

# Preceramic Organoboron–Silicon Polymers\*

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## SYNOPSIS

Several boron-containing organosilicon polymers were synthesized from a sodium-coupling reaction of silicon and boron halides with and without alkyl halide in hydrocarbon solvents. The B–Si preceramic polymers were characterized using techniques such as IR, UV, and NMR spectrometry, gel permeation chromatography, elemental analysis, molecular weight measurement, and thermal analyses (TGA, DSC, DTA, and TMA). The chemical structures of the preceramic polymers were postulated based on the analytical results. Black ceramic materials were obtained from the precursor polymers upon thermal degradation at temperatures above 1000°C in an inert atmosphere. The precursor polymers had a ceramic yield of up to 70%. Thermogravimetric analysis of the ceramic material in air at a flow rate of 100 mL/min showed it was stable up to 1000°C with little weight gain or loss. Several methods were used to characterize the ceramic materials: XRD, solid NMR, high-temperature DTA, elemental analysis, and acid digestion. The analyses indicated that the ceramic materials comprised a mixture of silicon carbide (SiC), silicon borides (SiB<sub>4</sub>, SiB<sub>6</sub>), and amorphous Si–B–C ceramics, with small amounts of silica and free silicon.

## INTRODUCTION

Non-oxide ceramics such as silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), silicon borides (SiB<sub>4</sub>, SiB<sub>6</sub>), and boron nitride (BN) offer high thermal stability, high oxidative stability, a high degree of hardness, and a wide range of electronic properties. However, fabrication of these ceramics into desired shapes is very difficult and requires sintering their powders at high temperatures (> 1500°C), often under high pressure and in an inert environment. Another technique currently being commercialized to make ceramics is chemical vapor deposition/infiltration (CVD/CVI), where one deposits atomic or molecular species generated by pyrolysis of low-molecular-weight organic molecules. The CVD/CVI process is slow, equipment- and energy-intensive, and has many basic limitations, particularly in the fabrication of complex structures.

Making high-temperature, non-oxide ceramics by the pyrolysis of organometallic polymers or other precursors has recently begun to attract considerable attention. Such processing shows great promise for producing improved ceramics and has expanded the applications for new ceramics. Polymers containing elements such as Si, C, N, or B can be pyrolyzed under certain conditions to produce high-temperature ceramics of SiC, Si<sub>3</sub>N<sub>4</sub>, B<sub>4</sub>C, SiB<sub>x</sub>, C–N–B, and BN.<sup>1–3</sup>

Silicon carbide was the first successful ceramic material made by the polymer–pyrolysis route.<sup>4</sup> Recently, high-strength silicon nitride fibers were made from polymeric precursors upon pyrolysis.<sup>5–7</sup> Despite these successes, the preparation of other non-oxide ceramics by polymer pyrolysis is an area which remains to be explored. One of the potential advantages of polymer processing is the formation of parts without the need for additives or binding agents.

Our objective was to synthesize polymers with boron–silicon bonds in their backbones (Si–B polymers or Si–C–B polymers). These polymers yield non-oxide, high-temperature silicon borides, silicon carbide, boron carbide, and/or Si–B–C ceramics upon pyrolysis.<sup>8,9</sup> A ceramic material containing

\* Part of this work was presented at American Chemical Society meeting, Anaheim, CA, September 1986.

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both boron and silicon should be a thermo-oxidatively stable material. At elevated temperatures ( $> 1000^{\circ}\text{C}$ ) in an oxidative environment boron would be oxidized to boria and silicon would be oxidized to silica, forming a protective borosilicate glass on the surface to prevent further oxidation of the ceramic.

Only a few examples of materials with consecutive boron–boron bonds have been described in the literature. Low-molecular-weight polymeric boron–boron compounds have been reported from the reaction of alkyl or aryl boron dihalide with sodium.<sup>10</sup> A few examples of simple molecules with Si–B bonds were reported,<sup>11</sup> but no organic polymers with Si–B bonds can be found in the literature other than those previously reported by the authors.

We are reporting the synthesis of organoboron–silicon polymers that have ceramic yields of up to 70% when the ceramics are generated by the pyrolysis of the polymers.

## EXPERIMENTAL

### Materials

Boron trichloride was obtained from Matheson Gas Products. Methyl boron dibromide was from Alpha Products. All other chemicals were from Aldrich Chemical Co. Octane and xylenes (mixed) were distilled over sodium in a nitrogen atmosphere before use. Dimethyldichlorosilane and vinylmethyldichlorosilane were freshly distilled before use. Methyl iodide was distilled and stored in a nitrogen atmosphere.

### Characterization

Infrared spectra were recorded on a Nicolet MX-1 Fourier transform infrared spectrometer (FTIR). A Varian EM360 NMR spectrometer was used for proton NMR spectra. Magic-angle spinning-solid (MASS) NMR was performed by Spectral Data Services, Champaign, IL. A Du Pont 1090 thermal analyzer was used for thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and thermal mechanical analysis (TMA). Molecular weights of the polymers were measured by the vapor–pressure–osmometry method in chloroform, using Wescan Molecular Apparatus Model 233-200. Elemental analyses were performed by Huffman Laboratories, Wheat Ridge, CO, and Galbraith Laboratories, Knoxville, TN. Gel permeation chro-

matography (GPC) work was performed by Modchrom, Inc., Mentor, OH.

