

## Silicon-based ceramics from polymer precursors\*

L. V. Interrante<sup>1,‡</sup>, K. Moraes<sup>1</sup>, Q. Liu<sup>1</sup>, N. Lu<sup>1</sup>, A. Puerta<sup>2</sup>, and L. G. Sneddon<sup>2</sup>

<sup>1</sup>Departments of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA; <sup>2</sup>University of Pennsylvania, Philadelphia, PA 19104, USA

*Abstract:* A hyperbranched polycarbosilane of the type  $[R_3SiCH_2-]_x[-SiR_2CH_2-]_y[-SiR(CH_2-)_{1.5}]_z[-Si(CH_2-)_{2}]_1$  ( $R = H, -CH_2CH=CH_2$ , or OR) has been prepared, which was used as a source of inorganic/organic hybrid materials and, through pyrolysis, as a precursor to inorganic solids with unusual microstructures and properties. A partially allyl-substituted derivative “AHPCS”, nominally  $[Si(allyl)_{0.1}H_{0.9}CH_2]_n$ , has been extensively studied as a precursor to silicon carbide (SiC) and is now used commercially as a SiC matrix source for C- and SiC-fiber-reinforced composites and binder for particulate ceramics. The alkoxy derivatives,  $[Si(OR)_2CH_2]_n$ , ( $R = Me, Et$ ) yield, after hydrolysis and condensation, carbosilane/siloxane gels with unusually high surface areas (700–900 m<sup>2</sup>/g) and microporosity that is retained in the resultant  $SiO_xC_y$  ceramics formed after pyrolysis to 1000 °C. The fully condensed  $[Si(O)CH_2]_n$  gel in the latter case was obtained as thin, adherent films on Si surfaces by spin coating and was found to exhibit dielectric constants as low as 2.0 after heating to 400 °C. The SiC precursor, AHPCS, has also been used recently, along with other polymeric precursors, to make two-phase (SiC/C and SiC/BN) amorphous ceramics that exhibit unusual microstructures and thermal/mechanical properties. These microstructures are formed during the mixing and thermosetting of the constituent polymers, which undergo phase separation due to their immiscibility. Certain of the SiC/C composites, which have the C phase uniformly distributed as ca. 1- $\mu$ m droplets in a  $SiC_x$  matrix, exhibit high oxidation resistance, and microindentation tests on the SiC/BN system suggest unusual toughness.

### HYPERBRANCHED POLYCARBOSILANES AS A SOURCE OF SiC AND $SiO_xC_y$ CERAMICS

Ranging from the sol-gel processing of metal alkoxides and the pyrolysis of inorganic backbone polymers such as poly-siloxanes, -carbosilanes, -silazanes, and -borazynes, to chemical vapor deposition (CVD) with volatile molecular precursors, molecular, and more generally macromolecular systems have been widely exploited as a source of novel inorganic solid-state materials [1]. In most instances, the main motivation for resorting to this, usually more expensive, way of obtaining inorganic solids lies in the special advantages that are afforded by molecular systems in processing these materials in particular shapes (continuous fibers, films, molded monoliths, etc.) or with special microstructures (from homogeneous, multicomponent, amorphous solids and ordered micro- to meso-porous structures to epitaxial, single-crystal films) that are difficult, or even impossible, to obtain by more conventional, non-molecular approaches. A prime example in the case of macromolecular precursors is the fabrication of

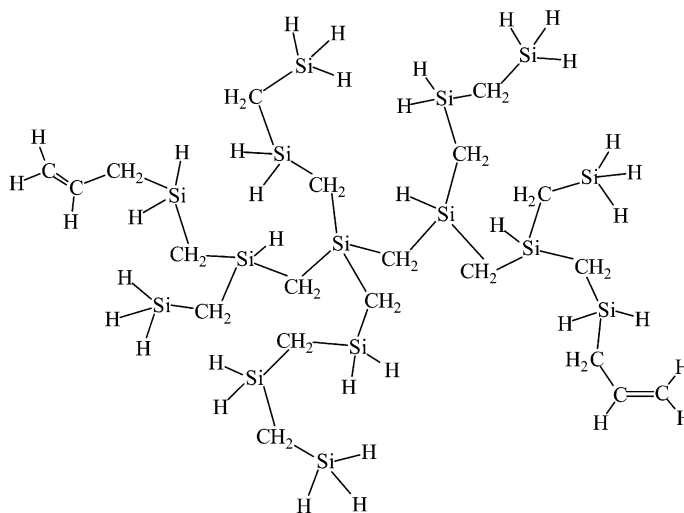
\*Lecture presented at the 5<sup>th</sup> Conference on Solid State Chemistry (SSC 2002), Bratislava, Slovakia, 7–12 July 2002. Other presentations are published in this issue, pp. 2083–2168.

