

Olefin hydroboration of borazine with vinylsilanes as precursors of Si–B–C–N ceramics

Jong-Kyu Jeon ^a, Quoc Dat Nghiem ^{a,*}, Dong-Pyo Kim ^{a,*}, Jinyoung Lee ^b

^a Department of Fine Chemicals Engineering and Chemistry, Chungnam National University, 220 Kung Dong, Yusong-Gu, Daejeon 305-764, Republic of Korea

^b Advanced Technology Research Center, Agency for Defense Development, Yuseong, P.O. Box 35-5, Daejeon 305-764, Republic of Korea

Received 1 February 2004; accepted 13 April 2004

Abstract

A processible polymeric precursor for Si–B–C–N ceramics was prepared by a hydroboration reaction between borazine and dimethyldivinylsilane using no catalyst with a synthetic yield 85%. The synthesized liquid polymer with an approximately 40% ceramic yield changed to an insoluble solid via a cross-linking reaction of the unreacted vinyl groups to the B–C alkyl bridges between the borazine ring and silane as post-heated from 200 to 600 °C. The insoluble solid was then transformed to SiCN and BN amorphous structures when pyrolyzed to 1400 °C. The synthetic and ceramic conversion chemistry was thoroughly investigated by infrared, ¹H, ¹¹B, ¹³C and ²⁹Si nuclear magnetic resonance spectroscopy, X-ray diffraction and thermal gravimetric analysis.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Hydroboration; SiCBN ceramic; Borazine; Vinylsilanes; Polymeric precursor

1. Introduction

The synthesis of processible polymeric precursors for multipart ceramics such as the Si–E–C–N (E = Al, B, P, Ti, Zr, etc.), B–C–N, or Al (or Ti)–B–N systems are interesting methods for fabricating composites, fibers, films, or bulk ceramics since the superior thermal and mechanical properties of multinary systems were reported [1–3].

Recently, it was reported that the amorphous phase of Si–C–B–N ceramics containing various elemental compositions from organosilanes, organosilazanes, and borane compounds have excellent thermal stability up to 2000 °C without a loss of mass and/or any crystallization [4–6]. The role of boron is believed to enhance the high-temperature stability of boron modified polyorganosilazane derived materials and retard the crystallization and decomposition of silicon nitride at temperatures >1500 °C [7,8]. In addition, the relative ratio and chemical environment of boron within the

precursors might affect the thermal behavior of ceramic materials regardless of the fact that these remarkable properties are not completely understood.

Since the synthetic route of silazane-substituted borazines via a reaction of the silazanes with borane dimethyl sulfide was introduced by Seyferth and Plenio [9], various synthetic routes for producing the preceramic polymers for Si–B–C–N ceramic materials have been reported. Riedel et al. [5] reported the ammonolysis of $B[C_2H_4Si(CH_3)Cl_2]_3$, which is a precursor for the Si–B–C–N ceramic material, was stable for a limited time at temperatures >2000 °C. Riedel and co-workers [7] later described the synthesis of polymers with a higher boron content using either $HBCl_2 \cdot SME_2$ or $H_2BCl \cdot SME_2$ instead of $BH_3 \cdot SME_2$. Aldinger and co-workers [10] synthesized boron-modified polysilazanes of the general type $\{B[C_2H_4Si(R)NH]_3\}_n$ using an oxide-free sol–gel process, the derived ceramic materials showed a resistance toward oxidative attacks up to 1700 °C.

Borazine, which is one of the widely used precursors for *h*-BN, was also used to synthesize the polymeric precursors for Si–B–C–N ceramics. Paine and co-workers [11] described the synthetic route of Si–B–C–N polymers by reacting B-chloroborazines with

* Corresponding authors. Tel.: +82-42-821-7684; fax: +82-42-823-6665.

E-mail addresses: nqdat@cnu.ac.kr (Q.D. Nghiem), dpkim@cnu.ac.kr (D.-P. Kim).

$\text{LiSi}[\text{Si}(\text{CH}_3)_3]_3$ followed by the subsequent polymerization with hexamethyldisilazane. Sneddon and co-workers [12] also reported the preparation of Si–B–C–N preceramic polymers via the thermal dehydrocoupling of polysilazanes and borazine.

However, most of the reported preceramic polymers for Si–C–B–N ceramics have been extremely pyrophoric and are insoluble in most solvents, which make them difficult to handle and limits their ability to be processed. In addition, a synthetic route of the Si–B–C–N polymer via the olefin hydroboration of borazine without catalysts has attracted little attention, even though it is a simple and promising route due to its mild reaction conditions. Recently, we reported the synthetic route of polymer derived Si–C–B–N ceramics via the hydroboration from borazine and trivinylcyclotrisilazane [13].

This paper reports the synthesis and characterization of an alternative soluble polymeric precursor for Si–C–B–N ceramics without the use of a catalyst or byproducts, which involves a reaction between the vinyl groups of the vinylsilanes and the B–H groups of borazine via hydroboration. In addition, the microstructural change during pyrolytic conversion to ceramic materials from the polymeric phase was also investigated thoroughly using various solid state NMR techniques.

