

Synthesis and Thermal Behavior of Polymeric Precursors for Si–B–C–N Ceramic

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ABSTRACT: Polyborosilazanes (PBSZs) were synthesized by co-ammonolysis of 2,4,6-trichloroborazine and dichloromethylsilane and used as precursors for Si–B–C–N ceramics. The pyrolyzed products were characterized with Fourier transform infrared, X-ray photoelectron spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction, and scanning electron microscopy (SEM). The results indicated the content of B or Si plays an important role in con-

trolling the high temperature behavior of the precursors. The resistance of the ceramics, which were obtained from pyrolysis of PBSZs at 1500°C, toward oxidative attack up to 1000°C was also investigated by TGA and SEM/EDX. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3400–3406, 2010

Key words: synthesis; thermal properties; pyrolysis; polyborosilazane; Si–B–C–N ceramic

INTRODUCTION

Precursor-derived Si–B–C–N quaternary ceramics have received much attention because of their high temperature stability and resistance to crystallization, as well as high resistance toward oxidative attack at elevated temperature.^{1–6} Since Takamizawa et al.^{7–12} reported, for the first time, on the high-temperature stability of Si–B–C–N composites, intense research has been focused on preparation of these materials from pyrolysis of polyborosilazane precursors. According to the reaction pathways, the various synthetic routes for polyborosilazanes can be sorted into two categories, “polymer route” and “monomer route.” The polymer route is characterized by functionalization of a polymeric precursor, generally, polysilazane,^{13–18} whereas the monomer route is characterized by conversion of Si- and/or B-functionalized monomer into preceramic polymers.¹⁹ The excellent examples for the second route are the work of German scientists. Jansen et al. synthesized polyorganoborosilazanes by ammonolysis or aminolysis reactions of 1,1,1-trichloro-*N*-(dichloroboryl)silane Cl₃SiNHBCl₂ (TADB).^{20–23} Riedel et al. obtained Si–B–C–N precursors by ammonolysis of tris(methyldechlorosilylethyl)borane.^{24–26} Starting from tris(hydridosilylethyl)boranes, B[C₂H₄-Si(R)Cl₂]₃ (R=H, CH₃), and with bis(trimethylsilyl)carbodiimide as N-

source, Weinmann et al. also prepared highly-cross-linked Si–B–C–N precursors, polysilylcarbodiimides, via a new developed nonoxide sol-gel process.^{11,27,28} In these cases, all the polymeric precursors were synthesized from monomers with special structures, which contain both Si and B in one molecule.

On the other hand, in the synthesis of polysilazanes, the precursors to silicon nitride or silicon carbonitride ceramics, co-ammonolysis of mixed chlorosilanes has been the most used simple method. By choice of chlorosilanes with different substituents, or adjustment of the ratio of chlorosilanes, various polysilazanes having different processing properties can be prepared. Recently, Hasegawa²⁹ described preparation of polyorganoborosilazanes with a wide range of B/Si/C ratio simply by co-ammonolysis of various organochlorosilanes and boron trichloride. By pyrolysis of dichlorodimethylsilane (SiMe₂Cl₂) or dichloroethylsilane (SiHC₂H₅Cl₂)-based polyorganoborosilazane with limited B/Si/C ratios in an inert atmosphere, amorphous borosilicon carbonitrides with good thermal stability and excellent oxidation resistance were prepared. However, compared with the research of polysilazanes, the report on preparation of polyorganoborosilazanes by co-ammonolysis of chlorosilanes and chloroboranes is still quite rare, probably due to the limitation of commercially available B–Cl containing compounds.

In this article, we would like to describe our attempt on synthesis of new polymeric precursor for Si–B–C–N ceramics by using the co-ammonolysis methodology. B-containing polysilazanes, viz. polyborosilazanes, with different B/Si ratio were

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TABLE I
Details of PBSZ Precursors

Sample	HMeSiCl ₂ / TCB ratio	Si/B ratio	Yield %	M _n ^a	Appearance
PBSZ-1	1.5	0.5	46.5	516	White solid
PBSZ-2	3	1	50.2	544	Viscous, colorless liquid
PBSZ-3	6	2	57.6	645	Viscous, colorless liquid
PBSZ-4	12	4	64.9	763	Viscous, colorless liquid

M_n, number-average molecular weight.