<sup>‡</sup>Corresponding author: E-mail: interl@rpi.edu

continuous SiC fiber by melt spinning of a polycarbosilane precursor, followed by cross-linking and pyrolysis to form a continuous ceramic fiber [2]. A more recent example in this same general area of Si-based ceramics, involves the conversion of polymer fibers containing Si, C, N, and B to an amorphous  $\text{Si}_x\text{C}_y\text{N}_z\text{B}_b$  fiber that is thermally stable to ca. 2000 °C [3]. In addition to processability and a high conversion yield to the desired ceramic product, the ability to control the composition and microstructure of the final ceramic material is often critical to the success of a particular molecular precursor. In the specific case of silicon carbide precursors, where the ceramic product, SiC, is a “line compound” with a 1:1 Si:C ratio [4], the ability to generate a single-phase, crystalline, SiC final product, while also achieving a high ceramic yield, ultimately depends on the stoichiometry of the initial precursor, as well as the sequence of chemical reactions that occur on pyrolysis. For many applications, this control of the stoichiometry at the 1:1 Si:C ratio is critical to the successful application of the precursor method.

In 1991, we reported the synthesis of a polycarbosilane that had a 1:1 Si:C ratio, with H as the only other component, and which underwent pyrolysis in reasonably high yield with retention of this initial 1:1 stoichiometry [5]. This precursor (AHPCS), which had a relatively low molecular weight ( $M_n = 600\text{--}1000$  AMU), hyperbranched,  $[\text{H}_3\text{SiCH}_2\text{-}]_x[\text{-SiH}_2\text{CH}_2\text{-}]_y[\text{-SiH}(\text{CH}_2\text{-})_{1.5}]_z[\text{-Si}(\text{CH}_2\text{-})_2]_1$  structure [5,6] and a “[SiCH<sub>4</sub>]” overall composition, was obtained by Grignard coupling of chloromethyltrichlorosilane, followed by reduction with  $\text{LiAlH}_4$ . Later work resulted in improvements in the synthesis method, enhancing both the purity and yield of the product, as well as the ability to produce it on a large scale [7], and also the recognition that the Si-X substituted intermediate carbosilane obtained from the Grignard coupling reaction was amenable to facile structural modification [6]. One such modification was the replacement of a portion of the remaining Si-X groups with Si-allyl or -vinyl groups prior to the reduction with  $\text{LiAlH}_4$ . For example, it was found that the addition of a small amount (ca. 10 %) of allyl groups prior to the reduction with  $\text{LiAlH}_4$  resulted in a precursor with improved thermal cure characteristics, as well as enhanced ceramic yield, with only a slight increase in the C/Si ratio in the resultant “SiC” product. This precursor, called AHPCS {nominally  $[\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2\text{CH}_2]_{0.1}[\text{SiH}_2\text{CH}_2]_{0.9}$ } [6,9] (Fig. 1), has now become commercially available and is under evaluation worldwide as a coating material, a binder for ceramic powders, and a matrix source for polymer-derived, ceramic matrix composites through polymer infiltration and pyrolysis [8,9].

