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Nanostructured Non-oxide Ceramics Templated via Block Copolymer Self-Assembly

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Research directed toward materials comprising ordered ceramic mesostructures by means of self-assembly is gaining momentum due to the prospect of realizing new and/or improved properties that are not accessible by conventional microstructured materials. Self-assembly with structure-directing agents, such as surfactants or block copolymers, has been successfully applied to the synthesis of a large number of ordered mesoporous inorganic materials, mostly based on silica and transition metal oxide systems.[1−11] Very few attempts have been made to template nanoscale ordered structures with high-temperature non-oxide ceramics.[12−15] Ordered non-oxide ceramics such as silicon nitride and silicon carbide hold great promise in applications requiring high temperatures and structural integrity such as next-generation aircraft engines and gas turbines. The synthesis of this type of materials, however, faces substantial challenges due in part to the lack of precedent for their self-assembly into nanostructures. In oxide ceramics, hydrolysis of precursors such as metallic salts or alkoxides can be used as the basis of forming ceramics in confined nanoscale domains. No equivalent reaction exists for nitrides or carbides, where polymeric ceramic precursors are required. Recently, Wiesner and co-workers demonstrated that block copolymers (BCPs) can be used as structure directing agents to template liquid polymeric precursors in order to form ordered mesoporous silicon carbonitrides.[14,15] This is the first report on the synthesis of non-oxide ceramics using bottom-up self-assembly techniques.

Here we apply a similar approach to the synthesis of nonporous nanostructured silicon carbonitride ceramics. The protocol starts with the self-assembly of a polymeric ceramic precursor into an ordered structure, using an amphiphilic block copolymer as a template. This ordered nanostructure is stabilized via cross-linking of the precursor in order to endure subsequent high-temperature processing without undergoing an order-to-disorder transformation. Controlled pyrolysis is then performed in such a way that the ordered structure is conserved while pores are eliminated during the decomposition of block copolymer and the ceramization of the polymeric precursor. The end result of this process is an ordered, high density, nanostructured ceramic with silicon carbonitride as the major component.

The ceramic precursor used in this study is a commercially available polysilazane (PSZ) commonly known as Ceraset (Kion Corp., NY). This precursor can produce SiCN ceramics upon pyrolysis in a nitrogen atmosphere. Polybutadiene-*block*-poly(ethylene oxide) (PB-*b*-PEO) serving as the template has a molecular weight (M_n) and polydispersity index (M_w/M_n) of 27 000 and 1.05, respectively. The volume fraction of PEO is equal to 0.20 based on ^{1}H NMR analysis. This block copolymer was selected due to its miscibility with PSZ and the fact that crystallization of PEO chains is unlikely at this molecular weight. This is considered critical in order to prevent macro-phase separation in the BCP/precursor mixtures. PB-*b*-PEO, PSZ, and dicumyl peroxide initiator (2 wt % of polysilazane) were dissolved in a 1:1 mixture of tetrahydrofuran and chloroform. Several solutions with a mass fraction of PSZ ranging from 0.17 to 0.89 were prepared. After evaporation of the solvents, these homogeneous mixtures were annealed at 100 °C for 12 h to allow for self-assembly of PB-*b*-PEO and PSZ to occur.

Figure 1a illustrates the TEM bright field images of the pure block copolymer and a series of compositions containing differing amounts of PSZ. The morphology of pure block copolymer is hexagonally packed cylindrical in which PEO cylinders are surrounded by a PB matrix. Incorporation of PSZ leads to an increase in the size of the PEO/PSZ domain and transforms the cylindrical structure to a lamellar morphology. This is consistent with prior observations in which a uniformly dissolved homopolymer into a minority phase increases the effective volume fraction of that phase and changes the curvature of the interface, thereby shifting the morphology from cylindrical toward a more symmetric lamellar structure.[16,17] In these lamellar structures, the

