Single-source-precursor Synthesis and High-temperature Behavior of SiC Ceramics Containing Boron

Abstract: In this paper, a hyperbranched polyborocarboxasilane (HPBCS) was prepared by a one-pot synthesis with Cl₅Si(CH₃)CH₂Cl, Cl₃SiCH₂Cl and BCl₃ as the starting materials. The obtained HPBCS was characterized by GPC, FT-IR and NMR, and was confirmed to have hyperbranched structures. The thermal property of the resulting HPBCS was investigated by TGA. The ceramic yield of the HPBCS is about 84% and that of the counterpart hyperbranched hydridopolycarbosilane is only 45%, indicating that the introduction of boron into the preceramic polymer significantly improved the ceramic yield. With the polymer-derived ceramic route, the final ceramics were annealed at 1800 °C in argon atmosphere for 2 h in order to characterize the microstructure and to evaluate the high-temperature behavior. The final ceramic microstructure was studied by XRD and SEM, indicating that the introduction of boron dramatically inhibits SiC crystallization. The boron-containing SiC ceramic shows excellent high-temperature behavior against decomposition and crystallization at 1800 °C.

Keywords: boron, hyperbranched polymer, SiC, single-source precursor

1 Introduction

Since the 1960s, silicon-based polymer-derived ceramics (PDCs) have been synthesized directly by the pyrolysis of organosilicon polymers and gain more and more attention in the past decades [1–4]. In comparison with the conventional powder-based ceramic processing, the PDC route has many important advantages because the structures, compositions, and properties of PDCs can be tailored at atomic, molecular, and nanoscales by changing the chemistries of precursors [2, 3]. Silicon carbide (SiC) is an advanced ceramic material with high thermal and chemical stability, low density, high mechanical strength and hardness, and high thermal conductivity [5]. Recent investigations have shown that in some special cases, namely in boron-containing SiC-based ceramics, Si-B-C-N ceramics and composites are attracting more and more attentions in various applications such as dielectric, EMI shielding and EM absorption [6–9]. Moreover, the incorporation of <1 wt% boron into SiC ceramics has been shown to significantly improve sintering and to enhance ceramic yield [10, 11]. Boron is believed to enhance the high-temperature stability of boron-modified silicon-based ceramics and also retards the crystallization and decomposition at high temperatures [12, 13]. Therefore, the aforementioned work has spurred interests in the incorporation of boron into polymeric precursors to SiC ceramics.

Recently, single-source precursors (SSPs) to boron-modified SiC have been paid more attention due to the improved homogeneity of the ceramics [14–17]. Generally, two different approaches to the design of the SSPs have been explored, namely polymer route and monomer route. The polymer route involves chemical modification of silicon-containing polymers or oligomers with boron-containing compounds. It was reported by Sneddon et al. [14] that the hydroboration reactions of the allylhydridopolycarbosilane (AHPCS) with BH₃·THF (or BH₃·SMe₂) led to boronated polymers, but those polymers were extensively cross-linked and no longer processible. In their study, the 9-BBN-modified AHPCS has proven to be an excellent processible single-source precursor to dense SiC ceramics. Yu et al. [15, 16] used the hydroboration reactions of the AHPCS (or ethynylhydridopolycarbosilane) with the 9-BBN to prepare the boron-modified preceramic precursors. Their results indicate that the introduction of 1 wt% boron significantly inhibits SiC crystallization and improves density of final ceramics. The monomer route involves the synthesis of polymers from boron-containing monomer units. Hsu et al. [17] synthesized several boron-
containing organosilicon polymers via a sodium-coupling reaction of silicon and boron halides with and without alkyl halide in hydrocarbon solvents. The obtained preceramic polymers contained Si-B bonds in their backbones and yielded 56–70% ceramic product in an inert atmosphere above 800 °C. However, little attention was paid on the backbone polyborocarbosilane prepared by the monomer route.