2. Results and discussion

2.1. Polymer synthesis

The polymeric precursors for the SiCBN ceramics have been mostly synthesized from various organoboranes as a boron sources. However, there are few reports on the preparation of processable polymers by hydroboration using cyclic boron hydrides as a borazine [13]. In our experiments, it was observed that vinylsilanes reacted smoothly with liquid borazine at moderate temperatures to produce borazine containing copolymers. The novel polymers were isolated by vacuum evaporation of excess borazine after refluxing at 70 °C for 3 h. The polymer, denoted as **DVSB** from the below, obtained from dimethyldivinylsilane (DVS) and borazine, which is a moisture sensitive and transparent viscous liquid, is soluble in common organic solvents such as benzene and ethers. However, it became an insoluble colorless gel when cross-linked as a result of the post-treatment at 120 °C. The molecular weight distribution of the as-synthesized **DVSB** polymer was determined to be $M_n = 671$ and $M_w = 3101$ with a polydispersity of $M_w/M_n = 4.621$. Elemental analysis of the polymer exhibited 40.6 (32.23) for Si, 30.48 (37.1) for C, 11.1 (10.10) for B, 11.12 (13.08) for N and 6.61 (7.48) for H, which are relatively consistent with theoretical values in parentheses. As the **DVSB** cross-linked and pyrolyzed at higher temperature under an inert atmosphere, the whitish gel turned to a yellowish

solid, and ultimately to blackish ceramic phase. Alternatively, the polymers referred to as **MVSB** and **TVSB**, respectively, obtained from methyltrivinylsilane (MVS) and tetravinylsilane (TVS) reacted with borazine, which were mainly insoluble in common organic solvents presumably due to the highly cross-linked structure, while the soluble part showed only the lower molecular weight below $M_w = 300$. Therefore, this work focused on the processible **DVSB** polymer in order to understand the synthesis and ceramic conversion chemistry.

Fig. 1 shows the infrared spectra of the starting substances and the various **DVSB** polymers annealed at different temperatures. By comparing the IR spectra obtained in this study to the literature, the IR spectra of dimethyldivinylsilane matched the characteristic $=\text{CH}_2$ stretching band at 3054 cm^{-1} , $=\text{CH}$ stretching band at 3010 cm^{-1} , and $\text{C}=\text{C}$ stretching band at $1610\text{--}1590\text{ cm}^{-1}$, while borazine to N–H band at 3400 cm^{-1} , B–H band at 2500 cm^{-1} , B–N band at $1385\text{--}1310\text{ cm}^{-1}$. The as-synthesized polymer from the two reactants showed a broad absorption at $2965\text{--}2856\text{ cm}^{-1}$. It is believed that this new band correlates with the aliphatic C–H stretch, $\nu_{\text{as}}(\text{CH}_3) = \nu_{\text{as}}(\text{CH}_2) = 2965\text{ cm}^{-1}$ and $\nu_{\text{as}}(\text{CH}) = 2900\text{ cm}^{-1}$ [14]. Besides, the sharp absorptions at 3054 and 3010 cm^{-1} for the olefin C–H of the vinyl group could barely be observed, and the B–H stretching vibration at 2500 cm^{-1} became significantly broad as a result of polymerization. Furthermore, when the synthesized polymer was cured at 200 °C, the intensities of the absorption bands assigned to the vinyl and B–H groups decreased, which completely disappeared at 300 °C. This suggests that the B–H bonds of borazine with a relatively low reactivity compared to the organoboranes partially reacted at the α - or β -positioned carbon atom and converted to B–C bonds via hydroboration to produce the polymeric products. For the polymer samples treated at 400 °C, the IR absorption bands of the CH_x ($x = 1, 2, 3$) units almost disappeared, indicating that the transformation of the original polymeric phase into the ceramic phase had begun.

This was confirmed by the ^{29}Si NMR spectra of the vinylsilane monomer and the as-synthesized polymer, as shown in Fig. 2. The spectrum of the as-synthesized polymer shows two major peaks at -0.9 and -13.8 ppm. The latter peak can be assigned to silicon atoms containing vinyl groups, as seen from the spectrum of the monomer, which almost disappeared at 200 °C. The former peak was generated by the hydroboration of the vinyl groups to form silicon atoms with alkyl group, which became the dominating species when cured at higher temperatures [8].

Fig. 3 shows the ^1H NMR spectra of starting materials and the as-synthesized polymer. The dimethyldivinylsilane monomer showed the characteristic resonances of the vinyl protons as a multiplet ranging from 5.76 to 6.32 ppm, and Si– CH_3 at 0.21 ppm. In the borazine

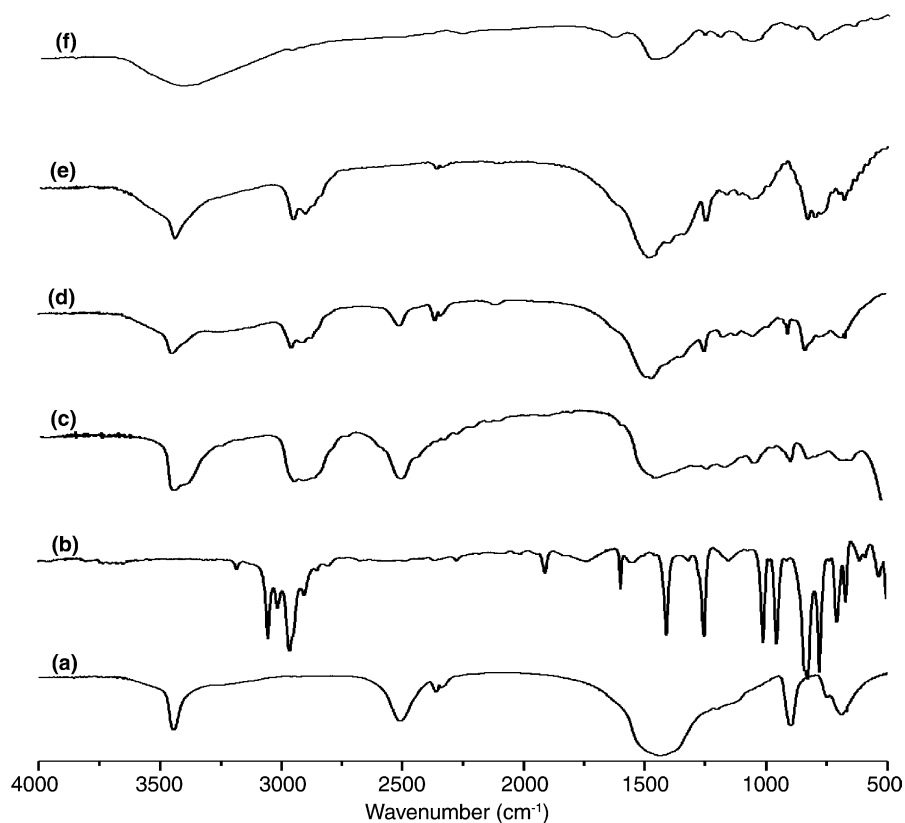


Fig. 1. IR spectra of the starting substances: (a) borazine, (b) dimethyldivinylsilane, and of copolymers pyrolyzed at various temperatures (c) as-synthesized, (d) 200 °C, (e) 300 °C, and (f) 400 °C.

