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Synthesis of Inorganic–Organic Diblock Copolymers as a Precursor of Ordered Mesoporous SiCN Ceramic**

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A wide variety of synthetic approaches have been proposed for the fabrication of mesoporous materials for a range of applications such as catalysis, separation, and sensing, as well as for various optical and electronic systems.^[1–3] There are many reports on mesoporous carbon and oxides prepared using various hard and soft templates. However, the low oxidation resistance of carbon and the poor hydrothermal stability of silica have limited their use. On the other hand, the preparation of mesoporous silicon carbide with a unique stability and strength using hard templates has attracted considerable interest.^[4–8] However, hard-template routes are not suitable for the industrial production of powder materials due to engineering difficulties, and require a harmful etching step, most commonly with strong acid, which limits the coating processibility to substrates. Therefore, soft-template routes using surfactants and block copolymers have attracted substantial attention for the creation of well-ordered nanostructured materials with facile applications on a large scale.^[9–14] Wiesner and co-workers reported mesoporous SiCN ceramic materials with an organic diblock copolymer amphiphile through the preferential interaction of inorganic precursors.^[15,16] On the other hand, the complete removal of an organic template by pyrolysis can cause serious volume shrinkage, which can reduce the mechanical and dimensional stability of the ceramic products obtained. Manners and co-workers reported the formation of nanostructures using poly(ferrocenylethylmethylsilane)-*block*-poly(styrene) as an organic–organometallic block copolymer.^[17] Recently, Matsumoto et al. reported the preparation of ceramic particles from inorganic–organic block copolymers.^[18] In particular, Malenfant et al. coincidentally and separately reported the synthesis of nanostructured boron car-

bonitride (BCN) and mesoporous boron nitride (BN) ceramics based on hybrid organic–inorganic block copolymers.^[19] However, there is no report of the direct synthesis of an inorganic–organic block copolymer as a precursor of a stereostructural mesoporous SiC-based ceramic.

Herein, poly((vinyl)silazane)-*block*-poly(styrene) (PVSZ-*b*-PS) as the inorganic–organic diblock copolymer precursor for an ordered mesoporous nonoxide ceramic via living free-radical polymerization was newly developed using dithiocarbamate derivatives as reversible addition fragmentation chain transfer (RAFT) agents and 2,2'-azo-bis-isobutyronitrile as an initiator. During pyrolysis under an inert atmosphere, the block copolymer with a self-assembling behavior transformed from an inorganic block to a ceramic wall, and the pores in the organic block formed an ordered mesoporous SiCN ceramic.

The molecular weight of the PVSZ block was controlled from 3000 to 10 000 g mol⁻¹ with a narrow polydispersity of <1.5 while the PS block had a molecular weight <20 000 g mol⁻¹ (see Supporting Information, Fig. S1). The volume fraction of the inorganic block was controlled from 0.5 to 0.7,^[20] which is expected to form a lamella or hexagonal structure under the phase diagram, as calculated by Leibler^[21] and Matsen and Bates.^[22] The ¹H, ¹³C, and ²⁹Si NMR spectra of the block copolymer, PVSZ-*b*-PS, were consistent with the structure suggested in Figure 1.

The ¹H NMR spectra (Fig. 1) indicated the presence of unreacted vinyl groups and Si–H groups in the PVSZ block at $\delta = 5.79$ – 6.22 and 4.47 – 4.78 ppm, respectively. The consumption of vinyl groups became clearer with decreases in the relative integral ratio of –CH=CH₂/Si–H from ca. 0.86 to ca. 0.77 compared with the starting vinylcyclohexylsilazane (VSZ). The methylene protons of the saturated vinyl groups formed by using RAFT polymerization at 1.85 ppm was not observed due to overlap with the relatively broad peaks of the polymer backbone. The peaks at $\delta = 0.98$ and 0.29 ppm were assigned to N–H groups and methyl protons of the Si–CH₃ groups in the inorganic block, respectively. From the PS block, the signals corresponding to C₆H₅–, CH₂, and CH protons were observed at $\delta = 6.5$ – 7.2 and 1.5–1.9 ppm, respectively. The two weak singlets at $\delta = 3.7$ and 4.05 ppm were assigned to dithiocarbamate (–N(CH₂CH₃)₂) groups^[23] at the end of the polymer chain. Alternatively, the signals at $\delta = 2.3$, 7.5, and 8.05 ppm were assigned to the benzyl CH₂ and the aromatic protons of the benzyl group, respectively, which is evident for the incorporation of the chain transfer agent fragment as the other end group in the polymer chain. These results are con-