Another modification in the synthesis process for HPCS involves the replacement of the (Si)–Cl groups in the intermediate chlorocarbosilane obtained from the Grignard coupling reaction by (Si)–OR



**Fig. 1** AHPCS “average” structure, as derived from NMR and GPC studies.

(R = Me, Et) to yield an alcohol-soluble, hyperbranched, alkoxy-substituted polycarbosilane  $\{[(\text{OR})_3\text{SiCH}_2-]_x[-\text{Si}(\text{OR})_2\text{CH}_2-]_y[-\text{Si}(\text{OR})(\text{CH}_2-)]_{1.5}[-\text{Si}(\text{CH}_2-)_2]_1\}$  that can be cross-linked through sol-gel processing to produce a “[Si(O)CH<sub>2</sub>]<sub>n</sub>” gel [10,11]. This gel has a high Brunauer–Emmett–Teller (BET) surface area (750–900 m<sup>2</sup>/g) with a sharp peak in the pore size distribution at ca. 20 Å. Moreover, it undergoes pyrolysis to form a silicon oxycarbide product that retains a high surface area (ca. 250 m<sup>2</sup>/g) and a peak in the pore size distribution at ca. 20 Å [11]. Recently, we have succeeded in using this precursor to prepare uniform thin films of the “[Si(O)CH<sub>2</sub>]<sub>n</sub>” gel by spin coating that exhibit low dielectric constants [12]. These films are currently under evaluation for possible use as low  $\kappa$  dielectric materials.

## NOVEL CERAMIC MICROSTRUCTURES DERIVED BY BLENDING POLYMER PRECURSORS

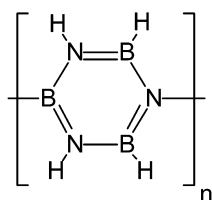
The characteristically low entropy of mixing for high-molecular-weight, linear polymers has long been used as a means of controlling the microstructures and physical properties of polymer blends. For example, hard, relatively brittle polymers such as polystyrene (PS) can be effectively “toughened” by blending in a “soft” polymer such as polybutadiene, which, when properly formulated to allow a slight degree of mixing, forms a widely dispersed second phase in the PS matrix. This has led to the development of a number of strong, tough, thermoplastic materials that are used extensively in industry [13].

When two such linear homopolymers are connected through a covalent linkage to form block-copolymers, this tendency to undergo phase separation leads, in the case of monodisperse homopolymer blocks, to specific, well-ordered, nanostructures that depend on the relative sizes of the component blocks. Such block copolymers have been used previously in several cases to prepare organic/inorganic hybrid materials, and after removal of the organic phase by calcining or in an oxygen plasma, inorganic materials with novel nanostructures [14]. However, the only prior example that we are aware of for the direct pyrolytic conversion of a phase-separated mixture of polymeric precursors to a ceramic composite, which retains the microstructure developed in the polymer mixture, has been our prior preparation of a C/SiC composite by pyrolysis of mixtures of the SiC precursor, AHPCS, with pitch as the C precursor [15]. In this case, the oxidation of the C phase was found to be significantly retarded by encapsulation as micron-size particles in a SiC matrix. We have subsequently found that when AHPCS is mixed with polyborazylene (B<sub>3</sub>N<sub>3</sub>H<sub>4-x</sub>; PB), a similar type of phase separation occurs, leading to SiC/BN ceramic composites with equally unusual microstructures and properties.

### SiC/BN composites derived from AHPCS/PB mixtures [16]

PB is a well-known polymer precursor to BN that has been used as a matrix source for fiber-reinforced, BN matrix composites and as a source of BN films in Si and SiO<sub>2</sub> substrates [17,18]. This low-molecular-weight, hydrolytically sensitive polymer, usually represented by the *para*-linked structural formula shown below, appears to have a complex structure, containing linear, branched, and fused-ring (naphyl-like) segments [17]. As produced, by thermally induced dehydrocoupling of borazine, it is soluble in ether solvents, such as tetrahydrofuran (THF) and ethyleneglycoldimethylether (glyme).