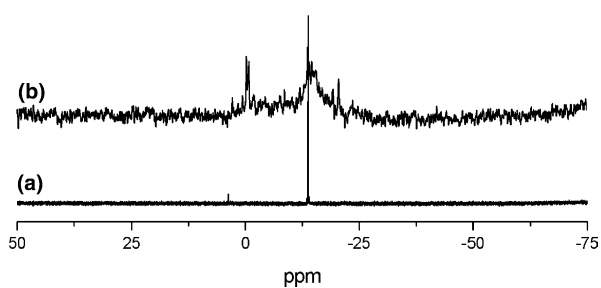


Fig. 2. ^{29}Si NMR spectra of (a) dimethyldivinylsilane and (b) as-synthesized copolymer.

monomer, the B–H peaks between 3.75 and 4.75 ppm, as a quartet, and N–H peaks between 5.25 and 5.75 ppm, as a triplet, were observed. However, the as-synthesized polymer exhibited comparatively weak and broad resonances for the vinyl protons at 5.76–6.32 ppm, which might be a terminal vinyl group attached to the polymer backbone. In addition, the new signals at 0.5–1.9 ppm are consistent with the literature [6]. The broad multiplet peaks at 0.64 were assigned to SiCH_2 signals coupling, and the peak at 1.25 ppm was assigned to the BCH_2 signals due to β -hydroboration, and the others peaks at 0.9 and 1.7 ppm can be attributed to CHCH_3 and CHCH_3 protons due to α -hydroboration, respectively. These results suggested that β -hydroboration

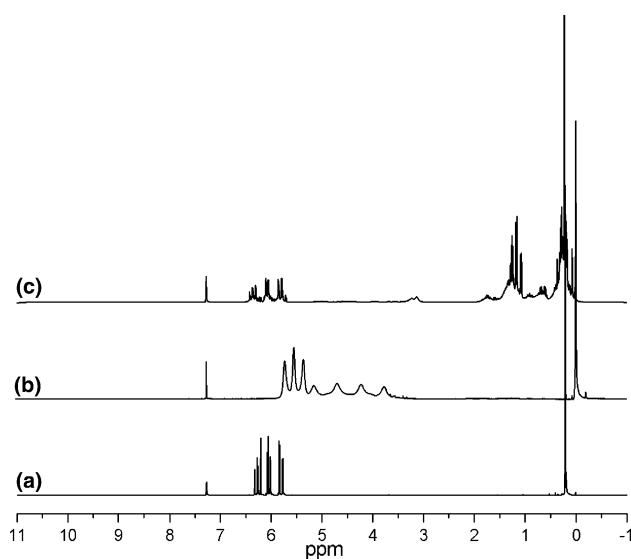


Fig. 3. ^1H NMR spectra of the starting materials and as-synthesized polymer: (a) dimethyldivinylsilane, (b) borazine, and (c) as-synthesized copolymer.

dominates with higher peak intensity due to less steric hindrance.

The hydroboration reaction between dimethyldivinylsilane and borazine was also investigated by ^{13}C NMR measurements. By comparing the spectrum of the

as-synthesized polymer to the vinylsilane monomer, as shown in Fig. 4, new signals at ranging from -3 to 30 ppm were observed. This is reasonably assigned to the CHCH_3 and CH_2CH_3 peaks at 7.5 – 12.4 and 15 – 32 ppm as a result of α -hydroboration. The resonances for the SiCH_2 groups at 1 – 2 ppm, the resonances for BCH_2 at 10.7 ppm are observed as a result of β -hydroboration, as previously reported [6]. However, the remaining peaks at 132 and 138 ppm were attributed to the presence of terminal vinyl carbons while the $\text{Si}-\text{CH}_3$ peak at -3.2 ppm became diffused with polymerization.

On the other hand, it is known that ^{13}C DEPT NMR is a useful technique that can distinguish among the three types of carbons such as methyl, methylene, and methine groups [7]. In Fig. 5(b), the DEPT 45 experiment yielded a positive for every carbon with attached protons. The peaks at 8 and 15 – 29 ppm were assigned to CHCH_3 and CH_2CH_3 , respectively, while the peaks at 12 ppm to CH_2 .

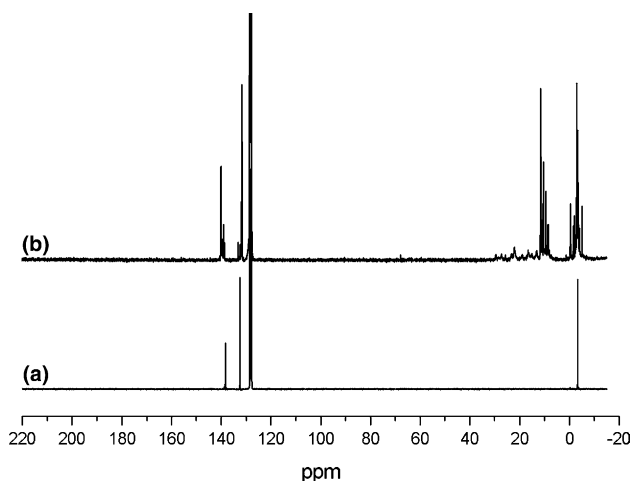


Fig. 4. ^{13}C NMR spectra of (a) starting substance (dimethyldivynylsilane) and (b) as-synthesized copolymer.