^a By GPC analysis.

synthesized from co-ammonolysis reaction of 2,4,6-trichloroborazine and dichloromethylsilane. Thermal behavior of these new precursors, phase evolution and, oxidative resistance of the pyrolytic residue were also investigated, respectively.

EXPERIMENTAL

Materials

All reactions were carried out under nitrogen atmosphere using standard Schlenk technique.³⁰ Dichloromethylsilane was purchased from Xinghuo Chemical Plant (Jiangxi, China) and freshly distilled before use. Dichloromethane was dried by refluxing over CaH₂ and distilled before use. 2,4,6-trichloroborazine Cl₃B₃N₃H₃ (TCB) was prepared according to literatures³¹ and purified by sublimation.

Characterization

Fourier transforms infrared (FTIR) spectra were recorded with a Bruker IFS 45 spectrometer. ¹¹B, ¹³C, and ²⁹Si NMR spectra in CDCl₃ solution were measured on a Bruker Avance 400 or Avance 300 spectrometer at 128, 100, and 59 MHz, respectively. Molecular weights of polymeric precursors were estimated by a gel permeation chromatography (GPC) equipped with a Waters 2414 refractive index detector and s-Styrigel columns, using tetrahydrofuran as an eluent and polystyrene as a standard. Thermal gravimetric analyses (TGA) and derivative thermal gravimetric (DTG) were performed on a Netzsch STA 409PC under nitrogen flow at a heating rate of 5°C/min. X-ray powder diffraction (XRD) patterns were obtained using CuKα radiation (40 KV, 200 mA, λ = 0.154056) with a Rigaku D/MAX 2400 diffractometer. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. Scanning electron microscopy (SEM) was conducted on a HITACHI S-4800 with 15 kV electrons. The samples were sputter-coated with a layer of gold to enhance their conductivity before observation.

Synthesis of polyborosilazanes

To a mixture of H₃CSiHCl₂ and TCB in CH₂Cl₂, NH₃ was introduced under vigorous stirring through a gas inlet at -10°C. Ammonolysis was carried out until no further NH₃ was absorbed. The mixture was subsequently stirred for another 2 h at -10°C and allowed to warm to room temperature. The precipitated NH₄Cl was removed by filtration, followed by condensation under reduced pressure to remove solvent. The residue was further dried in a vacuum at 50°C to give polyborosilazanes (PBSZs). The products were characterized by FTIR, ²⁹Si-NMR, ¹¹B-NMR, ¹³C-NMR, and GPC. By changing molar ratio of HMeSiCl₂ to TCB from 1.5 to 3, 6, and 12, four PBSZs, namely, **PBSZ-1**, **PBSZ-2**, **PBSZ-3**, and **PBSZ-4**, with different B/Si ratio were synthesized, respectively. The results were summarized in Table I.