### Syntheses

The synthesis and isolation of the polymers were conducted in a dry/inert atmosphere because the starting materials and the boron-containing silicon polymers were sensitive to oxygen and moisture.

#### *Synthesis of Polymer I (reaction between boron trichloride and dimethyldichlorosilane)*

Sodium, 44 g (1.91 mol), and 400 mL of dry xylenes or octane were placed in a 1000 mL, 3-neck, round-bottom flask equipped with a magnetic stirrer, low-temperature ( $-30^{\circ}\text{C}$ ) condenser, thermometer, dropping funnel, and nitrogen gas inlet. Nitrogen gas flowed through the system for at least 1 h, and a slight positive pressure of nitrogen was maintained during the synthesis. The flask was heated to  $125\text{--}138^{\circ}\text{C}$ . One hundred milliliters of xylenes or octane, 55.5 mL of dimethyldichlorosilane (0.45 mol), and 26.1 mL of boron trichloride (0.3 mol) were placed into the dropping funnel. The liquid in the dropping funnel was added to the heated flask dropwise over a period of 2–3 days at above  $120^{\circ}\text{C}$ . The reaction mixture was refluxed for 22 h. Five milliliters of methyl iodide or trimethylchlorosilane were added to the flask and continued to reflux for another 2–20 h. After cooling, the reaction mixture was filtered in an inert atmosphere. The solvent of the filtrate was distilled off at  $125\text{--}140^{\circ}\text{C}$  (vacuum was applied at the end) to yield a solid polymer I (50–60% yield).

#### *Synthesis of Polymer II (reaction between methyl boron dibromide and dimethyldichlorosilane)*

Thirteen grams of sodium (0.565 mol) and 100 mL of xylenes or octane were placed in a 500 mL, 3-neck flask equipped with a condenser, nitrogen-inlet tube, magnetic stirrer, and dropping funnel. The flask was heated to the reflux temperature of the solvent. Over a period of 4–8 h, 17.4 g of dimethyldichlorosilane (0.135 mol) and 25 g of methyl boron dibromide (0.135 mol) in 50 mL of xylenes or octane were added dropwise to the reaction flask through the dropping funnel. The reaction mixture was refluxed for 20 h, and a purple–blue precipitate was formed. One-half milliliter of methyl iodide was added to the flask, and the reflux was continued for 2 h. After cooling, the reaction product was filtered. The brown filtrate was distilled under reduced pressure to remove the solvent. A gummy polymer II was collected (50–61% yield).

**Synthesis of Polymer III (reaction of boron trichloride, methyl iodide, and dimethyldichlorosilane)**

Sodium, 44 g (1.91 mol), and 400 mL of xylenes or octane were placed in a 1000 mL, 3-neck, round-bottom flask equipped with a magnetic stirrer, low-temperature circulated-liquid condenser, thermometer, dropping funnel, and nitrogen gas inlet. The flask was heated to 120–138°C. One hundred milliliters of xylenes or octane, 37 mL of dimethyldichlorosilane (0.3 mol), 13.8 mL of methyl iodide (0.3 mol), and 26.1 mL of boron trichloride (0.3 mol) were placed into the dropping funnel. The liquid in the dropping funnel was added to the heated flask dropwise over a period of 8–20 h at or above 120°C. The reaction mixture was refluxed for another 24 h. After cooling, the reaction mixture was filtered. The filtrate was evaporated until dry (vacuum was applied to remove the solvent at the end) to yield a solid polymer III (45–55% yield). Polymer III was soluble in toluene, chloroform, xylenes, alkane, THF, etc.

**Synthesis of Polymer III-0.5 (reaction of boron trichloride, methyl iodide, and dimethyldichlorosilane)**

Polymer III-0.5 was synthesized similarly as above by reacting sodium (52 g, 2.26 mol) in octane with dimethyldichlorosilane (0.5 mol), methyl iodide (0.25 mol), and boron trichloride (0.25 mol). A solid polymer III-0.5 with a 45–50% yield was isolated.

**Synthesis of Polymer IV (reaction of boron trichloride, methyl iodide, vinyl methyl dichlorosilane, and dimethyldichlorosilane)**

Sodium, 72.5 g (3.15 mol), and 900 mL of dry octane were placed in a 2000 mL, 3-neck, round-bottom flask equipped with a magnetic stirrer, low-temperature circulated-liquid condenser, thermometer, dropping funnel, and nitrogen gas inlet. The flask was heated to 125°C. The material in the dropping funnel [180 mL of octane, 54.6 mL of dimethyldichlorosilane (0.45 mol), 6.5 mL of vinyl methyl dichlorosilane (0.05 mol), 31 mL of methyl iodide (0.5 mol), and 43 mL of boron trichloride (0.5 mol)] was added to the heated flask dropwise over a period of 2 days at or above 122°C. The reaction mixture was refluxed overnight. Trimethylchlorosilane (5 mL) was added to terminate the reaction. After re-

flux for another day, the reaction mixture was cooled and the solution was filtered in an inert atmosphere. The filtrate was evaporated until dry to give a solid polymer IV with a 45–55% yield.