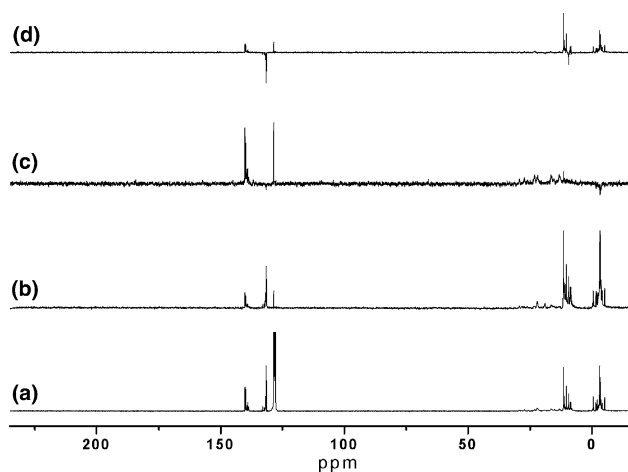


Fig. 5. ^{13}C DEPT NMR spectra of as-synthesized copolymer: (a) ^{13}C NMR, (b) DEPT 45°, (c) DEPT 90°, and (d) DEPT 135°.

These methyl and methylene groups were formed from the vinyl groups reacting with the borane groups of borazine via α - and β -hydroboration. In the variant of the DEPT 90 experiment, only the CH yielded peaks. The CH_2 , and CH_3 carbons were invisible. In Fig. 5(c), only the low intensity peaks centered at ca. 15 – 29 ppm was assigned to the CHCH_3 signals. In a variant of the DEPT 135 experiment, CH_2 yields negative peaks, whereas CH and CH_3 were positive. As shown in Fig. 5(d), the negative peak at 12 ppm was attributed to the $\text{SiCH}_2\text{CH}_2\text{B}$ signals and the positive peaks at 8 and 15 – 29 ppm were assigned to CHCH_3 and CH_2CH_3 signals, respectively. In addition, the peak centered at -3.2 ppm was attributed to $\text{Si}-\text{CH}_3$ signals. This suggests that both hydroborations on the α - and β -positioned carbon atoms took place simultaneously as a result of the partial negative charge on the α -C atom, resulting from an electron withdrawing effect of the silyl group by a $(p-\sigma)_\pi$ conjugation of the β -vinyl carbon in $\text{C}=\text{CSiVi}(\text{CH}_3)_2$ as well as the steric effect by the structure of borazine and vinylsilane environment [6,7]. Moreover, the B–H signal of borazine changing from a quartet signal to a singlet signal indicates that the B–H bonds of borazine had partially reacted with the α - and β -positioned carbon atoms on the silicon and formed B–C bonds, as mentioned above.

2.2. Ceramic conversion chemistry of polymeric precursor

The thermal conversion of the polymer to a ceramic product was investigated using solid-state ^{11}B , ^{13}C , and ^{29}Si MAS NMR spectroscopy. Fig. 6 shows the ^{11}B MAS NMR spectra of the thermally annealed polymers at different temperatures. At 200 °C, the range of signals observed between 17.2 and 28.7 ppm assigned to the N_2BH and N_2BC bonds might indicate that most of the B–H bonds of borazine participated the hydroboration of the α - or β -vinyl carbon atoms, which formed N_2BC bonds [8,12,14,15]. After heating to 400 °C, the relative intensity of the peak at 28.7 ppm decreased and that of the peak at 17.2 ppm increased. After the polymer was heated to 600 °C, a broad peak at 17.2 ppm with a shoulder peak at 21.5 ppm was observed. This conversion is most notable, which shows a microstructural change from an organoborazine to a BN-based ceramic phase. After the polymer was pyrolyzed at 1100 °C, a broad signal between 15 and 30 ppm assigned to the BN_3 and N_2BC species was observed. This suggests that the partial conversion from N_2BC or N_2BH to BN_3 took place as the temperature was increased even if the determination of N_2BC , N_2BH , and BN_3 was uncertain due to the broadness of signals in this region [8,12,14–16]. It is a remarkable point that the B–C bridges between borazine and silane were rearranged during the ceramic conversion so that *h*-BN and amorphous carbon formed after pyrolysis at high temperatures. At

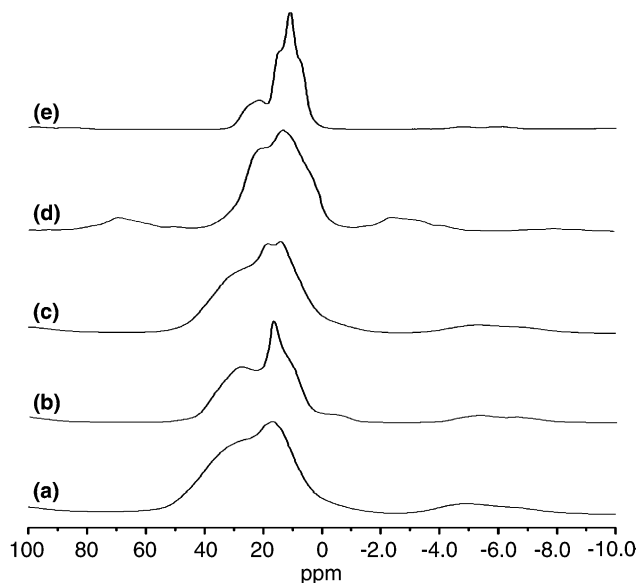


Fig. 6. Solid-state ^{11}B MAS NMR spectra of cross-linked polymer at different temperatures: (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 1100 °C, and (e) 1400 °C.

