Preparation of high-temperature stable Si−B−C−N fibers from tailored single source polyborosilazanes

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Abstract

Bulk Si−B−C−N ceramics derived from polyborosilazanes of the type $[B(C_2H_4SiRNH)_3]_n$ (**1a**, R = CH$_3$; **2a**, R = H; C$_2$H$_4$ = CHCH$_3$, CH$_2$CH$_2$) exhibit an exceptional structural stability at high temperature. Therefore, such quaternary systems are of great scientific and technical interest as fibrous reinforcements intended for high-temperature applications. In this context, the design of novel polyborosilazanes, which display properties tailored for the preparation of Si−B−C−N fibers, is studied. Boron-modified polysilazanes of the type $[B(C_2H_4SiRNCH_3)_3]_n$ (**1b**, R = CH$_3$; **2b**, R = H) are prepared via aminolysis of the tris(dichlorosilylethyl)boranes $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH$_3$; **2**, R = H). It is shown that the functionalisation of the precursors with =N−CH$_3$ units improves their processability (i.e. solubility) compared to that of their ammonolysed analogs $[B(C_2H_4SiRNH)_3]_n$ (**1a**, R = CH$_3$; **2a**, R = H). In addition to the influence of the =N−CH$_3$ units, the presence of the ≡Si−CH$_3$ functions in such polymers offers the best potential for the preparation of fibers by melt-spinning. As-spun fibers are then converted under controlled atmosphere into high-temperature stable Si−B−C−N fibers according to the polymer-derived ceramic route.
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1. Introduction

Polymer-derived Si−B−C−N ceramics play a major role in the development of materials for high-temperature applications.[1–9] Indeed, the chemical modification of the silazane system by the incorporation of elemental B is reported to yield ceramics in the quaternary system Si−B−C−N with high thermal stability in inert or oxidative atmosphere. In particular, single source boron-modified polysilazanes such as C−B−C-bridged polysilazanes,[4,7] pinacolborane and borazine-hydridopolysilazanes[10] as well as N−B−N-bridged polysilazanes[3,11] have been shown to be promising pre-ceramic polymers for providing such materials. The former compounds of the type $[B(C_2H_4SiRNH)_3]_n$ (**1a**, R = CH$_3$; **2a**, R = H; C$_2$H$_4$ = CHCH$_3$, CH$_2$CH$_2$) are prepared by ammonolysis of the monomeric tris(dichlorosilylethyl)boranes $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH$_3$; **2**, R = H) via a monomer route.[4,7] As-synthesised boron-modified polysilazanes are best suited to the preparation of bulk materials which retain an amorphous ceramic structure above 1700 °C and exhibit a high thermal and oxidation resistance at that temperature. Therefore, Si−B−C−N ceramics should provide the possibility of extending the practical upper temperature limit of 1200–1400 °C for currently available binary and ternary phase-based ceramic fibers. The general process scheme for the preparation of ceramic fibers is based on the multistep polymer-derived ceramic (PDC) route by including an additional shaping processing, i.e. the spinning.[12] The spinning generally consists of a melt-spinning of the starting polymer followed by stretching of the resulting polymer green fibers to reduce the fiber diameter. As-spun fibers are then cured and pyrolysed into ceramic fibers with fine diameters.

Since a controllable rheology is the most desirable polymer property for the melt-spinning, polyborosilazanes of the type $[B(C_2H_4SiRNH)_3]_n$ (**1a**, R = CH$_3$; **2a**, R = H) have to

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exhibit suitable melt-processability allowing them to be spun into fibers. A simple method for displaying this essential requirement is given by decreasing the cross-linkage of such polymers. With this aim in mind, this paper is devoted to the synthesis of novel C−B−C-bridged polysilazanes of the type $[B(C_2H_4SiRNCH_3)_3]_n$ (**1b**, R = CH$_3$; **2b**, R = H) by aminolysis of the tris(dichlorosilylethyl)boranes $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH$_3$; **2**, R = H). Their synthesis as well as their processability are investigated and discussed. Based on the melt-behaviour of the polymers, polymer green fibers can be provided by melt-spinning. They are subsequently cured and pyrolysed under controlled atmosphere into high-temperature stable Si−B−C−N fibers.