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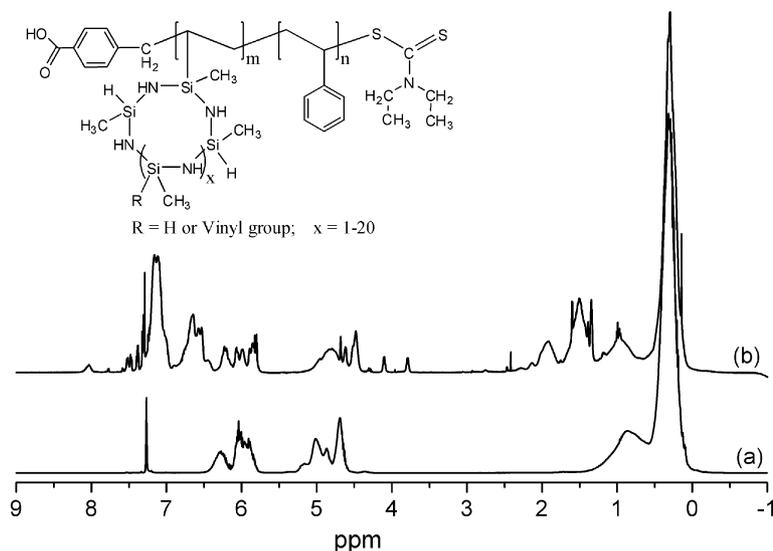


Figure 1. ^1H NMR spectra and chemical structure (inset) of the polymers in CDCl_3 , a) the starting VSZ and b) PVSZ-*b*-PS.

sistent with the presence of a benzoic moiety at the methylene terminus of the polymer chain. The bonding of the PVSZ and PS block was confirmed by the signals at $\delta = 1.34$ and 2.14 ppm in the ^1H NMR spectra as well as by the signals at $\delta = 22.8$ and 39.5 ppm in the ^{13}C NMR spectra (see Supporting Information, Fig. S2). In addition, the ^{13}C NMR peaks for the end groups $-\text{S}(\text{S})\text{CN}(\text{CH}_2\text{CH}_3)_2$ were also observed at $\delta = 196.3$, 12.2, and 44.6 ppm. In the ^{29}Si NMR spectra (see Supporting Information, Fig. S3), the relative peak intensity at -32 ppm for $\text{SiCH}=\text{CH}_2$ bonds decreased with the consumption of vinyl groups to bridge the blocks, and shoulder peaks in the range from -14.5 to -18 ppm were also observed with the newly generated Si-methylene groups via the α - or β -addition of radical polymerization. The major peak at -23.2 ppm, which was assigned to HSiCN_2 groups, became broader owing to the increased molecular weight of the silazane block. These spectroscopic results revealed that the PVSZ-*b*-PS block copolymer was obviously formed with the end of the polymer chain by dithiocarbamates and a benzoic moiety, which is consistent with the general synthetic mechanism of RAFT polymerization, as previously reported.^[23,24]