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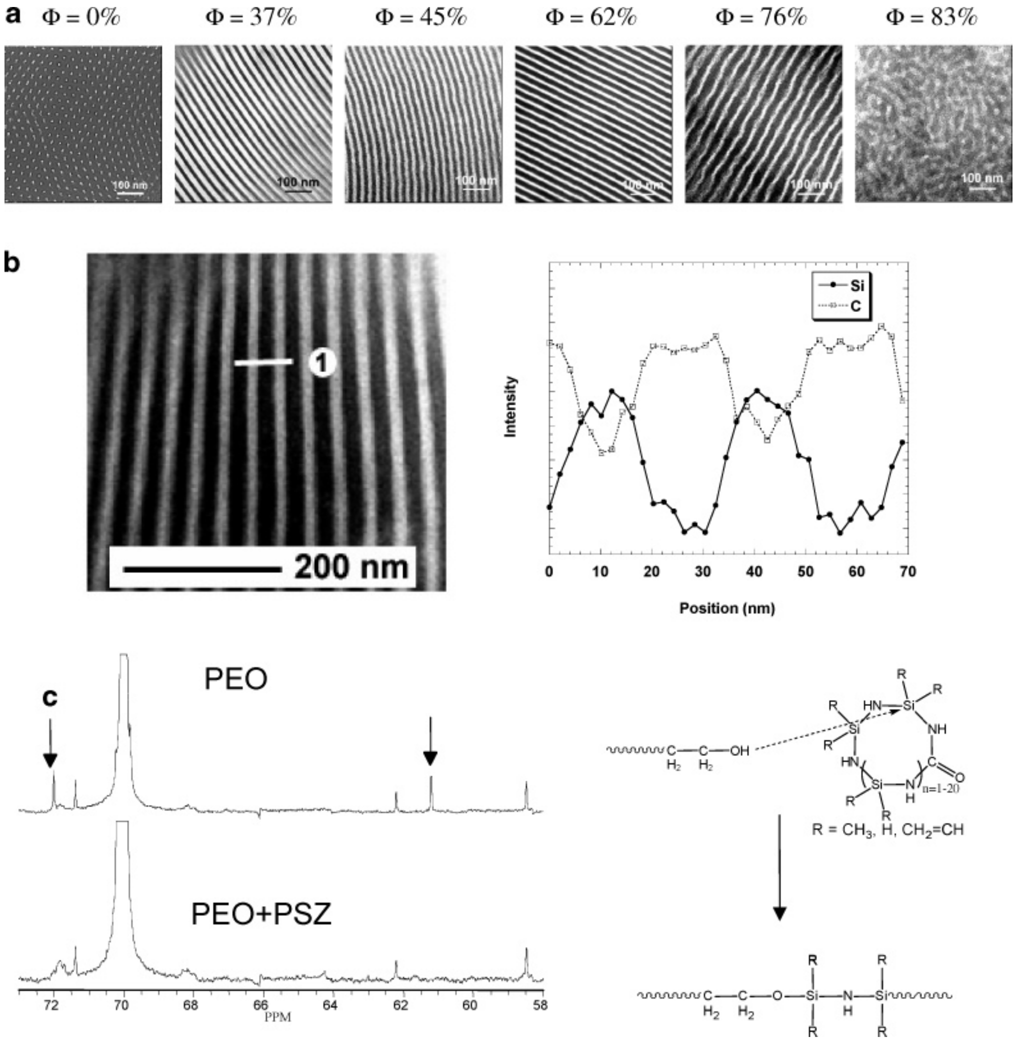

Figure 1. (a) TEM bright field images of pure PB-*b*-PEO and PB-*b*-PEO/PSZ mixtures self-assembled at 100 °C for 12 h (Φ is the composition of polysilazane in wt %), sample prepared from cryomicrotoming without staining. For all mixtures, the bright phase corresponds to the PB phase, while for the pure block copolymer, bright phase correspond to the PEO domains. (b) Dark field STEM image and associated EELS chemical line profile from PB-*b*-PEO/PSZ mixture (Φ = 62 wt %) demonstrating preference for PSZ to target PEO phase. The PSZ-containing PEO phase appears bright in the DF-STEM image. (c) Proposed ring-opening reaction and network formation in mixtures of PB-*b*-PEO and PSZ (arrow highlights resonance assigned to terminal CH_2-CH_2-OH groups).

thickness ratio between the PEO (with PSZ) and PB phases increases with increasing PSZ. The lamellar morphology persists for blends over a wide range of PSZ concentrations. Furthermore, for PSZ contents higher than 70 wt %, the sample exhibits a distorted (undulated) lamellar morphology, and for PSZ > 80 wt %, a micellar wormlike structure is formed.