1400 °C, two sharp peaks were observed. The major peak at 11.2 ppm was assigned to *h*-BN, and the minor peak at 21.5 ppm due to the formation of a turbostratic BN [8].

In Fig. 7, the solid-state ^{13}C MAS NMR spectra of the pyrolyzed polymers at various temperatures may provide an obvious view on the microstructural development during the conversion from a polymer to a ceramic. At 200 °C, signals of the aliphatic carbon atoms due to hydroboration assigned to 10 ppm for the

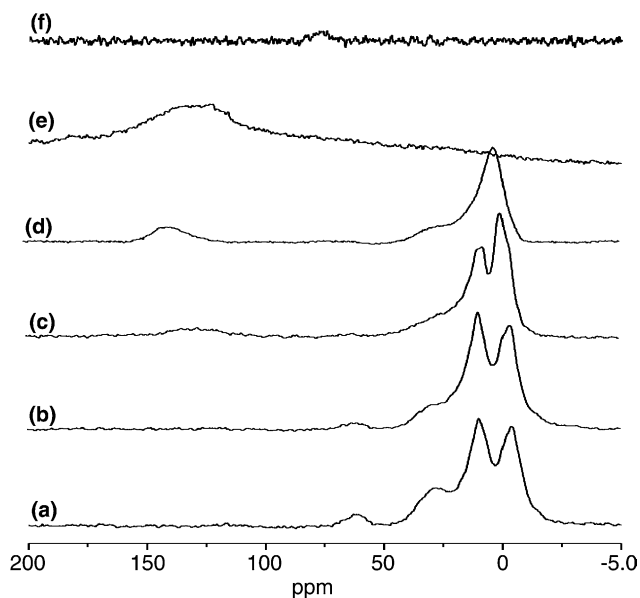
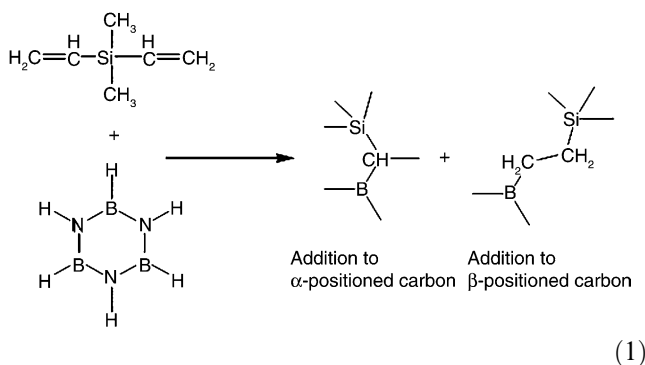


Fig. 7. Solid-state ^{13}C MAS NMR spectra for cross-linked polymers at various temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 600 °C, (e) 1100 °C, and (f) 1400 °C.

$\text{SiCH}_2\text{CH}_2\text{B}$ units, and 28 ppm for the CH_3CHBSi units were observed [6,8], while the peak at -3.2 ppm was assigned to CH_3 . These can be explained by the addition of borane groups of the borazine ring to both the α - and β -vinyl carbon atoms, as shown by Eq. (1). At 300 °C, the intensity of the hydroborated aliphatic carbon peaks at 10 and 28 ppm increased substantially. It is interesting that the aliphatic carbons gradually converge to methyl types presumably due to thermal decomposition of the various B–C bonds as annealed up to 400 °C [14].

In addition, the silicon-bonded methyl groups at -3.2 ppm were retained up to 400 °C with no thermal degradation. Remarkably, a new signal at 59 ppm, which could be assigned to a tertiary amine ($\text{B}_2\text{N}-\text{C}$), was monitored. It is possible that this amine formed as a result of hydroamination between a vinyl group on a silicon atom and N–H in borazine. However, the intensity of this peak decreased significantly when annealed at 300 °C due to thermal composition of the N–C bonds.



In the spectra pyrolyzed at 600 °C, an obvious change in the molecular structure was observed by appearance of new broad resonance at 127 ppm with a drastically reduced aliphatic resonance. This suggests that the B (or N)–C alkyl bridge and the methyl group attached to the silicon had transformed to amorphous graphite as a result of the atomic rearrangement during the ceramic conversion. Between 600 and 1100 °C, a total loss of the organic moiety occurred, and only the graphitic carbon is identifiable at the 1100 °C sample at 120–130 ppm. It is worth noting that it does not exclude the presence of SiC in these specimens due to the extremely long relaxation time of ^{13}C in SiC even if the existence is not confirmed in either spectrum of the specimens pyrolyzed at 1100 °C [8]. Eventually, the most drastic changes in the polymeric precursor occurred in temperature range, 400–900 °C, to form a ceramic network.

Fig. 8 shows the solid-state ^{29}Si MAS NMR spectra. As the polymers were cross-linked at higher temperatures beginning at 200 °C, a dominating peak at -2.4 ppm for Si atoms saturated with alkyl groups increased in the relative intensity while a minor peak at -15.4 ppm for the unreacted vinyl moiety vanished completely on heating to 300 °C. In addition, the shoulder

