Preceramic Polymer for Si—B—N—C Fiber Via One-Step Condensation of Silane, BCl$_3$, and Silazane

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ABSTRACT: A preceramic polymer for Si—B—N—C fiber, polyborosilazane, has been synthesized by one-step condensation reaction of dichloromethylsilane, BCl$_3$, and hexamethyldisilazane with high yield. The reaction mainly involves the condensation of Si—Cl and B—Cl with N—SiMe$_3$ followed by SiMe$_3$Cl evaporation and dehydrogenation between N—H and Si—H. The resulted polymer is a soluble colorless transparent solid with melting point of 70°C and molecular weight of 10,800. The backbone of the polymer is mainly composed of —Si—N—B-bridge with some borazine rings. The polymer exhibits good processability and flexible polymer fibers with diameter of 15–20 μm were obtained by melt spinning. Pyrolysis of the as-synthesized polymer to 1000°C under nitrogen atmosphere results in a ceramic yield of 63 wt %, and the obtained Si—B—N—C ceramic remains fully amorphous up to 1700°C, and only small amount of poorly crystallized BN, Si$_3$N$_4$, and SiC phases were observed upon heating at 1850°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 921–928, 2008

Key words: amorphous; fibers; high temperature materials; polycondensation; pyrolysis

INTRODUCTION

Nonoxide ceramics, such as silicon carbide, silicon nitride, and boron nitride have been used in a variety of hostile environments because of their refractory, high performance, and oxidation resistant properties. Compared to these single-component ceramics, multielement systems composed of Si, B, N, and C represent a novel class of ceramics with superior high-temperature durability with potential applications in the fields of aviation and aerospace. However, the lack of general synthesis routes that allow for the generation of these materials with controlled composition, under moderate conditions, and in processed forms, has hampered both scientific studies and their practical applications. Preceramic polymer route is the only effective approach known for the fabrication of Si—B—N—C ceramic fibers. Many researchers[1–11] synthesized different kinds of preceramic polyborosilazanes (PBSZs) for Si—B—N—C ceramic. However, most of the PBSZs are insoluble and infusible, which makes them impossible in application to fiber fabrication. Some research groups reported the synthesis of processible PBSZs by aminolysis or ammonolysis of a single source precursor. Sneddon and coworkers[3] synthesized PBSZs with appropriate rheological properties and thermal stability for a melt-spinning process. These polymers were prepared by chemical modification of hydridopolysilazanes with various monofunctional borane or borazine derivatives (pinacolborane or B-diethylborazine). The final material was amorphous at 1600°C. Jansen and coworkers[8] prepared N-methyl PBSZs by aminolysis of trichlorosilylamino-dichloroborane via a monomer route. These PBSZs can be tailored to be meltable and spinnable by melt- or solution-spinning processes. The resulting green fibers were cured in HSiCl$_3$ and pyrolysed up to 1500°C under nitrogen atmosphere. Such Si—B—N—C fibers remained thermally stable up to ~ 1750°C in a nonoxidizing atmosphere. Bernard and coworkers[10] reported a process of aminolysis of a single-source precursor B(C$_2$H$_4$SiCH$_3$Cl$_2$)$_3$ for the synthesis of boron-modified C—B—C-bridged polysilazane [B(C$_2$H$_4$SiCH$_3$ NCH$_3$)$_3$]$_n$. These polymers can be formed into green fibers by melt-spinning process. Pyrolysis of the cured fibers up to 1400°C in

nitrogen atmosphere produced Si—B—N—C fibers remaining amorphous up to 1600°C.

However, the synthesis of single source precursors usually requires several steps and the following processes such as separation of the byproducts can be complex. This is not suitable for the preparation of precursors intended to be used for mass production.

An alternative access to Si—B—N—C precursors was developed by Lee and coworkers.[11] They synthesized a PBSZ polymer by reacting boron trichloride (BTC), trichlorosilane (TCS) with hexamethyldisilazane (HMDZ). The process proves to be simpler and cheaper, because no additional crosslinking agents were needed, and the elimination of the byproducts was directly achieved successfully. In this synthesis route, the polymerization step proceeds quickly and provides polymers with a high degree of crosslinking and highly branched due to the polycondensation ability of the trifunctional monomers, that is, BTC and TCS. Both the highly crosslinked structure and the capability of these polymers to thermally crosslink allow us to obtain high-performance bulk materials in high ceramic yields. For example, bulk amorphous ceramics derived from such polymers can be thermally stable up to 1600°C in an argon environment. In return, an important disadvantage of such polymers is their insufficient softening on heating and their insolubility, each of which prevents the preparation of fibers requiring either melt or solution processing.[11] These observations point out that one of the demanding problems for processing fibers is to develop polymers with the appropriate rheology and melt stability to allow for continuous melt spinning. A simple method for displaying this essential requirement is provided by decreasing the crosslinkage of such polymers. With this aim in mind, our strategy was to avoid excessive reactive groups in the synthesis of preceramic polymer. Therefore, on the basis of Lee's process,[11] we used bifunctional $MeHSiCl_2$ as one of the monomers, which will improve the structural linearity and thus the chain flexibility of the polymer. This article is devoted to a detailed study on the synthesis of processable N—B—N-bridged PBSZs with a one-step condensation process. It will be shown that the rheology and melt stability of the polymer can be ideally tailored for the melt-spinning process. In addition, the thermal stability of the preceramic polymer was preliminarily discussed.

