ELSEVIER

Polymer derived Si–C–B–N ceramics via hydroboration from borazine derivatives and trivinylcyclotrisilazane

Quoc Dat Nghiem [a], Jong-Kyu Jeon [a], Lan-Young Hong [b], Dong-Pyo Kim [a],*

[a] Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Daejon 305-764, South Korea
[b] Advanced Materials Research Center, Chungnam National University, Daejeon 305-764, South Korea

Abstract

2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane (VSZ) and borazine ($B_3N_3H_6$) were used as starting materials to synthesize a preceramic polymer for a Si–C–B–N ceramic. The product was obtained as a soluble gel polymer by hydroboration between vinyl and B–H groups at 0 °C to room temperature for 30 h by the standard Schenk technique. The polymer-to-ceramic conversion at a ceramic yield of 70–75% was investigated by simultaneous TG/DTA, ^{13}C and ^{29}Si MAS-NMR, IR, XRD, TEM and XPS. The polymer-derived SiCBN ceramic remained as an amorphous solid up to 1400 °C, and crystallized slightly at 1800 °C to show mixed XRD patterns for Si_3N_4, SiC and BN. The ceramic product obtained at 1000–1400 °C exhibited excellent oxidation resistance in air. In addition, it was demonstrated that dense and smooth ceramic films were readily prepared by spin-coating the liquid polymer.
© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Composite phase of ceramics with some specialties has been involved with various elemental combinations including nitrogen and carbon in addition to main group elements (E = B, P, O, Al, Si) [1,2]. It has been demonstrated that the use of preceramic polymers is beneficial for controlling the chemical compositions of ceramics. Thus, significant research effort has been expanded to design novel ceramics with ultra high temperature stability or extraordinary hardness. Different synthetic pathways have been reported for the synthesis of the polymeric precursors from various starting materials.

Recently, Si–C–B–N ceramics from organosilanes, organosilazanes and borane compounds have been reported and the amorphous phases of these materials have shown excellent thermal stability up to 2000 °C without mass loss or oxidative damage [3–5], although the reasons for these remarkable properties are not completely understood. Takamizawa et al. reported first, on the high temperature stability of Si–C–B–N ceramics [6]. Soon after, Seyferth et al. reacted silazanes with borane methyl sulfide to obtain silazane-substituted borazines as a Si–C–B–N precursor [7]. Sneddon and co-workers obtained Si–C–B–N preceramics that are also based on borazine by dehydrogenation and dehydrosilylation of hydridosilazane with borazine [8]. Recent publications by Müller et al. reported the reaction of polymethylvinylsilazane with borane dimethylsulfide to obtain Si–C–B–N preceramics [9,10], and Riedel and co-workers reported new ceramic materials in the quaternary Si–C–B–N system derived from the synthesis of silyl-substituted organoboranes by the hydroboration of vinylsilanes [2]. However, it is a disadvantage that most of the preceramic polymers for Si–C–B–N ceramics are extremely pyrophoric and insoluble in most solvents, which makes them difficult to handle and limits their processabilities.

In this paper, we report on the synthesis of a soluble polymeric precursor for Si–C–B–N ceramics, without catalyst or byproducts, which involves reaction between the vinyl groups of organosilazane and the B–H groups

---

* Corresponding author. Tel.: +82-42-821-7684; fax: +82-42-823-6665.
E-mail address: dpkim@cnu.ac.kr (D.-P. Kim).

of borazine via hydroboration. In addition, the polymer produced was investigated in an attempt to understand the conversion chemistry to the ceramic and the thermal stability of pyrolyzed specimens at high temperatures.

2. Results and discussion

2.1. Conversion chemistry from polymer to ceramic

The hydroboration of unsaturated groups have been investigated using various organoboranes. However, little has been published on the preparation of processable polymers by hydroboration using cyclic boron hydrides, except transition metal catalyzed alkylation of borazine via hydroboration [11]. In our experiment, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane (VSZ) was found to react smoothly with liquid borazine at moderate temperatures to produce borazine copolymer. The product was isolated as a moisture sensitive colorless gel by the vacuum evaporation of solvent, which is soluble in common organic solvents, including benzene and tetrahydrofuran. The molecular weight distribution of the as-synthesized polymer were found to be the number-average molecular weight (M_n) = 1155 and the weight-average molecular weight (M_w) = 2915 with a polydispersity M_w/M_n = 2.52. Elemental analysis produced 29.07 (26) for Si, 23.59 (30) for C, 12.29 (10) for B, 25.83 (26) for N and 7.68 (8) for H, which are relatively consistent with theoretical values in parentheses. When cured at elevated temperature, the color of the polymer changed from colorless to white then yellow, and finally to a blackish ceramic when subsequently pyrolyzed.

Fig. 1 shows Fourier transform infrared spectra of the polymeric products obtained at various temperatures up to 900 °C. A comparison of the as-synthesized polymer with two starting materials of VSZ and borazine revealed that the band intensities of the vinyl group at 3047, 1594 cm^{-1} and B–H group at 2500 cm^{-1} were slightly decreased, and that absorption bands of N–H group at 3420 cm^{-1} and of the B–N group at 1442 cm^{-1} broaden on polymerization. Moreover, a weak and broad absorption band in the range 2800–3000 cm^{-1} was created. It is believed that this new band correlates with aliphatic C–H stretching, i.e. $v_{as}(CH_3) = v_{as}(CH_2) = 2956$ cm^{-1} and $v_{as}(CH) = 2900$ cm^{-1} [12], which could be formed from both α- and β- addition reaction the vinyl and borane groups.