Polyborazylene:



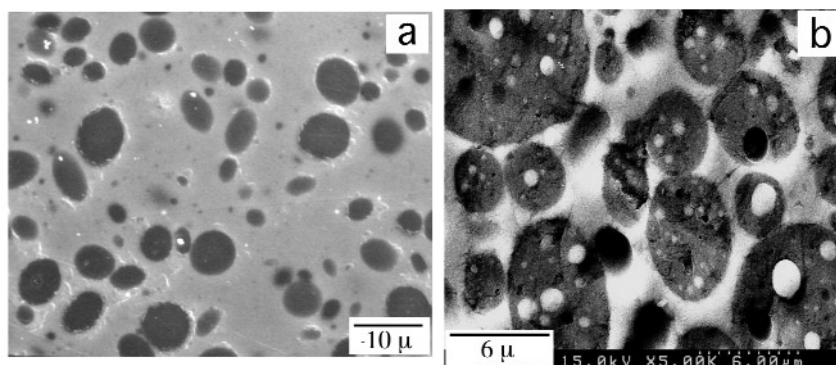
We have found that a glyme solution of PB also readily dissolves AHPCS to form a clear, homogeneous solution. After a few hours of stirring, the solvent was removed under vacuum to yield a cloudy, yellow gel. In this manner, mixtures of AHPCS with 20 and 50 wt % PB were prepared and pyrolyzed directly in bulk form by heating (slowly) to 1000 °C under flowing, high-purity argon. These polymer mixtures were found to undergo pyrolysis in remarkably high yield (88 % for the 50:50 mixture, as compared to ca. 70–80 % for AHPCS alone), suggesting, along with their gel-like nature, some as-yet unidentified chemical interaction between these two polymers that may start as low as room temperature. The presence of both Si–CH<sub>2</sub>CH=CH<sub>2</sub> and Si–H groups in AHPCS could allow either (or both) thermally induced hydroboration or dehydrocoupling to occur between these two polymers; however, based on prior indications of a substantial improvement in ceramic yield for “polycarbosilane” [2,19], which is known to have Si–H groups but no olefinic groups, when blended with as little as 1 % of PB [20], it seems likely that at least the latter process, involving the Si–H groups of AHPCS and the N–H groups of PB, may be involved here.

The resultant 3–4-mm-sized chunks of the AHPCS/PB-derived SiC–BN ceramics, along with AHPCS derived SiC alone, were further heat-treated to 1600 °C in flowing, high-purity argon. These different samples were then encapsulated in epoxy and cross-sectioned for examination by optical microscopy and scanning electron microscopy (SEM), as well as elemental analysis by scanning Auger spectroscopy and microindentation hardness tests by using a diamond indenter. Several of the indents, in each sample, were studied at high magnification by using SEM.

#### *Specimen microstructure*

AHPCS–SiC, without any PB, is monolithic and homogeneous. As is clear from the SEM micrographs (Fig. 2b) and electron microprobe analysis of the initially obtained (on pyrolysis to 1000 °C) 50:50 mixture, AHPCS–SiC/PB–BN on the other hand is composed of two distinct phases—a lighter SiC-rich phase and a darker BN-rich phase. In the 80:20 AHPCS/PB samples (Fig. 2a), the SiC-rich material forms the continuous phase, and BN forms the imbedded phase as, typically, 1–10- $\mu$ m-size droplets in the SiC-rich matrix. In some larger BN regions, smaller regions of SiC (lighter in color) can be seen dispersed.

Electron microprobe chemical analysis of the two regions indicates that the dark regions are predominantly composed of boron and nitrogen with small amounts of silicon and carbon (ca. 6 % each). On the other hand, the bright region, while being richer in silicon and carbon (in a 1:1 ratio), also contains a significant amount of boron and nitrogen (20 atom % each; balance Si and C). Because there is no overlap of elements between the two starting precursors, it is reasonable to assume that the bright regions were formed from a mixture of AHPCS and PB, which was richer in AHPCS than PB and the



**Fig. 2** Optical (a) and SEM (b) micrographs of the as-prepared 80:20 (a) and 0:50 (b) SiC/BN composites, respectively (polished cross-sections of 3–4-mm pieces).

dark regions were formed predominantly from PB. The electron microprobe chemical analysis suggests that some level of mixing has occurred between the two polymers in both regions, although it is clearly much higher in the SiC-rich areas. The smaller atomic percentage of silicon and carbon in the dark BN-rich regions compared to the boron and nitrogen in the SiC-rich regions suggests that the PB is more soluble in the AHPCS phase compared to AHPCS in the PB phase.