EXPERIMENTAL

Synthesis of preceramic polymer

All reactions were carried out under dry nitrogen atmosphere using Schlenk-type techniques as described by Shriver.[12] All the monomers were handled without air contact and stored in a moisture-free environment. BTC, DCS, and HMDZ were purchased from Guangming Special Gas Corp., Xinghuo Chemical Corp., and Guibao Chemical Corp., respectively. BTC was maintained in n-hexane in refrigerator until the synthesis. Hexane was dried with sodium-benzophenone mixture under reflux. DCS and HMDZ were distilled before use. In a typical reaction, the molar ratio between monomers was set at 1 : 2 : 6 (BTC : DCS : HMDZ). BTC in 1.5M hexane solution was introduced with a syringe from the bottle. The proper amount was weighed on a balance and injected into a precooled reactor through a septum. DCS was added into the reactor in the same manner. HMDZ was injected into a dropping funnel with a septum and carefully added dropwise to the mixed solution under vigorous stirring, whereby a cloudy solution with no precipitation was observed. The temperature of mixture was kept below 0°C during the addition of monomers. After the addition of HMDZ was completed, the reaction mixture was then heated, resulting in volatilization of $SiMe_3Cl$, b.p.58°C, until the reactor reached $\sim$ 140°C. Continued heating resulted in volatilization of a mixture of $SiMe_3Cl$ and HMDZ, b.p. 126°C, which changed in composition from $SiMe_3Cl$-rich initially, to HMDZ-rich at the maximum reactor temperature of 200–350°C. The product may be held at the maximum temperature for 6–20 h. The final traces of starting reagents, solvent, byproducts, and low molecular oligomers were removed at 100–200°C by application of a vacuum for 1 h. After cooled to ambient temperature, the product attached itself to the inner surface of the reactor in the shape of a colorless transparent bulky solid that is sensitive to moisture and air. The yield of product was typically >92% of theory, based on the weight of BTC and DCS. The bulk product was transferred into a glove box, placed in a vial full of nitrogen, and finally stored in vacuum dry-sealing desiccators.

Polymer fiber preparation

Polymer fibers were prepared using a lab-scale melt-spinning system setup inside a nitrogen-filled glove box. The as-synthesized polymer was fed into an extruder, where it is heated, sheared, and pressured through a filtering system to eliminate any gels or unmelts that may be present in the extrudate. The molten polymer then passed through a spinneret that has a single 0.25-mm capillary. The extrudate flow was then uniaxially drawn in nitrogen atmosphere to filament, which was subsequently stretched and collected on a rotating spool.

Pyrolysis of the preceramic polymer

The polymer was powdered under nitrogen atmosphere in a glove box before pyrolysis. Pyrolysis of the polymer powders was performed under flowing 99.999% ultra-high pure nitrogen atmosphere using a high-temperature alumina tube furnace. Before adding to the samples, the furnace tube was purged by a vacuum and subsequently filled with ultra-high pure nitrogen repeatedly at room temperature to remove the residual air. The furnace was heated from room temperature to 1000°C at a heating rate 10°C min^{-1}, dwelling for an additional 2 h at 1000°C, and then finally simply cooling in ambient air to room temperature. Additional heat treatment for the crystallization of the obtained ceramics was carried out in a 99.999% ultra-high pure argon atmosphere in graphite furnace (AStro Furnace) using a graphite crucible heated to 1200, 1500, 1700, and 1850°C at a heating rate 20°C min^{-1} and held for 2 h at each temperature.

Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet Avatar 360 in a KBr pellet. X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical compositions and the bonding structure on an XSAM 800 multifunctional X-ray photoelectron spectrometer with an Al Kα energy source. ^{1}H-, ^{11}B-, and ^{29}Si-nuclear magnetic resonance (NMR) spectra were performed in CDCl$_3$ with a Bruker Avance 400. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H NMR and ^{29}Si NMR. The chemical shift of ^{11}B NMR was referenced to BF$_3$ · OEt$_2$. The molecular weight of PBSZ was measured by gel permeation chromatography (GPC, Waters 2690) with polystyrene as a standard. Quantitative analyses of nitrogen have been carried out in a Leco TC-436N/S Determinator, whereas carbon was measured in an Elemntar Vario EL, ELTRA CS-444 C/S analyzer. Silicon and boron were quantified by means of ICP-AES in an Arl 3580B spectrometer after digestion of the ceramic samples using a mixture of bases. O was measured in an IRO-I oxygen determinator. Thermal properties (polymer softening and decomposition) were studied by differential scanning calorimetry (DSC, CD2-34P) under nitrogen atmosphere between −50 and 280°C at a heating rate 10°C min^{-1} in alumina crucibles. Melt behavior was investigated by thermomechanical analysis (TMA, DMTA-V) on polymer pellets using a compressive load under nitrogen atmosphere from 30 to 280°C at a heating rate of 5°C min^{-1}. Scanning electron microscopy (SEM) images of PBSZ fibers were taken with a JSW5600LV. Thermogravimetric analysis (TGA, NETZ SCH-STA-449C) of the polymer to ceramic conversion was carried out under nitrogen atmosphere (50 cm^3 min^{-1}) from 25 to 1000°C at a heating rate 10°C min^{-1} in silicate crucibles. The obtained pyrolyzed specimens were characterized by powder X-ray diffraction (XRD, D8 ADVANCEX), using Cu Kα radiation.

RESULTS AND DISCUSSION

Synthesis of the PBSZ

Most of the processes to polyborosilazane (PBSZ) always involve aminolysis or ammonolysis of a single source precursor. Potential problems included are the elimination of byproducts, such as ammonium chloride. The cleavage of HMDZ offers a rather convenient and versatile access to precursors containing a nitrogen bridge between the electropositive elements, for example, silicon and boron.[2] A major advantage of this reaction pathway lies in the formation of volatile byproduct, that is, chlorotrimethylsilane, which can easily be distilled off. It should be noticed that by reacting the byproduct Me$_3$SiCl with ammonia, the reactant HMDZ can be recovered, which is of particular interest for ecological as well as for economic reasons. In our experiment, BTC, dichloromethylsilane (DCS), and HMDZ were chosen as the starting materials. BTC act as boron source for the target polymer. Bifunctional DCS was chosen to ensure mild crosslinking degree in the polymer. HMDZ was found to react smoothly with BTC and DCS at moderate temperature to produce Si—B—N—C polymer. After vacuum evaporation of low-weight oligomers and final traces of starting reagents, the product was isolated as a moisture and air-sensitive colorless transparent solid, which is soluble in common organic solvents, including benzene and chloroform. The molecular weight distribution of the as-synthesized polymer were found to be the number–average molecular weight (M_n) = 10,800 and the weight–average molecular weight (M_w) = 16,210 with a polydispersity M_w/M_n = 1.50. Elemental analysis produced 32.71 for Si, 8.55 for B, 29.09 for N, 21.10 for C, 0.71 for O, and 7.84 for H. The impurity O element was contaminated during the transfer of the polymer. The X-ray photoelectron spectroscopy of as-synthesized PBSZ shown in Figure 1 supports the elemental analysis results qualitatively. No residual chlorine is detected by element analysis and XPS, which confirm the elimination of salts, especially ammonium chloride, during the synthesis of PBSZ. Most importantly, the elimination of the salts was successfully achieved by a direct reaction without an additional step. So, we can speculate that the precursor polymers from our route has a higher purity compared with those polymers synthesized from other methods,[1] which always has such impurities as NH$_4$Cl.
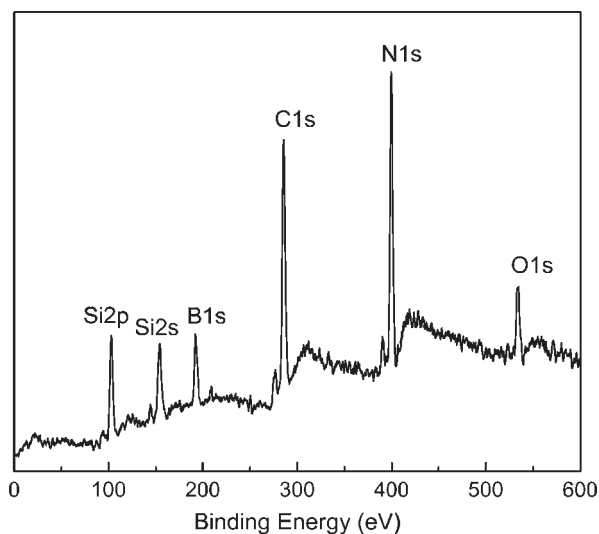
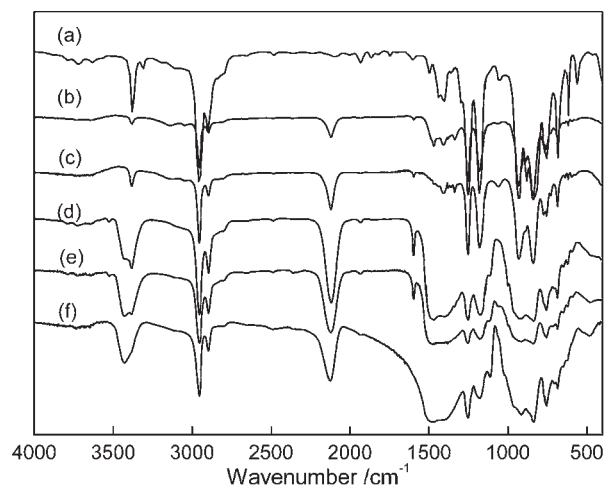**Figure 1**   XPS spectrum of as-synthesized PBSZ.

