperatures as high as 1500 °C for conversion into the high-temperature ceramic material.

Blending the silazane with the block copolymer is expected to lead to preferential segregation of the silazane within the PDMAEMA domains, primarily due to the polar nature of the molecule (see Figure 1). This increases the effective volume fraction of the PDMAEMA domains. By taking a block copolymer of a given composition, different morphologies should thus be accessible by simply increasing the amount of the silazane oligomer added, similar to what was observed in systems described earlier.^{6,9,10} Polymerization of the silazane is then started through the thermally activated radical initiator, dicumyl peroxide, within the PDMAEMA/Ceraset domains. This generates a nanostructured composite consisting of PI and PDMAEMA/cross-linked polysilazane mixed domains.

Small-angle X-ray scattering (SAXS) experiments were performed on a Bruker-AXS Nanostar (Cu K α , 1.54 Å) operated at 40 kV, 40 mA in transmission mode. In the SAXS pattern of composite **MK1/1** after cross-linking at 120 °C (Figure 2a), peaks

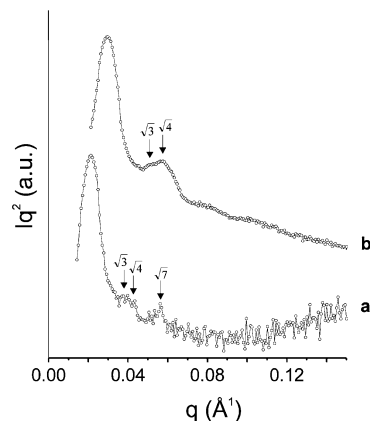


Figure 2. SAXS traces of the as-made composite (a) and ceramic after calcination to 1500 °C (b). Peak positions as expected for a hexagonal cylinder morphology are indicated by tics.

with q spacing ratios of 1, $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{7}$ are discernible, consistent with hexagonally packed domains. Transmission electron microscopy (TEM) was performed on a JEOL 1200EX operating at 120 keV to corroborate this assignment. Bulk samples were embedded in epoxy and 50–100 nm sections cut using a Leica Ultracut UCT microtome at –60 °C for composites and at room temperature for ceramics. Sections were subsequently transferred

to copper grids for analysis. A representative TEM image of the composite is shown in Figure 3a. The contrast in this micrograph arises from the electron density difference between PI and PDMAEMA/polysilazane domains, the latter appearing darker. The image of MK1/1 clearly shows hexagonally packed cylinders.

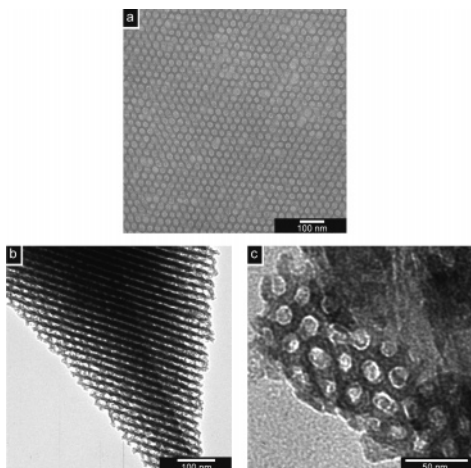


Figure 3. Bright-field TEM images of the as-made composite (a) and ceramic calcined to 1500 °C (b), demonstrating that the hexagonal structure is preserved during heat treatment.

The SAXS diffractogram of sample MK1/1 after heat treatment to 1500 °C is shown in Figure 2b. Although for both traces (a) and (b) the measuring time was about 1 h, the signal-to-noise ratio is clearly better for trace (b), expected from a higher electron density contrast in this sample. Besides the first-order peak, two higher order reflections at q spacing ratios of $\sqrt{3}$ and $\sqrt{4}$ of the first-order maximum are clearly visible for the ceramic, consistent with preservation of a hexagonal structure. There is a significant shift of the spectrum to higher q -values compared to the composite, indicating sample shrinkage upon high-temperature treatment. The (10) plane spacing is found to decrease from 31 to 22 nm on going from the composite to the ceramic material. That the hexagonal structure is preserved upon heating to 1500 °C is corroborated by the TEM images in Figure 3b and c, which show different projections of hexagonally packed cylinders. From Figure 3c, the average pore diameter can be estimated as ~ 13 nm.