To confirm that PSZ is selectively incorporated into the PEO phase during micro-phase separation, qualitative chemical line profiles generated from electron energy loss spectra (EELS) were acquired across the cross-section of the lamellae. This is shown along with a STEM dark-field image for a mixture containing 62 wt % PSZ in Figure 1b. This profile indicates that the silicon signal, characteristic of PSZ, is confined to the PEO phase and is uniform throughout that domain. No trace of PSZ was found in the PB phase, whose domains are revealed by a heightened C signal in the line profile.

An interesting feature of the PB-*b*-PEO/PSZ system is that it can incorporate large amounts of PSZ (up to ∼90 wt %) without causing macro-phase separation. Significant incorporation of PSZ precursor into the PEO phase contrasts with previously published reports in a similar system.[14] ^{13}C NMR experiments suggest that the incorporation of PSZ in the PEO domains is in part driven by the reaction of PEO chain-end hydroxyl groups with the silicon moieties in the polysilazane backbone. This is consistent with the enthalpic driving force at play upon going from Si−N to Si−O bonds. The proposed reaction and the ^{13}C NMR spectra of pure PEO and that of a 1:1 mixture of PEO and PSZ after thermal processing are depicted in Figure 1c. A comparison between the ^{13}C NMR spectra supports the proposed reaction due to the disappearance of the resonances at 61 and 72 ppm, which are assigned to the terminal methylene groups (CH_2-CH_2-OH) at the PEO chain-end. Furthermore, in a series of control experiments, we synthesized PB-*b*-PEO block copolymers where the PEO block is chain-end terminated with an acetate ester functionality, anticipating that an ester moiety, unlike hydroxyl, would be unreactive toward PSZ. Upon mixing and

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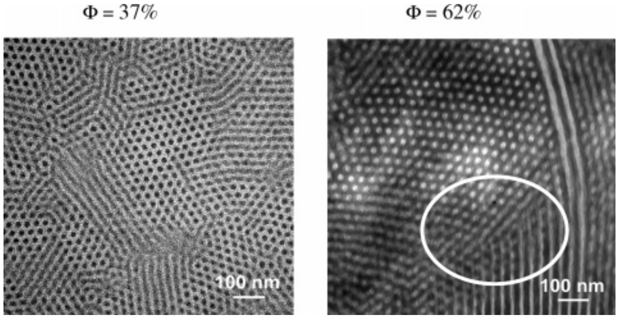

Figure 2. TEM bright field images of PB-*b*-PEO/PSZ mixtures with 37 wt % (left) and 62 wt % (right) of polysilazane after annealing at 200 °C for 4 h reveal cylindrical and inverse cylindrical morphologies, respectively. The dark phase corresponds to the silicon-containing phase (PEO plus PSZ), while the bright phase is the PB phase.

annealing ester terminated PB-*b*-PEO block copolymers with PSZ, we observed extensive macro-phase separation regardless of the mixture composition, thus supporting the hypothesis that a reactive chain-end on the PB-*b*-PEO is necessary for high PSZ loading into the PEO phase. As a control, pure ester terminated PB-*b*-PEO block copolymer was found to self-assemble into highly ordered hexagonal arrays of PEO cylinders in a PB matrix, indicating that the polymer modification does not preclude its self-assembly.

