

Synthesis of Polyborosilazane and Its Utilization as a Precursor to Boron Nitride

Zeng-Yong Chu, Chun-Xiang Feng, Yong-Cai Song, Xiao-Dong Li, Jia-Yu Xiao

Key Laboratory of New Ceramic Fibers and Composites, National University of Defense Technology, Changsha, 410073, People's Republic of China

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ABSTRACT: A new kind of polyborosilazane was synthesized from hexamethylcyclotrisilazane by exposure to boron trichloride. The pyrolysis of the precursor was carried out at 1250, 1600, and 1800°C in nitrogen for a dwelling time of 1 h. Characterizations were performed with Fourier transform infrared, X-ray photoelectron spectroscopy, thermogravimetric analysis, and XRD techniques, and the results showed that the boron content of the precursor increased as the exposure time increased, whereas the C/Si ratio re-

mained constant. Minor amounts of Si and C remained in residue pyrolyzed at 1250°C, but they were completely removed when their residue was further sintered at 1800°C. At that point, it only consisted of hexagonal BN crystals. Therefore, the polymer could be used as a precursor to BN in some special applications. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 105–109, 2004

Key words: pyrolysis; sintering; synthesis

INTRODUCTION

Precursor pyrolysis is a process by which suitable polymers with inorganic skeletons are converted into a wide variety of ceramics.^{1–10} The development of polycarbosilane (PCS)-derived SiC fibers (Nicalon, Nippon Carbon Co., Tokyo, Japan) marks a considerable breakthrough in this field. Recent progress in precursor synthesis has been focused not only on the improved selectivity, reduced cost, and production of phase-pure ceramics such as silicon carbide or silicon nitride but also on the evolution of multiple-component ceramics.^{3–5} For example, hetero elements such as N, Ti, Zr, B, and Al have been added to PCS precursors to make Si–C–N, Si–Ti–C, Si–Zr–C, Si–B–C, Si–Al–C, and Si–B–C–N ceramic fibers.^{6–8} The incorporation of these hetero elements can improve the thermal stability of SiC fibers more or less through sintering or the shifting of the decomposition temperature to a higher value.

Sacks et al.⁹ revealed that a small amount of boron content can sufficiently modify the high-temperature resistance of SiC fibers. However, the addition of boron to the fibers usually produces a reaction between polysilane and polyborazine (PBN), which is too active to be processed,¹⁰ or the curing of PCS fibers in an

atmosphere of NO₂/BCl₃, which causes a nonuniform distribution of boron atoms.^{11,12} Therefore, we explored a novel approach by simply mixing PCS with a boron-containing polymer to make a hybrid precursor.¹³

The new polymer should be soluble or meltable and compatible with PCS. On the basis of extensive research on the synthesis of polyborosilazanes (PBSNs) and PBNs,^{5,14–16} we synthesized a new processable PBSN from hexamethylcyclotrisilazane (HMCTS) by exposure to BCl₃. The synthesis is based on the idea that polysilazanes (or silazane oligomers) can be cured by BCl₃,^{10,17} and so BCl₃ can crosslink HMCTS and form a processable PBSN. The precursor was successfully blended into PCS to produce a Si–C–O–N–B fiber with much higher thermal stability.¹⁸

EXPERIMENTAL

Materials

Dimethyldichlorosilane (DMDCS) was purchased from Xinghuo Chemical Plant (Jiangxi, China) and purified by distillation. Xylene was dried via refluxing over sodium and distilled under a nitrogen atmosphere. High-purity gases (NH₃, 99.999%; N₂, 99.999%; Ar, 99.999%; and BCl₃, 99.9%) were purchased from Dalian Special Gas Co. (Dalian, China) and were used via flowing through a drying tower. The reactions were carried out in oven-dried glass equipment with flowing high-purity N₂ as the protecting gas.

Correspondence to: Z. Y. Chu (z.y.chu@163.net).

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TABLE I
Details of PBSN precursors

Sample	Exposure time (min)	M_n^a	Chemical formula ^b	Appearance
HMCTS	0	217 ^c	SiC ₂ NH ₇ ^c	Viscous, light yellow liquid
PBSN-1	10	360	SiC _{2.0} N _{0.8} B _{0.1} O _{0.2} H _x	Viscous, brown liquid
PBSN-2	20	680	SiC _{2.0} N _{0.9} B _{0.3} O _{0.2} H _x	Viscous, brown liquid
PBSN-3	30	950	SiC _{2.0} N _{0.8} B _{0.7} O _{0.3} H _x	White solid
PBSN-4	40	1510	SiC _{2.0} N _{0.8} B _{0.9} O _{0.4} H _x	White solid

M_n = number-average molecular weight.

