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Synthesis and characterization of a new liquid polymer precursor for Si–B–C–N ceramics

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Abstract A new liquid polyborosilazane precursor for Si–B–C–N ceramic was synthesized by co-condensation reaction of boron trichloride, organodichlorosilanes, and hexamethyldisilazane. The structure and properties of polyborosilazane were studied by means of Fourier transform-infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), rheology, and thermogravimetric analysis (TGA). The conversion of polymer to ceramic and the high-temperature behavior of the new polymer-derived ceramic were investigated by TG–MS, FT-IR, X-ray diffraction (XRD) and high-temperature TGA (HTGA). The ceramics showed good oxidative resistance and thermal stability with weight gain of 1.8 wt% at 1350 °C under air atmosphere and weight loss of 2.6% at 1900 °C under Ar atmosphere.

Introduction

As an alternative approach to synthesize ceramics, pyrolysis of polymer precursors (PDCs route) has drawn remarkable interest [1–6]. With this strategy, a series of new ternary and multinary ceramics have been developed. Among them, Si–B–C–N quaternary ceramics have received much attention due to their excellent thermal stability and resistance to oxidation at high temperature [7–10]. Since the first example of molecular precursor reported by Takamizawa [11], various polyborosilazane precursors for Si–B–C–N ceramic have been prepared from different synthetic routes.

Due to its simplicity, ammonolysis reaction of Si–Cl and B–Cl containing compounds has been the most widely used method in the preparation of polyborosilazanes. Jansen et al. [8, 12] synthesized polyborosilazanes by ammonolysis reactions of 1,1,1-trichloro-*N*-(dichloroboryl)silane (TADB). Riedel et al. [7, 13] obtained Si–B–C–N polymer precursors by ammonolysis of tris[(dichloromethylsilyl)ethyl] borane. In these cases, preparation of multifunctional monomers that contain both Si and B in one molecule is the key and essential step. In addition, to get polymer precursors, separation of amine or ammonium salts from reaction mixture is also unavoidable. Weinmann and co-workers [14–16] prepared highly crosslinking Si–B–C–N precursors, polysilylcarbodiimides, via an elegant non-oxide sol–gel process by ammonolysis of $B[C_2H_4–Si(R)Cl_2]_3$ ($R = H, CH_3$) with bis(trimethylsilyl)carbodiimide as amine source. In this process, byproduct Me_3SiCl is easy removed, however, preparation of the multifunctional monomer $B[C_2H_4–Si(R)Cl_2]_3$ in advance is still needed.

Lee and coworkers [17] developed a novel and simple one-step process to synthesize polyborosilazane by reaction of boron trichloride, trichlorosilane, and hexamethyldisilazane. The strategy excludes the preparation of multifunctional monomer, and is easy to eliminate byproducts. However, the obtained polymer is a highly crosslinking solid and difficult to melt or dissolve in solvent, which prevents its use as impregnant or fiber precursor. Tang and coworkers [18] modified the method by using

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dichlorodimethylsilane instead of trichlorosilane to decrease the crosslinking density of polymer and obtained a hot-melt product. Though the one-pot procedure provides a simpler and easily scale-up strategy to prepare polyborosilazanes, to our surprise, the research related to the method is quite limited.

To develop liquid polyborosilazanes that suitable for preparation of ceramic matrix composites as impregnant, we have extended the method to synthesize polyborosilazane containing multi-functional groups. In this contribution, we would like to report synthesis and characterization of a new vinyl containing liquid polyborosilazane. The conversion of polymer to ceramic and the high-temperature behavior of the new polymer-derived Si–B–C–N ceramic will be discussed.

Experimental

Synthesis

Methylvinyldichlorosilane (MVDCS), methyldichlorosilane (MDCS), and hexamethyldisilazane (HMDZ) (Zhejiang Hutu Silicon Co., Ltd.) were purified by distillation before use. Boron trichloride (BTC, 1 M in hexane) was purchased from Beijing Multi Technology Corp. Dicumyl peroxide (DCP) was obtained from Sinopharm Chemical Regeant Co. Ltd. and recrystallized from ethanol. All reactions were performed under dry nitrogen atmosphere using Schlenk techniques.

The molar ratio of reactants was set as 1:1:1:6 (MVDCS:MDCS:BTC:HMDZ). In a typical synthesis, to a mixture of MVDCS, MDCS and BTC solution, HMDZ was added dropwise at 0 °C. After the addition of HMDZ was complete, the reaction mixture was allowed to warm to room temperature. Then the mixture was slowly heated to 200 °C to remove by-product of Me_3SiCl, solvent, and unreacted starting materials. The resulting transparent liquid was further dried at 200 °C for 1 h in vacuum. After cooled down to room temperature, a polymer precursor, **PSNB**, was obtained as a light yellow viscous liquid in 80% yield.