Figure 2 IR spectra of (a) starting monomer HMDZ, oligomers at different temperatures (b) 140°C, (c) 170°C, (d) 200°C, (e) 230°C, and (f) as-synthesized PBSZ.

To observe the progress in the process of synthesis, several intermediate oligomers were taken when the reaction temperature reaches 140, 170, 200, and 230°C, respectively. Figure 2 shows Fourier transform infrared spectra of the oligomer products obtained at various temperatures during the synthesis of PBSZ. A comparison of the as-synthesized polymer with one of the starting materials HMDZ revealed that absorption bands of N—H group at 3383 cm^{-1} and the B—N group at 1404 cm^{-1} broaden on polymerization. IR absorption peaks of N—H groups at 3383 cm^{-1} are sharp singlet in the HMDZ and in the oligomers below 200°C; however, they are broaden when a new absorption band at 3429 cm^{-1} appears in the oligomers above 200°C and in PBSZ, which may result in the formation of new structure. Referring to the literatures,[13,14] the absorption peak of N—H groups on the borazine ring, which falls in the range of 3435–3525 cm^{-1}, shift to higher wavenumbers relative to N—H groups on the linear chain, from which we can assign this peak to the N—H group in the borazine ring, and therefore the formation of borazine ring can be speculated in the polymer. Most importantly, the characteristic N—B—N vibration mode of the B_3N_3 ring is observed in the oligomers above 200°C and in PBSZ at about 1472 cm^{-1}.[5,7,13] Therefore, we can deduce the formation of borazine ring starts at 170–200°C. Moreover, the intensity of the absorption band at 3429 cm^{-1} increases as the temperature is raised, which indicates that the number of the borazinic structure increases in the polymer. Consistently, the concurrent decrease of the intensity of linear chain band centered at 3383 cm^{-1} further confirms the formation borazinic structure unit in PBSZ. Accordingly, the ^{11}B NMR spectrum of PBSZ in $CDCl_3$ (in Fig. 3) show a single peak centered at

27.8 ppm, illustrating that only borazinic BN_3 environment exists in the polymer.[15–18]

The elimination of $SiMe_3Cl$ formed by the reaction between Cl-containing groups (i.e., B—Cl and Si—Cl) and —$SiMe_3$ groups during the initial stage and the liberation of HMDZ by self-condensation of intermediate molecules in the second stage of the reaction, which was reported by Lee,[11] was also found in our experiment. Therefore, the formation of borazinic six-membered ring may result from the intermolecular condensation by release of HMDZ, as illustrated in Scheme 1.

Besides, we found that the Si—H bond also participate reactions during the formation of polymeric network. Figure 4 shows the dependence of the relative IR absorption intensity ratios of Si—Me (1256 cm^{-1}) to Si—H (2126 cm^{-1}) and to N—H (1179 cm^{-1}) on reaction temperature. The analyses
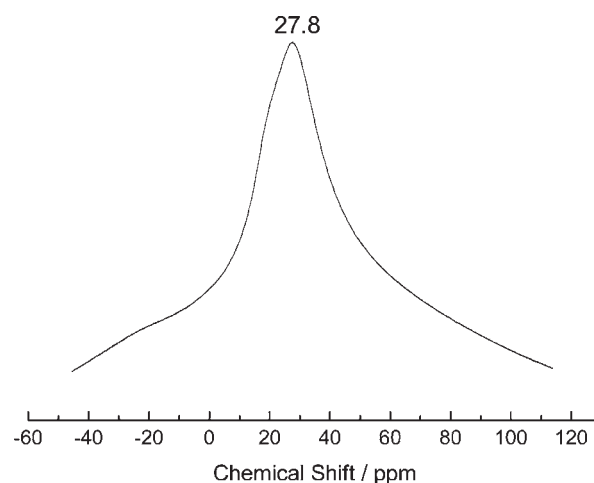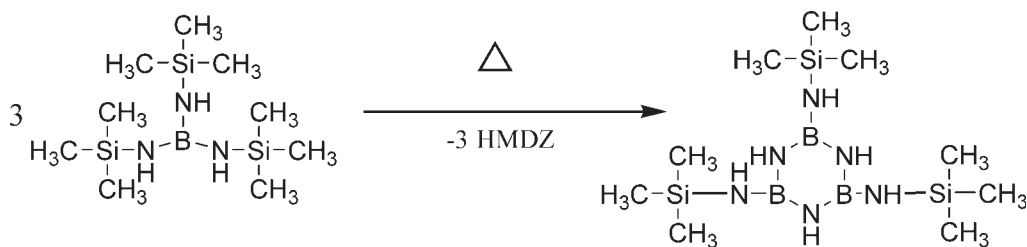

Figure 3   ^{11}B NMR spectrum of as-synthesized PBSZ in $CDCl_3$.