The thermal behavior of the block copolymer (number average molecular weight (M_n) = 15 300 g mol^{-1} , polydispersity index (PDI) = 1.22 and PVSZ volume fraction of 0.69) was characterized by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 2). The first weight-loss stage that ended at ca. 300 °C with a loss at ca. 20 wt % was associated with the crosslinking reaction^[25] of the PVSZ block, which is consistent with the presence of an exothermic peak at 295 °C in the DSC thermogram. The highly crosslinkable VSZ as an inorganic block is a well-known precursor for SiCN ceramics.^[26] In contrast, the organic PS block rapidly decomposed as the second weight-loss stage (ca. 30 wt %) was reached at the narrow temperature

range 370–430 °C, which is consistent with TGA results of both the block copolymer and the PS homopolymer. The final weight loss of ca. 5 wt % was presumably due to a transformation to the dense ceramic phase. In addition, it is reasonable that the addition of 1 wt % of the dicumyl peroxide (DCP) initiator facilitated the curing reaction at the lower temperature of 184 °C, resulting in a significant improvement of ceramic yield from 43 to 51 %, as shown in the TGA results. Therefore, the presence of crosslinkable vinyl and silane groups in an inorganic block are beneficial to enhance the dimensional stability of the developed microstructure without thermal agitation during pyrolysis.

In order to demonstrate the microphase segregation of the synthesized block copolymer, the cast films of PVSZ-*b*-PS ($M_n = 15\,300\ \text{g mol}^{-1}$, PDI = 1.22 and PVSZ volume fraction of 0.69) were examined by small-angle X-ray diffraction (SAXRD). The films annealed at 200 and 400 °C (Fig. 3a) showed a shape peak with the relative position of hexagonally packed domains with a *d*-spacing of 13.3 and 12.4 nm, respectively, indicating nearly no shrinkage due to the formation of a rigid solid network via a crosslinking step. In particular, a transmission electron microscopy (TEM) image of the sample annealed at 400 °C (Fig. 3b) clearly shows an array of hexagonally packed cylinders consisting of aligned pores with a circular shape, as expected from the phase diagram.^[21] The average pore diameter was estimated to be ca. 10 nm and the wall thickness 5 nm. As the cast film was annealed at 800 °C, the mesoporous structure was retained with a sharp peak at higher 2θ (1.15°) and a shoulder peak at $2\theta = 1.84$, indicating a dramatically decreased *d*-spacing to 7.6 nm due to high volume shrinkage as a result

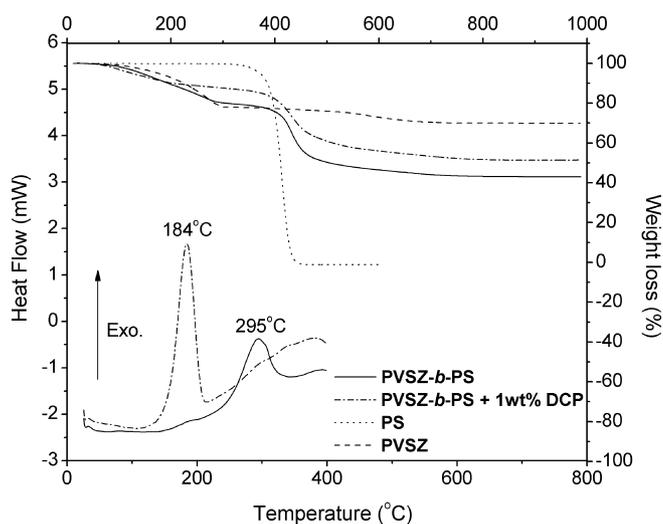


Figure 2. Thermal properties of PVSZ-*b*-PS and homopolymers: Top and right-hand axes are the temperature and weight lost for TGA. The left-hand and bottom axes show the heat flow and temperature for DSC thermograms.