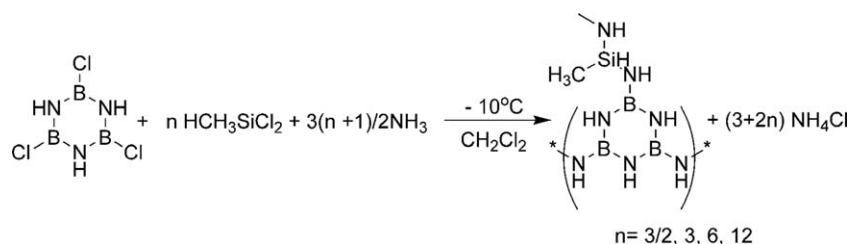
Pyrolysis of precursors PBSZs

Pyrolysis of **PBSZ-1**, **PBSZ-2**, **PBSZ-3**, and **PBSZ-4** were performed in a tube furnace (model GXL 1600X, WEIDA) equipped with a controller and an alumina tube. Fused alumina boats were used to contain the precursor in the tube. The heating rate was 5 K/min and the holding time at 1200°C under flowing N₂ was 2 h. Further annealing up to 1300, 1400, and 1500°C was performed under an argon flow at a heating rate of 3 K/min for a dwelling time of 2 h at the final temperature, respectively. The residues annealed at 1500°C were named as **PBSZ-1C**, **PBSZ-2C**, **PBSZ-3C**, and **PBSZ-4C**, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of the precursors

The co-ammonolysis reaction of dichloromethylsilane and TCB with ammonia was performed in CH₂Cl₂ at -10°C and shown in Scheme 1. The as produced polyborosilazanes were easily separated from ammonium chloride by filtration. After removal of solvent, polyborosilazanes were obtained



Scheme 1 Synthesis of polyborosilazanes (PBSZs).

in moderate yields as colorless liquid or white solid, depending on the ratio of TCB to dichloromethylsilane. The polymers were characterized by IR and NMR spectroscopy. As shown in Figure 1, all precursors show absorption peaks around 2135 cm^{-1} attributed to Si—H stretching vibration.³ N—H stretching and Si—N—H deformation vibrations are detected around $3380\text{--}3400\text{ cm}^{-1}$ and $1170\text{--}1177\text{ cm}^{-1}$, respectively.²⁹ The maintenance of borazine rings in all four polymers was proven by existence of absorption bands at 1450 cm^{-1} and 760 cm^{-1} .³²

NMR spectra for polymers **PBSZ-1-4** were also measured to confirm the structure. The ^{11}B -NMR spectrum exhibits single resonance at 27.70 ppm assigned to the B surrounded by three N atoms.²⁹ In the ^{13}C -NMR of the precursors, one signal at 4.30 ppm is observed, which can be assigned to C atom of methyl group that bonded to silicon. The single resonance in ^{29}Si -NMR spectrum at -21.74 ppm is assigned to the $-\text{Si}(\text{HMe})\text{-NH}$ -group.³

The numeric molecular weights of the precursors were estimated by GPC measurements using polystyrene standards and listed in Table I. In all cases, the quite low number-average molecular weight was found, suggesting low polymerization degree. The synthetic yields of precursor were increased from

PBSZ-1 to **PBSZ-4** with decreasing in the ratio of B to Si. This is due to the reduction of insoluble products with the decrease on content of tri-functional TCB. **PBSZ-1** with the highest B:Si ratio of 2 : 1 is a solid, which suggests a high crosslinking degree for this precursor, whereas the other three precursors having lower B/Si ratio are viscous liquids.

Thermal properties

The thermal properties of precursors **PBSZ-1**, **PBSZ-2**, **PBSZ-3**, and **PBSZ-4** were studied by TGA and their thermograms are shown in Figure 2. The precursors possess comparable ceramization progressions, marked by two-step decomposition. The first step takes place in the range of $100\text{--}350^\circ\text{C}$, whereas the second step occurs between 400 and 700°C . The main weight loss is detected in the first step. It is probably induced by evaporation of volatile silicon-containing small molecules, such as silazanes. This behavior is somewhat similar to that of PBNs which are converted into ceramics at about 300°C .^{16,29} In addition, the evolution of NH_3 and H_2 that caused by transamination⁶ and dehydrocoupling reaction between Si—N/N—H and N—H/Si—H units, respectively, is also responsible for the weight loss. From 700 to 1000°C , the weight loss of all these samples is negligible. The ceramic yields at 1000°C were 62%,