**Synthesis of Polymer IV-0.5 (reaction of boron trichloride, methyl iodide, vinylmethyldichlorosilane, and dimethyldichlorosilane)**

The procedure was the same as above, except less sodium (52 g), methyl iodide (0.25 mol), and boron trichloride (0.25 mol) were used. The yield of polymer IV-0.5 was 45–50%.

**Pyrolysis**

The boron-silicon polymer was pyrolyzed in a quartz tube in an inert atmosphere and heated at 10–20°C/min to 1100°C and was held at 1100°C for 1 h.

**Acid Digestion**

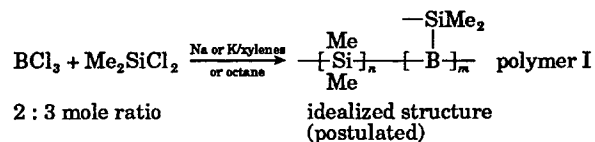
The ceramic product from the pyrolysis of each boron-silicon polymer was digested in a platinum crucible with hydrofluoric acid and heated until all the acid evaporated. The sample weight loss was the amount of silica present. The sample was then digested with a 50 : 50 mixture of nitric acid and hydrofluoric acid at the boiling point of the acid mixture. After the acid evaporated and the sample was washed with water, the weight loss represented the amount of silicon borides and silicon-boron-carbon compounds present in the sample.

**RESULTS AND DISCUSSION**

**Polymer Synthesis**

To obtain high ceramic yields, this effort concentrated on the synthesis of polymer precursors with small substituent groups. Four Si-B polymers, based on the sodium-coupling reaction of methyl boron dibromide or boron trichloride and dimethyldichlorosilane, vinyl methyl dichlorosilane with or without methyl iodide, were studied.

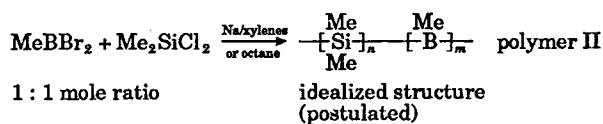
1. Polymer I, a crosslinked polymer, was synthesized from the sodium-coupling reaction of boron trichloride and dimethyldichlorosilane in xylenes or octane.



where  $n, m \geq 1$

Different mole ratios of boron trichloride and dimethyldichlorosilane yield different polymers with various values for  $n$  and  $m$ . The yield of the soluble polymer I was 60% when xylenes was used as the solvent and 40–50% when octane was used as the solvent.

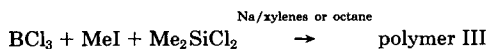
2. Polymer II, a methyl-containing boron–silicon polymer, was synthesized from the sodium-coupling reaction between methyl boron dibromide and dimethyldichlorosilane in xylenes or octane.



where  $n, m, \geq 1$

The soluble polymer II was isolated, with a yield of 50–60%.

3. Polymer III was similar to polymer II. Since methyl boron dibromide was not available in large quantities, a reaction using methyl iodide, boron trichloride, and dimethyldichlorosilane as starting materials was carried out in Na/xylenes or octane to synthesize a partially crosslinked polymer III. An equimolar ratio of the starting materials was used in the synthesis of polymer III. Polymers could also be synthesized from different molar ratios of the starting materials. For example, polymer III-0.5 was synthesized in octane by using 1 mol of silane and 0.5 mol of boron trichloride.



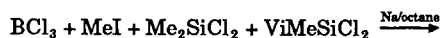
1 : 1 : 1 mole ratio

or 0.5 : 0.5 : 1 mole ratio to give polymer III-0.5

The chemical structure of polymer III is similar to that of polymer II. For polymer III-0.5,  $n = 2m$ ,  $m \geq 1$ . The major polymeric fractions were soluble in the organic solvents, and the yield of the polymer synthesized in xylenes was 10% higher than those synthesized in octane.

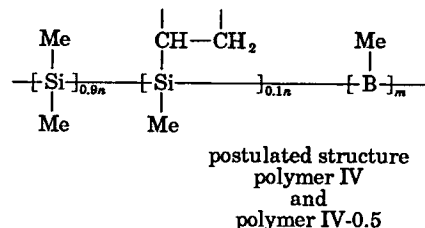
4. Polymer IV, a vinyl modification of polymer III, was synthesized from the sodium-coupling reaction of methyl iodide, boron trichloride, dimethyldichlorosilane, and vinylmethyldichlorosilane in octane. It has been found that an addition reaction takes place over the double bond, and no vinyl group is present in the polymer.

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1 : 1 : 0.9 : 0.1 mole ratio

0.5 : 0.5 : 0.9 : 0.1 mole ratio



$n = m$  or  $n = 2m$  for polymers IV and IV-0.5, respectively. The yield of the octane-soluble polymer was 40–50%.