With the PDC route, an important consideration when choosing a ceramic precursor is the ceramic yield because this ultimately determines the utility, bulk properties, and shape retention in the resulting ceramics [18]. Hyperbranched polymers are different from linear ones in terms of the dimensionality of molecular architecture, the former being three-dimensional spheres while the latter is one-dimensional chains. They were found superior, in terms of the ceramic yield, to the linear ones as ceramic precursors [19]. Recently, hyperbranched polycarbosilanes (HBPCSs) have drawn great attention as precursors to SiC [20]. The first HBPCS was originally synthesized by Greber et al. through Grignard self-addition of Cl-SiR2(CH2)CH2MgCl, followed by the reduction of the residual chlorine groups with lithium aluminum hydride (LiAlH4) [21]. In an analogous route, a series of liquid HBPCSs were prepared [22–30]. Yu and co-workers synthesized a series of hyperbranched polycarbosilanes via a one-pot synthesis, including two steps: a Grignard coupling of chlorosilanes and unsaturated halogenated hydrocarbons (such as allyl chloride or propargyl chloride) occurred, and then it was followed by reduction with lithium aluminum hydride [29–33].

Based on these considerations that combine a backbone polyborocarbosilane with a hyperbranched structure, we tried to synthesize a new hyperbranched polyborocarbosilane (HPBCS) via the Grignard coupling route for the first time. The molecular structure and reaction mechanism of the obtained HPBCS were studied in detail. The thermal properties of the HPBCS and the high-temperature behavior of the final ceramics were investigated as well.

2 Experimental

2.1 Raw materials

Cl2Si(CH3)CH2Cl and Cl3SiCH2Cl are industrial grade and distilled before use. BCl3:THF solution (1 mol/L) was obtained from Guangzhou Rui He Chemical Science and Tech. Co. Ltd and used as received. Magnesium (Mg, 99% purity) and lithium aluminum hydride (LiAlH4, 99% purity) were stored in inert ambience. THF was distilled from a sodium benzophenone ketyl prior to use. All other reagents are analytical grade and used as received. All manipulations involving air and/or water sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technology [31].

2.2 Synthesis

A series of experiments of synthesizing liquid HPBCSs were designed with molar ratios of Cl2Si(CH3)CH2Cl to Cl3SiCH2Cl as 1/2, and different molar ratios of BCl3 to the overall amount of the two chlorosilanes as 0.1, 0.2, and 0.3. The resultant polymers are abbreviated as HPBCS-1, HPBCS-2, HPBCS-3, correspondingly. To make a comparison, a hyperbranched polycarbosilane (HPCS) was synthesized via the same route, in the absence of BCl3.

One typical synthesis of HPBCS was achieved with the following procedure: Dry THF (500 mL) and 22.6 g of magnesium powder (0.94 mol, 30% excess) were added to a 2 L, four-neck flask equipped with an argon inlet, mechanical stirrer, a constant pressure drop funnel, and a reflux condenser with an argon outlet. The mixture of Cl3SiCH2Cl (86.4 g, 0.48 mol), Cl2Si(CH3)CH2Cl (40.0 g, 0.24 mol) and BCl3:THF solution (72 mL, 0.072 mol) in the drop funnel was added to the flask over about 1 h. After the addition was complete, the reaction mixture was heated at 60 °C oil bath for 12 h to obtain brownish yellow slurry as large amounts of MgCl2 precipitated. In our case, the reactive intermediate was not separated from the reaction slurry except that small amount of the reaction mixture was separated and used to measure FT-IR and 11B NMR. And then, the resulting slurry was reduced by LiAlH4. LiA1H4, 15.0 g (0.39 mol, 30% excess) suspended in 200 mL of THF was added to the reaction slurry over 30 min, with an ice/water bath under rapid stirring. The resulting light gray suspension was refluxed overnight under argon. At last, the reduced mixture was stripped of as much ether as possible under vacuum with heating to 50 °C. The resulting solids were extracted with pentane and allowed to settle, and the clear, yellow pentane solution was transferred by cannula to remove the polymer from the lithium and aluminum salts. The solution remained clear yellow during removal of the solvent under vacuum. Finally, a viscous, yellowish, air-sensitive polymer (22.3 g) was recovered in an overall yield of 62.3%.

2.3 Pyrolysis

According to TGA results the conversion of the preceramic polymer into the inorganic state is completed at a tem-
temperature close to 900 °C, so this temperature was selected for the synthesis of ceramics. The polymer samples were put in an alumina boat and heated in a self-made tube furnace in argon flowing at 200 cm³/min. The temperature was progressively raised up to 900 °C at a rate of 5 °C min⁻¹ and kept at this value for 2 h. After pyrolysis, the 900 °C ceramics were annealed at 1800 °C in argon atmosphere for 2 h in order to characterize the microstructure and to investigate the high-temperature behaviors. The 900 °C ceramic sample was put in a graphite crucible and heated in a tube furnace in argon, heated rapidly to the predetermined temperature at a rate of 5 °C/min and hold for 2 h, and finally cooled to room temperature. The 1800 °C ceramics derived from HPBCS-1, HPBCS-2 and HPBCS-3 are abbreviated as SiCB-1, SiCB-2 and SiCB-3, respectively.