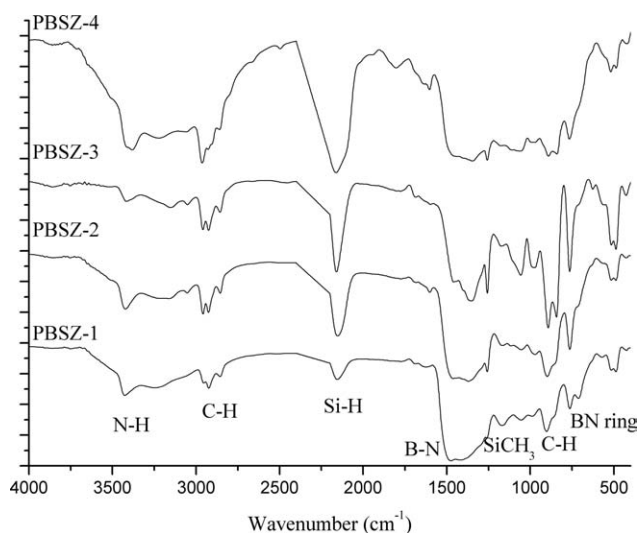


Figure 1 FTIR spectra of PBSZs.

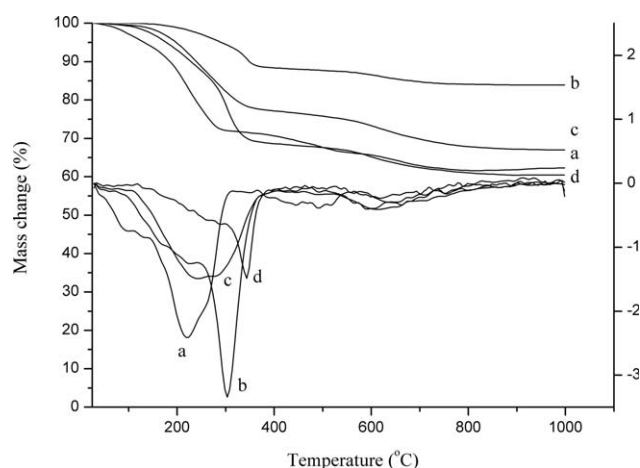


Figure 2 TGA and DTG curves of polymeric precursors PBSZs: (a) **PBSZ-1**, (b) **PBSZ-2**, (c) **PBSZ-3**, and (d) **PBSZ-4**.

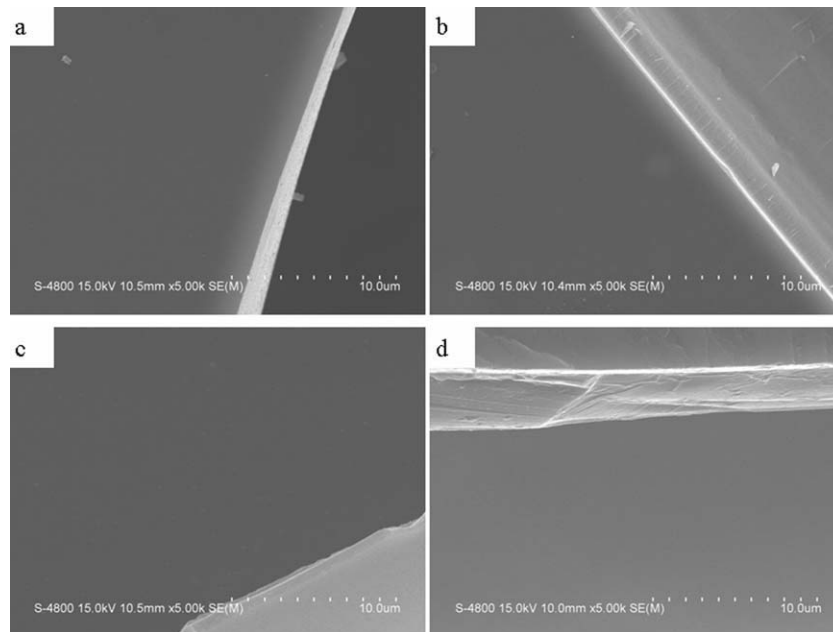


Figure 3 SEM images of (a) PBSZ-1C, (b) PBSZ-2C, (c) PBSZ-3C, and (d) PBSZ-4C.