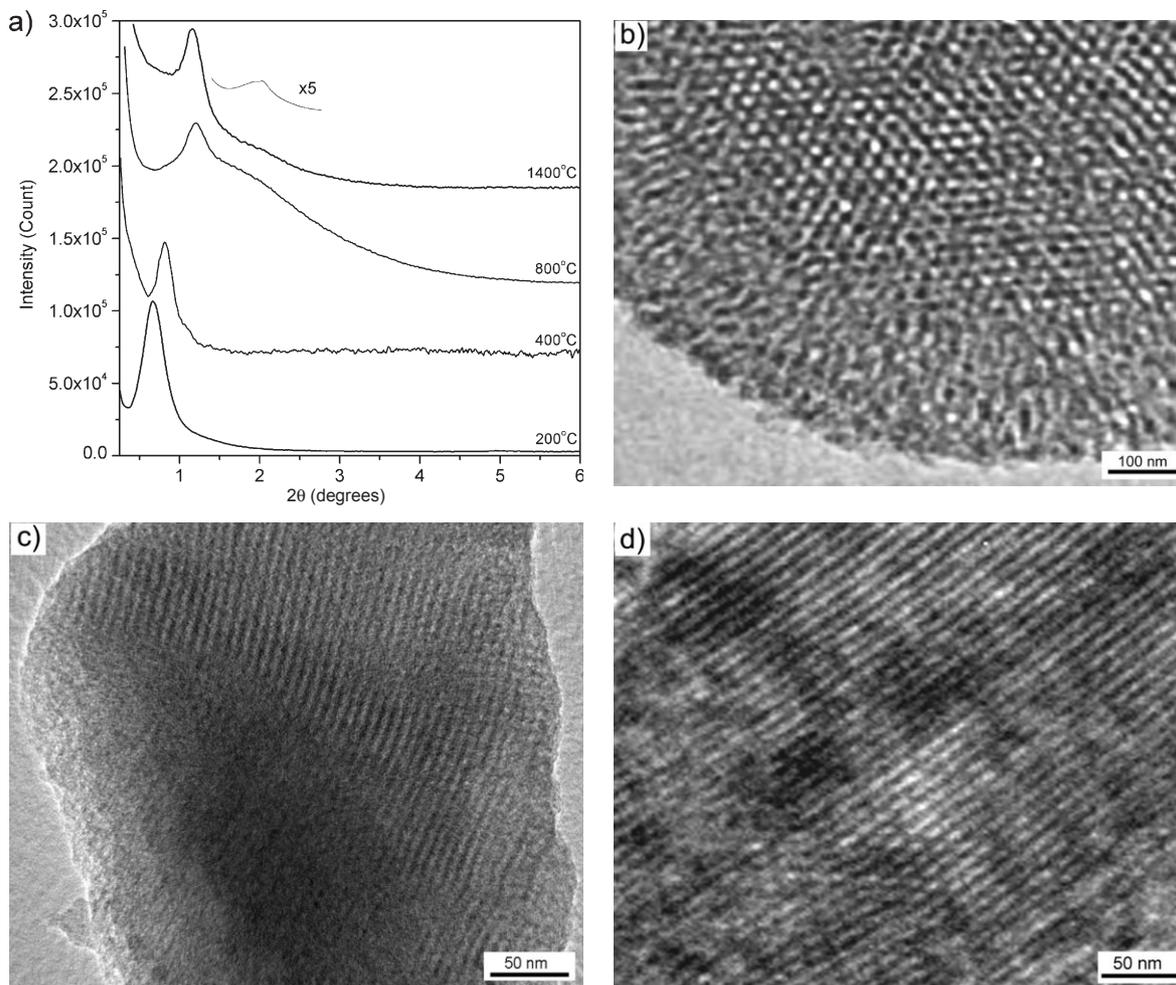


Figure 3. a) Small-angle XRD patterns and TEM images of the mesoporous SiCN ceramic annealed at different temperatures: b) 400 °C, c) 800 °C, and d) 1400 °C.

of total disappearance of organic blocks. Furthermore, it is surprising that, upon heating to 1400 °C, the mesoporous structure was preserved with a sharp peak at 2θ (1.20) and d -spacing of 7.3 nm (Fig. 3a), which is consistent with the TEM image shown in Figure 3d. Furthermore, a weak higher ordered peak at 1.95° is convincing evidence for a high level of ordering. It is most likely that the preservation of ordered mesoporous structures even with a thin solid wall at high temperatures is mainly attributed to the lower organic portion of this block copolymer, unlike the organic–organic block copolymers^[14–16] and the reported inorganic–organic block copolymers.^[18]