Scheme 1 Formation reaction of borazine ring in the polymer.

below are based on the hypothesis that the reactivity of Si—H is too low to react when the temperature is below 200°C.[19] The decrease of both Si—Me/Si—H and Si—Me/N—H may be attributed to the elimination of HMDZ, because SiMe₃Cl, b.p.58°C, may be distilled off when the reactor reaches 140°C.[20] Moreover, the almost linear decrease of the Si—Me/Si—H and Si—Me/N—H, or the almost fixed changing rate of Si—Me/Si—H and of Si—Me/N—H at 140–200°C suggests that there is no other reaction involved in the Si—Me and N—H except the elimination of HMDZ at this temperature range. It should be pointed out that the formation of borazinic ring resulting from the elimination of HMDZ as described earlier will not alter the changing rate of Si—Me/N—H. The Si—Me/N—H has a slight increase as the temperature reaches to 230°C, whereas the Si—Me/Si—H remains decreasing but with a slower rate. Because the Si—Me bonds decrease during the whole synthesis due to the release of HMDZ, the lowered decreasing rate of Si—Me/Si—H may be interpreted as the consumption of both N—H and Si—H bonds, which may probably result in the dehydrogenation reaction between Si—H and N—H groups with the formation of SiN₃C as shown in Scheme 2.[19] The ²⁹Si NMR spectrum of the solution of PBSZ in CDCl₃ (Fig. 5) provide further evidence for the formation of

structure unit of SiN_3C, which always shows resonances at −22 to −24 ppm.[21–23] The sharp increase of both Si—Me/Si—H and Si—Me/N—H as the temperature is raised to 240°C may be due to the acceleration of the dehydrogenation reaction.

Besides the SiN_3C environment, the ²⁹Si NMR spectrum of PBSZ show several other resonances among which the peaks at ∼ 0.5 ppm and at −2.8 to −3.5 ppm can be assigned to SiC_3N environment,[24] which is formed through the cleavage of HMDZ. The broad peak centered at ca. −19.8 ppm results from $Si(H)CN_2$ groups.[21–23]

Figure 6 shows the ¹H NMR spectrum of the soluble polymer, from which we can see that PBSZ has a complex microstructure. The multiplet peaks at 0–0.41 ppm can be attributed to CH_3, and broad resonances at 4.8–5.2 ppm result from SiH bonds.[5] The multiplet broad peaks at 1.5–1.8 ppm are consistent with the BNHSi group.[17,18] The broad peak around 0.45 ppm can be attributed to SiNH groups on the linear chain,[5] and the broad peak at 3.4 ppm can be assigned to protons of B_2NH[17,18] in the borazine ring. All these environments confirm the mechanism of the reaction.
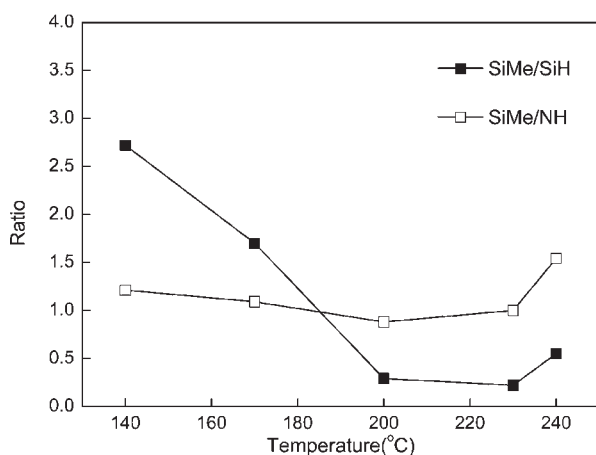
Properties of the PBSZ

A controllable rheology for good processability is a prerequisite for polymer that would be used as precursor for ceramic fiber, and the thermal behavior is also an important property for a preceramic polymer. To study the ability of polyborosilazanes (PBSZs) for melt spinning, the softening properties of the polymer as well as its thermal degradation were investigated by means of TMA using the compression mode with a load of 0.4N and DSC. Thermal behavior of the polymer was measured by TGA.

Figure 4 Dependences of IR absorption intensity ratios (Si—CH₃/Si—H, and Si—CH₃/N—H) on temperature in the oligomers during the synthesis of PBSZ.
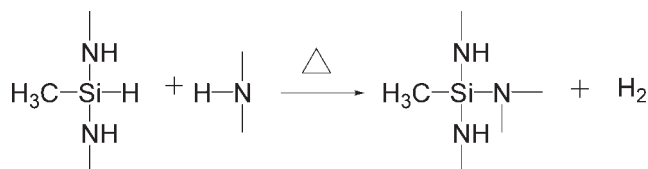
Scheme 2 Formation of SiN₃C structure unit in PBSZ.