84%, 67%, and 60% for **PBSZ-1**, **PBSZ-2**, **PBSZ-3**, and **PBSZ-4**, respectively.

The ceramic yields for all samples were also estimated by pyrolysis up to 1200°C in tube furnace under nitrogen atmosphere. To ensure complete ceramization, the samples were held for 2 h at the

final temperature. The data are almost identical with that observed from TGA measurement. The further annealing of the obtained residues to 1300, 1400, and 1500°C under argon atmosphere was performed, respectively, and black ceramic materials were received in all cases (Fig. 3).

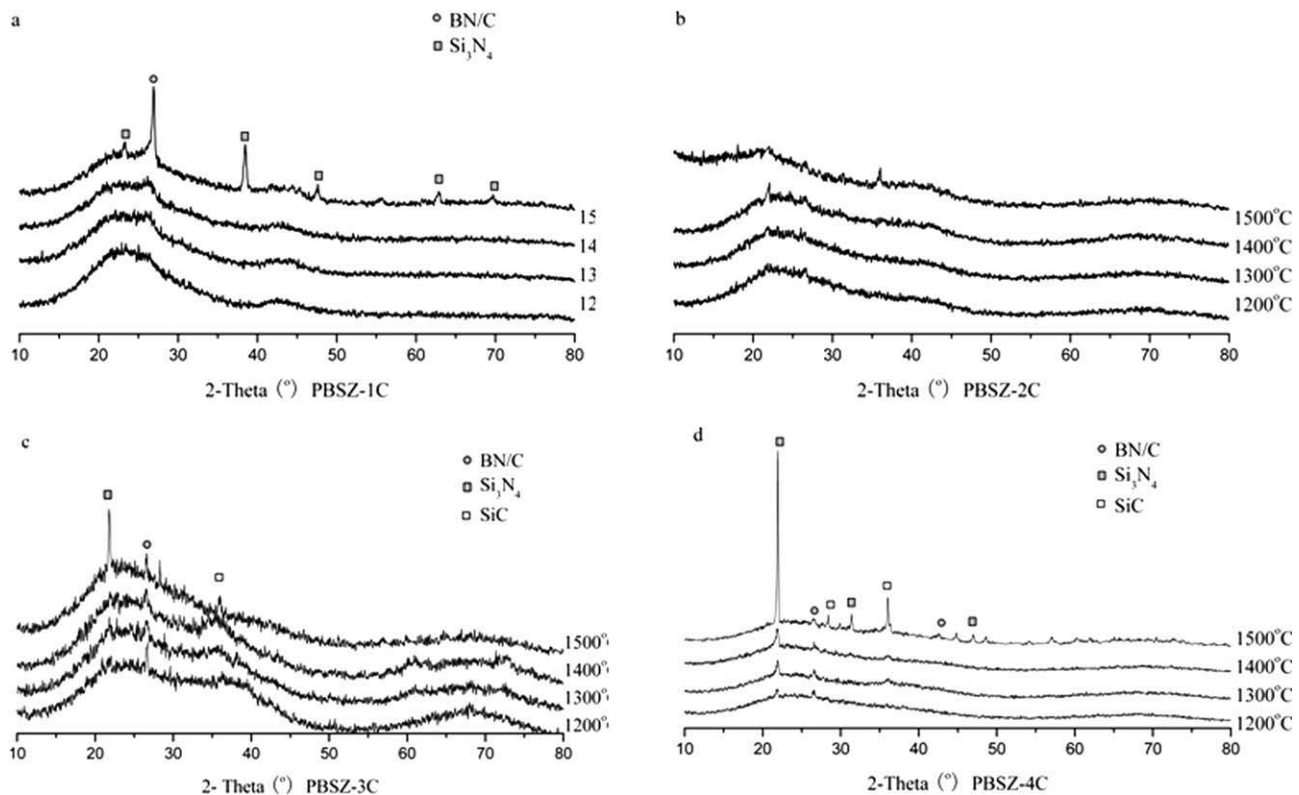


Figure 4 XRD patterns of the pyrolytic product of PBSZs at 1200, 1300, 1400, and 1500°C: (a) **PBSZ-1C**, (b) **PBSZ-2C**, (c) **PBSZ-3C**, and (d) **PBSZ-4C**.