Curing

Formation of crosslinking framework before decomposition or volatilization of the precursors is an effective way to increase the ceramic yield. To cure **PSNB**, dicumyl peroxide (DCP) of 0.5 wt% was added. Then, the **PSNB** was heated to 170 °C at a heating rate of 10 °C/min, with a dwell time of 2 h under N_2 atmosphere. After cooled down, a hard bulk cured **PSNB** (**PSNB170**) with light yellow color was obtained.

Pyrolysis

The cured bulk precursors were pyrolyzed in a high-temperature sintering furnace (Joint-Stock Company, HIGH-MULIT 5000, Japan) from room temperature to the schemed temperature in a flowing Ar atmosphere at a heating rate of 5 °C/min, followed by holding at the final temperature for additional 2 h, and then cooled down to room temperature at a rate of 5 °C/min. Below 1600 °C, alumina crucible was used, and above 1600 °C (including 1600 °C), graphitic crucible was adopted to keep samples.

Characterization

FT-IR spectra were obtained from a Bruker Tensor-27 FT-IR spectrometer in the wavenumber range of 4000–400 cm^{-1} with KBr pellets. ^{1}H-NMR spectra were recorded in $CDCl_3$ solution with Bruker AVANCE 400 spectrometer. ^{29}Si and ^{11}B-NMR spectra were recorded in $CDCl_3$ solution with Bruker AVANCE 300 spectrometer. Complex viscosity was obtained using a TA AR 2000 Rheometer with a 20-mm diameter parallel plate at a heating rate of 4 °C/min. TGA-MS was performed on a PerkinElmer Diamond TGA–MS equipment at a heating rate of 10 °C/min under Ar atmosphere from 30 to 1000 °C. The high-temperature stability of the ceramic under argon atmosphere was evaluated with a Setaram Setsys EV24 HTGA from 30 to 1900 °C at a heating rate of 10 °C/min. The anti-oxidation behavior was recorded on a SII EXSTAR TG/DTA6300 at a heating rate of 10 °C/min under air atmosphere from 30 to 1350 °C. XRD measurements were carried out on a Rigaku D/M4X 2500 diffractometer with Cu Kα radiation. Elemental analysis was done at Shanghai Institute of Ceramics, Chinese Academy of Sciences.

Results and discussion

Synthesis and properties of **PSNB**

The use of $HMeSiCl_2$ and $MeViSiCl_2$ as starting materials results in a polymer precursor containing both Si–H and Si–Vi groups, which can be confirmed by ^{1}H-NMR spectra (Fig. 1). The broad resonances at 4.6-–5.1 and 5.7–6.1 ppm are characteristic resonances of Si–*H* [17] and Si–(*CH=CH₂*) [19], respectively. The multiplet peaks at 0–0.3 ppm are attributed to Si-–CH_3, and a medium-intensity peak at 0.4 ppm can be attributed to SiN*H* on the linear chain. The broad peak at 1.5–1.9 ppm is assigned to BN*H*Si, and 3.3 ppm belongs to B_2NH in borazine ring, respectively [17].

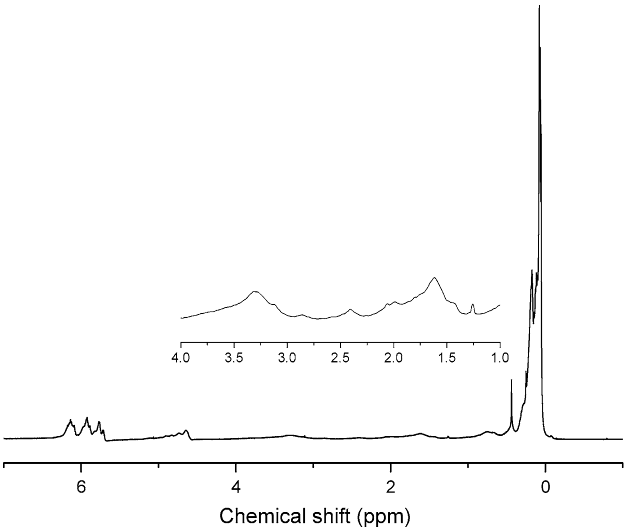

Fig. 1 ^{1}H-NMR spectrum of **PSNB**

The ^{29}Si-NMR spectrum (Fig. 2) of **PSNB** provides evidence for the formation of $\mathit{Si}\mathrm{N_3C}$ unit, which shows resonances at around −22.8 ppm [17, 18, 20]. The sharp doublet at −17.2 ppm originates from $\mathrm{CH_3CH_2{=}CH}\mathit{Si}\mathrm{N_2}$. The medium-intensity peak at −14.6 ppm can be assigned to $\mathit{Si}\mathrm{HN_2C}$ [20], and the peaks between 2.4 and 3.3 ppm are assigned to $\mathit{Si}\mathrm{(H){-}CH_3}$ and $\mathit{Si}\mathrm{(CH_2{=}CH){-}CH_3}$. The peak at 0 ppm belongs to $\mathrm{Si{-}(CH_3)_3}$ [21].