When the synthesized polymer was cured at 200 °C, the intensities of the absorption bands assigned to vinyl groups and B–H groups decreased, and completely disappeared when the polymer was cured at 300 °C. For polymers treated at 400 and 600 °C the IR vibration bands of the CH$_x$ ($x = 1, 2, 3$) units almost disappeared, indicating the transformation of the original polymeric
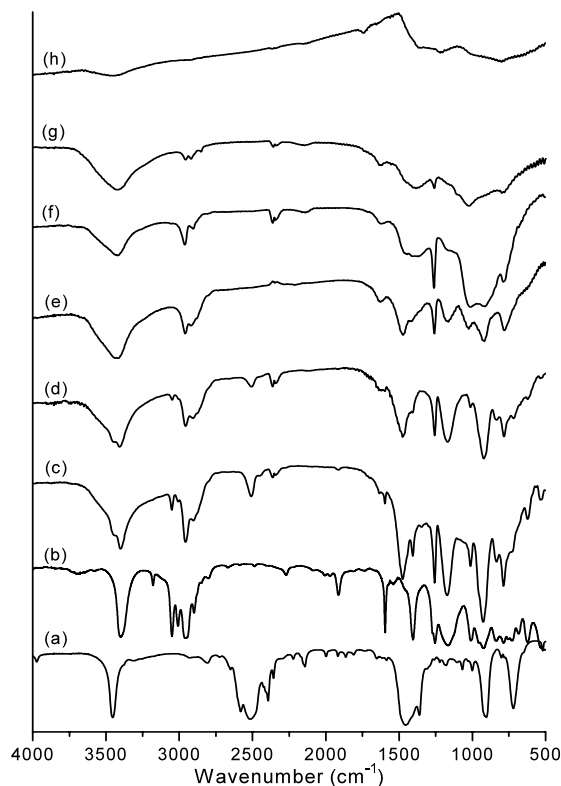

Fig. 1. IR spectra of the starting materials (a) borazine, (b) 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane, and of copolymers pyrolyzed at various temperatures (c) as-synthesized, (d) 200 °C, (e) 300 °C, (f) 400 °C, (g) 600 °C and (h) 900 °C.

phase into the ceramic intermediate phase. In the amorphous ceramic at 900 °C, the band at about 3400 cm^{-1} due to N–H bonds almost disappeared. It was interesting to observe that the N–H bonds displayed high thermal stability, and they reportedly survived up to 800 °C in a recent literature [13].

Fig. 2 shows the ^{1}H-NMR spectra of the soluble polymeric product. The as-synthesized polymer showed the vinylic hydrogen of the VSZ monomer at around 5.9 ppm as a multiplet is significantly reduced, which becomes clearer on decreasing the relative intensity ratio of –CH=CH$_2$/CH$_3$–Si from ca. 0.26 to ca. 0.15. Moreover, new peaks appeared in the range 0.8–1.5 ppm, which are attributed to the formation of an alkyl bridge via two possible routes of hydroboration [5]. Broad peaks at 0.9–1.2 ppm can be assigned to BCH$_2$ protons and the peaks at around 0.4 ppm can be assigned to SiCH$_2$ protons due to β-addition of borazine ring, and the others at 1.07 and 1.4 ppm can be attributed to CHCH$_3$ and CHCH$_3$ protons due to the α-addition, respectively. The B–H quartet of borazine around 3.75–4.75 ppm almost disappeared due to the partial formation of B–C bonds, which is consistent with a literature report [5].

The hydroboration reaction between VSZ and borazine was confirmed by ^{13}C-NMR. By comparing the

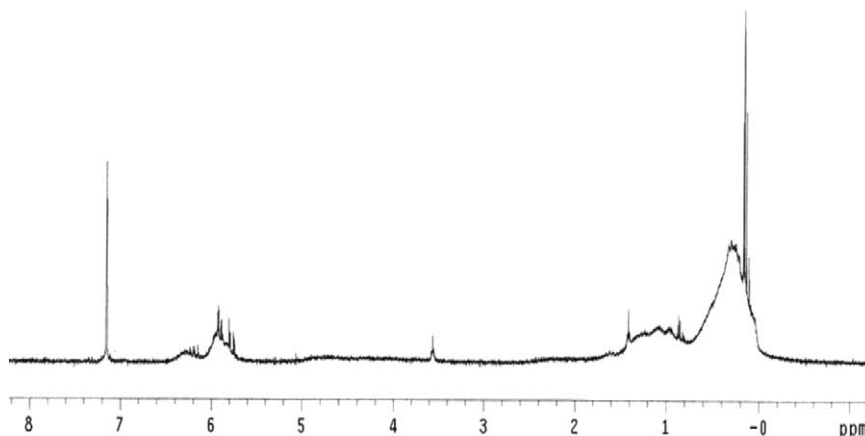Fig. 2. ^{1}H-NMR spectra of as-synthesized copolymer in C_6H_6.

as-synthesized polymer with VSZ, as shown at Fig. 3a, new weak peaks were found at 12.4–13.7 ppm and at 29.2–29.5 ppm due to the formation of methyl and methylene groups from vinyl groups reacted with borane groups of borazine ring via α- or β-addition [5,14]. The peak centered at 2.3 ppm was assigned to Si–CH_3, and the peaks at 131.9 and 142.0 ppm to unreacted vinyl groups. As the polymers became insoluble upon curing at intermediate temperatures, solid-state NMR was be only way to investigate the chemical structural changes at the molecular level. In Fig. 3b, the sample annealed at 200 °C generally showed signals that were identical with