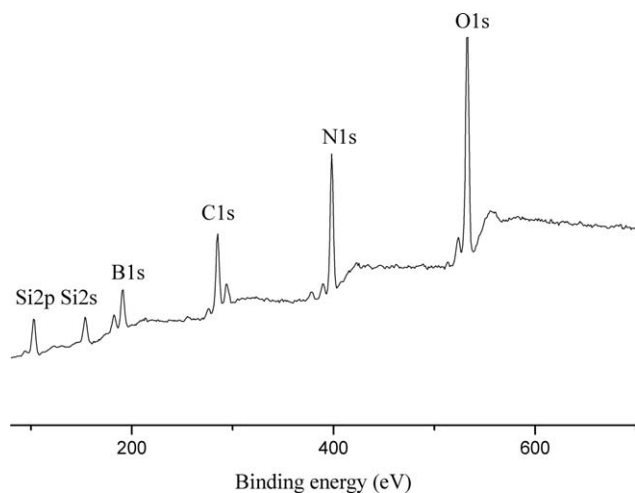


Figure 5 XPS wide-scan profile of PBSZ-2C.

Analysis of ceramics

To elucidate phase transformation of the new precursor derived ceramics, XRD investigations were performed for the ceramics obtained at different pyrolytic temperature with the patterns shown in Figure 4. The ceramics derived from all precursors demonstrate amorphous character up to 1200°C; however, their crystallization behavior are depended on the composition of precursors. After annealing at 1300°C, the diffraction diagram for the pyrolytic product of **PBSZ-4**, the precursor with the highest ratio of Si to B, shows three reflections at $2\theta = 22^\circ$, 26° , and 36° with low intensity that trace back to Si_3N_4 and BN/C, respectively. The XRD diagrams of the pyrolytic residues of **PBSZ-1** and **PBSZ-3** are some similar, for example, both samples annealed at 1400°C show weak, broad reflections at $2\theta = 26^\circ$ and 22° , respectively. The sample annealed at 1500°C (**PBSZ-1C**) exhibits sharp reflections of Si_3N_4 and BN/C, whereas **PBSZ-3C** shows Si_3N_4 , SiC, and BN/C reflections. The ceramic derived from **PBSZ-2** shows the best thermal stability, which still remains amorphous at 1500°C. These results indicate that the content of B or Si plays an important role in controlling the high temperature behavior of the precursor derived ceramics.

XPS investigations of **PBSZ-1C**, **PBSZ-2C**, **PBSZ-3C**, and **PBSZ-4C** displayed the similar chemical bonding, with **PBSZ-2C** as an example as shown in Figure 5. The spectrum suggests the existence of B–N, Si–N, Si–C, B–O, and Si–O in the SiBCN network. The oxygen was probably introduced during the processes of the curing and the annealing treatment.

The existence of B–N, Si–C, and Si–N bonds in pyrolytic products of PBSZs were also detected by FTIR, with that of the samples obtained by pyrolysis of **PBSZ-2** at different temperature as an example