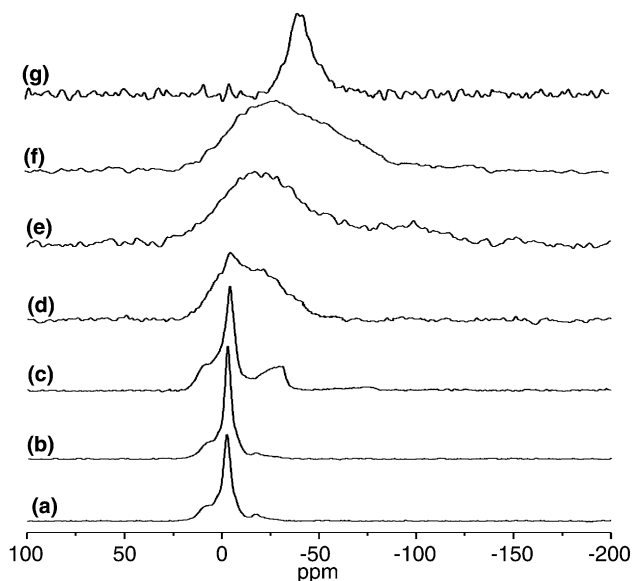


Fig. 8. Solid-state ^{29}Si MAS NMR spectra of a cross-linked copolymer at various temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 600 °C, (e) 900 °C, (f) 1100 °C, and (g) 1400 °C.

peak centered at 12.5 ppm suggests that hydroamination with a vinyl group on the silicon atom took place, which is consistent with the ^{13}C NMR results. At 600 °C, two overlapping peaks were observed at -4.2 and -21.6 ppm, which could be assigned to $\text{Si}(\text{Csp}^3)_2\text{N}_2$ sites and $\text{Si}(\text{Csp}^3)\text{N}_3$ sites, respectively [17]. At 900 and 1100 °C, only one signal with greater width peak was observed, which represents the superposition of the NMR line due to three main structural components, namely $\text{SiC}_x\text{N}_{4-x}$ units with $x = 0, 1$ or 2 . This indicates heterogeneity of the local environment around the Si atoms in the amorphous SiCBN phase [18,19]. Finally, a broad peak at -42.2 ppm was observed after heating to 1400 °C, which involved the formation of Si_3N_4 (-49 ppm) phase [14]. In addition, peak broadening and a peak shift to higher fields were generally observed from the overall NMR spectrum during the conversion to the ceramic phase. This was possibly caused by a decrease in the number of protons as a consequence of thermal decomposition [17].

Finally, the B, C, and Si environments dramatically changed from those of an organic/inorganic polymeric material to that of an amorphous or nanocrystalline ceramic. Therefore, thermogravimetric analysis (TGA) was used to investigate the corresponding thermal behavior of the hydroborated polymers, as shown in Fig. 9. The ceramization progressions of the polymers consist of a two-step decomposition. The weight loss between 70 and 200 °C might be due to the evaporation of the low-molecular weight polymer. A high mass loss was observed in temperature range 300–600 °C due to the atomic rearrangement involved with the simultaneous ceramization and depolymerization processes [20]. The ceramic yield,

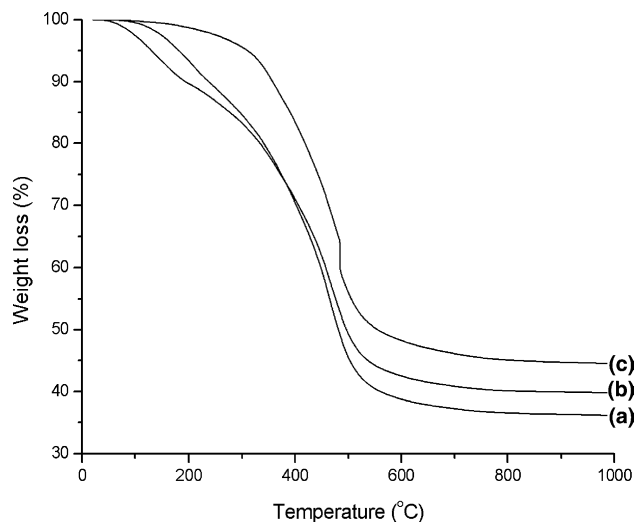


Fig. 9. Thermogravimetric analysis of the polymer-to-ceramic transformation of polymers cross-linked at different temperatures: (a) as-synthesized polymer, (b) cross-linked at 150 °C, and (c) cross-linked at 200 °C.

36.1%, of the as-synthesized polymer was relatively low compared to those of other reported preceramic polymers. In addition, the cured polymers at 150 and 200 °C displayed only slightly improved yields to 39.8% and 45.1%, respectively. It is believed that the low thermal stability of alkyl bridges in the copolymer and the absence of an additional cross-linkable group might result in the high formation of volatile fragments resulting in a high mass loss during the early stage of pyrolysis.

Fig. 10 shows the XRD patterns of the pyrolyzed specimens at 900, 1100 and 1400 °C. The ceramic products retained their amorphous phase up to 1100 °C, and slight crystallization began at 1400 °C with broad bands centered at approximately 26.5° and 43° as 2θ . The diffraction pattern is similar to that of the layered graphite with the (002) $\{2\theta = 26.5^\circ\}$ and (101) $\{2\theta = 44.6^\circ\}$, or *h*-BN phase with the (002) $\{2\theta = 26.7^\circ\}$ and (100) $\{2\theta = 41.6^\circ\}$ planes. This suggests that some borazine rings accompanying the B–C

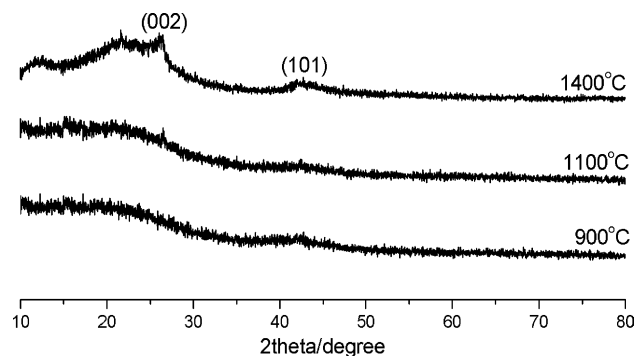


Fig. 10. X-ray diffraction patterns of the Si–B–C–N ceramics pyrolyzed at different temperatures.