those of the as-synthesized polymer; 1.6 ppm assigned to Si–CH_3 sites, the broad overlapping peaks in the 11–28 ppm range to two types of aliphatic carbon bridge, and the doublet at 125–150 ppm to C=C sites [15,16]. In particular, the peak at around 28 ppm in the aliphatic region attributed to the CH_3CHBSi unit, whereas the $SiCH_2CH_2B$ group was assigned to the resonance at ca. 12 ppm. These can be explained by the addition of the borazine ring to the α- and β-vinyl carbon atoms as shown by Eq. (1) [14,17]. When heated at 300 °C, the signals at 125–150 ppm vanished completely, which is consistent with the IR result, whereas the hydroborated
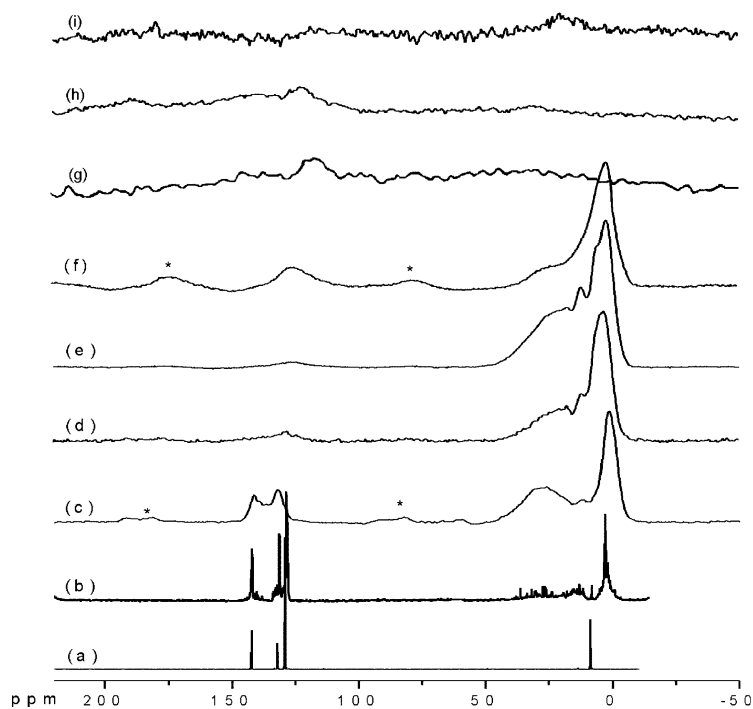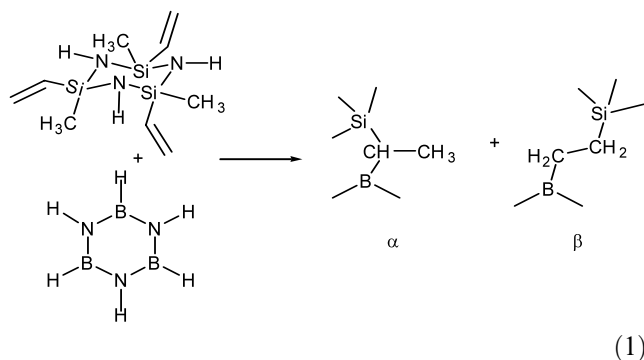

Fig. 3. ^{13}C-NMR spectra of (a) monomer VSZ, (b) soluble as-synthesized polymer in C_6D_6, and the solid-state NMR spectra of insoluble polymers treated at various temperatures under MAS conditions: (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 600 °C, (g) 1100 °C, (h) 1400 °C and (i) 1800 °C. (*) Spinning side bands.

aliphatic carbon peaks at 27.7 ppm and 11.6 ppm substantially increased.

$$(1)$$

Upon heating to 400 °C the intensity of the signals of the hydroborated carbons decreased, and almost disappeared at 600 °C, due to the thermal decomposition of the organic structures. The transformation of the polymeric phase into the ceramic phase was indicated by a new broad spectral component at ca. 125 ppm, which was assigned to amorphous carbon [12,18]. In the amorphous ceramic at 1100 °C the carbon is found to exist in one main fraction, namely as graphite like domains, given by the resonance centered at 122 ppm, as well as CH_xSi_{4-x} units ($x = 0$, 1 or 2). As total loss of aliphatic carbons had occurred in the 1400 °C specimen, only graphitic carbon was clearly identifiable at 123.16 ppm [19]. In the crystalline ceramic at 1800 °C, the presence of carbidic carbon is not confirmed in the ^{13}C MAS-NMR spectra, but this does not preclude the existence of SiC in these samples; others have noted similar difficulty due to the extremely long relaxation of ^{13}C in SiC [19]. In summary, the most drastic changes in ^{13}C-NMR spectra are registered from 400 to 600 °C, and the result from the disintegration of the polymeric precursors and formation of an amorphous preceramic network.

The ^{29}Si-NMR spectra of the monomer and of the hydroborated products annealed at different temperatures are shown in Fig. 4. The spectrum of the as-synthesized polymer shows two major peaks at -3.16 and -14.99 ppm, and a minor peak at 16.3 ppm. Since the -14.99 chemical shift is seen in the solution ^{29}Si-NMR spectrum of VSZ, it can be assigned to silicon atoms in intact silazane rings with vinyl groups of within the polymer. The new peak centered at -3.16 ppm was generated by the saturation of the vinyl groups on the Si atoms in the ring, and the peak at 16.3 ppm suggests B–N bonding with the silazane ring, resulting in a silicon environment [19].