2. Experimental section

2.1. General comments

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques.[13] Dichlorovinylsilanes $H_2C = CHSiRCl_2$ (R = CH$_3$ and H) were obtained from ABCR chemicals and freshly distilled before use. Borane dimethylsulfide (2 M solution in toluene) was obtained from Sigma Aldrich. Methylamine was dried with KOH prior to its use. Toluene and tetrahydrofuran (THF) were purified by distillation from potassium.

Fourier transform infrared (FT-IR) data were obtained with a Bruker IFS66 spectrometer as KBr pellets. Chemical analysis was performed using a combination of different analysis apparatus (ELEMENTAR Vario EL CHN-Determinator, ELTRA CS 800 C/S Determinator, LECO TC-436 N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus). Thermogravimetric analysis (TGA, Netzsch STA 409) was carried out in a flowing argon atmosphere (25–1400 °C; heating rate: 5 °C/min) in alumina crucibles.

Differential scanning calorimetry (DSC, Mettler Toledo DSC TA 8000) was conducted in an argon atmosphere (−50 to 150 °C; heating rate: 10 °C/min) in aluminium crucibles. Thermomechanical analysis (TMA, Mettler Toledo TMA/SDTA 840) was carried out in a nitrogen atmosphere (30–140 °C; heating rate: 5 °C/min).

Fiber morphology was observed by scanning electron microscopy (SEM) with field emission equipment, Hitachi S800.

High-temperature thermogravimetric analysis (HT-TGA, Netzsch STA 501 equipment) of Si−B−C−N fibers was performed in a nitrogen atmosphere (500–2150 °C; heating rates: 5 °C/min (T < 1400 °C) and 2 °C/min (T > 1400 °C)) using graphite crucibles.

2.2. Synthesis of the polymers

The synthesis of the tris(dichlorosilylethyl)boranes $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH$_3$; **2**, R = H; C_2H_4 = CHCH$_3$, CH$_2$CH$_2$) was described previously.[14,15]

2.2.1. Synthesis of $[B(C_2H_4SiCH_3NCH_3)_3]_n$ (**1b**)

In a 2-l Schlenk flask equipped with a water-cooled reflux condenser, a gas inlet tube and a magnetic stirrer, 30.80 g of **1** (70.5 mmol) were dissolved in 500 ml of THF and cooled to 0 °C. Under vigorous stirring, 19.82 g (638.1 mmol) of CH$_3$NH$_2$ were introduced through the solution, which immediately caused the precipitation of methylamine hydrochloride. After the addition of CH$_3$NH$_2$ was completed, the reaction mixture was allowed to warm to room temperature and the polymer solution was filtered through a pad of celite. The filtrate and the extract were combined, concentrated and dried at room temperature in a high vacuum (10^{-2} mbar) to produce 20.90 g of a white powder **1b** (67.10 mmol, 96%).

Chemical analysis [Si$_3$C$_{12}$H$_{30}$N$_3$B]: M = 311.46 g/mol, found (calculated, wt.%): C 45.8 (46.3), H 9.6 (9.7), N 16.1 (13.5), Si 22.1 (27.1), B 2.9 (3.9), O 1.5 (0.0) [Si$_3$C$_{14.5}$H$_{36.3}$N$_{4.4}$B$_{1.0}$O$_{0.4}$].

IR (KBr/cm^{-1}): 3425, 3313, 3235 w (ν N−H); 2951 s (ν_{as} CH$_3$, ν_{as} CH$_2$); 2889 s (ν SiC−H); 2800 m (ν NC−H); 1596 m (ν NH); 1460 m (δ NCH$_3$); 1407 i (δ_{as} (C−) CH$_3$); 1359 m (δ_s (C−) CH$_3$); 1254 s (δ_s (Si−) CH$_3$); 1181 m (δ C−B−C); 1145 (δ SiCH$_2$C); 1076 s (ν C−N); 913 sh-870 vs (δ N−Si−N).

2.2.2. Synthesis of $[B(C_2H_4SiHNCH_3)_3]_n$ (**2b**)

In contrast to the procedure described for **1b**, the aminolysis of **2** was carried out in toluene.

26.56 g of **2** (67.24 mmol) were dissolved in 500 ml of toluene.

18.80 g (605.2 mmol) of CH$_3$NH$_2$ were added to the mixture solution.

After filtration, the precipitate was extracted several times and the combined solutions were concentrated and dried at 50 °C in a high vacuum to yield 15.63 g of a white powder **2b** (58.02 mmol, 86%).