2.4 Characterization

Gel permeation chromatography (GPC) measurements were performed at 35 °C with THF as the eluant (1.0 mL/min) using an Agilent 1100 system. The spectrum was calibrated with narrow polystyrene standards. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Avaror 360 apparatus (Nicolet, Madison, WI) with KBr plates for liquid samples. Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AV300MHz spectrometer operating at 300.13 MHz for hydrogen-1, 59.63 MHz for silicon-29 (¹H decoupling), and 96.96 MHz for boron-11 (¹H decoupling). The specimens used for NMR were dissolved in CDCl₃ solution. The ¹H and ²⁹Si chemical shifts were all referred to tetramethylsilane. The chemical shift of ¹¹B NMR was referenced to BF₃·OEt₂. Thermal analysis of the polymers was carried out on a thermal gravimetric analysis (TGA) (Netzsch STA 409EP) in argon gas with a ramping rate of 10 °C/min ranging from room temperature to 1000 °C. X-ray diffraction (XRD) was carried out by using a PANalytical X’Pert PRO diffractometer (PANalytical, Netherlands) with CuKα radiation. The specimens were continuously scanned from 10° to 90° (2θ) at a speed of 0.01678°/s. The morphologies of the ceramics were examined with a scanning electron microscope (SEM) (Model 1530, LEO, Germany).

3 Results and discussion

3.1 Polymer characterization

Viscous liquid products were obtained via Grignard coupling of Cl₃SiCH₂Cl, Cl₂Si(CH₃)CH₂Cl and BCl₃, followed by reduction with LiAlH₄. The weight-average molecular weight (Mw) and polydispersity index (PDI) of the resulting polymers were measured by GPC (Fig. 1). The Mw of HBPCS and HPCS are 900 and 1800, and the PDI of HBPCS and HPCS are 1.6 and 8.9, respectively. Compared with the HPCS, the HPBCS has larger molecular weight and wider molecular distributions. The GPC results indicate that the boron should be introduced into the polymer matrix, resulting in the molecular weight increasing.

The as-synthesized polymers were characterized by means of FT-IR and NMR. As shown in Fig. 2, the functional groups in HPCS including Si-CH₃, Si-CH₂-Si, Si-H were identified by FT-IR, as followed: 2950, 2873 cm⁻¹ (s, CH₃ stretching), 2920 cm⁻¹ (s, CH₂ stretching), 1400, 1250 cm⁻¹ (Si-CH₃ deformation), 1355 cm⁻¹ (s, Si-CH₂-Si deformation), 1040 cm⁻¹ (vs, Si-CH₂-Si stretching), 800 cm⁻¹ (vs, Si-C stretching), 2100 cm⁻¹ (vs, Si-H stretching), 940 cm⁻¹...
With respect to the HPBCS, it shows characteristic peaks of HPCS including the above-mentioned Si-CH₃, Si-CH₂-Si, and Si-H groups. It is worth mentioning that the rectangle-labelled area (a) and (b) significantly changed (including peak shape and intensity), comparing the HPBCSs and HPCS. According to the literatures, the area (a) and (b) are corresponding to CH₂ stretching and B-C stretching in a -BCH₂- units, respectively [17]. The intensities of the area (a) and (b) obviously increased with the increase in the BCl₃ amount in feed. Moreover, the small bands appear at 2500 cm⁻¹, which is due to the B-H absorption [17]. The results indicate that the boron was successfully introduced into the obtained polymer chains, which will be further confirmed by the NMR analysis.