Upon heating to 300 °C, the peak at -14.99 ppm showed only a weak intensity while the peak at -3.16 ppm became broader, and the peak at 16.3 ppm almost disappeared. After heating at 400 °C, the peak at -14.99 ppm essentially disappeared, indicating that

hydroboration was nearly completed at this temperature, with a consequent increase in the relative intensity of the peak at -3.16 ppm. It is resonably consistent with results of ^{13}C-NMR. At 600 °C, two peaks were observed at -6.62 and -21.6 ppm, which could be assigned to $Si(Csp^3)_2N_2$ sites and $Si(Csp^3)N_3$ sites, respectively [20]. It has also been reported that observation of broadened signals and signals shifted to higher fields was possibly caused by a decrease in the number of protons as a consequence of thermal decomposition [20]. At 900 and 1400 °C, only a signal with greater width peak was observed, thus represents a superposition of NMR line due to three main structural components namely SiC_xN_{4-x} units with $x = 0$, 1 or 2. This indicates heterogeneity of the local environment around the Si atoms in the amorphous material, regardless of the distribution of bond lengths and angles [15,21]. Finally, after heating to 1800 °C, a major peak at -18.95 ppm and a minor peak at -49 ppm were observed. These peaks were attributed to the formation of Si_3N_4 (-49 ppm) and SiC (-19 ppm) crystallites [12]. We interpret that the conversion of SiC_xN_{4-x} units to SiC between 1400 °C and 1800 °C in an argon atmosphere can be explained by redistribution reaction of different silicon site, as shown by the reaction between SiCN and the free carbon phase $2SiCN + 2C \rightarrow 2SiC + 2C + N_2$, which is consistent with a report that Si_3N_4 reacts with free carbon at over 1450 °C, according to the reaction: $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$ [20].

2.2. Characterization of materials

Thermal behavior of the hydroborated copolymer was measured by the thermogravimetric analysis and differential thermal analysis (TGA/ DTA) as shown Fig. 5. The polymeric products exhibited a high ceramic yield of 73–77% at 1000 °C even given a major weight loss at 400–700 °C, compared to 55% of reported SiCBN polymers [19]. This result is highly promising from the application point of view for the fabrication of dense ceramic parts. In addition, the mass loss at 70–200 °C might be mainly caused by the vaporization of low molecular weight polymers, whereas sample cross-linked at 200 °C showed almost no weight loss over the same region. The significant weight loss in the range 400–700 °C suggests that the hydroborated copolymer was decomposed or rearranged to transform the polymeric structure to the ceramic phase, which involved the thermal decomposition of the aliphatic bridges or methylene groups, as observed by ^{13}C and ^{29}Si MAS-NMR. Moreover, as detected by DTA the broad exotherm over the temperature range 100–600 °C was attributed to cross-linking hydroboration and pyrolytic decomposition. In the temperature range 700–1400 °C, the produced ceramic phase became thermally stable only with slight weight loss, and a broad endothermic
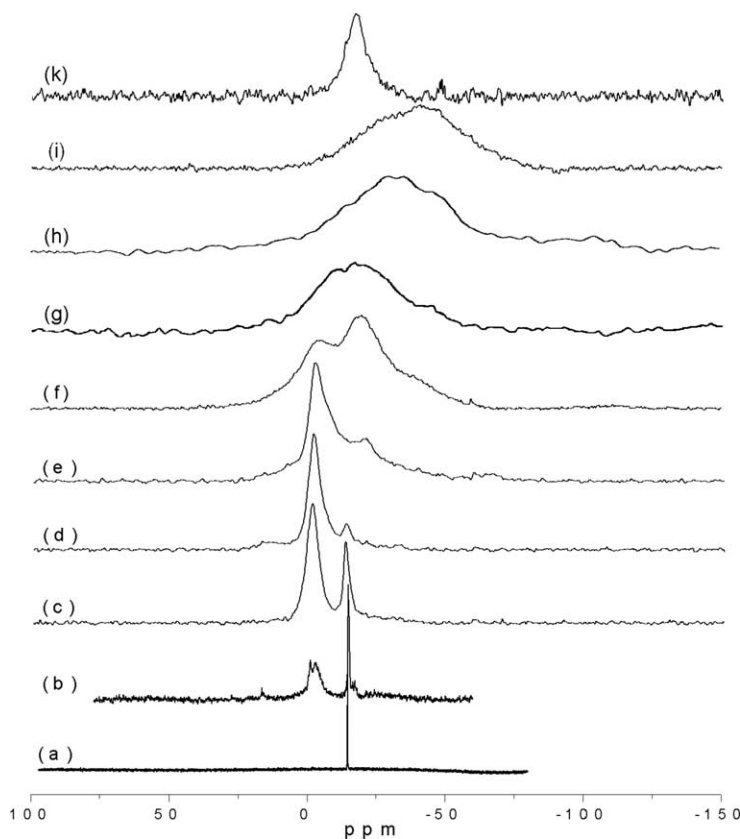
Fig. 4. ^{29}Si-NMR spectra of (a) monomer VSZ, (b) soluble as-synthesized polymer in C_6D_6, and the solid state NMR spectra of insoluble products treated at various temperatures under MAS conditions: (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 600 °C, (g) 900 °C, (h) 1100 °C, (i) 1400 °C and (k) 1800 °C.

peak at 1150 °C was observed, presumably due to the redistribution reactions, which led to the amorphous SiCBN ceramic. This compares with the redistribution reaction of SiCN glass, which is observed at the lower temperature of 980 °C [20].

In order to investigate crystallization behavior, polymeric precursors annealed at different temperatures for 2 h were analyzed by X-ray diffraction as shown in Fig. 6. The pyrolyzed sample from 900 to 1400 °C was fully amorphous, which demonstrates an unusual crystallization-resistance, and it is comparable with that different polymer-derived SiCBN ceramics retain the amorphous phase up to 1600–1700 °C, as observed by Riedel et al. [4], Weinmann et al. [5] and Schmidt et al. [19]. In our own work, the obtained ceramic phase at 1600 °C showed evidence of an early crystallization stage, as diffraction at broad bands at $2\theta = 35.4$ and 60.35°, which are characteristic of SiC [19]. When the polymer was heated to 1800 °C, it proceeded to form higher crystalline composite ceramic phases, which involved SiC as well as Si_3N_4 at $2\theta = 34.8$ and 35.7°, and BN at $2\theta = 26.7$ and 41° [19]. It recently speculated that the presence of atomic boron might retard the diffusion of other atoms and hinder the formation of crystalline ceramics [10,12,22]. In addition, it is interest-

ing that boron in the cyclic borazine might play a similar role to stabilize the amophous state at high temperatures.