^a Derived from GPC analysis.

^b Derived from XPS analysis with Si = 1.0.

^c In theoretical aspect.

Synthesis

HMCTS was synthesized through the ammonolysis of DMDCS according to the literature.¹⁹ Then, in a 250-mL, three-necked flask equipped with a reflux condenser, a dropping funnel, and a gas inlet tube, freshly distilled xylene (100 mL) and HMCTS (10 mL) were charged by syringe into a flask under N₂. The reaction mixture was refluxed, and a constant volume fraction of BCl₃ (20 vol %) in a flow of N₂ (80 mL/min) was added to the solution. The unreacted BCl₃ was ab-

sorbed by water at the end of the equipment. After a period of time, the solvent was removed by distillation under N₂, and a white solid (PBSN) was obtained after drying *in vacuo* with a molecular weight of approximately 1500.

Pyrolysis

The pyrolysis was carried out at 1250°C under N₂ in a tube furnace equipped with a controller and a quartz

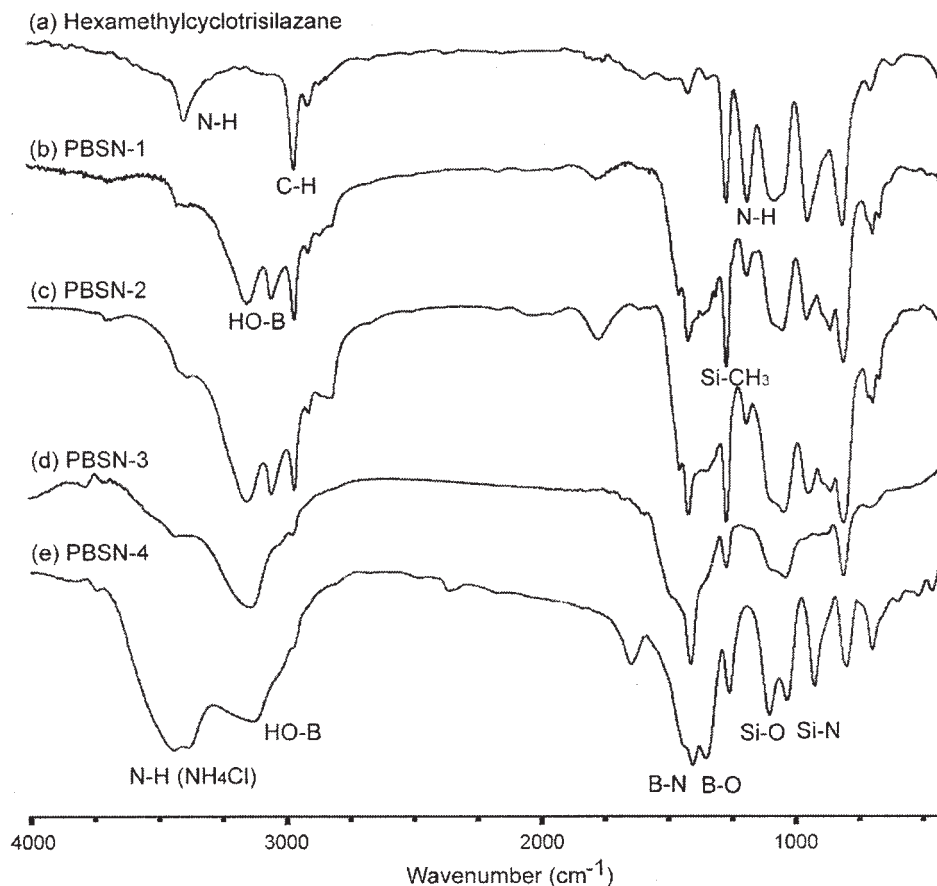
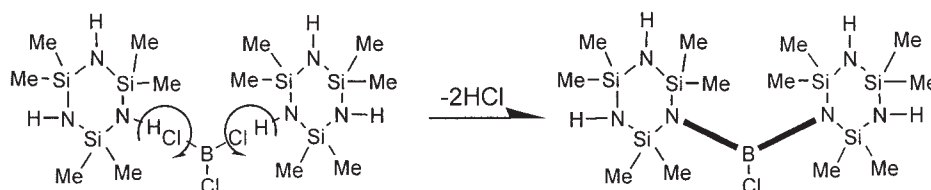


Figure 1 FTIR spectra of (a) HMCTS and (b–e) its reaction products with BCl₃.