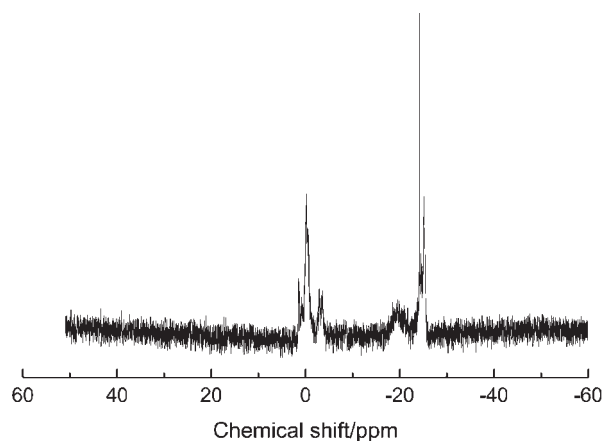**Figure 5** ^{29}Si NMR spectrum of as-synthesized PBSZ in CDCl$_3$.

Figure 6 ^{1}H NMR spectrum of as-synthesized PBSZ in CDCl$_3$.

The TMA curve of PBSZ measured between 30 and 280°C is shown in Figure 7. It is interesting that the curve is very similar to that of the polymer reported by Bernard[10] except the temperature range. It is shown in the TMA that the polymer melts starting at 70°C (T_m) with large dimensional change extending over 180°C from 70 to 250°C. Obtaining the glass transition temperature (T_g) of polymers from DSC is useful to assess the extent of the cross-linkage of such polymers. From the DSC, we can see that the T_g of PBSZ is centered at 42°C. Upon heating, PBSZ transforms into a softened compound through the glass transition, which extends over 26°C going from 30 to 56°C. The wide range of the glass transition may be interpreted as the molar mass dispersion in the polymer. The observed low softening point of PBSZ indicating high chain flexibility results in the low crosslinking density of the polymeric network. Increasing temperature above T_g led to a slight deviation in the TMA curve, and then a significant decrease in the curve is observed due to the melting of the polymer starting from 70 to 250°C, after which point a strong exothermic peak appears resulting from the polymer crosslinking or decomposition. PBSZ exhibits thermoplastic behavior in the temperature up to 250°C and recovers its initial physical and chemical features when it is cooled to room temperature. Therefore, the as-synthesized polymer can be considered stable as a melt from 42 to 250°C without change in its physical and chemical composition.

From these results, it is obvious that PBSZ appears to be a potential candidate for the preparation of polymer green fibers, which is impossible for the polymers reported by Lee et al.,[11] for our knowledge. It exhibits a low glass transition temperature and, because of the use of monomers with reduced reactive groups, neither thermal crosslinking nor decomposition occurs in the 42–250°C temperature
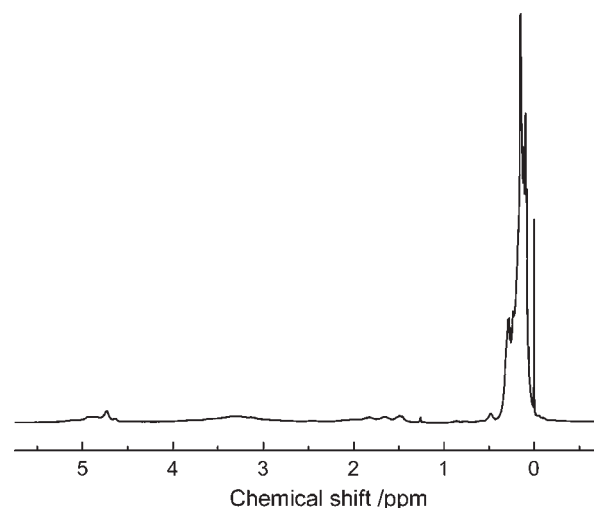
range in which the polymer is in the molten state. Because of the low T_g and the high dimensional change when heated, PBSZ exhibits good softening property qualifying it as a potential precursor for polymer fibers in the viscous region shown on the TMA curve (70–250°C). As an illustration, PBSZ shows good melt spinnability and uniform and defect-free green fibers can be easily obtained by spinning the polymer at 80–86°C from a lab-scale melt-spinning system, having a single 0.25-mm capillary. In a typical condition without optimized, endless polymer green fibers are extruded from the melt at 3.2 cm min^{-1}. Resulting polymer green fibers with an adjustable diameter of 15–20 µm can be continuously stretched from the melt by a rotating spool (Fig. 8).