In addition, transmission electron microscopy (TEM) image in Fig. 7 demonstrated that the SiCBN ceramic annealed at 1800 °C consists of SiC, Si_3N_4 and BN nanocrystallites with grain sizes in the range 25–40 nm, which is consistent with the XRD results.

Preliminary investigations on oxidation resistance of the SiCBN ceramics was performed using high temperature TGA in air up to 1400 °C as shown in Fig. 8. The ceramic product pyrolyzed at 1100 °C displayed only a slight mass gain of 0.3% on heating in air. This is probably due to the passive oxidation of the ceramic, which is accompanied by the formation of a protective Si(C)O surface layer [5]. It should be pointed out that the amorphous SiCBN ceramic prepared at 1400 °C did not show any mass loss, indicating excellent resistance to oxidation. It is a promising property to utilize the soluble SiCBN precursor for high temperature application.

The chemical bonding within a specimen annealed at 1800 °C was investigated by X-ray photoelectron spectroscopy (XPS). In Fig. 9a, the peaks at 102.1 and 100.58 eV on Si 2p spectrum are assigned to Si–N, and
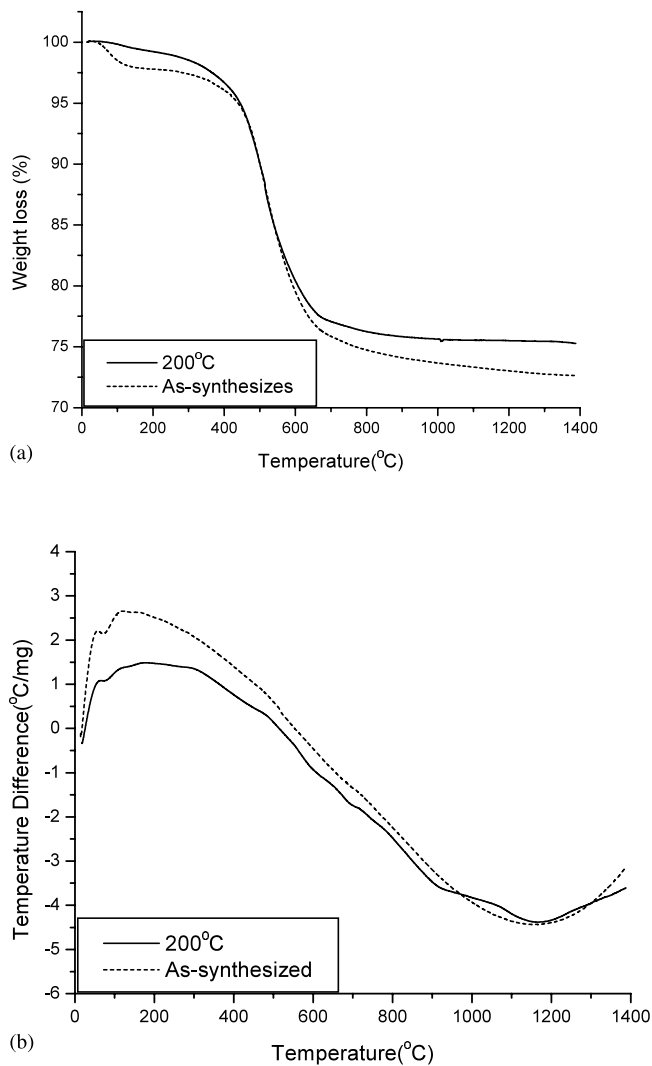
(a)

(b)

Fig. 5. (a) TGA and (b) DTA curves of the as-synthesized polymer and the cured at 200 °C in argon.
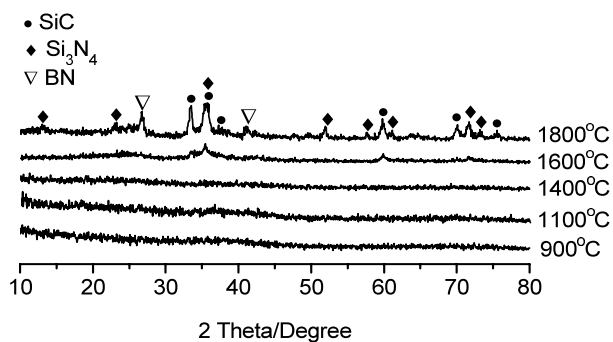

Fig. 6. XRD patterns of polymer-derived ceramic specimens at different temperatures.
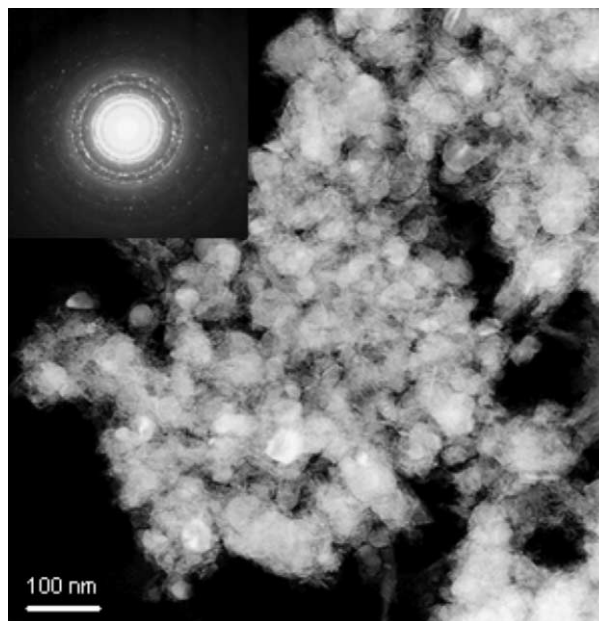