Scheme 1 Reaction process between HMCTS and BCl_3 .

tube. Fused silica boats were used to contain the precursor in the tube. The heating rate was $100^\circ\text{C}/\text{h}$, and the holding time at 1250°C was 1 h. Further sintering up to 1600 and 1800°C was performed in a graphite furnace under an argon flow at a heating rate of $300^\circ\text{C}/\text{h}$ and for a holding time of 1 h at the target temperature.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a PerkinElmer 2000 IR spectrometer in the wave-number range of $4000\text{--}400\text{ cm}^{-1}$ with standard procedures. The molecular weight distributions were determined by gel permeation chromatography (GPC) with a Waters 244 analyzer, Milford, USA, *s*-Styragel columns calibrated with polystyrene standards, and tetrahydrofuran (THF) as a diluent at a flow rate of $0.5\text{ mL}/\text{min}$. X-ray photoelectron spectroscopy (XPS) was recorded with an FRR XPS spectrometer (Kyoto, Japan) with Al $K\alpha$ as the excitation source on a freshly fractured surface of PBSN. The pressure in the spectrometer was 10^{-9} Pa . The elemental contents were analyzed instrumentally at the National Key Laboratory of Powder Metallurgy of China. A thermogravimetric analysis (TGA) was obtained with a Netzsch STA 449C thermal balance (Tokyo, Japan) in a $40\text{ mL}/\text{min}$ nitrogen flow up to 1400°C at a heating rate of $10^\circ\text{C}/\text{min}$. Scanning electron microscopy (SEM) was conducted on a JEOL (Japan) JSM-6300 microscope (Tokyo, Japan). The samples were sputter-coated with a layer of gold to enhance their conductivity before observation.

RESULTS AND DISCUSSION

Synthesis and characterization of the precursors

Table I lists some typical PBSN precursors, prepared from HMCTS by exposure to BCl_3 for various times, and their molecular weights and chemical formulas. FTIR spectra of the precursors are shown in Figure 1.

A B—N bond can be formed between B—Cl and N—H bonds by the elimination of hydrogen chloride.¹⁷ Therefore, as shown in Figure 1, the N—H absorption (3400 and 1180 cm^{-1}) decreases sharply

with increasing exposure time. Meanwhile, absorptions corresponding to B—O—H ($3050\text{--}3200\text{ cm}^{-1}$), B—O (1350 cm^{-1}), and B—N bonds (1450 cm^{-1}) emerge and become stronger with time. The reaction between HMCTS and BCl_3 is shown in Scheme 1. Two cyclic HMCTSs are crosslinked by two B—N bonds, and a great increase in the molecular weight is obtained. However, the remaining unreacted B—Cl bonds may react with water and form B—OH bonds, as confirmed by FTIR. Also, PBN may be formed because of the reaction between NH_3 and BCl_3 .¹⁶ In fact, NH_3 cannot be absolutely avoided in HMCTS, and a white solid (NH_4Cl) is formed in the reflux condenser, a result of the reaction between NH_3 and HCl. After 40 min of exposure, the molecular weight of the precursor (PBSN-4) increases to 1510, and it is still soluble in common solvents, such as xylene, toluene, THF, and hexane.

The XPS profile of PBSN-4 is shown in Figure 2. In addition to the peaks (Si, C, N, and O) assigned to HMCTS,¹⁴ the PBSN precursor displays an additional B peak at $192\text{--}194\text{ eV}$, evidence of the presence of B.⁵ Based on element-sensitive ratios, a chemical formula such as $\text{Si}_{2.0}\text{N}_{0.8}\text{B}_{0.9}\text{O}_{0.4}\text{H}_x$ can be proposed for PBSN-4; the hydrogen content could not be identified because of the limitations of the instrument. Through a comparison of the chemical formulas of the synthesized precursors shown in Table I, a constant C/Si ratio of 2.0 can be found. This is in good agreement with that of HMCTS, and this indicates that the Si— CH_3 group is very stable in this synthesis reaction. However, the contents of Si and C decrease as the B content increases.