It should be noted that in compositionally asymmetric mixtures of PB-*b*-PEO/PSZ (where the volume ratio between the PB phase and the combined phase of PEO and PSZ deviates significantly from 1:1), the lamellar phase established at self-assembly temperatures as low as 100 °C may not be stable at certain higher temperatures. In such cases, annealing these self-assembled mixtures at 200 °C for 4 h under a nitrogen atmosphere induces an order-to-order phase transition from lamellar to cylindrical, as evidenced by TEM images in Figure 2. In contrast, blends with symmetric compositions do not exhibit order-to-order phase transformation upon heating. The order-to-order phase transformation observed here is similar to that reported previously in other asymmetric block copolymer systems, such as polystyrene-polybutadiene (PS-*b*-PB) among others.[18,19] In particular, akin to polystyrene−polybutadiene block copolymers, lamellar to cylindrical transition in PB-*b*-PEO/polysilazane blends is mediated by an intermediate “undulated lamellar” phase (see Figure 2). Unlike in systems such as PS-*b*-PB, lamellar to cylindrical phase transformation in PB-*b*-PEO/PSZ mixtures is a thermally nonreversible transition, since at temperatures above 130 °C the polymer mixture cross-links extensively. Owing to the kinetic hindrances by this cross-linking, the lamellar to cylindrical transition may not be complete by 200 °C heat-treatment, normally a mixture of lamellar and cylindrical regions can be found. The kinetically influenced nature of this transition is further evidenced by the fact that, when the asymmetric lamellar structure is heated continuously to high temperatures (e.g., 400 °C) at higher heating rates (e.g., 5 °C/min), the transition to cylindrical structure can be avoided.

Pyrolysis experiments were conducted by heating the self-assembled samples in a tube furnace at a constant rate of 0.5−20 °C/min to final temperatures of 700−1500 °C under nitrogen flow. Typically, a 1-h dwell time at about 400 °C was done to ensure full cross-linking of the PSZ. Upon pyrolysis, decomposition of the organic components occurs with gradual weight loss caused by the emission of methane, ethane, hydrogen, carbon monoxide, ammonia, and water as revealed by mass spectrometry. Pyrolysis of PB domains between 400 and 500 °C results in the formation of an amorphous carbon phase. FTIR and TGA analyses suggest that thermolysis of PEO/polysilazane domains initiates by decomposition of PEO chains between 350 and 400 °C. The conversion of the polysilazane network into an amorphous silicon carbonitride network occurs in the temperature range of 400−800 °C.

Brunauer−Emmett−Teller (BET) adsorption−desorption experiments were performed to monitor the evolution of porosity during pyrolysis. The absorption−desorption isotherms of N_2 for a PB-*b*-PEO/PSZ mixture containing 62 wt % PSZ are shown in Figure 3a. At temperatures up to 400 °C, the material is fully dense, while at intermediate temperatures (ca. 500 °C), a large quantity of pores develops in the material. Increasing the pyrolysis temperature leads to closure of the pores due to viscous flow of the PSZ. It should be noted that the pore closure process is temperature dependent. BET results and wide-angle X-ray scattering (WAXS) data for pure PSZ samples (without block copolymer, not shown here) show that smaller pores (with an estimated size of ∼1 nm, by WAXS) are intrinsic to the decomposition of PSZ developing at around 500 °C and being mostly removed at 600 °C. Higher temperatures are required for the removal of larger pores that result from PB-*b*-PEO decomposition. These observations are consistent with previous investigations of pyrolysis/pore closure behavior in bulk polysilazane compacted from precursor powders, in which complete closure of pores smaller than 20 nm occurs upon heat treatment.[20] Therefore, unlike the pyrolysis of mesoporous oxides, the pores generated in the present systems form only temporarily and close upon pyrolysis, yielding materials with high density. Nonetheless, some fraction of the larger pores may persist even after pyrolysis is complete. The estimated pore volume fractions in the ceramic samples with PSZ composition of 62 and 45 wt % are equal to 2% and 7%, respectively, while the average pore size is approximately equal to 10 nm as determined by BET. It should be noted that BET can only reveal open pores; closed pores that are not accessible from the surface are unaccounted for, and the existence of the latter is apparent from the SEM image of Figure 3b. Finally, the pyrolyzed ceramic phase contains Si, C, N, and O and its composition depends on the initial concentration of the block copolymer/precursor blend. The ceramic composition pyrolyzed from samples containing 62 and 45 wt % PSZ have empirical formulas of $Si_{1.00}C_{0.66}N_{1.30}O_{0.27}$ and $Si_{1.00}C_{0.60}N_{1.17}O_{0.48}$, respectively, according to semiquantitative X-ray fluorescence (XRF) analysis. Bright-field TEM and SEM images of