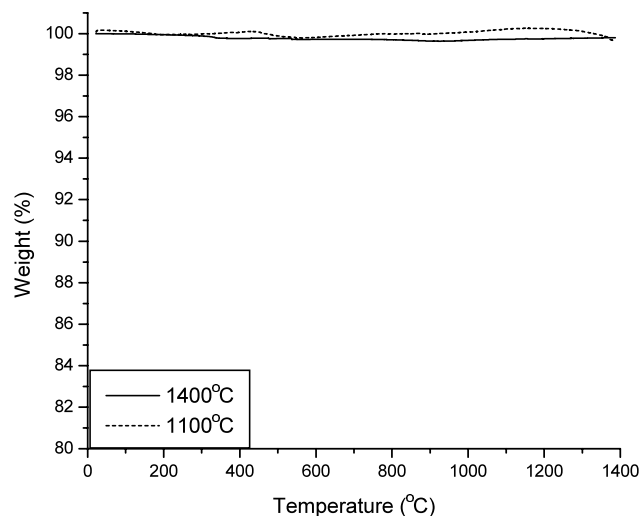Fig. 7. Bright field lattice image and electron diffraction pattern of powdery SiCBN ceramic annealed at 1800 °C

Fig. 8. Oxidation behaviors (TGA) of polymer-derived SiCBN ceramics prepared at different temperatures.

Si–, respectively, which is consistent with presence of the SiC and Si_3N_4 crystalline phases [23]. In accord with the C 1s binding energy (Fig. 9c), the peaks at 283.97 and 284.7 eV were assigned to the C–Si bond of SiC and the C–C bond of graphite, respectively [23]. In terms of

the B 1s spectrum, shown in Fig. 9b, the peaks at 190.48, 190.03 and 189.58 eV were assigned to the B–N bonds of h-BN. The same argument was applied to assign the N 1s peaks at 397.3 and 397.77 eV to mixtures of N–B and N–Si bonds, respectively (Fig. 9d).

Finally, we demonstrate the outstanding processibility of the polymeric precursor to produce high quality SiCBN films by simple spin-coating process. Fig. 10 shows the morphology of SiCBN films on SiO_2–Si or Si substrates after being pyrolyzed at 900 °C in a vacuum. The films showed smooth surfaces and dense structures with no crack in the thickness range $0.15 \sim 2$ μm,
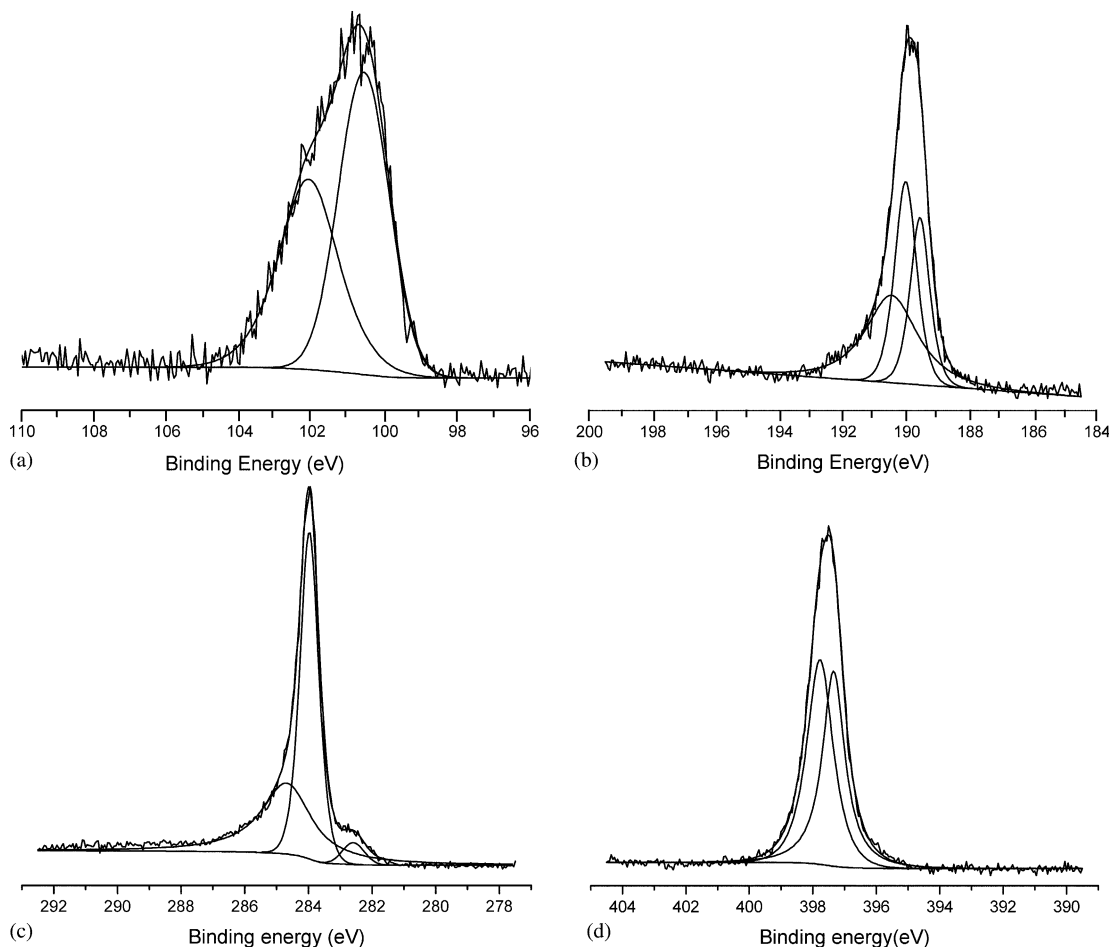
Fig. 9. X-ray photoelectron spectroscopy of polymer-derived SiCBN ceramic prepared at 1800 °C: (a) Si_{2p}, (b) B_{1s}, (c) C_{1s}, (d) N_{1s}.