In consistent with the melt stability of PBSZ up to 240°C, a good reproducibility of the extrusion operation and high-quality green fibers can be easily obtained. However, the low softening temperature,
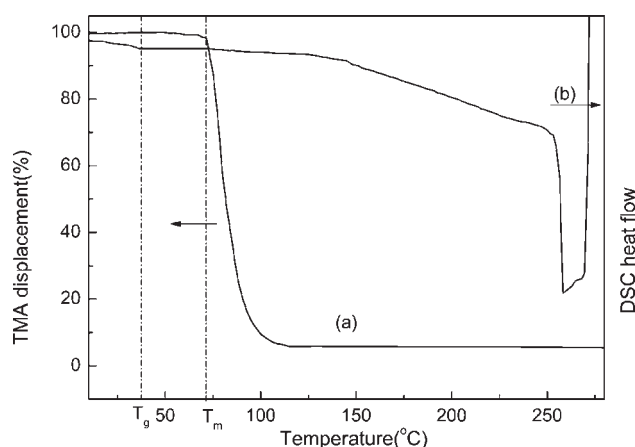

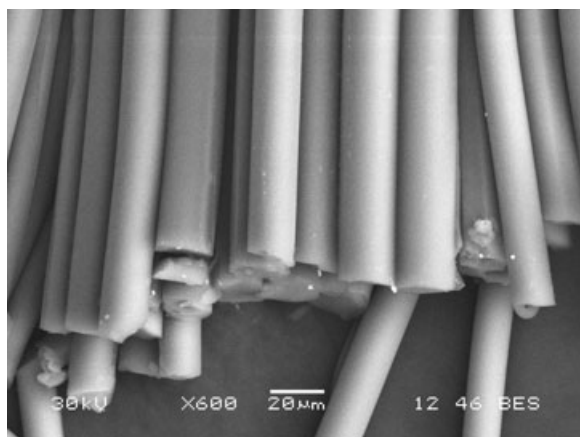**Figure 7** Plots of (a) TMA and (b) DSC of as-synthesized PBSZ.

Figure 8   SEM image of as-spun PBSZ fibers.

Figure 10   XRD patterns of polymer-derived ceramics specimens annealed at different temperatures: (a) 1000°C, (b) 1200°C, (c) 1500°C, (d) 1700°C, and (e) 1850°C.

wide glass transition, and the high-dimensional change upon heating contribute to the good melt processability of the preceramic polymer.[10]

Thermal behavior of the as-synthesized PBSZ was measured by TGA upon heating up to 1000°C under nitrogen atmosphere as shown in Figure 9. The polymer shows almost no weight loss up to 230°C, which is consistent with the TMA and DSC results. The polymeric products exhibited a ceramic yield of 63 wt % at 1000°C even given a major weight loss at 300–600°C. In addition, the observed mass change at 300–400°C may be attributed to insufficient crosslinking within the polymer or the inadequate reaction conditions. This may lead to the formation and evaporation of small molecules. The significant mass loss of the polymeric product detected at 400–600°C suggests that the polymer decomposed or rearranged to transform the polymeric structure to the ceramic phase, which involved the thermal decomposition end group CH_3. It should be noticed that the ceramic yield is lower than that of a reported borazine-based polymer,[24] but it is expected to increase if the as-synthesized preceramic polymer is cured before pyrolysis.
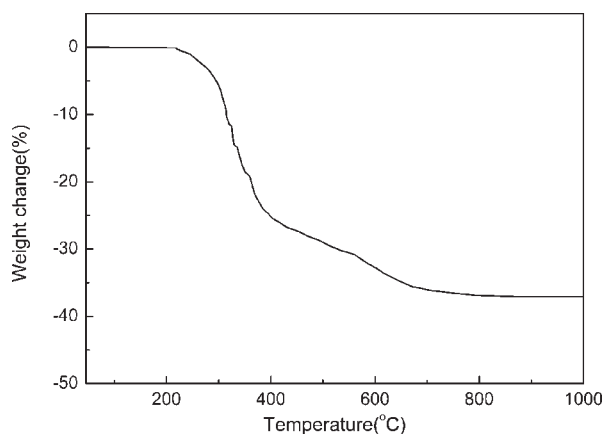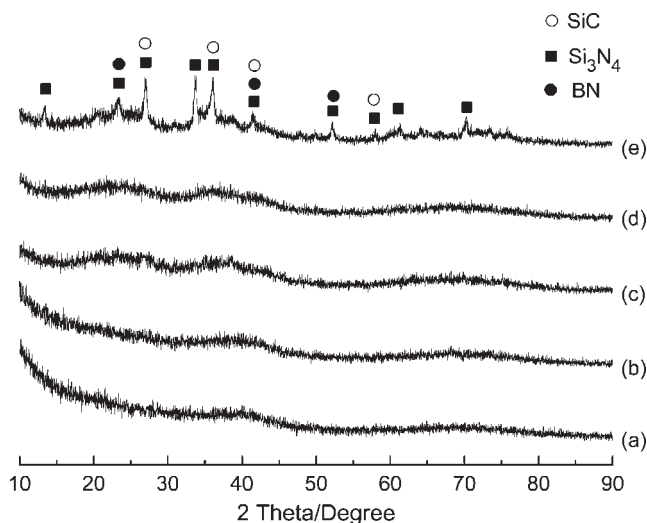
To investigate crystallization behavior, polymeric precursors annealed at different temperatures for 2 h were analyzed by X-ray diffraction and Fourier transformation infrared spectra as shown in Figures 10 and 11, respectively. The pyrolyzed samples from 1000 to 1700°C were fully amorphous, demonstrating an unusual crystallization resistance, which is consistent with those different polymer-derived Si—B—N—C ceramics reported in the literatures.[4,21,22] Interestingly, we found that the crystallization temperature of our polymer is higher than those borazine-based polymers in which the borazine ring is introduced by the intact ring in the starting materials. The latter polymers[5,14,25,26] are amorphous only to 1400–1500°C. This may be attributed to the inhomogeneous introduction of the