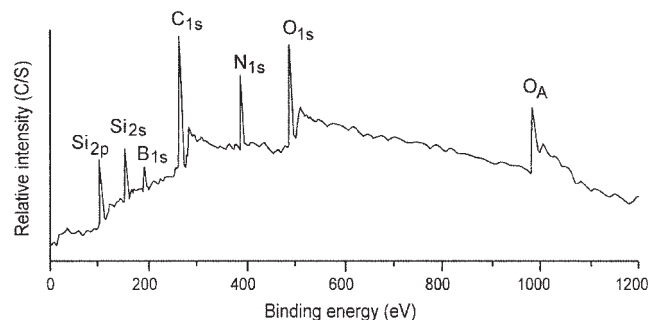


Figure 2 XPS wide-scan profile of PBSN-4.

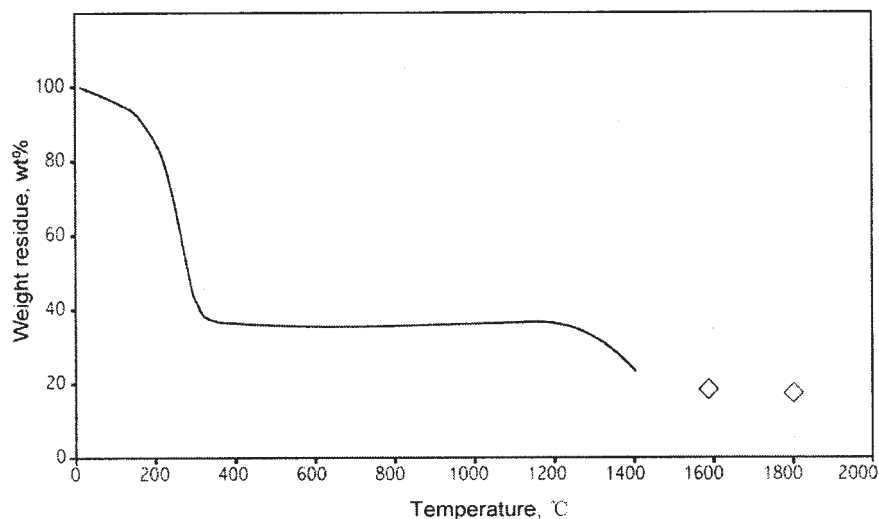


Figure 3 TGA curve of PBSN-4.

Pyrolysis of the precursor

The thermal pyrolysis behavior of PBSN-4 was studied with TGA, as shown in Figure 3. Unlike the weight loss of polysilazanes, which mainly occurs in the range of 300–700°C,^{14–16} the weight loss of PBSN-4 mainly occurs below 300°C. This behavior is somewhat similar to that of PBNs, which are converted into ceramics at about 300°C.^{16,20} With additional information on the composition of the residue pyrolyzed at 1250°C (i.e., 18.5 wt % for Si and 15.6 wt % for C), we can conclude that most Si and C are lost below 300°C in the form of silanes or silazanes.^{14,15} A slight weight loss up to 1200°C can be attributed to the decomposition of $\text{SiC}_x\text{O}_y\text{N}_z$ multiphases.^{3,4}

As shown in Figure 4, FTIR spectra present more information about further heat-treated ceramics. Absorption peaks attributable to Si—O—Si (1080 cm^{-1}) and Si—N—Si (925 cm^{-1}) asymmetric stretching can be both detected after pyrolysis at 1250 and 1600°C, whereas they are not detectable any more after treatment at 1800°C. The final ceramic only shows two strong peaks centered at 1370 and 810 cm^{-1} , which are typical absorption peaks of BN.^{16,20} Composition analysis also confirms that the produced ceramic contains only B and N, whereas the others are very few and can be ignored.

XRD patterns of the pyrolyzed residue of PBSN-4 are shown in Figure 5, which indicates that the residue crystallizes quickly from about 1600 to 1800°C. The diffraction of the final ceramic results in a very sharp BN(002) peak and two weak peaks corresponding to BN(101) and BN(102), which clearly indicate the presence of hexagonal BN crystals.^{16,20} Therefore, it can be inferred from the aforementioned results that the final

ceramic after sintering at 1800°C is only composed of hexagonal BN crystals. However, as shown by the SEM image in Figure 6, the BN ceramic has porosity as high as 51.2 vol % and can hardly be used as a structural ceramic directly.