### Polymer Characterization

The polymers prepared with xylene as a solvent contained small amounts of xylenes which could not be removed by vacuum distillation at temperatures up to the boiling point of xylenes (140°C). Although the xylenes could have been removed at temperatures above 200°C, the higher temperatures would also have caused the polymer to begin to decompose. Infrared spectra of the polymers synthesized in xylenes showed small xylene absorption peaks (aromatic CH band and aromatic carbon absorption band). For the polymers prepared with octane, the solvent was removable by vacuum distillation at 130–140°C.

The infrared spectra of polymers I–IV are similar. A typical infrared spectrum of polymer I (synthesized in octane) is shown in Figure 1. The absorption at 2900–3000  $\text{cm}^{-1}$  is the aliphatic C–H band. The small bands appearing at 2100 and 2500  $\text{cm}^{-1}$  are Si–H and B–H absorption bands, respectively. The intensities of the 2100 and 2500  $\text{cm}^{-1}$  absorptions are not strong, indicating that the polymer contained only small segments of Si–H and B–H. The intensities of the Si–H and B–H absorption bands for polymers II–IV are less than those for polymer I. According to theoretical calculations, the Si–B band should be around 650  $\text{cm}^{-1}$ .<sup>12</sup> One of the three absorption peaks between 620–690  $\text{cm}^{-1}$  may be attributed to an Si–B band. A new absorption band at around 1315  $\text{cm}^{-1}$  for all of the polymers is assigned to B–C stretching. The small, broad absorp-

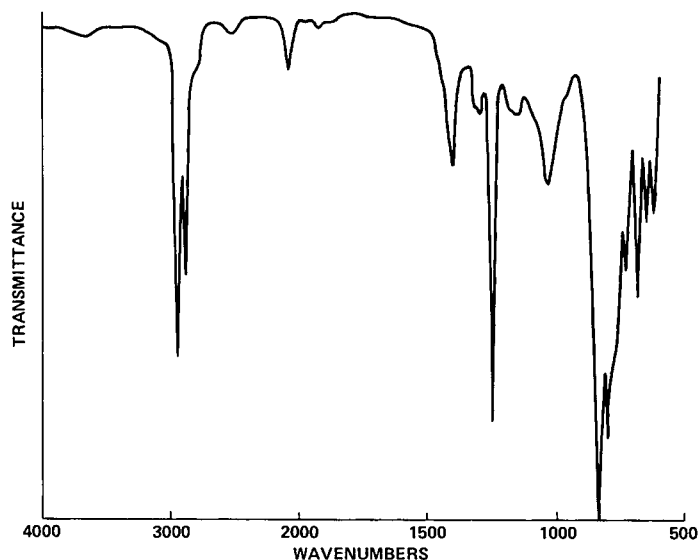


Figure 1 Infrared spectrum of polymer I.

tion band at around 1040 cm<sup>-1</sup> is probably due to the absorption of the Si-O-Si and Si-CH<sub>2</sub>-Si and/or Si-CH<sub>2</sub>-B bands. Theoretical calculations indicated that weak Si-Si and B-B IR absorption bands should have been present at 425 and 960 cm<sup>-1</sup>, respectively.<sup>12</sup> No IR absorption peaks appeared at the latter two frequencies, an indication that little Si-Si or B-B structure was present in the polymers.

Polydialkylsilanes have a UV absorption at 300-350 nm.<sup>13</sup> The UV spectra of polymers I-III show an absorption tail and a small shoulder at 280 nm,

with no UV absorption peak in the 300-350 nm region. These results suggest that the polymers do not have long, consecutive Si-Si bonds, but may have alternating boron and silicon structures, block random structures with short Si-Si and B-B blocks, or rearranged structures with -Si-C-Si- or -Si-C-B- chains in their backbones.

All the boron-containing silicon polymers are sensitive to oxygen and moisture. Figure 2 shows the infrared spectra of polymer III-0.5 before and after exposure to air. After the polymer sample was

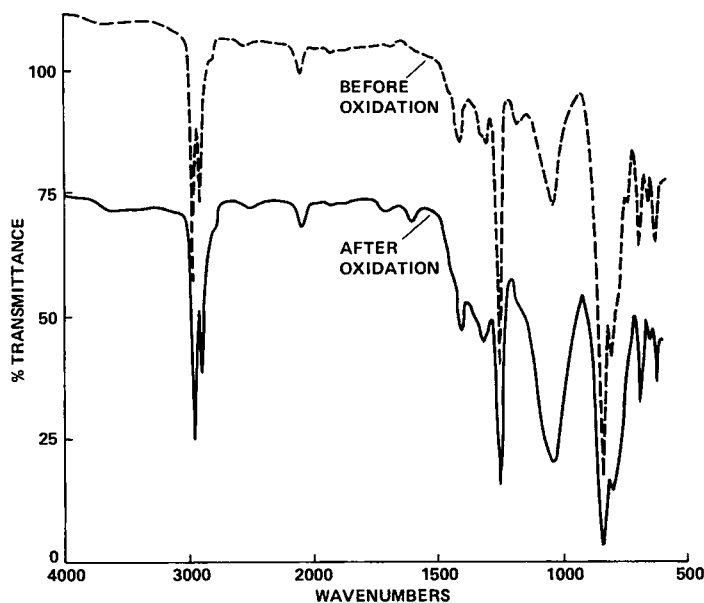


Figure 2 Infrared spectra of polymer III-0.5 before and after oxidation.