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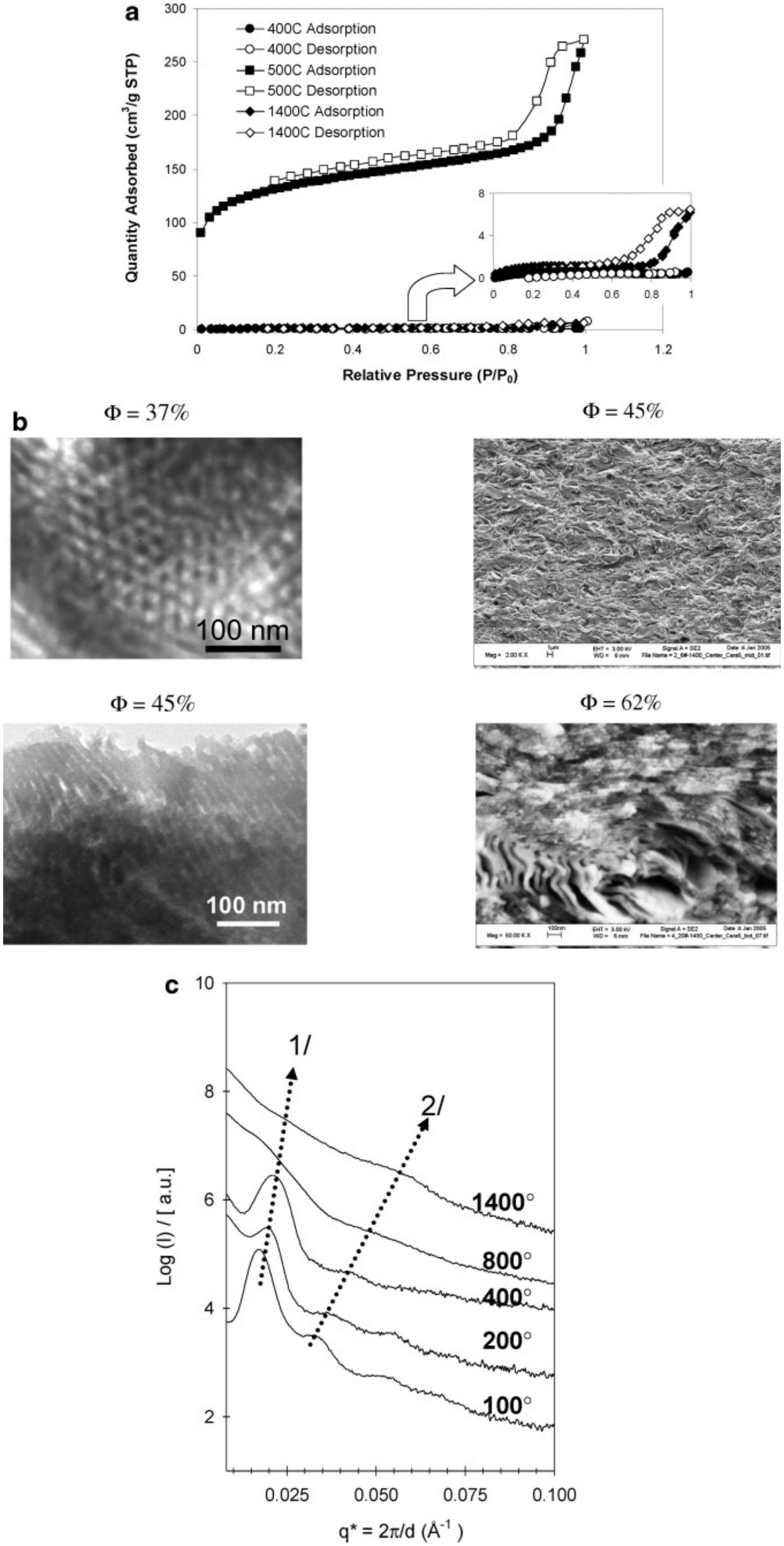