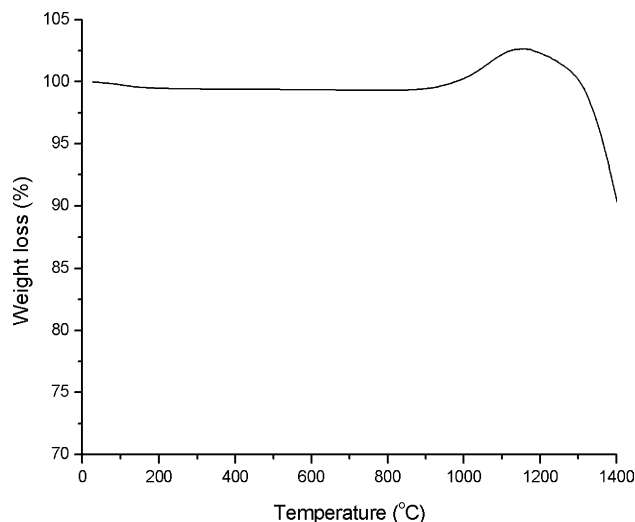


Fig. 11. Oxidation behavior (TGA) of the polymer-derived SiCBN ceramic annealed at 1400 °C.

alkyl bridge had converted to amorphous carbon incorporated BN throughout the pyrolysis. In comparing the crystallization behavior, the obtained SiCBN ceramic began to crystallize earlier than the other SiCBN ceramics, which were fully amorphous at 1400 °C [8,13].

Finally, preliminary investigations on the oxidation resistance of the SiCBN ceramics were performed using high-temperature TGA in air up to 1400 °C, as shown in Fig. 11. The ceramic product displayed a mass gain of 2.5 wt% upon heating to 1100 °C presumably due to passive oxidation of the BN phase, which is stable only up to 850 °C in air. In addition, the drastic weight loss over 1300 °C was due to evaporation of the boron oxide phases.

3. Experimental

All the reactions were performed in a purified argon atmosphere using standard Schlenk techniques to minimize oxidation and/or contamination by atmospheric moisture [21]. All glassware was stored in a drying oven for several hours at 120 °C. Tetrahydrofuran was dried with a sodium–benzophenone mixture under reflux. Borazine ($B_3N_3H_6$), as a monomeric precursor for hydroboration, was synthesized using a method reported previously [22]. The commercially available dimethyldivinylsilane, methyltrivinylsilane, and tetravinylsilane (97%, Aldrich) were used without purification.

3.1. Polymer DVSB from dimethyldivinylsilane and borazine

Into a precooled solution of 10 ml (7.31 g, 65.12 mmol) dimethyldivinylsilane dissolved in 50 ml tetrahydrofuran, 6.47 ml (6.81 g, 65.12 mmol) of borazine

was carefully dropped at a temperature of approximately 0 °C. The temperature of the mixture was kept below 5 °C for over 5 h and was then gradually warmed to room temperature. After stirring for 30 h at room temperature, the solution was refluxed at 70 °C for 3 h and then cooled to room temperature. After evaporating the solvent, 10.6 g of the transparent DVSB liquid polymer was obtained with high viscosity at a yield of 85.4% based on DVS weight.

3.2. Polymer MVSB from methyltrivinylsilane and borazine

6.28 g (60.03 mmol) of borazine was added dropwise to a precooled mixture of 7.69 g (60.03 mmol) of methyltrivinylsilane and 50 ml tetrahydrofuran. The reaction was performed using identical conditions for synthesizing the above DVSB polymer. Finally, 8.5 g (85%) of the white xero-gel type of the MVSB polymer was obtained.

3.3. Polymer TVSB from tetravinylsilane and borazine

The synthesis of TVSB was carried out using the same condition of DVSB. Into a solution of 8 g (56.93 mmol) of tetravinylsilane and 50 ml tetrahydrofuran, 7.94 g (75.9 mmol) of borazine was added. After completing the reaction at the identical conditions for the above DVSB polymer, 9.6 g (82%) of the TVBS polymer was obtained as a white solid.

For the comparison study, some of the as-synthesized DVSB polymer was cross-linked at 120 or 150 °C for 3 h. The cross-linked polymers became either a white gel or mostly insoluble dry gel. The various polymer samples were then annealed at 900, 1100, and 1400 °C for 3 h in an argon atmosphere at a heating rate of 5 °C min⁻¹ (2 °C min⁻¹ over the temperature range 200–600 °C due to the characteristic weight loss). A black porous solid was then eventually obtained after pyrolysis.

Fourier transform infrared (FT-IR) spectra were obtained using a Mattson Genesis II spectrometer in a KBr matrix. ¹H-, ¹³C-, ²⁹Si-, and ¹³C distortionless enhancement by polarization transfer (DEPT) nuclear magnetic resonance (NMR) spectra were performed in C₆D₆ with a Bruker DMX600. The ¹¹B-, ¹³C-, and ²⁹Si-magic angle spinning (MAS) NMR experiments were performed on an FT Wide Bore (600 MHz) Unity NOVA600. Tetramethylsilane (TMS) was used as an internal standard while the ²⁹Si and ¹³C chemical shifts were determined relative to an external standard, sodium 2,2-dimethyl-2-silapentane-5-sulfonate and adamantane, respectively. These values were then expressed relative to the reference compound TMS ($\delta = 0$ ppm). The ¹¹B MAS spectra were calibrated relative to an aqueous solution of H₃BO₃ ($\delta = 19.6$ ppm) as external standard, and are given relative to BF₃·OEt₂ ($\delta = 0$

ppm). The molecular weight of the synthesized polymer was investigated by gel permeation chromatography (GPC, Waters 2850) with polystyrene as a standard. The thermal properties of the polymer samples were measured with TGA (thermogravimetric analysis, TA Instrument 2050), using a platinum crucible up to 1000 °C in an argon atmosphere at a heating rate of 5 °C min⁻¹. The molecular weight distribution of the synthesized polymers was investigated using GPC (gel permeation chromatography, Waters 2850) with polystyrene as the standard. The obtained pyrolyzed specimens were characterized by powder X-ray diffraction (XRD, Rigaku miniflex), using Cu K α irradiation. The elemental composition was determined by elemental analysis (CE instrument, EA 1110).