In Fig. 3, ^{11}B-NMR spectrum of **PSNB** shows a broad peak with the maximum at 28.8 ppm, implying the existence of borazinic $\mathit{B}\mathrm{N_3}$ in the polyborosilazane [22–24]. After deconvoluted, other four peaks are distinguished in the spectrum, which are centered at 17.5, 39.5, 48.2, and 57.6 ppm, respectively. These results indicate that the polymer **PSNB** has a complex structure. However, it is not easy to assign the ^{11}B peaks to specific structure due to lack of the related data.

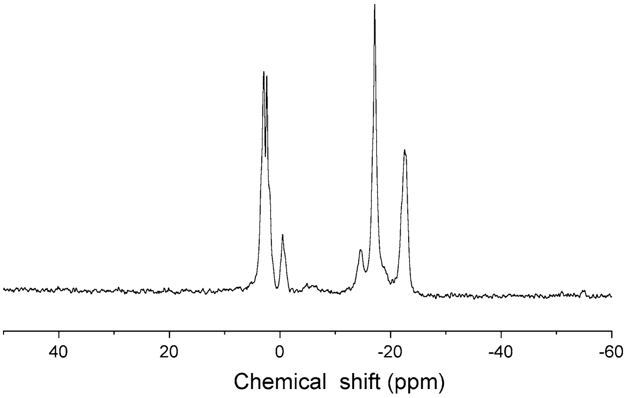

Fig. 2 ^{29}Si-NMR spectrum of **PSNB**

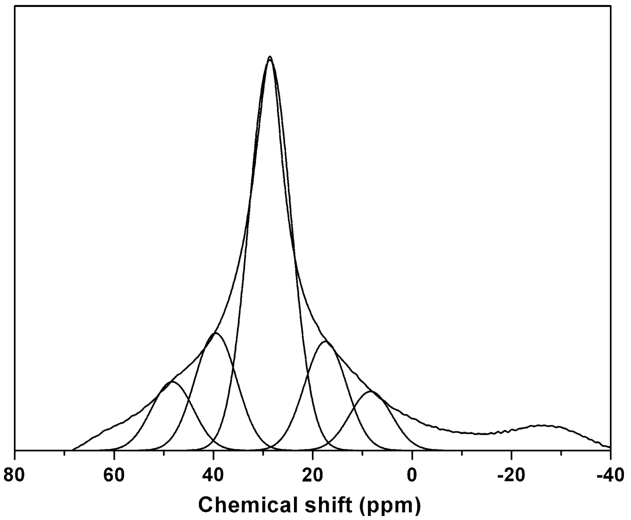

Fig. 3 ^{11}B-NMR spectrum of **PSNB**

The FT-IR spectrum of as-synthesized **PSNB** is shown in Fig. 4a. There is a broad band between 1300 and 1500 cm^{-1} due to overlap of B–N stretching at 1403–1408 cm^{-1}, 1380 cm^{-1} and $\mathrm{{-}CH_2{-}}$ bending vibration at 1350 cm^{-1} [21]. Asymmetric stretching bands of N–H and Si–H units are observed at 3393, 1170, and 2128 cm^{-1}, respectively [18]. Absorption bands at 3047, 3006, and 1593 cm^{-1} are characteristic $\mathrm{{=}CH_2}$, =CH, and C=C stretching bands of vinyl group [19]. The sharp bands at 2956 and 2899 cm^{-1} are assigned to C–H stretching. The band at 1254 cm^{-1} originates from the stretching mode of $\mathrm{Si{-}CH_3}$ bonds [19, 21]. A broad band at 844 cm^{-1} is due to Si–N bond attached to boron, and the signal at 950 cm^{-1} belongs to Si–N–Si bond [14, 25]. A minor band at 790 cm^{-1} is ascribed to B–N bending vibration. Besides, the bands of Si–O–Si (1010 cm^{-1}) and Si–OH (530 cm^{-1}) appear in the spectrum, which is due to the hydrolysis of Si–NH during testing in the air. After cured under N_2 atmosphere, these peaks attributed to Si–O–Si and Si–OH do not show again (Fig. 4b), implying the crosslinking structure decreases the sensitivity of the polymer to air.