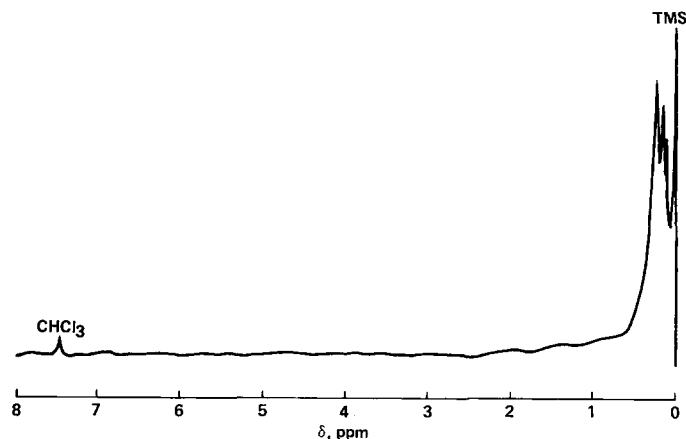


Figure 3 NMR spectrum of polymer IV.

exposed to air/moisture, the intensity of the band at  $1040\text{ cm}^{-1}$  increased to form a broad peak at  $1020\text{--}1080\text{ cm}^{-1}$  due to the formation of an Si-O-Si structure. After oxidation, the absorption band at  $1150\text{ cm}^{-1}$  disappeared, and the B-O absorption band at  $1320\text{ cm}^{-1}$  increased. The intensity of the  $1040\text{ cm}^{-1}$  band was related to the extent of oxidation. After oxidation, the intensities of the Si-H and B-H decreased slightly, and a broad OH band appeared at  $3300\text{ cm}^{-1}$ . A new band also appeared at  $1600\text{ cm}^{-1}$  and was not assigned.

The infrared spectra of polymer IV and polymer IV-0.5 are similar to the IR spectrum of polymer III with no vinyl peak. Since polymers IV and IV-0.5 were synthesized using vinyl methyl dichlorosilane as one of the starting materials, the absence of a vinyl peak indicates that the vinyl double bond reacted during the polymerization process.

The proton NMR spectra of polymers I-IV showed a weak, broad peak at around 0.2 ppm, indicating methyl or methylene groups attached to silicon and boron. A small amount of xylene was

Table I Elemental Analysis of Boron-Containing Silicon Polymers\*

Sample	% of Element						Mole Ratios of Elements, C : H : B : Si
	C	H	B <sup>b</sup>	Si <sup>b</sup>	Cl/Br	O	
<b>Polymer I</b>							
Theoretical value	36.74	9.18	11.22	42.86	0	0	2 : 6 : 0.67 : 1
Found	35.44	7.77	8.99	42.29	0.58	3.26 <sup>c</sup>	1.96 : 5.14 : 0.54 : 1
<b>Polymer II</b>							
Theoretical value	42.86	10.71	13.10	33.33			3 : 9 : 1 : 1
Found	42.50	7.63	11.10	30.40	< 0.3	NA	3.26 : 7.03 : 0.93 : 1
<b>Polymer III</b>							
Theoretical value	42.86	10.71	13.10	33.33			3 : 9 : 1 : 1
Found	44.87	8.70	12.99	33.31	0.31	3.55 <sup>c</sup>	3.14 : 7.31 : 0.99 : 1
<b>Polymer III-0.5</b>							
Theoretical value	42.25	10.56	7.75	39.44			2.5 : 7.5 : 0.5 : 1
Found	38.72	8.26	8.23	37.72	0.01	2.94 <sup>c</sup>	2.39 : 6.13 : 0.56 : 1
<b>Polymer IV</b>							
Theoretical value	43.50	10.88	12.87	32.75			3.1 : 9.3 : 1 : 1
Found	39.76	7.95	14.00	33.01	0.01	3.11 <sup>c</sup>	2.81 : 6.74 : 1.08 : 1
<b>Polymer IV-0.5</b>							
Theoretical value	43.03	10.76	7.59	38.62			2.6 : 7.8 : 0.5 : 1
Found	42.28	8.98	7.66	38.02	0.07	4.02 <sup>c</sup>	2.59 : 6.61 : 0.51 : 1

\* The theoretical values were calculated based on the amounts of starting material used.

<sup>b</sup> Polymer was dissolved in *o*-xylene and analyzed by ICP.

<sup>c</sup> Oxygen value was measured by neutron-activation method.