From the SAXS and TEM results, heat treatment up to 1500 °C of the bulk composite preserves the nanostructure and leads to a mesoporous material. Separate microprobe studies (JEOL 8900 EPMA) of the composition of these materials treated up to 1400–1500 °C under Ar/H₂ typically showed the following number percentages: 29% C, 9% O, 30% N, and 32% Si. To check whether the pores are open and accessible, nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 at 77 K after outgassing at 100 mPa for 15 h at 300 °C. In Figure 4, the porous ceramic exhibits a nitrogen sorption isotherm of type IV according to BDDT classification, with a specific surface area of 51 m² g⁻¹ according to the Brunauer–Emmett–Teller (BET) method.¹¹ Calculation of the pore size distribution from the adsorption branch of the isotherm reveals an average pore diameter according to Barrett–Joyner–Halenda¹² (BJH) of 13 nm, which is in excellent agreement with the TEM results. The measured surface area per gram of the mesoporous ceramic is considerably lower than what is typically observed in block copolymer-directed mesoporous silica, where both meso- and micropores are present.^{3,9} The contribution from the mesopores to surface area in the present material can be estimated from the structural information obtained from SAXS and TEM. The calculation is based on the pore diameter

of 13 nm, determined from TEM (consistent with results of the nitrogen sorption/desorption experiments), the (10) plane spacing of the hexagonally packed cylindrical pores from SAXS (22 nm), and an approximate density of 2.5 g/cm³.¹³ The resulting surface area of 38.2 m² g⁻¹ is in good agreement with the value obtained from the BET analysis and suggests that wall microporosity contributions are probably small.

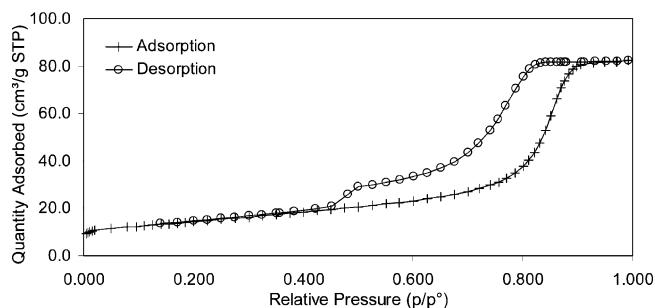


Figure 4. Nitrogen adsorption (+)–desorption (O) isotherms of the mesoporous ceramic after heat treatment to 1500 °C. STP, standard temperature and pressure.

In summary, we have demonstrated that when the block copolymer PI-*b*-PDMAEMA is employed as a structure-directing agent for Cereset, a precursor for high-temperature ceramics, a nanocomposite with hexagonal morphology is obtained. High-temperature treatment up to 1500 °C under nitrogen results in a mesoporous ceramic with open and accessible pores. To the best of our knowledge, this is the first time an ordered mesoporous high-temperature ceramic material has been obtained through a block copolymer type bottom-up approach. This exciting result has the potential to open a new field for the generation of nanostructured high-temperature ceramics with novel property profiles.

Acknowledgment. This work was funded by the Gates Millennium Fellowship (CG), the National Science Foundation (DMR-0312913), and the Cornell Center for Materials Research (CCMR) (DMR-0079992). The work made use of the Cornell Center for Materials Research X-ray diffraction facility, the Hudson mesoscale facility, and the electron and optical microscopy facility, all supported through the National Science Foundation Materials Research Science and Engineering Centers Program (DMR-0079992). We also thank Ruediger Dieckmann, Hongxia Lu, Surbhi Mahajan, Sabine Renker, and Yuanming Zhang for help in synthesis and characterization.

References

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712.
- (2) Göltner, C. G.; Antonietti, M. *Adv. Mater.* **1997**, *9*, 431–436.
- (3) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548–552.
- (4) Templin, M.; Franck, A.; Du Chesne, A.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädlér, V.; Wiesner, U. *Science* **1997**, *278*, 1795–1798.
- (5) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152–155.
- (6) Garcia, C. B. W.; Lovell, C.; Curry, C.; Faught, M.; Zhang, Y.; Wiesner, U. *J. Polym. Sci. B: Polym. Phys.* **2003**, *41*, 3346–3350.
- (7) Matsumoto, R. L. K. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 797–800.
- (8) Creutz, S.; Teyssié, P.; Jérôme, R. *Macromolecules* **1997**, *30*, 6–9.
- (9) Simon, P. F. W.; Ulrich, R.; Spiess, H. W.; Wiesner, U. *Chem. Mater.* **2001**, *13*, 3464–3466.
- (10) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, UK, 1998.
- (11) Brunauer, S.; Deming, L. S.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732.
- (12) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.
- (13) Shah, S. R.; Raj, R. *Acta Mater.* **2002**, *50*, 4093–4103.

JA046795H