The new polymer **PSNB** is a liquid under ambient condition. As shown in Fig. 5a, with increase of temperature, viscosity of the polymer decreases until 90 °C and then keeps lower than 500 mPa s over the range of 90–160 °C. From 160 °C, the viscosity dramatically increases because of the thermal-induced crosslinking reaction of vinyl groups. **PSNB** contains both Si–H and Si–Vi groups, which also permits us to get cured polymer by other manners, such as hydrosilylation reaction catalyzed by Pt or radical polymerization initiated with peroxide. In this work, the rheological behavior of **PSNB** with 0.5 wt% DCP as initiator was also investigated and shown in Fig. 5b. Before 140 °C, the variation on the viscosity of **PSNB**/DCP is similar to that of pure **PSNB**, while the viscosity increases rapidly from 140 °C, which is much earlier than that of pure **PSNB** due to crosslinking reaction

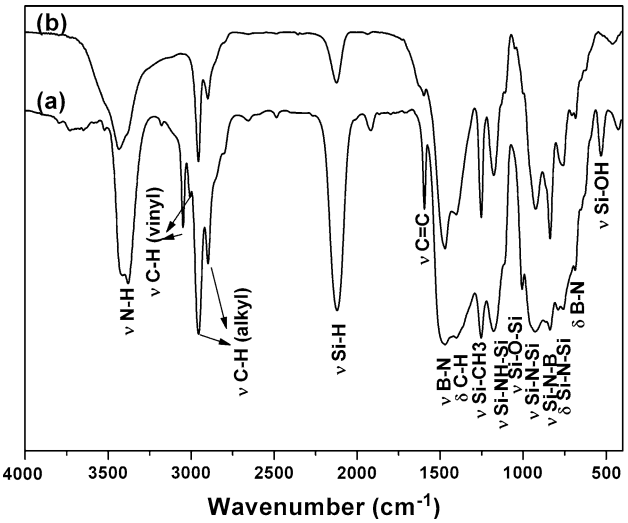

Fig. 4 IR spectra of (*a*) the as-synthesized **PSNB** and (*b*) cured **PSNB**

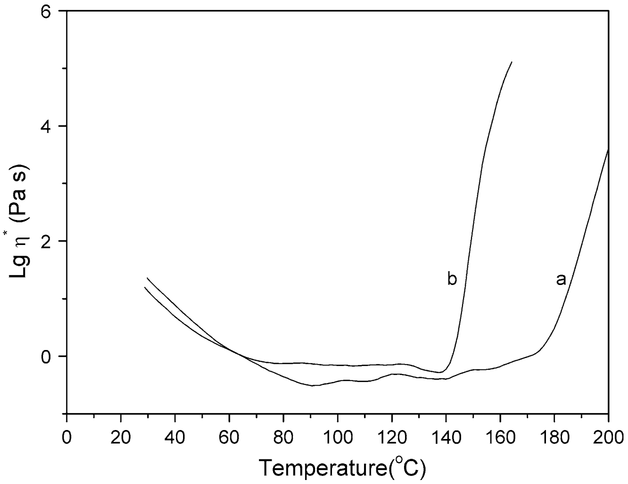

Fig. 5 Dependence of viscosity on temperature of **PSNB** (*a*) without DCP, (*b*) with 0.5 wt% DCP

of vinyl groups initiated by DCP. The fact that the viscosity keeps stable and lower than 800 mPa s over a broad range of temperature suggests a proper processing window in preparation of composites with **PSNB** as an impregnant.

Conversion of **PSNB** to Si–B–C–N ceramics

The pyrolysis behavior of the as-synthesized **PSNB** and **PSNB170** was investigated by TG–MS. For as-synthesized sample (Fig. 6a), the weight losses are 23.5% in the range of 30–300 °C and 32.7% in the range of 300–800 °C, respectively, with ceramic yield of 45.6% at 1000 °C. For **PSNB170** (Fig. 6b), though the weight loss is only 1.2% during curing process, the sample shows a small weight loss of 5.5% between 30 and 300 °C, which is much lower than that of the as-synthesized **PSNB** in the same temperature range. This suggests the crosslinking structure is formed. The weight loss of the **PSNB170** is 36.2% between 300 and 800 °C, and the final ceramic yield at 1000 °C is 59.6%, which is higher than that of uncured **PSNB** by 14.0%.