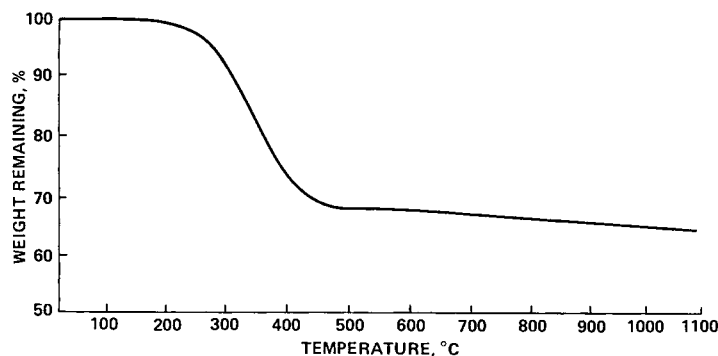


Figure 4 Thermogravimetric analysis of polymer I.

detected from polymers I–III by NMR when the polymers were synthesized in xylenes. Since the polymerization conditions are highly acidic, in the Lewis acid sense, and provide conditions similar to those in Friedel–Crafts reaction, the broad peak of aromatic protons suggests that xylenes are probably incorporated into the polymer structure. When the polymers were synthesized in octane and after vacuum distillation to remove volatile materials, no octane peak could be detected in the NMR spectra. Again, no olefinic proton could be detected in the proton NMR of polymer IV (see Fig. 3).  $^{13}\text{C}$ -NMR spectra of polymers I and II confirmed the presence of methyl carbon at 2.08 ppm and methylene carbon at 21.26 ppm. The  $^{29}\text{Si}$ -NMR spectrum of polymer I showed several complicated peaks, indicating that different types of silicon were present in the polymer.  $^{11}\text{B}$ -NMR spectra of polymer I and II showed two major peaks at 11.4 and 1.36 ppm, corresponding to at least two kinds of boron that were present in the polymer.

Elemental analyses of boron-containing silicon polymers were difficult using conventional wet-analysis techniques to get a good material balance. The elemental analysis data for polymers synthesized in octane are shown in Table I. The measured carbon contents for polymers I–IV were somewhat lower than expected, except for polymer III. Also, the measured hydrogen contents of all of the polymers were lower than the calculated values based on the expected structures or the amounts of the starting materials used. The lower hydrogen contents suggest that perhaps some methyl groups were rearranged into methylene groups, thereby eliminating some hydrogen. When the polymer samples were dissolved in organic solvent and analyzed directly by inductively coupled plasma (ICP), satisfactory results were obtained for the boron and silicon contents. These agreed with the expected re-

sults as shown in Table I. Although the measured carbon and hydrogen contents were lower than expected, the total contents of boron, silicon, carbon, and hydrogen were above 95%, indicating that the polymer samples had low oxygen contents. The oxygen contents of the polymers could be measured accurately by the neutron activation method, and it was found that the oxygen contents (Table I) were 3–4%.

Various thermal analyses of the synthesized polymers were performed. Thermogravimetric analyses (TGA) of the polymers showed that the decomposition temperatures of the materials commenced at about 200–300°C. A typical TGA curve of polymer I is shown in Figure 4. The ceramic yield at > 1000°C depends on the silicon and boron content of the polymer: the higher the silicon and boron content, the higher the ceramic yield. Ceramic yields of 56–70% were observed for various polymers, as shown in Table II. All of the ceramic products were stable in air, with less than a 2% weight gain at 1000°C for 1 h. In an inert environment the ceramic material showed a weight loss of less than 2% after 1 h at 1000°C. Polymer I, prepared from a trifunctional boron compound (boron trichloride) and a difunctional silane compound (dimethyldichlorosilane), was the most crosslinked or branched polymer. Polymer III may have had more branching than polymer II. The ceramic yields of the polymers were in the following order: polymer I > polymer III > polymer II > polymer IV.

Differential scanning calorimetry (DSC) curves of polymers I, II, III, and IV showed exothermic peaks at above 220°C because of the crosslinking reaction. In each case, after the sample was heated at 250°C for 15 min in nitrogen, the exothermic peak was reduced, and because of the crosslinking reaction, the sample became insoluble in organic solvents.

**Table II Ceramic Yield from Silicon-Boron Polymers**

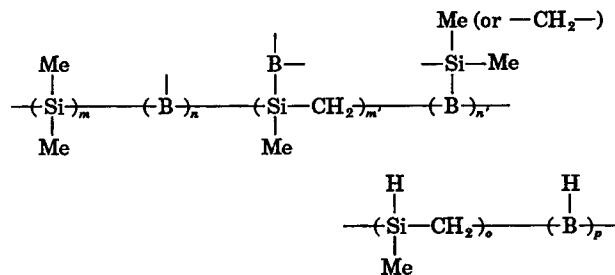
Polymer	Theoretical Ceramic Yield SiC + Si-C-B, %	Found, %
I	72.4	64-70
II and III	60.7	57-62
IV	60	56-60

Thermal mechanical analysis (TMA) was used to determine the softening points or melting points of the polymers. The data are shown in Table III. The polymers containing less boron (polymers III-0.5 and IV-0.5) softened or melted at lower temperatures than the corresponding polymers containing more boron (polymers III and IV). The most cross-linked, polymer I, showed a higher softening point.