4. Conclusions

A novel polymer, as a precursor of Si–B–C–N ceramics, was successfully prepared from a hydroboration reaction between dimethyldivynylsilane and borazine, resulting in the formation of a processible colorless liquid polymer with a synthetic yield >85%. The tendency of B–H reduction and the extinction of the vinyl group in the IR and NMR spectra can be explained by the formation of some B–C alkyl bridges via α - or β -vinyl addition. It was partly observed that hydroamination of the N–H bonds of borazine and the unreacted vinyl group occurred above 200 °C. The polymer showed a relatively lower ceramic yield below 45%, compared to the other preceramic polymers in range 60–80%. This was attributed to thermally weak B–C bridges formed by the hydroboration without an alternative cross-linkable route. The pyrolyzed products were confirmed to be mainly amorphous ceramic phases consisting of BN, free carbon, and SiC_xN_{4-x} units, with $x = 0, 1, \text{ or } 2$, by XRD and multinuclear solid-state NMR investigations. Finally, the high-temperature stability of the obtained ceramic in air was comparatively lower than that reported for Si–B–C–N ceramics prepared from organoborane or silazanes sources.

Acknowledgements

This research was funded by Agency for Defense Development (UD030023AD). We thank to the Korea

Basic Science Institute (KBSI) for carry out the ¹H, ¹³C, ¹¹B, and ²⁹Si NMR investigations.

References

- [1] J. Bill, F. Aldinger, *Adv. Mater.* 7 (1995) 775.
- [2] R.T. Paine, C.K. Narula, *Chem. Rev.* 90 (1990) 73.
- [3] D. Seyferth, W.S. Rees, *Chem. Mater.* 3 (1991) 1106.
- [4] H.P. Baldus, M. Jansen, O. Wagner, *Key Eng. Mater.* 75 (1994) 89–91.
- [5] R. Riedel, A. Kienzle, W. Dressler, L.M. Ruwisch, J. Bill, F. Aldinger, *Nature* 382 (1996) 796.
- [6] M. Weinmann, T.W. Kamphowe, J. Schuhmacher, K. Müller, F. Aldinger, *Chem. Mater.* 12 (2000) 2116.
- [7] L.M. Ruwisch, P. Dürichen, R. Riedel, *Polyhedron* 19 (2000) 323.
- [8] W.R. Schmidt, D.M. Narsavage-Heald, D.M. Jones, P.S. Marchetti, D. Raker, G.E. Maciel, *Chem. Mater.* 11 (1999) 1455.
- [9] D. Seyferth, H.J. Plenio, *J. Am. Ceram. Soc.* 73 (1990) 2131.
- [10] M. Weinmann, J. Schuhmacher, H. Kummer, S. Prinz, J. Peng, H.J. Seifert, M. Christ, K. Müller, J. Bill, F. Aldinger, *Chem. Mater.* 12 (2000) 623.
- [11] D. Srivastava, E.N. Duesler, R.T. Paine, *Eur. J. Inorg. Chem.* (1998) 855.
- [12] (a) K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, *Chem. Mater.* 5 (1993) 547;
(b) K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, *Polym. Prepr.* 34 (1993) 334;
(c) T. Wideman, K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, *Chem. Mater.* 7 (1995) 2203;
(d) P.J. Fazon, E.E. Remsen, J.S. Beck, P.J. Carroll, A.R. McGhie, L.G. Sneddon, *Chem. Mater.* 7 (1995) 1942;
(e) T. Wideman, E. Cortez, E.E. Remsen, G.A. Zank, P.J. Carroll, L.G. Sneddon, *Chem. Mater.* 9 (1997) 2218.
- [13] Q.D. Nghiem, J.K. Jeon, L.Y. Hong, D.P. Kim, *J. Organomet. Chem.* 688 (2003) 27–35.
- [14] J. Schuhmacher, F. Berger, M. Weinmann, J. Bill, F. Aldinger, K. Müller, *Appl. Organomet. Chem.* 15 (2001) 809.
- [15] C. Gervais, J. Maquet, F. Babonneau, C. Duriez, E. Framery, M. Vaultier, P. Florian, D. Massiot, *Chem. Mater.* 13 (2001) 1700.
- [16] D. Sauter, M. Weinmann, F. Berger, P. Lamparter, K. Müller, F. Aldinger, *Chem. Mater.* (2002) 2859.
- [17] M.A. Schiavon, G.D. Sorary, I.V.P. Yoshyda, *J. Non-Crystal. Solids* 304 (2002) 76.
- [18] C. Gérardin, F. Taulelle, D. Bahloul, *J. Mater. Chem.* 7 (1997) 117–126.
- [19] Y.El. Kortobi, H. Shihi, A.P. Legrand, E. Musset, N. Herlin, M. Cauchetier, *Colloid Surface A15* (1996) 319.
- [20] A. Müller, A. Zern, P. Gerstel, J. Bill, F. Aldinger, *J. Eur. Ceram. Soc.* 22 (2002) 1631.
- [21] This preparative method is based on experiments developed by the German chemist Wilhelm Schlenk. All apparatus are equipped with side arms for pumping out the air and moisture and introducing inert gas. See also: D.F. Shriver, M.A. Drezdz. *The Manipulation of Air-Sensitive Compounds*, second ed., Wiley, New York, 1986.
- [22] K.T. Moon, D.S. Min, D.P. Kim, *Bull. Korean Chem. Soc.* 19 (1998) 222.