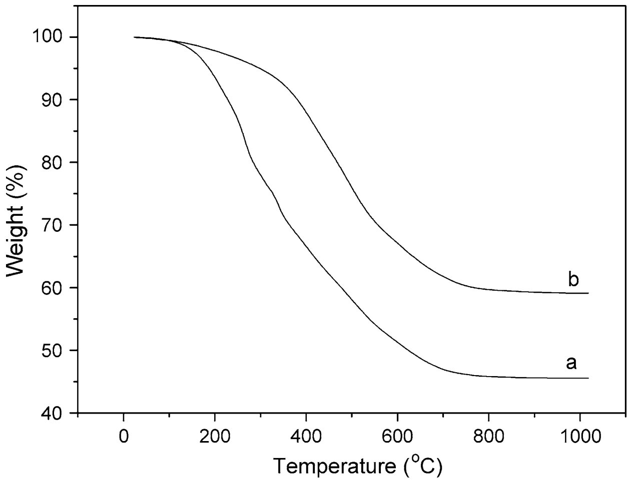

Fig. 6 TG curves of **PSNB** (*a*) as-synthesized, (*b*) cured

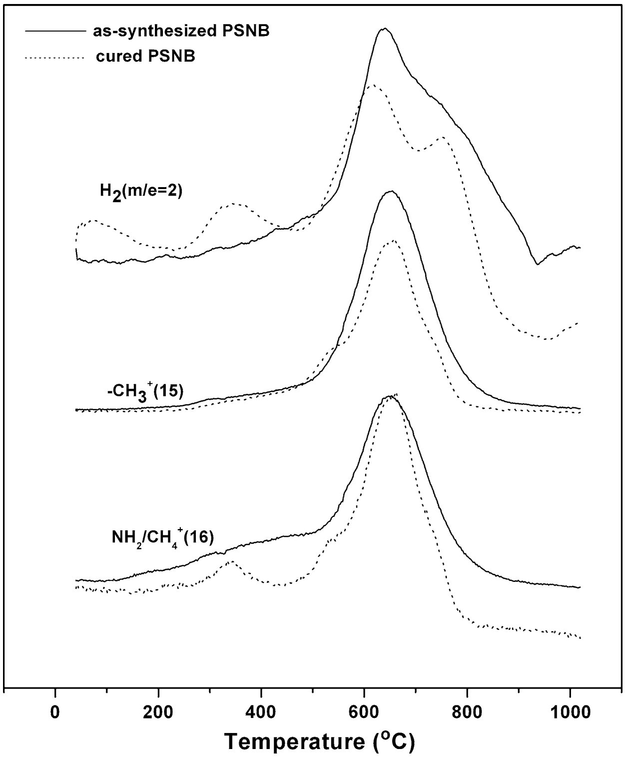

Fig. 7 MS spectra of the as-synthesized **PSNB** and cured **PSNB**

As revealed by MS spectra, for as-synthesized **PSNB** and **PSNB170**, hydrogen, ammonia, and methane are the major gaseous by-products during pyrolysis (Fig. 7). For as-synthesized **PSNB**, H_2 evolution occurs in a wide

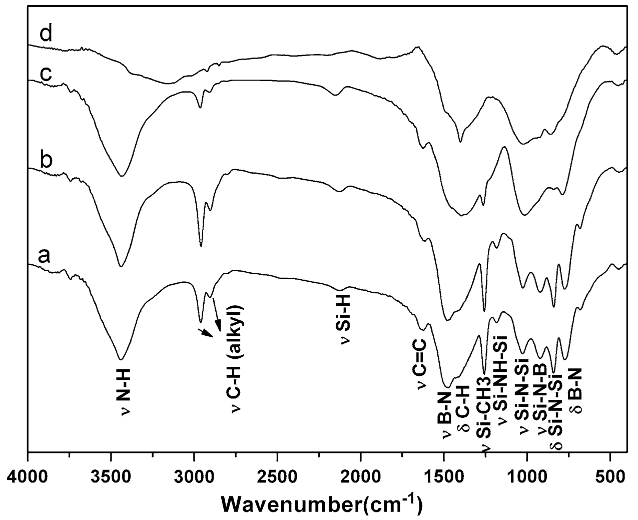

Fig. 8 IR spectra of **PSNB** pyrolyzed at (*a*) 300 °C, (*b*) 500 °C, (*c*) 700 °C, (*d*) 900 °C under Ar atmosphere