A similar type of two-phase microstructure, consisting of droplets of a C-rich phase in a predominantly "SiC" matrix was observed previously in the case of SiC/C composites that were obtained by mixing AHPCS with certain pitch samples (which served as the C source), followed by thermal cross-linking and pyrolysis [15]. In both cases, the appearance of the resultant microstructure resembles strongly that observed for mixtures of two immiscible viscous liquids, or for blends of high-molecular-weight polymers. In the latter case, it is well known that, in the absence of specific interactions (such as ionic or hydrogen bonding) between the two polymers, as their number average molecular weight increases, phase separation occurs at lower levels of intermixing [13]. In the case of AHPCS, and presumably also PB, the molecular weight is relatively low; therefore, a significant amount of intermixing apparently occurs prior to phase separation. Nonetheless, there is a substantial difference in the composition and properties of the two phases, resulting in distinct interfaces between the BN- and SiC-rich phases. Moreover, it is also apparent that this phase separation has occurred prior to ceramization of the component polymers, either immediately upon removal of the glyme solvent or upon thermally induced cross-linking of the polymer mixture, and that this initial, polymer miscibility-determined, microstructure is retained as the two polymers undergo conversion to ceramics upon heating to 1000 °C.

### *Hardness*

The Vickers hardness of the as-produced 80:20 and 50:50 SiC/BN samples, as well as after annealing to 1400 and 1600 °C, were measured by using a diamond indenter [16]. Among the key findings from this study was the observation that both the hardness values and the tendency to form cracks in these ceramic mixtures upon indentation was substantially reduced relative to that of AHPCS-derived SiC alone. For each of the three thermal treatment temperatures, the SiC/BN ceramic composites showed a substantially lower hardness as compared to the AHPCS-SiC material. Moreover, it was found that, in contrast to AHPCS-derived SiC alone, where extensive radial and lateral cracking was observed at the indent, for all of the SiC/BN composites tested, not only were the indentation impressions significantly larger than in the unadulterated AHPCS-SiC material, as would be expected from their lower hardness, but, unlike the AHPCS-SiC samples, which showed substantial radial and lateral cracking at the indent, very few cracks, if any, were observed for the SiC/BN composites under the same indentation conditions. Moreover, in contrast to the originally obtained 1000 °C samples and the 80:20 SiC/BN sample at 1600 °C, where the two phases appear to be strongly bonded together and deformation occurs without failure at the interface, in the 1600 °C 50:50 SiC/BN material, the two phases no longer behave as a monolithic material, and separation of the two phases at their interface can be seen in the region of the indent. For this 50:50 SiC/BN sample prepared at 1600 °C, in some cases, radial cracks produced by the indentation are blunted, and terminate at the weakly bonded second phase. This separation at the interface between the BN- and SiC-rich phases presumably reflects the differing amount of shrinkage of the two phases that accompanies the increasing densification/crystallization of the component materials as they are heated to 1600 °C, which may be magnified by the higher volume fraction of the dispersed phase in the case of the 50:50 composite. Indeed, X-ray diffraction (XRD) measurements carried out on this system evidence at least partial crystallization of the SiC (but apparently not the BN) under these conditions. This combination of decreased hardness, decreased crack formation, and crack blunting are suggestive of unusual toughness for this precursor-derived SiC/BN mixture, at least after annealing to 1600 °C. Further studies are needed in order to verify these preliminary conclusions; however, if this is indeed the case, such a system would be of considerable interest as either an interphase or as the matrix phase in ceramic fiber-reinforced, ceramic matrix composites (such as SiC<sub>f</sub>/SiC<sub>m</sub>).

Clearly, much remains to be determined about the processes of phase separation, cross-linking, pyrolysis, and crystallization that occur during the conversion of this polymer mixture to the two-phase BN- and SiC-rich phases; however, it is clear that this approach of using mixtures of immiscible polymer precursors has quite general applicability and that it offers unique opportunities for microstructural (and thereby property) control in ceramic composites.

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