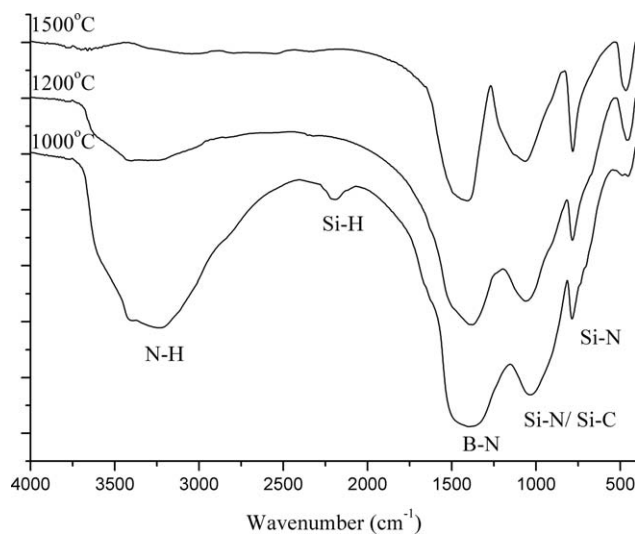


Figure 6 FTIR spectra of the pyrolytic product of PBSZ-2 at 1000, 1200, and 1500°C.

and shown in Figure 6. The main absorption bands of B–N, Si–N, and Si–C are denoted. All spectra show a strong, broad peak centered at 1400 cm^{-1} and a medium-intensity band at 800 cm^{-1} for B–N. Absorptions at 1050 and 470 cm^{-1} are caused by Si–N and Si–C, respectively. In the sample pyrolyzed at 1200°C, N–H absorption at 3450 cm^{-1} was detectable, which decreased upon treatment of the sample at higher temperature and disappeared for the sample obtained at 1500°C. The signal at 2140 cm^{-1} , which is attributed to Si–H, disappeared in the temperature range between 1000 and 1200°C.

The oxidative stability of the ceramic materials **PBSZ-1C**, **PBSZ-2C**, **PBSZ-3C**, and **PBSZ-4C** were also examined in air over a temperature range of 30–1000°C with thermogravimetric analysis. The TGA results (Fig. 7) suggest that the ceramics possess excellent thermo-oxidative stability. The mass

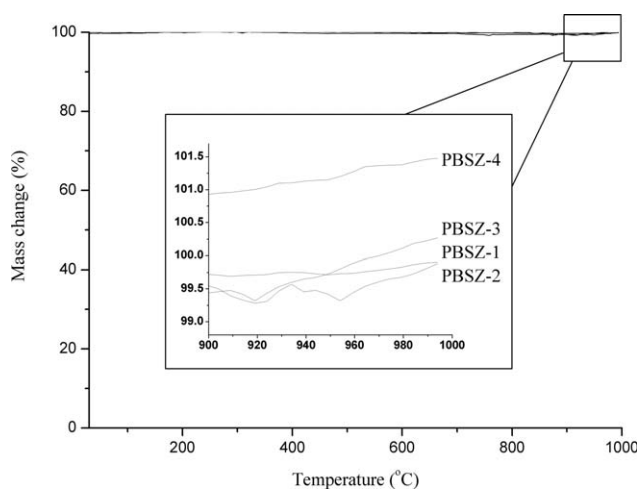


Figure 7 TGA curves of the ceramic obtained from **PBSZ-1C-4C** annealed under air at 1000°C.

TABLE II
Compositions of Ceramics PBSZ-1C, PBSZ-2C, PBSZ-3C, PBSZ-4C and Their Counterparts Annealed Under Air at 1000°C

Sample	Si%	B%	C%	N%	O%	Empirical formula ^a
PBSZ-1C	15.23	23.85	18.70	36.34	5.88	Si _{0.64} BC _{0.78} N _{1.53} O _{0.25}
PBSZ-1C air	14.77	23.49	19.96	35.56	6.22	Si _{0.63} BC _{0.85} N _{1.51} O _{0.26} (air)
PBSZ-2C	22.03	23.48	14.98	33.43	6.08	Si _{0.94} BC _{0.64} N _{1.42} O _{0.26}
PBSZ-2C air	23.23	23.21	14.62	32.73	6.21	Si _{1.00} BC _{0.63} N _{1.41} O _{0.27} (air)
PBSZ-3C	26.18	15.85	16.41	37.61	3.95	Si _{1.65} BC _{1.04} N _{2.38} O _{0.25}
PBSZ-3C air	27.98	15.23	16.19	36.39	4.21	Si _{1.84} BC _{1.06} N _{2.39} O _{0.27} (air)
PBSZ-4C	31.15	9.16	18.30	38.63	2.77	Si _{3.40} BC _{2.00} N _{4.22} O _{0.30}
PBSZ-4C air	30.46	9.48	17.69	38.91	3.46	Si _{3.21} BC _{1.87} N _{4.07} O _{0.36} (air)