The molecular weights of all the synthesized polymers were determined by vapor-pressure osmometry (VPO) in chloroform at 40°C. The molecular weights of the polymers were in the range of 800-1500. Since the molecular weights of the polymers were measured in air, oxidation of the polymers probably occurred. The gel permeation chromatography (GPC) of polymer I was measured using THF as the solvent and using polystyrene as the standard. The GPC chromatograms showed a broad peak with  $M_n = 785$ . The number average molecular weight ( $M_n$ ) of polymer I determined by GPC was smaller than the average molecular weight (1400) determined by VPO in chloroform. The low molecular weights of the polymers indicated that the extents of the reactions were limited, or cyclic structures could have been formed.

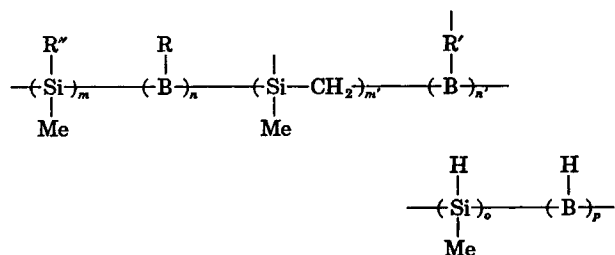
The molecular weight distributions of polymers II and III were also measured by GPC using Modchrom GPC 10X3A + 500A columns and THF as the solvent. The GPC curves all showed one broad peak for the polymers. The average molecular weights were  $M_n = 600$  and  $M_w = 850$  for polymer II, and  $M_n = 700$  and  $M_w = 960$  for polymer III.

Based on the analytical data and literature,<sup>13,14</sup> the chemical structures of the polymers may be postulated. Infrared spectra of the samples suggest the presence of small amounts of Si-H and B-H in the polymers. Infrared and NMR spectra and elemental analyses of the samples suggest the presence of methylene groups. Ultraviolet spectra of the samples indicate the lack of long consecutive Si-Si bonds. The following branched structure is postulated for polymer I:

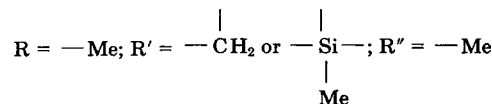


where  $m, n, m', n', o, p > 0$  and  $< 10$ ; and  $m, n, m', n' \gg o, p$

Polymers II, III, and IV may have the following structures:

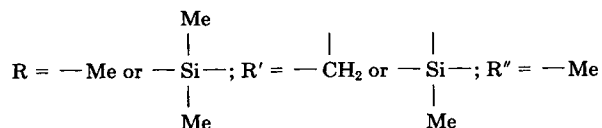


For polymer II:



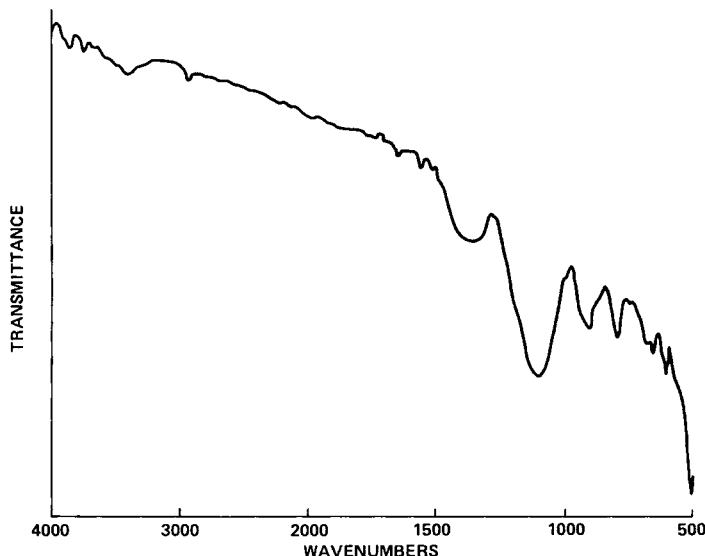
$m, n, m', n', o, p > 0$  and  $< 10$ ; and  $m, n, m', n' \gg o, p$

For polymer III,

**Table III Thermomechanical Analysis of Polymeric Precursors**

Sample	Softening Point, °C
Polymer I	100-180
Polymer II	< 20
Polymer III	70-130
Polymer III-0.5	50-100
Polymer IV	70-120
Polymer IV-0.5	45-90

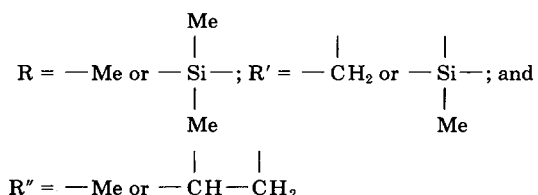




**Figure 5** Infrared spectrum of ceramic product from the pyrolysis of polymer I up to 1300°C in argon.

$m, n, m', n', o, p > 0$  and  $< 10$ ; and  $m, n, m', n', \gg o, p$

For polymer IV,



$m, n, m', n', o, p > 0$  and  $< 10$ ; and  $m, n, m', n', \gg o, p$

Since the molecular weights of the polymers are less than 1500, another likely structure would be cyclic structures.