Chemical analysis [Si$_3$C$_9$H$_{24}$N$_3$B]: M = 269.38 g/mol, found (calculated, wt.%): C 41.2 (40.1), H 8.6 (9.0), N 18.5 (15.6), Si 24.2 (31.3), B 3.5 (4.0), O 1.0 (0.0) [Si$_3$C$_{12}$H$_{29.5}$N$_{4.6}$B$_{1.1}$O$_{0.2}$].

IR (KBr/cm^{-1}): 3421, 3317, 3265, w (ν N−H); 2933 s (ν_{as} CH$_3$, ν_{as} CH$_2$); 2876 s (ν SiC−H); 2799 m (ν NC−H); 2155 br (ν Si−H); 1588 m (δ NH); 1460 m (δ NCH$_3$); 1424 w (δ_{as} (C−) CH$_3$); 1372 m (δ_s (C−) CH$_3$); 1187 m (δ C−B−C); 1145 (δ SiCH$_2$C); 1079 s (ν C−N); 913 sh-870 vs (δ N−Si−N).
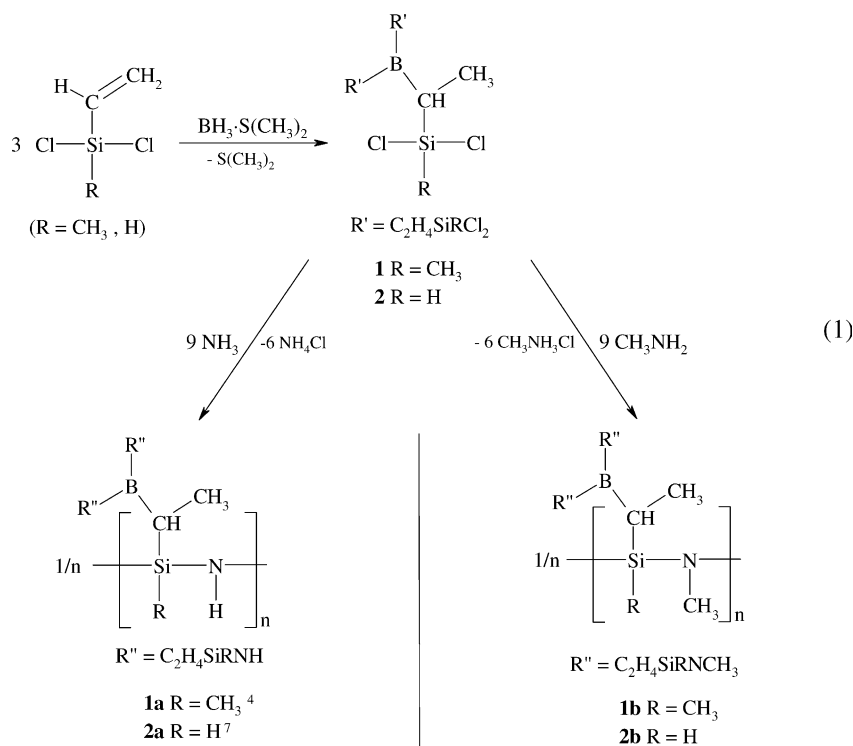
2.3. Si−B−C−N fiber preparation

Green fibers were prepared in a nitrogen atmosphere using a lab-scale melt-spinning apparatus set up in a glove-box. The polymer is melt-spun through a spinneret having a single 0.2 mm capillary and the resulting endless filament was subsequently stretched and collected on a rotating spool. As-spun fibers were cured in a mixture of ammonia and nitrogen (70/30) atmosphere (25–200 °C; heating rates: 25 °C/h (T < 70 °C) with a dwell time of 2 h and 15 °C/h (T > 70 °C) with

a dwell time of 1 h) in a silicate tube furnace. The heat treatment was followed by pyrolysis in a pure nitrogen atmosphere (200–1000 °C; heating rate: 50 °C/h, dwell time 30 min). An additional heat treatment was carried out in a graphite furnace in a nitrogen atmosphere (25–1400 °C; heating rate: 100 °C/h, dwell time 2 h).

3. Results and discussion

3.1. Polymer synthesis

Following the monomer route, dichlorovinylsilanes $CH_2 = CHSiRCl_2$ (R = CH_3 and H) react with $BH_3·S(CH_3)_2$ to yield moisture and air-sensitive $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH_3; **2**, R = H; C_2H_4 = $CHCH_3$, CH_2CH_2) as colourless liquids. Based on the well-established ammonolysis reaction of **1** and **2** with NH_3 leading to polymers **1a** and **2a** [Eq. (1)], aminolysis with CH_3NH_2 yields polymers of the type $[B(C_2H_4SiRNCH_3)_3]_n$ (**1b**, R = CH_3; **2b**, R = H) which are composed of silazane chains that are cross-linked via C−B−C bridges [Eq. (1)].