The pore characteristics of the sample annealed at 1400 °C were confirmed by measuring the N₂ adsorption–desorption isotherm. The mesoporous ceramic product showed a type IV behavior (see Supporting Information, Fig. S4) with a large Brunauer–Emmett–Teller (BET) surface area of 428.17 m² g^{−1} and a narrow pore size distribution with an average pore size of 5.6 nm, which was in good agreement with the TEM and SAXRD results. Compared with other synthetic processes, for

example, using organic block copolymers as a template,^[15,16] the prepared SiCN product exhibited a higher BET surface area with high temperature stability. The observed high BET surface area even at 1400 °C clearly demonstrates that an inorganic–organic block copolymer could be the most reliable route with essential design of curing chemistry to prepare versatile mesoporous nonoxide ceramics with excellent thermal stability. Finally, the ²⁹Si CP-MAS NMR spectrum of the SiCN sample pyrolyzed at 1400 °C showed broadening of the peak at −35 ppm (see Supporting Information, Fig. S3(c)), which was assigned to the three structural components of the amorphous SiC_xN_{4−x} units with $x = 0, 1, \text{ or } 2$ as reported at the bulk product.^[26] Scanning electron microscopy/energy dispersive spectrometry analysis estimated the weight ratios to be 44.72 % for Si, 25.68 % for C, 22.88 % for N, and 6.73 % for O, which corresponds to Si_{2.8}C_{3.7}N_{2.8}O_{0.7}.

In summary, a block copolymer, PVSZ-*b*-PS, with self-assembling behavior was synthesized using the RAFT polymerization route, which was then converted into an ordered mesoporous SiCN ceramic with high temperature stability at

1400 °C. To the best of our knowledge, this is the first report of the synthesis of an inorganic–organic diblock copolymer that was transformed directly to a mesoporous SiCN ceramic phase. Moreover, it is highly plausible that this result can lead to the development of alternative SiC, Si₃N₄, and BN mesoporous ceramics and hybrid compositions. In addition, it is believed that these ceramic precursors have significant potential in the generation of various nanostructured nonoxide ceramics, in combination with the advanced chemistry and processes of organic–organic diblock copolymers.

Experimental

In a typical synthesis, a stock solution containing 5 g (16.7 mmol) of VSZ (KiON VL20, KiON Corp.), 93 mg (0.57 mmol) of 2,2'-azobis(isobutyronitrile) (AIBN), 462 mg (1.63 mmol) of 4-diethylthiocarbamoylsulfanyl-methyl-benzoic acid as a RAFT agent, and 3 mL of toluene were added to a Schlenk tube. The solution was degassed with three freeze–evacuate–thaw cycles and then sealed. The tube was heated at 120 °C in an oil bath for 48 h. A solution containing 4.5 g (43.0 mmol) styrene and 31 mg (0.18 mmol) AIBN was then added. The resulting solution was kept at 120 °C for 4 h. The volatiles were removed under reduced pressure to give poly(vinyl)silzane-*block*-polystyrene. The resulting polymer was diluted in tetrahydrofuran and precipitated by adding *n*-hexane. The purified poly(vinyl)silzane-*block*-polystyrene (6.8 g, 71.6% conversion, $M_n = 15\,300\text{ g mol}^{-1}$, and PDI = 1.22) was filtered out, followed by drying in vacuum.

To investigate the microsegregation and the formation of mesoporous SiC-based ceramic, ca. 0.5 mm thick PVSZ-*b*-PS films were cast over 3–4 days from a 1 to 5 wt % solution in toluene in a 100 mm diameter Teflon disk. The films were then annealed in an argon atmosphere at 180 °C for 3 h. The cast film was pyrolyzed at temperatures up to 1400 °C at a heating rate of 1 °C min⁻¹ in an argon atmosphere to allow the conversion of the films to ceramic materials. More detail in the synthesis and characterization of the RAFT agent and block copolymer are presented in the Supporting Information.

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