temperature range from 150 to 930 °C with a maximum around 640 °C. Methane evolution appears between 490 and 880 °C with a maximum at 648 °C. It has been reported that ammonia evolution of the polysilazane-related polymer occurs before 500 °C due to transamination reaction [19]. Therefore, the slope between 109 and 498 °C in MS spectra (*m*/*e* = 16) is attributed to ammonia evolution. While the broad evolution (*m*/*e* = 16) between 610 and 830 °C is methane. For **PSNB170**, hydrogen evolution also appears in a wide temperature range with three maximum at 345, 611, and 753 °C, respectively. Methane evolution (*m*/*e* = 15, 16) appears between 457 and 830 °C with a maximum at 656 °C. Ammonia evolution shows an obvious maximum peak at 357 °C. Comparing the MS spectra of as-synthesized with that of the **PSNB170**, we can find that uncured sample exhibits wider range of gaseous by-products evolution, indicating that crosslinking structure decreases the possibility of the formation of gas by-products, and thus enhances the thermal stability.

To further monitor the conversion process of the cured polymer to ceramic, FT-IR was performed on samples obtained at different pyrolysis temperatures (Fig. 8). The intensity of absorption bands attributed to Si–CH_3 (2960/2890/1250 cm^{-1}), Si–Vi (1620 cm^{-1}), and N–H (3393 cm^{-1}) decreases with rising of the temperature. For the sample pyrolyzed at 900 °C, the infrared spectrum shows two broad overlaps, one from 1530 to 1227 cm^{-1} and another from 1193 to 609 cm^{-1}. The former band belongs to B–N bond and the latter originates from Si–N and Si–C bonds [26], respectively.

Combing the results of TG–MS and FT-IR analyses, we attribute the mass loss of cured sample to the reactions shown in Scheme 1. During the curing process, the vinyl polymerization reaction is initiated by DCP [19]. Simultaneously, dehydrogenation reaction between Si–H and

Scheme 1 Possible reactions of PSNB during curing and pyrolysis process

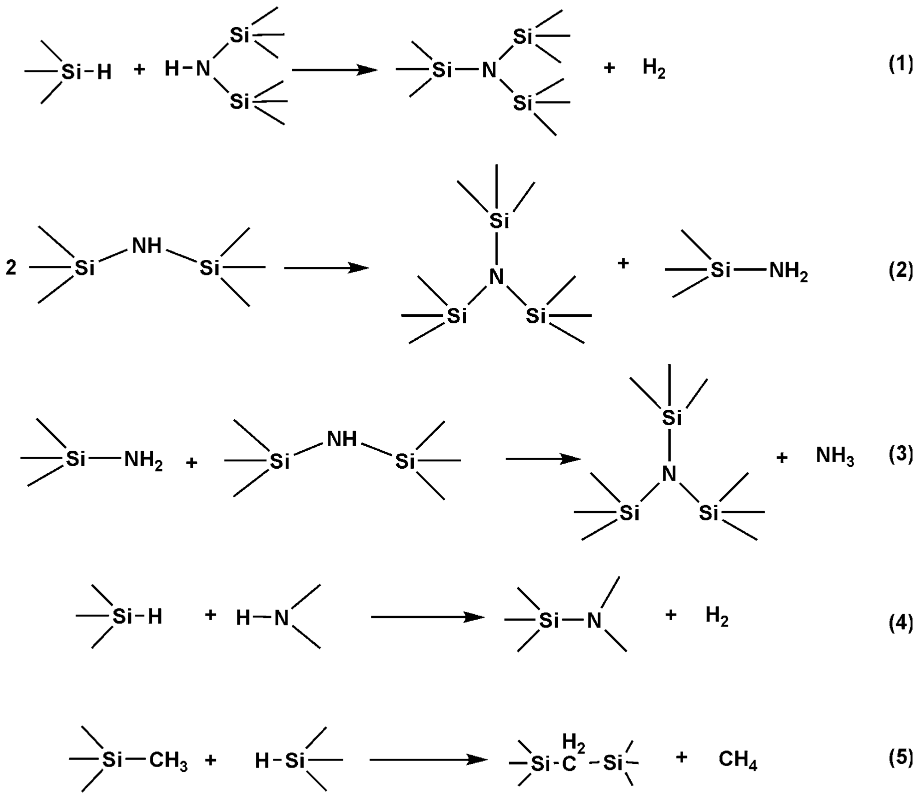

Table 1 Elemental analysis data of cured **PSNB** and pyrolytic products at 1000 °C

	%Si	%N	%B	%C	%O	%H	Empirical formula
PSNB170	37.14	23.55	1.26	23.72	6.73	6.40	$Si_{1.00}N_{1.27}B_{0.09}C_{1.49}O_{0.32}H_{4.83}$
PSNB1000	47.13	19.68	3.01	18.13	4.06	1.93	$Si_{1.00}N_{0.84}B_{0.16}C_{0.90}O_{0.15}H_{1.15}$

N–H also takes place (Scheme 1 (1)). As a result, the absorption intensity of N–H, Si–H, CH_2=CH–, and =C–H in the cured **PSNB** decreases sharply (Fig. 4b). The initial weight loss before 500 °C arises from a transamination reaction between NH group in the polymer backbone and Si–N linkages (Scheme 1(2, 3)) [18, 25]. In the range of 500–850 °C, the larger weight loss is due to the evolution of methane and hydrogen (Scheme 1(4, 5)) [19]. Above 800 °C, weight change is negligible, indicating the completion of ceramic conversion.