In the ¹H NMR spectra (Fig. 3), the groups of signals around 0 ppm in the labeled area (c) are assigned to the various the Si-CH₃ and Si-CH₂ functionalities [25–27]. The three peaks in the labeled area (a) ranging from 3.5 to 4.5 ppm are attributed to the proton absorption of Si-Hₓ (x = 3, 2 or 1) groups [25–27]. As reported previously, chlorosilanes underwent a side reaction with ether, resulting in the incorporation of methylene from THF into the polymer chain. The multiplets in the labeled area (b) ranging from 1.5 to 2 ppm is assigned to the methylene protons of SiOCH₂CH*₂CH*₂CH₂ segments derived from the side reaction between chlorosilanes and THF [26]. With the increasing of BCl₃ amounts in feed, the intensities of the multiplets in the area (c) dramatically decrease with the increasing of BCl₃ amounts, which can be due to that the contents of Si-CH₃ and Si-CH₂ units reduce after the introduction of boron into the polymer chains.

The ²⁹Si NMR is an important method to investigate the chemical environments around Si atoms. As shown in Fig. 4, complex multiplets from 5 to 0 ppm (SiC₄), from -10 to -20 ppm (C₃SiH), from -30 to -40 ppm (C₂SiH₂) and from -58 to -68 ppm (C₃SiH₃) are the direct evidence of a branched structure [25–28]. Based on the FT-IR and NMR results, the obtained polymer is confirmed to be the hyperbranched polyborocarbosilane.

### 3.2 Reaction mechanism of polymer

Previously, a series of HBPCs were successfully prepared via the following steps: a Grignard coupling of chlorosilanes occurred, and then it was followed by reduction with lithium aluminum hydride (LiAlH₄) [22, 23, 25–28]. In the present work, we believe the initial step in the polymerization is a formation of the intermediate R₃Si-CH₂MgCl (R=CH₃, Cl or another CH₂SiR₃ group), which is similar to the previous work. The second step is the formation of the complicated branched structure, namely hyperbranched chloropolyborocarbosilane, is generated by the reaction of the intermediate R₃Si-CH₂MgCl with remaining SiCl groups and with BCl groups. After reduction with LiAlH₄, the chloropolyborocarbosilane was converted to the target polymer hydridopolyborocarbosilane HPBCs.

To certify the transformation from the chloropolyborocarbosilane to the target HPBCs, their FT-IR and ¹¹B {¹H} NMR spectra were performed and the results are shown in Fig. 5 and Fig. 6, respectively. In Fig. 5, it is obviously
found that the characteristic Si-H peaks (at 2100 and 940 cm\(^{-1}\)) and B-H peak (at 2500 cm\(^{-1}\)) appear after the reduction of the intermediate choloropolyborocarbosilane.

In Fig. 6, the \(^{11}\)B \(^{1}\)H NMR spectrum of the choloropolyborocarbosilane shows a broad and strong signal from 0 to 20 ppm, indicating that complex boron environments including BCCl\(_2\) or BCCl\(_2\) units in the choloropolyborocarbosilane matrix besides small amount B-O units. After reduction, the broad boron signal splits into two signals from 10 to 20 ppm and from 20 to 35 ppm, which are due to boron signals of the BCH\(_2\) and BC\(_2\)H units in the target HPBCS, respectively.

Based on the FT-IR and \(^{11}\)B \(^{1}\)H NMR results, the reaction mechanism (Scheme 1) is further confirmed and the boron is successfully introduced into the hyperbranched polycarbosilane.

### 3.3 Thermal property of polymer

In order to understand the thermal behavior during the polymer-to-ceramic transformation of the preceramic polymers, the TGA of the HPBCS and HPCS was measured and the result is shown in Fig. 7. Below 300 °C, the HPCS lost 16.7% weight while the HPBCS lost 4.4%. In a case of pure PCS, the weight loss below 300 °C was attributed to the vaporization of low molecular weight oligomers [32], since the evolution of H\(_2\) derived from the dehydrocoupling reaction (Si-H/Si-H) started about 300 °C [3]. The introduction of boron enhanced the molecular weight of the obtained HPBCS (Fig. 1), inhibiting the evaporation of oligomers, which is responsible for the lower weight loss. Over the 300–500 °C region, the weight loss of HPBCS and HPCS were 3.9% and 26.7%, respectively. At temperatures between 500 and 1000 °C the 8% weight loss of the HPBCS...
closely matched that of HPCS (11%). It indicates that over the 300–500 °C region, significant differences in weight loss were found for the HPBCS and HPCS, which is responsible for the difference in final ceramic yields. According to the literature [14], it was found that over the 300–500 °C range, the evolution of volatile gases CH₃CH₃, SiH₄ and CH₃SiH₃ were suppressed in the boron-modified AHPSC, whereas the AHPSC showed loss of these three types gases. In our case, we believe that the introduction of boron into the preceramic polymer suppressed the gas evolution during the polymer-to-ceramic transformation, resulting in a higher mass residue. In conclusion, the ceramic yield of obtained HPBCS is about 84% and that of HPCS is only 45.5%. As expected, the introduction of a small amount of boron to the polymer precursor improved the final ceramic yield, which is an important consideration when choosing a ceramic precursor.