obtained by controlling preparation conditions. The work details will be reported in a separate paper.

3. Experimental

3.1. Synthesis and pyrolysis of polymer

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques [24]. All glasswares utilized were stored in a drying oven for several hours at 120 °C. Tetrahydrofuran was dried with sodium-benzophenone mixture under reflux. Borazine ($B_3N_3H_6$), a monomeric precursor for hydroboration, was synthesized as reported in our previous report [25]. 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane was obtained from Fluka and used without further purification.

Into a pre-cooled solution of 5 ml (4.4602 g, 17.5 mmol) 2,4,6-trimethyl-2,4,6-trivinylcyclosilazane dissolved in 20ml tetrahydrofuran, 5.31 ml (4.086 g, 52.5 mmol) of borazine was carefully dropped at ca. 0 °C.

The temperature of mixture was kept below 5 °C over 5 h and then gradually warmed to room temperature (r.t.). After stirring over 30 hr at r.t., tetrahydrofuran solvent was removed under vacuum (0.023 Torr) at r.t. 5.6 g of colorless homogeneous gel was obtained at a yield of 95%, based on VSZ weight.

Ceramic films were produced by spin-coating on 1×1 inch Si(100) wafers with ca. 0.1 μm-thick SiO_2 top coating. Substrates were flooded with the copolymer solution at 40 wt.% in THF and then spun at 2000 rpm for 1 min using a model PM101DT-R485 spinner (Head-way Research Inc.). Because the polymer is moisture sensitive, the coating process was carried out inside a glove bag, which was continuously purged with nitrogen or argon. The copolymer film and bulk product were cured at 200 °C, subsequently pyrolyzed in Al_2O_3 tubes under a flowing argon atmosphere at up to 1400 °C at a heating rate 5 °C min^{-1}, and then held for 2 h. The crystallization of the obtained amorphous ceramics was performed in graphite furnace (Astro Furnace) using a graphite crucible at 1800 °C for 2 h in an argon atmosphere.
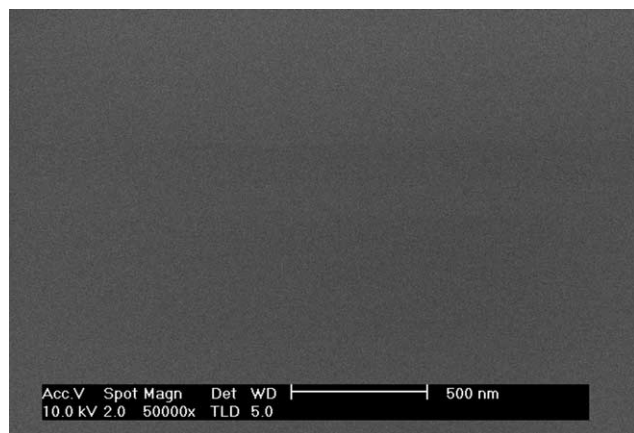
(a)
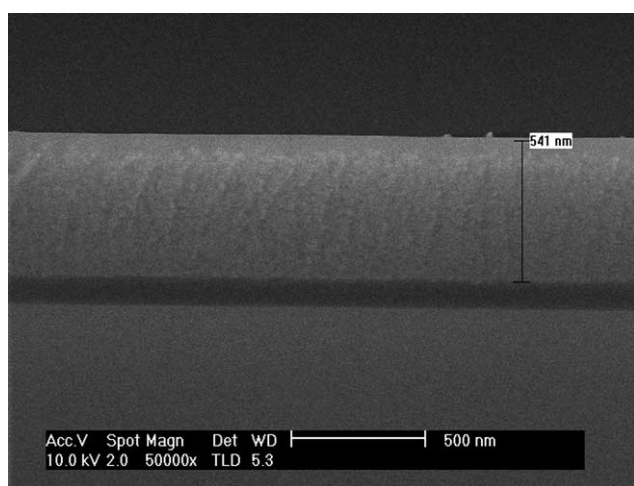
(b)

Fig. 10. SEM image of spin-coated SiCBN film pyrolyzed at 900 °C on a SiO_2–Si substrate under vacuum: (a) surface morphology and (b) cross section

3.2. Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Mattson Genesis II spectrometer in a KBr matrix. [1]H-, [13]C- and [29]Si-nuclear magnetic resonance (NMR) spectra were performed in C_6D_6 with a Bruker DMX600. [13]C- and [29]Si-magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed on an FT Wide Bore (600MHz) Unityl NOVA600. Tetramethylsilane (TMS) was used as an internal standard. The molecular weight of the synthesized polymer was investigated by gel permeation chromatography (GPC, Waters 2850) with polystyrene as a standard. And elemental analysis by Galbraith Inc. Thermogravimetric analysis was performed by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (TA Instrument 2050) at up to 1400 °C with a heating rate of 5 °C min^{-1}. The obtained pyrolyzed specimens were characterized by powder X-ray diffraction (XRD, Rigaku miniflex), using Cu–K_α

radiation. Bright field image and electron diffraction pattern were obtained using an energy filtering transmission electron microscope at 120 kV (EM 912 Omega, Carl Zeiss, Germany). X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical compositions and the bonding structure on an ESCA-LAB 250 X-ray photoelectron spectrometer with an Al–K_α energy source. Scanning electron microscopy (SEM) images were taken with a JSM-840 JEOL.