Elemental analysis is performed on both the **PSNB170** and the pyrolytic product at 1000 °C (**PSNB1000**). The contents of nitrogen, carbon, and hydrogen in **PSNB1000** are lower, while the contents of silicon and boron are higher than those of **PSNB170**, respectively (Table 1). The existence of oxygen in both samples is believed mainly due to partially hydrolysis of moisture sensitive precursor during synthesis and transfer processes, considering the low content of DCP (0.5%).

High-temperature behaviors of **PSNB**-derived ceramics

To investigate high-temperature behavior of **PSNB**-derived ceramics, the pyrolytic products obtained at different pyrolysis temperature were analyzed by XRD and FT-IR, as shown in Figs. 9 and 10. XRD diagrams show that the ceramics remain amorphous up to 1400 °C. The appearance of very weak peaks at 25° and 36° in the sample obtained at 1500 °C indicates formation of nanocrystalline phases. At 1600 °C, the samples start to crystallize and present broad peaks at 25°, 36°, 42°, 61°, and 72° (2θ). These peaks become sharper at 1700 °C, implying an increase of sample crystallization [17, 18]. For the sample pyrolyzed at 1800 °C, the peaks at 23°, 27°, 50°, 52°, 70°, and 73° belong to β-Si_3N_4 phases disappear, while the intensity of peaks at 36°, 60°, and 72° that corresponding to α/β-SiC phases increases. Moreover, in FT-IR spectra, the sample obtained at 1800 °C shows weaker intensity of Si–N band at 900 cm^{-1} and stronger Si–C band at 800 cm^{-1} than those of the sample obtained at 1700 °C [20]. This phenomenon is due to the decomposition and carbothermal reduction reaction of Si_3N_4 above 1600 °C as shown in Scheme 2 [27].

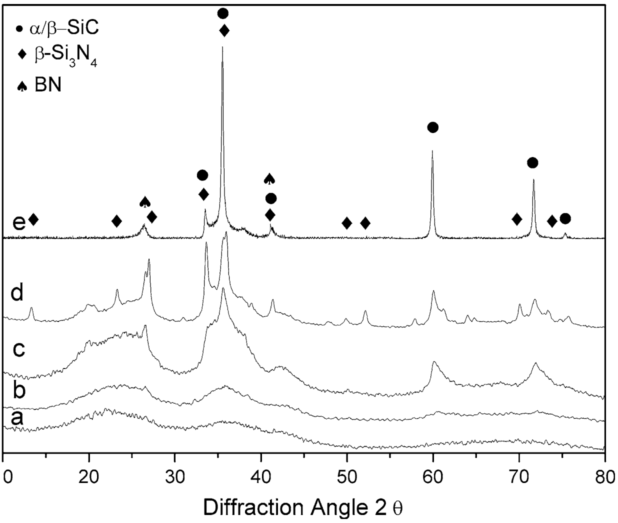

Fig. 9 XRD patterns of **PSNB** pyrolyed at (*a*) 1400 °C, (*b*) 1500 °C, (*c*) 1600 °C, (*d*) 1700 °C, (*e*) 1800 °C

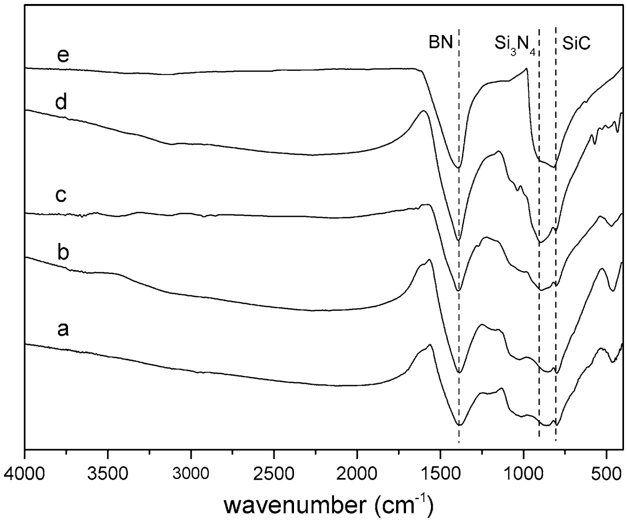

Fig. 10 IR spectra of **PSNB** pyrolyzed at (*a*) 1400 °C, (*b*) 1500 °C, (*c*) 1600 °C, (*d*) 1700 °C, (*e*) 1800 °C