CONCLUSIONS

A new kind of PBSN has been synthesized from HMCTS by exposure to BCl_3 . The pyrolysis of the precursor

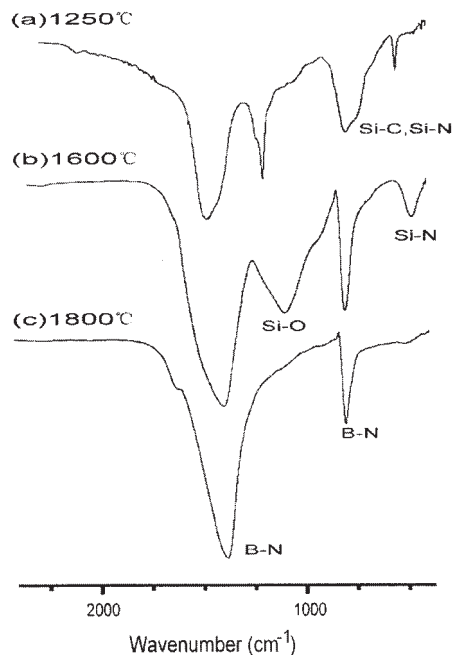


Figure 4 FTIR spectra of PBSN-4 pyrolyzed at (a) 1250, (b) 1600, and (c) 1800°C.

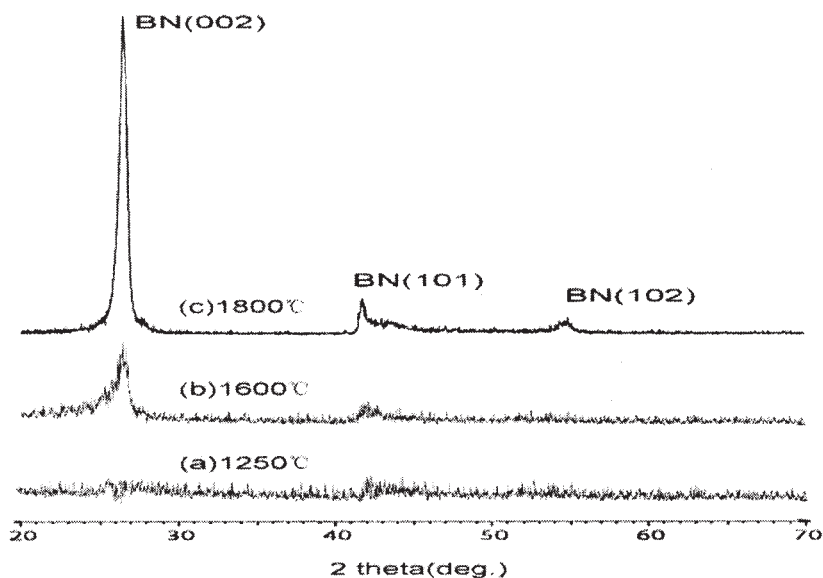


Figure 5 XRD patterns of PBSN-4 pyrolyzed at (a) 1250, (b) 1600, and (c) 1800°C.

sor under an inert atmosphere indicates that a pure hexagonal BN crystalline ceramic can be obtained after sintering at 1800°C. The polymer can be used as a precursor to BN in some special applications in view of our own work in the preparation of Si-C-O-N-B fibers. The advantage of using this polymer lies in its good handling and stability in comparison with intractable PBNs, but a disadvantage lies in its limited ceramic yield, which results in weakness and high porosity of the final ceramic.

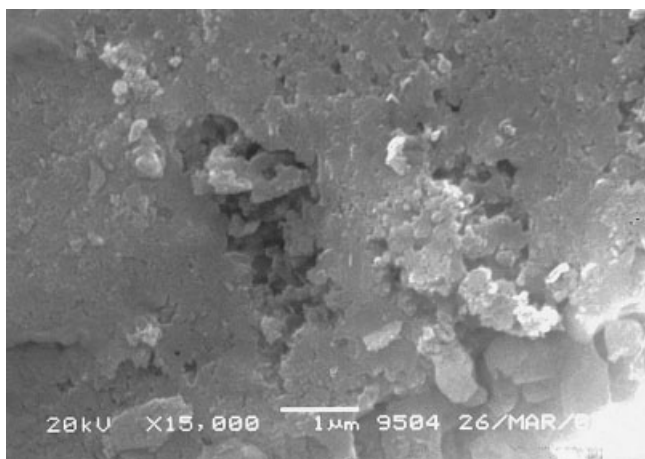


Figure 6 SEM image of PBSN-4 pyrolyzed at 1800°C.

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