Figure 3. (a) BET absorption−desorption N_2 isotherms of a PB-*b*-PEO/PSZ mixture after heat treatment at different temperatures. This mixture contains 62 wt % PSZ. (b) Microstructure of PB-*b*-PEO/PSZ mixtures pyrolyzed at 1400 °C under N_2 atmosphere, as revealed by TEM bright field images of samples with 37 wt % (top left) and 45 wt % (bottom left) of polysilazane, and SEM images of samples with 45 wt % (top right, low magnification) and 62 wt % (bottom right, high magnification). (c) SAXS curves of a PB-*b*-PEO/ PSZ mixture containing 45 wt % PSZ at different stages of pyrolysis.

pyrolyzed ceramic nanostructures derived from two block copolymer/precursor mixtures are illustrated in Figure 3b. The morphology of the pyrolyzed samples (Figure 3b) and original self-assembled nanostructures (Figures 1 and 2) clearly resemble each other. The lamellar or cylindrical ordered structure is maintained, although distortion of the structure in the ceramic samples is apparent after pyrolysis. We believe that the preservation of nanoscale order in lamellar and cylindrical block copolymer/precursor mixtures is mainly due to the full extent of cross-linking in both PB and PEO/polysilazane domains and that cross-linking and network formation in both PB and PEO/polysilazane domains suppresses the order-to-disorder transition commonly observed in block copolymers at elevated temperatures. Indeed, small-angle X-ray scattering and scanning electron microscopy experiments corroborate the TEM results in larger pyrolyzed specimens (approximately 1 in. diameter disks). Figure 3c shows a series of SAXS profiles for a mixture with 45 wt % of PSZ at different stages of cross-linking and pyrolysis. Higher order Bragg reflections, indicative of highly ordered lamellar structures, are observed in samples annealed and cross-linked at lower temperature. A continuous shift of the first- and second-order scattering peaks toward higher q values during the pyrolysis can also be observed. The increase in q vector is consistent with the expected shrinkage and weight loss of the ceramic nanostructure during pyrolysis. Upon full pyrolysis (temperature >800 °C), the higher level order (i.e., third-order) peaks disappear, and the remaining peaks becomes highly diffuse, which is consistent with a distorted, locally ordered structure as revealed by SEM and TEM.

The preservation of nanoscale order in silicon carbide ceramics, and the fact that the porosity can be managed (eliminated to a large extent), points to the possibility of making structural materials, similar to natural ceramics yet in non-oxide high-temperature ceramics. Natural ceramic systems such as nacre and conch exhibit fracture toughness values far in excess of their main constituent ceramic components, and it is believed that this unusual property is in part a result of hierarchical ordered structure (order at nano-, micro-, and millimeter scales) in such materials.[21−25] This type of ordered structure allows for cooperative participation of microstructural elements in the load transfer during formation and propagation of damage and cracks, thus alleviating deleterious effects arising from stress/strain concentration.[21−25] The process described in the present study offers a way of making the first-level of order (nanoscale) in carbides and nitrides, and this could be used as the basis for eventually achieving more complicated multilevel hierarchical ordered structures in these types of materials. We are currently refining the first-level of order. For example, in the present case, the interface material separating the silicon carbonitride ceramic layers is amorphous carbon stemming from decomposition of the PB phase. The low pyrolysis conversion rate of the PB (~2 wt %) leads to thin (<1 nm) interface layers and that may lead to structural discontinuity in some regions of the material. As carbon is not an ideal interface phase due to its poor oxidation resistance, efforts are underway to introduce a chemically tunable interface phase that best satisfies the chemical, geometrical, and physical requirements for maximum fracture energy dissipation and stability; these results will be presented in a subsequent report. Nonetheless, the ability to build and maintain nanoscale order in dense non-oxide high temperature ceramics, as demonstrated in this paper, should enable the realization of more sophisticated structures with greatly improved fracture resistance.

In summary, we have demonstrated the synthesis of ordered, dense nanostructured SiCN-based ceramics using block copolymers as structure directing agents. Although the nanostructured ceramic systems reported in this work exhibit hexagonal and lamellar morphologies, the versatility of block copolymer self-assembly combined with optimized processing techniques should enable the rational synthesis of other ceramic materials having ordered nanostructures with improved properties.

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Supporting Information Available: Details about the processing procedure and characterization by TEM and SAXS. This material is available free of charge via the Internet at http://pubs.acs.org.

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