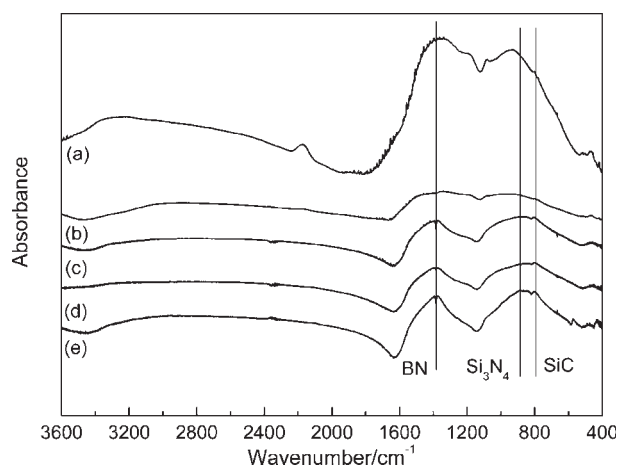

Figure 9   TG curve of as-synthesized PBSZ at 1000°C.

Figure 11   IR spectra (1800–400 cm^{-1}) of (a) PBSZ and polymer derived materials annealed at different temperatures: (b) 1000°C, (c) 1200°C, (d) 1500°C, (e) 1700°C, and (f) 1850°C.

borazine ring existing in the starting materials.[2] When the polymer was heated to 1850°C, the obtained ceramic showed the evidence of crystallization with the formation of crystalline composite ceramic phases, which involved SiC as well as Si_3N_4 and BN. It recently speculated that the presence of atomic boron might retard the diffusion of other atoms and hinder the formation of crystalline ceramics.[3,4,26,27] In addition, it is interesting that boron in the cyclic borazine might play a similar role to stabilize the amorphous state at high temperatures.[25]

In Figure 11, the IR spectra of the as-pyrolyzed and annealed materials, which were obtained in transmission mode, are shown. The positions of the main absorption maxima of crystalline BN, Si_3N_4, and SiC are denoted. All spectra show a very broad absorption at about 1380 cm^{-1} characteristic for hexagonal BN. The intensity of this band significantly increases as the annealing temperature is raised. The spectra exhibit a broad band between 1100 and 800 cm^{-1} the maximum of which is located at about 900 cm^{-1}. This position approximately corresponds to that of the main absorption of crystalline Si_3N_4 (920 cm^{-1}) with a small bathochromic shift, which can be expected in amorphous materials. The coordination sphere of silicon atoms is clearly dominated by Si—C bonds causing absorption maxima at 800 cm^{-1}. Compared to crystalline SiC (850 cm^{-1}), the shift to lower frequencies can be explained by the partly amorphous character of the materials.[28]

CONCLUSIONS

A soluble and meltable polymeric precursor for Si—B—N—C ceramic, having $M_n = 10800$ and $M_w = 16210$ in a high synthetic yield of >92%, was synthesized using a one-step condensation reaction between DCS, BTC, and HMDZ in hexane. The borazine ring detected by ^{11}B NMR in the polymeric network was formed at 170–200°C, as evidenced by IR. Dehydrogenation reaction between Si—H and N—H groups starts at 200–230°C. The polymer exhibits controlled viscoelastic properties to be readily melt spinnable into flexible and uniform fine diameter green fibers. Pyrolysis of the polymer under nitrogen atmosphere resulted in a ceramic yield of 63 wt % at 1000°C. Moreover, the polymer-derived Si—B—N—C ceramics retained a fully amorphous phase up to 1700°C, demonstrating better retention of amorphous state compared with those polymers with borazine ring, but introduced by the intact ring in the starting materials. Poorly crystallized composite

phase of SiC, Si_3N_4, and BN was formed at 1850°C. Such performance characteristics make this preceramic polymer excellent potential candidate for composite materials and for high-temperature applications.

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