Fig. 1. Thermo-mechanical analysis of **1b** and **2b** (heating rate 5 °C/min, N_2 atmosphere).

(1)

Aminolysis of **1** in THF at 0 °C produced **1b** as a white powder in an overall yield of 96%. In contrast to the aminolysis of **1**, the synthesis procedure of **2b** in THF was problematic since a thorough separation of the polymer from the methylamine hydrochloride was not possible. After filtration, the precursor contained significant levels of chloride impurities despite intensive efforts at dissolving and filtering. The aminolysis of **2** was best achieved in toluene solutions at 0 °C. The greater degree of cross-linking of the compound **2b** was directly manifested as a higher product loss during the filtration process than that of **1b**:**2b** was isolated as a white powder in 86% yield.
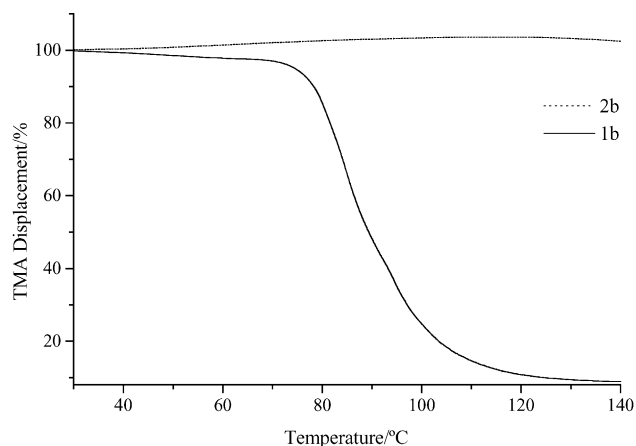
Both compounds were characterised by IR spectroscopy and elemental analysis as compiled in Section 2. Characterisation results show that the aminolysis reactions of **1** and **2** occurred in the expected pathway.

Compared to the synthesis yield of the ammonolysed derivatives **1a** and **2a** (Table 1),[4,7] the reaction between $B(C_2H_4SiRCl_2)_3$ and CH_3NH_2 proceeds much better. For example, the synthesis, i.e. the purification, of **2a** in which ≡Si−H and = N−H sites are present was particularly difficult due to its lower solubility and thus difficulties with the separation from the by-product ammonium chloride. Clearly,

Table 1
Properties of boron-modified polysilazanes of the type $[B(C_2H_4SiRNR')_3]_n$

Compound	Synthesis yield (mol.%)	Glass transition temperature (°C)	Ceramic yield (wt.%)
1a, R = CH$_3$, R$'$ = H	80–85	Not determined	62[a]
1b, R = CH$_3$, R$'$ = CH$_3$	∼96	38	22
2a, R = H, R$'$ = H	65–70	Not determined	88[a]
2b, R = H, R$'$ = CH$_3$	∼86	89	68

[a] Ceramic yield are obtained by TGA in a flowing argon at 1100 °C.

a decrease in the cross-linkage was achieved by the substitution of $=$N$-$H units in **1a** and **2a** with $=$N$-$CH$_3$ functions in **1b** and **2b**. Moreover, it is evident that, in addition to the influence of $=$N$-$CH$_3$ functions with cross-linkage, the sufficient steric bulk of the Si-bonded methyl groups in **1b** play a major role in the improvement of the polymer solubility.

3.2. Melt-spinning study

In order to study the ability of *N*-methyl polyborosilazanes for the melt-spinning, the melt-behaviour of **1b** and **2b** was investigated by means of differential scanning calorimetry (DSC, Table 1) and thermomechanical analysis (TMA, Fig. 1) using the compression mode of TMA with a load of 3 × 10^{-1} N. Obtaining the glass transition temperature (T_g) of polymers from DSC is useful to evaluate the extent of the cross-linkage of such polymers. The T_g of **1b** is centred at 38 °C. The observed low softening point indicating a high chain flexibility results from the low cross-link density of the polymer. Due to its higher degree of cross-linking, the softening point of **2b** is shifted to 89 °C. The differences in the degree of cross-linking of both polymers are directly reflected in TMA studies (Fig. 1).