^a Empirical formula are derived from EDX.

changes of **PBSZ-1C–4C** are very small under the experimental conditions. The weight losses of **PBSZ-1C**, **PBSZ-2C**, and **PBSZ-3C** at 1000°C are only 0.05%, 0.19%, and 0.27%, respectively. The mass gain of 1.5% was found for **PBSZ-4C** at 1000°C. These small differences are difficult to interpret because all data are in the range of experimental error. To get further insight into the oxidative stability of these ceramic materials, EDX analysis were performed and the results were summarized in Table II, together with that of untreated **PBSZ-1C–4C**, for comparison. No significant change was observed for the chemical composition between treated and untreated ceramic materials. The SEM images shown in Figure 8 suggest that the surface of the oxidized ceramics is smooth and pore-free, and similar as that of samples before treatment. The combination of the above

results suggests that the ceramic materials obtained from pyrolysis of the new precursors efficiently self-protect toward oxidation at 1000°C.

CONCLUSIONS

New polymeric precursors for Si–B–C–N ceramics were synthesized by co-ammonolysis of the mixture of dichloromethylsilane and 2,4,6-trichloroborazine. The ratio of Si/B in precursors was tunable by adjusting proportion of starting monomers. By pyrolysis of the new precursors in an inert atmosphere, Si–B–C–N ceramics were prepared. The investigation on phase transformation of pyrolytic residues indicates that the ratio of Si/B plays an important role in controlling the high temperature behavior of the precursor derived ceramics. The investigation of

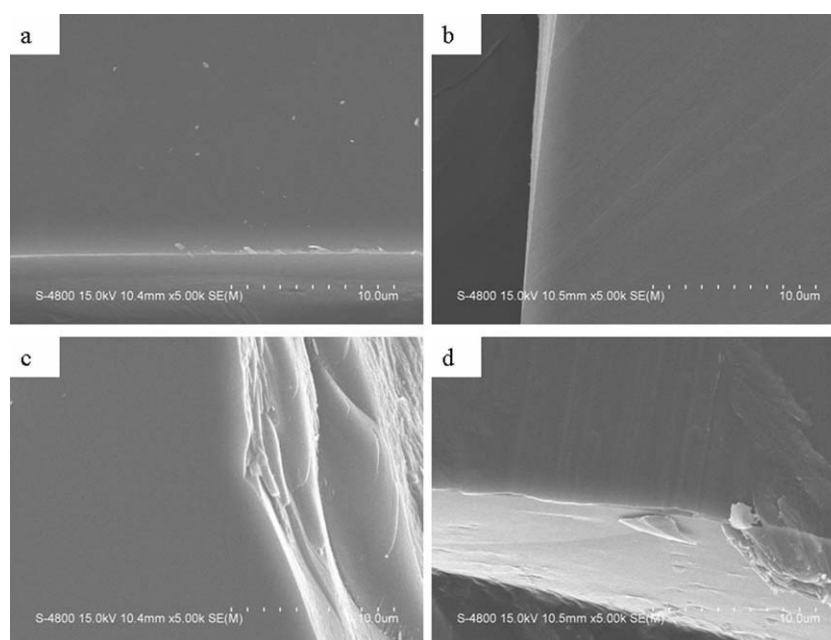


Figure 8 SEM images of the ceramic obtained from **PBSZ-1C–4C** after annealed under air at 1000°C: (a) **PBSZ-1C**, (b) **PBSZ-2C**, (c) **PBSZ-3C**, and (d) **PBSZ-4C**.

oxidation resistance indicates that the obtained ceramics efficiently self-protect under air over a temperature range of 30–1000°C.

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