**Polymer Pyrolysis and its Products**

Polymers I through IV were pyrolyzed in an argon atmosphere at a heating rate of 5–10°C/min from ambient to 500°C. From that point, the temperature was increased to 1000–1300°C at a heating rate of 20–50°C/min. The material was then held at 1000–1300°C for 1 h in argon. The pyrolyzed black rigid ceramic products from the polymers were analyzed by different techniques.

Infrared spectra of the pyrolyzed products from polymers I–IV showed broad absorptions at 1080 cm<sup>-1</sup> and small bands at 1300, 900, and 780 cm<sup>-1</sup>. A typical IR spectrum is shown in Figure 5. The

absorptions at 780 and 900 cm<sup>-1</sup> are associated with SiC absorption.

Both <sup>13</sup>C-NMR and <sup>29</sup>Si-NMR tests confirmed the presence of SiC in the ceramic materials; very little boron carbide was detected in the <sup>13</sup>C-NMR. Because the <sup>11</sup>B-NMR spectrum of the pyrolyzed material was very complicated, no simple boron compound was present in the ceramic products. Due to the quadruplet effect, the <sup>29</sup>Si-NMR was very noisy.

X-ray diffraction analyses of the samples pyrolyzed at 1300°C in argon also confirmed the presence of SiC.

Thermogravimetric analysis in air of the crushed ceramic products at a flow rate of 100 mL/min showed a 1% weight gain up to 1000°C, and no weight loss was observed at 650–750°C. These results indicate that little free carbon or silicon was present.

It was difficult to do an accurate elemental analysis of ceramic materials containing both boron and silicon using conventional wet-analysis techniques. A material balance could not be achieved, as shown in Table IV. High carbon contents were found in the ceramic products, indicating that some Si–B–C structures other than SiC are present in the material.

Acid digestion is a good method to determine the composition of the ceramic materials. The ceramic products from pyrolysis of the polymers were first digested by hydrofluoric acid to detect any silica or

**Table IV** Elemental Analysis of Ceramic Product from Pyrolysis of Boron-Containing Silicon Polymers

Sample	% of Element				
	C	H	B <sup>b</sup>	Si	O
Polymer I (1100°C)					
Found	30.32	0.08	7.84	53.65	8.11 <sup>a</sup>
Ratio	2.53	0.08	0.71	1.92	0.50
Polymer III (1300°C)					
Found	32.03	0.17	10.99	44.19	12.62 <sup>a</sup>
Ratio	2.67	0.17	1.00	1.58	0.79
Polymer IV (1300°C)					
Found	32.17	0.06	12.27	43.32	8.78 <sup>b</sup>
Ratio	2.68	0.06	1.12	1.55	0.55
Polymer IV-0.5 (1200°C)					
Found	35.94	0.13	6.92	45.10	12.04 <sup>a</sup>
Ratio	2.99	0.13	0.63	1.61	0.75

<sup>a</sup> Oxygen value was calculated by difference which may not be accurate.

<sup>b</sup> Oxygen value was measured by neutron activation method.

free silicon present in the ceramic products. The ceramic products were then digested with nitric acid-hydrofluoric acid to determine the amount of silicon borides and/or silicon-boron-carbon compounds. Any undigestible material was assumed to be silicon carbide and/or boron carbide. The results of the acid digestion are shown in Table V. It was found that little silica or free silicon was present in the ceramic products, and substantial amounts of nitric acid and hydrofluoric acid digestible silicon borides and/or silicon-boron-carbon compounds were present in the ceramic products.

Differential thermal analysis (DTA) of the acid-undigestible material in air showed an oxidation exothermic peak at 400–650°C with a weight loss of 15–18% resulting from the presence of free carbon. This indicated that silicon-boron-carbon compounds were present in the ceramic products. During nitric acid and hydrofluoric acid digestion, free carbon was formed from silicon-boron-carbon com-

pounds and mixed with other undigestible silicon carbide and/or boron carbide.

The ceramic material was probably primarily a mixture of silicon carbide, amorphous silicon borides, and silicon borocarbide with a small amount of boron carbide and free silicon.

## CONCLUSION

Pre-ceramic polymers with Si-B bonds in their backbones were synthesized from the Wurtz reaction of dialkyldichlorosilane and boron trichloride or methyl boron bromide with or without methyl iodide. The polymers softened at 40–180°C, started to decompose at 200–450°C and yielded 56–70% ceramic product in an inert atmosphere above 800°C. The ceramic products were stable in air at 1000°C for 1 h with less than 2% weight gain. The polymers have a high potential to form ceramic fibers or to

**Table V** Acid Digestion of Polymer Pyrolysis Ceramic Products

Sample	% of SiO <sub>2</sub>	% Silicon Borides and Si-B-C	% SiC and B <sub>4</sub> C
Ceramic from polymer I	1–6	54–78	14–45
Ceramic from polymer II	0.7–2	48–76	22–42
Ceramic from polymer III	2–6	55–69	25–43
Ceramic from polymer IV	2–8	47–68	24–51

be used as matrix resins for high-temperature applications such as ceramic matrix composites.

The authors thank Dr. Rick J. Brown of Chevron Research Company for ICP analysis of boron and silicon content in the polymer.

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Received January 15, 1990

Accepted April 9, 1990