Aminolysis of **1** yields a meltable polymer **1b**. As an illustration, increasing temperature above T_g leads to a slight deviation in the TMA curve then, starting from 75 °C, a significant decrease in the curve is observed due to the melting of the polymer. A quasi-linear response is obtained in the viscous region from 75 to 95 °C. The large penetration progress is stopped around 140 °C. After cooling, **1b** recovers its initial physical and chemical features. In contrast to the thermoplastic behaviour of **1b**, polymer **2b** is dimensionally stable under load up to 140 °C. Compounds **1b** and **2b** exhibit significant differences in melt-viscosity according to the nature of the substituents linked to the silicon atom. The substitution of the $\equiv$Si$-$CH$_3$ units in **1b** with the $\equiv$Si$-$H functions in **2b** involves a significant decrease in the fusibility of the polymer. Because of the sufficient latent reactivity of $\equiv$Si$-$H units, cross-linking is probably thermally activated in **2b** in the 25–140 °C temperature range. As a result, after cooling from 140 °C to room temperature, both T_g and elemental composition of the polymer change. This thermal behaviour disqualifies it as a potential precursor for polymer fibers. In addition to their favourable effect upon polymer solubility, the $\equiv$Si$-$CH$_3$ units in the polymer **1b** play also a crucial role on the polymer melt-spinnability. The polymer **1b** provides polymer fibers by spinning around 82 °C from a lab-scale spinning apparatus having a single 200 μm capillary. Resulting polymer fibers can be stretched from the melt by a spool with an adjustable diameter of about 55 μm.

3.3. Pyrolysis

The polymer-to-ceramic conversion of **1b** and **2b** was investigated by TGA up to 1400 °C in a flowing argon atmosphere. The ceramic yields of each compound was compared to those of **1a** and **2a** (Table 1).

As expected, it is observed that increasing the degree of cross-linking of polymers results in a lower volatility during the ceramic conversion. Considering the findings in the TGA investigations, the ceramic yields (Table 1) increase in the sequence **1b** (22 wt.%) < **1a** (62 wt.%) < **2b** (68 wt.%) < **2a** (88 wt.%). Due to the presence of $=$N$-$CH$_3$ units with a poor ability to condense the monomer units, *N*-methyl derivatives **1b** and **2b** are always converted in ceramic materials with lower ceramic yields than those of the ammonolysed compounds **1a** and **2a**.

In addition to a high degree of cross-linking, the incorporation of groups with sufficient latent reactivity such as $\equiv$Si$-$H units is a further requirement for increasing ceramic yields. As an illustration of this argument, compounds **2a** and **2b**, in which $\equiv$Si–H units are present, are converted in ceramics with lower weight loss than that of **1a** and **1b**. These results show that it is difficult to combine both good processability and high ceramic yields in boron-modified silazanes intended for the preparation of ceramic fibers. Indeed, due to the very low ceramic yield of the spinnable polymer **1b**, the integrity of polymer fibers could not be preserved during heat treatment. A curing process with ammonia was therefore applied at 200 °C to increase the cross-link density of the polymer after shaping and therefore, to prevent any inter-fiber fusion during the polymer-to-ceramic conversion. As-cured fibers were subsequently pyrolysed at 1400 °C in a nitrogen atmosphere to provide $Si_{3.0}B_{1.0}C_{5.0}N_{2.4}$ ceramic fibers. Circular and uniform fibers exhibit a glassy-like texture which results from the amorphous state of the ceramic (Fig. 2).

3.4. High-temperature stability

The thermal stability of as-prepared $Si_{3.0}B_{1.0}C_{5.0}N_{2.4}$ fibers was investigated by HT-TGA experiments up to 2150 °C in a nitrogen atmosphere (Fig. 3).