3.4 High-temperature behavior of ceramic

As is well-known, PDCs are amorphous materials which undergo different crystallization and decomposition processes upon annealing at high temperatures [1–4]. In our case, the ceramics pyrolyzed at 900 °C were annealed at 1800 °C to investigate the high-temperature behavior. The 1800 °C ceramics derived from HPCS, HPBCS-1, HPBCS-2 and HPBCS-3 are abbreviated as SiC, SiCB-1, SiCB-2 and SiCB-3, respectively. It is well accepted, decomposition and crystallization of PDCs is one of high-temperature behaviors besides energetics and high-temperature oxidation and corrosion [3]. Therefore, the crystallization behavior of the HPBCS and HPCS-derived ceramics annealed at 1800 °C was investigated by XRD. For the HPCS-derived ceramic, it shows the characteristic peaks of β-SiC. Among these peaks, the three major peaks at 2θ = 36° (111), 60° (220), and 72° (311), along with the weaker ones at 42° (200) and 75° (222), are attributed to β-SiC, and the shoulder at 34° is assigned to stacking faults like α-SiC in β-SiC. From a comparison of HPCS-derived ceramics with HPBCS-derived ceramics, the reflection of β-SiC of the latter becomes broader and weaker, which is attributed to the decreased crystallization degree and smaller crystallite size. The results indicate that the introduction of boron into the preceramic polymer significantly inhibits the crystallization of final ceramic. Moreover, the peaks corresponding to that of the β-SiC phase become broader and weaker as the boron content in the ceramics increases because of the decreased degree of crystallization, which further confirm that the introduction of boron into the preceramic polymer significantly inhibits the crystallization of SiC. For the SiC-based ceramics, the resistance to crystallization was found to be advantageous with respect to the thermal stability at high temperatures [3].

The microstructures of the 1800 °C ceramics were investigated by SEM and typical micrographs are shown in Fig. 9, taking the SiCB-3 as an example. It is evident that the crystal particle of HPBCS-derived ceramic is smaller than that of the HPCS-derived ceramic, indicating that small amount boron into ceramic significantly inhibits the crystallization of final ceramic. The results agree well with the XRD patterns.

Moreover, the decomposition of the SiC and boron-modified SiC was investigated and the results are shown in Fig. 10. After annealed at 1800 °C in argon atmosphere for 2 h, the mass residue of HPCS-derived SiC is 61.2%, while those of SiCB-1, SiCB-2 and SiCB-3 are 70.8%, 81.2%,
and 88.5%, respectively. Based on the XRD results and the decomposition analysis, the high-temperature property of the boron-modified SiC is significantly improved, comparing with SiC.

4 Conclusions

In this paper, a hyperbranched polyborocarbolane (HPBCS) was prepared by a one-pot synthesis with Cl$_2$Si(CH$_3$)CH$_2$Cl, Cl$_3$SiCH$_2$Cl and BCl$_3$ as the starting materials. The obtained HPBCS was characterized by GPC, FT-IR and NMR. It is proposed that the initial step in the polymerization is formation of the intermediate R$_3$Si-CH$_2$MgCl (R=CH$_3$, Cl or another CH$_2$SiR$_3$ group), and then the hyperbranched structure is formed by the Grignard coupling reaction of the intermediate with remaining SiCl and BCl groups. After reduction of SiCl and BCl bonds by LiAlH$_4$, the target HPBCS containing Si-H and B-H bonds, was successfully prepared. The thermal property of the resulting HPBCS was investigated by TGA. The ceramic yield of the HPBCS (84%) is about 40% higher than that of the counterpart hyperbranched hydridopolyacarbolane HPCS (45%), indicating that the introduction of boron into the preceramic polymer significantly improved the ceramic yield. Moreover, the introduction of boron dramatically inhibits SiC crystallization and decomposition, which are advantages for high temperature ceramics.

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References