4. Conclusions

A soluble gel polymeric precursor of SiCBN ceramic, having $M_n = 1155$ and $M_w = 2915$ in a high synthetic yield 95%, was synthesized using a hydroboration reaction between borazine, a cyclic boron hydride, and organosilazane containing vinyl groups, in THF solvent without a catalyst or byproducts. The polymerization was attributed to hydroboration via α- or β-addition of the borazine ring to the vinyl group, as evidenced by a reduction in vinyl group levels and by the formation of an alkyl bridge, detected by IR, and ^{1}H-, ^{13}C- and ^{29}Si-NMR. The subsequent transformation of the polymeric phase to the ceramic phase starting at 400 °C was accompanied by thermal decomposition of the organic carbon with a major weight loss up to 700 °C, finally resulting in 75% ceramic yield at 1000 °C. Moreover, the polymer-derived SiCBN films retained an amorphous ceramic phase up to 1400 °C, and had extremely high oxidation resistance with no weight change. Crystalline composite phase of SiC, Si_3N_4 and BN was formed at 1800 °C. In addition, we found that the polymer was easily processed to form high quality SiCBN films by spin-coating. Such performance characteristics, makes these ceramic films excellent potential candidates for composite materials and for high-temperature protective coating applications.

Acknowledgements

References

[1] J. Bill, F. Aldinger, Adv. Mater. 7 (1995) 775.
[2] L.M. Ruwisch, P. Dürichen, R. Riedel, Polyhedron 19 (2000) 323.
[3] H.B. Baldus, M. Jansen, O. Wagner, Key. Eng. Mater. 75 (1994) 89.
[4] R. Riedel, A. Kienzle, W. Dressler, L.M. Ruwisch, J. Bill, F. Aldinger, Nature 382 (1996) 796.
[5] M. Weinmann, T.W. Kamphowe, J. Schuhmacher, K. Müller, F. Aldinger, Chem. Mater. 12 (2000) 2112.

[6] M. Takamizawa, T. Kobayashi, A. Hayashida, Y. Takeda, US Patent 4,604,367 (1986).

[7] (a) D. Seyferth, H. Plenio, J. Am. Ceram. Soc. 73 (1990) 2131;
(b) D. Seyferth, H. Plenio, W.S. Rees, K. Büchner, Jr, in: A.R. Bassindale, P.P. Gaspar (Eds.), Frontiers of Organosilicon Chemistry, Royal Society of Chemistry, Cambridge, 1991, p. 15.

[8] (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. (Am. Chem. Soc. Div. Polym. Chem.) 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, K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, Mater. Res. Soc. Symp. Proc. 410 (1996) 185;
(f) T.T. Wideman, E. Cortez, E.E. Remsen, G.A. Zank, P.J. Carroll, L.G. Sneddon, Chem. Mater. 9 (1997) 2218.

[9] A. Müller, P. Gerstel, M. Weinmann, J. Bill, F. Aldinger, J. Eur. Ceram. Soc. 21 (2001) 2172.

[10] A. Müller, P. Gerstel, M. Weinmann, J. Bill, F. Aldinger, Chem. Mater. (2002) 14.

[11] P.J. Fazen, L.G. Sneddon, Organometallics 13 (1994) 2867.

[12] J. Schuhmacher, F. Berger, M. Weinmann, J. Bill, F. Aldinger, K. Müller, Appl. Organmetal. Chem. 15 (2001) 809.

[13] K.W. Volger, E. Kroke, C. Gervais, T. Saito, F. Babonneau, R. Riedel, Y. Iwamoto, T. Hirayama, Chem. Mater. 15 (2003) 755.

[14] M. Weinmann, T.W. Kamphowe, P. Fischer, F. Aldinger, Organomet. Chem. 592 (1999) 115.

[15] C. Gérardin, F. Taulelle, D. Bahloul, J. Mater. Chem. 7 (1997) 117.

[16] C. Gérardin, F. Taulelle, J. Livage, Chem. Phys. 89 (1992) 461.

[17] R. Jones, J.K. Myers, Organomet. Chem. 34 (1972) C9.

[18] J. Schuhmacher, M. Weinmann, J. Bill, F. Aldinger, K. Müller, Chem. Mater. 10 (1998) 3913.

[19] W.R. Schmidt, D.M. Narsavage-Heald, D.M. Jones, P.S. Marchetti, D. Raker, G.E. Maciel, Chem. Mater. 11 (1999) 1455.

[20] M.A. Schiavon, G.D. Sorary, I.V.P. Yoshyda, J. Non-Crystalline Solids 304 (2002) 76.

[21] Y. El Kortobi, H. Shihi, A.P. Legrand, E. Musset, N. Herlin, M. Cauchetier, Colloids Surf. A115 (1996) 319.

[22] 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.

[23] N.I. Fainer, E.A. Maximovski, Ydu.M. Rumyantsev, M.L. Kosinova, F.A. Kuznetsov, Nucl. Instrum. Method Phys. Res. A470 (2001) 193.

[24] D.F. Shriver, M.A. Drezdz, The Manipulation of Air-Sensitive Compounds, 2nd ed., New York, Wiley, 1986.

[25] K.T. Moon, D.S. Min, D.P. Kim, Bull. Kor. Chem. Soc. 19 (1998) 222.