Fibers show no mass changes up to 1700 °C whereas heat treatment at temperatures higher than 1700 °C results in a
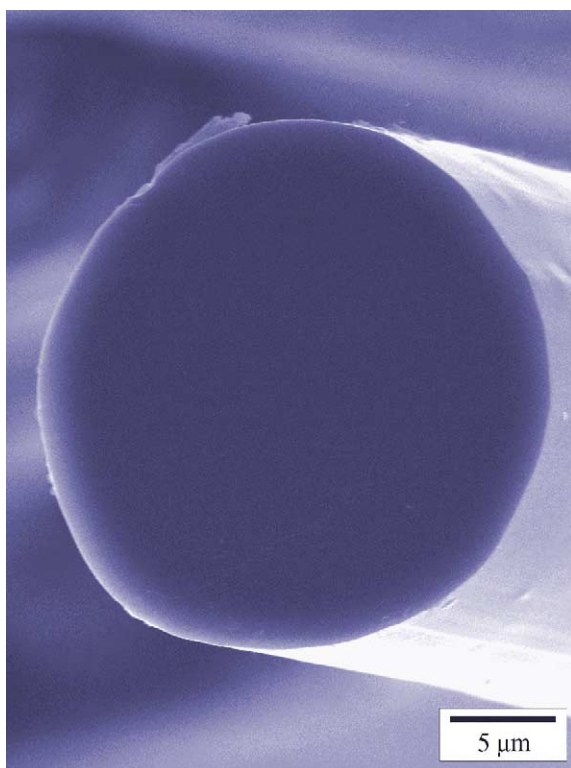
bility of Si−B−C−N bulk materials: decreasing the particle size from values >315 μm to values <32 μm involves a shift in the temperature of thermal decomposition from 1900 to 1680 °C, respectively.[16] Moreover, the weight loss was low (4 wt.%) at 2150 °C for coarse particles (size >315 μm) while it significantly increased for particle size <32 μm (17.5 wt.%) at such temperatures. Further investigations of the relationship between thermal stability and fiber diameter are therefore needed.

4. Conclusions

The C−B−C bridge containing polyborosilazanes $[B(C_2H_4SiRNCH_3)_3]_n$ (**1b**, R = CH_3; **2b**, R = H; C_2H_4 = $CHCH_3$, CH_2CH_2) prepared by hydroboration of dichlorovinylsilanes and subsequent aminolysis of the as-obtained tris(dichlorosilylethyl)boranes $B(C_2H_4SiRCl_2)_3$ (**1**, R = CH_3; **2**, R = H) offer processing advantages compared with typical polymers synthesised by ammonolysis of **1** and **2**. *N*-bonded methyl groups have a major impact on the polymerisation kinetics by limiting the progress of the condensation reactions and therefore by improving the required polymer solubility. Moreover, the Si-bonded methyl sites play a crucial role on the polymer spinnability since the methyl-substituted derivative $[B(C_2H_4SiCH_3NCH_3)_3]_n$ exhibits suitable melt-processability (i.e. fusibility) to be readily melt-spinnable and provide flexible and uniform fine-diameter green fibers. Subsequent curing in an ammonia atmosphere at 200 °C and pyrolysis in a nitrogen atmosphere at 1400 °C provides $Si_{3.0}B_{1.0}C_{5.0}N_{2.4}$ fibers which are stable up to 1700 °C in a nitrogen atmosphere.

Fig. 2. SEM micrograph of $Si_{3.0}B_{1.0}C_{5.0}N_{2.4}$ ceramic fibers derived from **1b**.

single decomposition step associated with a rapid and continuous weight loss up to 2150 °C. The decomposition rapidly leads to the gradual formation of thermodynamically stable phases with a weight loss of ~17% at 2150 °C. The thermally induced degradation of the materials at elevated temperatures is usually a function of both chemical composition, i.e. phase composition and surrounding atmosphere. Another important issue is probably the low specific surface area of fibers. Indeed, recent publications showed that the specific surface area of powders strongly influences the thermal sta-

Fig. 3. HT-TGA of the as-prepared $Si_{3.0}B_{1.0}C_{5.0}N_{2.4}$ fibers (500–2150 °C, N_2 atmosphere).

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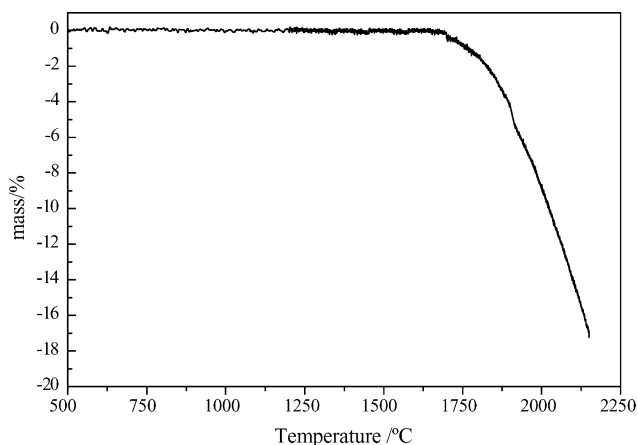
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