The pyrolytic product **PSNB1000** was adopted to investigate thermal properties of **PSNB**-derived Si–B–C–N ceramics. TGA trace (Fig. 11) shows that the **PSNB1000** has no obvious weight change up to 1500 °C under Ar atmosphere. Above 1600 °C, weight change takes place due to the decomposition and carbothermal reaction of Si_3N_4 as discussed above. The weight loss of **PSNB1000** at 1900 °C is only 2.6%, which demonstrates that the Si–B–C–N ceramic has excellent thermal stability.

The anti-oxidation property of **PSNB1000** was examined by TGA up to 1350 °C in dry air (Fig. 12). The weight

$$Si_3N_4 + 3C \longrightarrow 3SiC + 2N_2 \quad (6)$$

$$Si_3N_4 \longrightarrow 3Si + 2N_2 \quad (7)$$

Scheme 2 Carbothermal and decomposition reaction of Si_3N_4

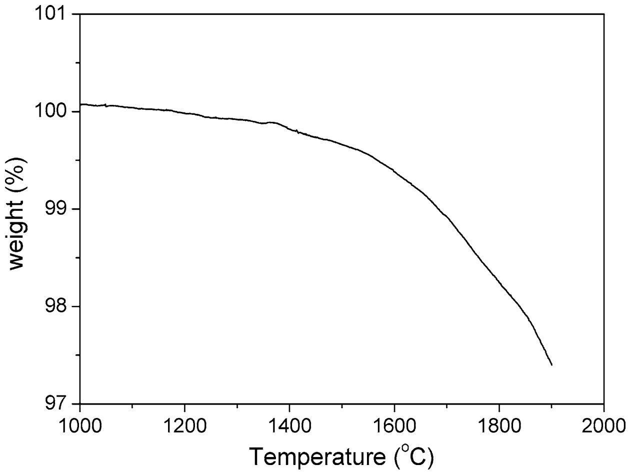

Fig. 11 TG curve of **PSNB1000** under Ar atmosphere

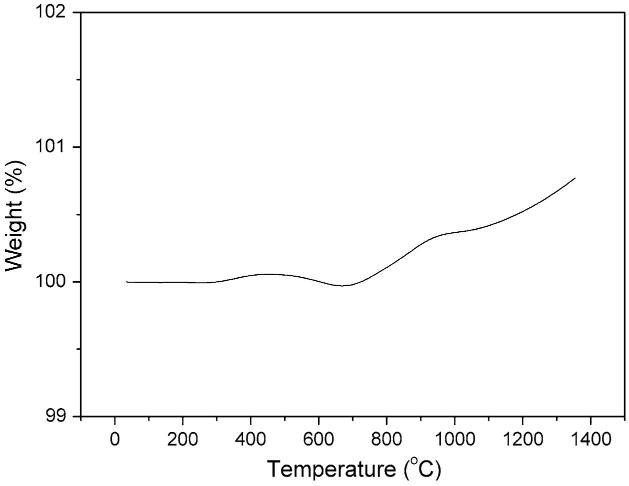

Fig. 12 TG curve of **PSNB1000** under air atmosphere

gain of the ceramics is only 1.8% at 1350 °C. As revealed in previous work [28], the formation of a passivating amorphous oxide layer offers resistance to further oxidation by hindering diffusion-controlled oxidation. The content of B and Si may be important for the excellent oxidation resistance of **PSNB1000**, which needs further study in future work.

Conclusions

A new low-viscosity liquid polymer precursor for Si–B–C–N ceramics was synthesized by co-amonolysis reaction of a mixture of BCl_3 and two dichlorosilanes with hexamethyldisilazane as amine source. The polymer shows potentials as impregnant due to a wide low-viscosity window of below 500 mPa s between 90 and 160 °C. The new precursor derived Si–B–C–N ceramics show good crystallization resistance. Under Ar atmosphere, the ceramics start to crystallize at 1600 °C and completely crystallized at 1700 °C, with a disappearance of Si_3N_4 crystalline phase at 1800 °C. The pyrolytic product at 1000 °C shows excellent thermal stability and oxidative resistance with weight loss of 2.6% at 1900 °C under Ar atmosphere and weight gain of only 1.8% at 1350 °C under air atmosphere.

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