The present invention relates to a polyorganoborosilane ceramic precursor polymer comprising a plurality of repeating units of the formula:

\[
\begin{array}{c}
R^1 \\
\hline
B \\
\hline
p
\end{array}
\]

with the segments being linked together by second units of the formula: 
\[
(R^2) \quad (\text{Si-R^3})_q
\]

where \( R^1 \) is lower alkyl, cycloalkyl, phenyl, or I, and \( R^2 \) and \( R^3 \) are each independently selected from hydrogen, lower alkyl, vinyl, cycloalkyl, or aryl, \( n \) is an integer between 1 and 100; \( p \) is an integer between 1 and 100; and \( q \) is an integer between 1 and 100. These materials are prepared by combining an organoborohalide of the formula \( R^4 \cdot (B \cdot (X^1)_2 \text{ where } R^4 \text{ is selected from halogen, lower alkyl, cycloalkyl, or aryl, } \text{ and } X^1 \text{ is halogen, lower alkyl, cycloalkyl, or aryl, and an organohalosilane of the formula: } R^3 \cdot (R^2 \cdot \text{Si}(X^2)_2 \text{ where } R^2 \text{ and } R^3 \text{ are each independently selected from lower alkyl, cycloalkyl, or aryl, and } X^1 \text{ and } X^2 \text{ are each independently selected from halogen, in an anhydrous aprotic solvent having a boiling point at ambient pressure of not greater than 160°C. With in excess of four equivalents of an alkali metal, heating the reaction mixture and recovering the polyorganoborosilane. These silicon boron polymers are useful to generate high-temperature ceramic materials, such as SiC, SiB₄, and B₄C, upon thermal degradation above 600°C.}
FIGURE 1 FTIR of POLYMER I

FIGURE 2 FTIR of POLYMER II
FIGURE 3 FTIR of POLYMER III

FIGURE 4 TGA of POLYMER II
BORON-CONTAINING ORGANOSILANE POLYMERS AND CERAMIC MATERIALS THEREOF

BACKGROUND OF THE INVENTION

Origin of the Invention

The invention disclosed herein was made in the performance of work under a NASA Contract and is subject to Public Law 96-517 (35 U.S.C. §200 et seq.). The contractor has not elected to retain title in this invention.

This is a division of application Ser. No. 06/890,577, filed July 30, 1986, U.S. Pat. No. 4,767,728.

Field of the Invention

The present invention relates to organic silicon-boron polymers which upon pyrolysis produce high-temperature ceramic materials. More particularly, it relates to the pyrolysis of a polyorganosilazane which produce high-temperature ceramic materials. They have high thermal and oxidation stability and are among the hardest materials that can be made. Other advantageous properties include low electrical conductivity, low co-efficient of thermal expansion, thermal shock resistance, creep resistance, high strength at elevated temperatures, and corrosion resistance. A few references which are of general interest follow:

D. Seyferth et al. disclose in the Communications of the American Ceramic Society, July 1984, pp. C-132 to C-133, the high-yield synthesis of Si₃N₄/SiC/C ceramic materials by the pyrolysis of a polyorganosilazane. The polyorganosilazane is prepared by the reaction of dichlorosilane, H₂SiCl₂, with gaseous ammonia. The ammonolysis product is pyrolyzed in nitrogen atmosphere to give a 70 percent yield of Si₃N₄.

In a similar manner, D. Seyferth et al. disclose in U.S. Pat. No. 4,482,669 the preparation of pre-ceramic polymers having repeating units of (NH-SiR₃)₉ and R-(CB₉H₁₀C)-(CH₂)₉-Si(X)₂-R' with water to form a polysiloxane (-Si-O-) polymer.

In U.S. Pat. No. 4,152,509, S. Yajima et al. disclose the preparation of a number of polysiloxanes by treating at least one boric acid composed with phenylsilane. Polysiloxanes are not disclosed. In U.S. Pat. No. 4,283,376, S. Yajima et al. disclose a process for producing polycarbosilane partly containing siloxane bonds (-Si-O-) wherein a part of the polycarbosilane comprises polysiloxane and a structure composed of boron, silicon, and oxygen. The polycarbosilane is converted into silicon carbide fibers by first preparing a spinning dope, treating the dope to render it infusible under tension or under no tension and firing the treated dope in a vacuum or in an inert atmosphere.

In U.S. Pat. No. 4,298,559, R. H. Baney et al. disclose the preparation of polysilanes having the average formula [(CH₃)₃Si][CH₃Si]. These polysilanes are prepolymers which produce silicon carbide ceramic materials when pyrolyzed in an inert atmosphere.

In U.S. Pat. No. 4,572,902, Matano et al. disclose a method for producing ceramics having a closed-pore size from a sintered body of a Si₃N₄-SiC composition. The process includes heating the ceramic sintered article in a flowing gas mixture of chlorine and nitrogen at 500°C to 1,500°C.

In U.S. Pat. No. 4,490,192, A. Gupta et al. disclose the preparation of finely divided particles of less than 1 micron in diameter having the composition of B₇Si₆, B₉N₆, P₃Si₉, P₃N₉, and the like. These particles are prepared in flowing argon with pyrolysis occurring using a laser.

Takamiza et al. in Japanese patent publications Nos. 80500/78 and 101099/78 disclose the preparation of polymers made from methylchlorosilanes, however, no mention is made of the yields of ceramic material generated by the decomposition of the polycarbosilanes. More recently in Japanese Kokai Nos. 79/114460 and 79/83098 suggest that the preparation of silicon carbide precursor polymers having a silicon-carbon (Si-C-Si-) bond are prepared by heating organosilicon compounds including (CH₃)₃Si-Si(CH₃)₂Cl in the presence of B, Al, Si, Ge, Sn and Pb compounds or H and its salts at high temperatures.


None of the above references disclose or suggest the polymer precursors the polyorganosilazanes or silicon-boron ceramic polymers of the present invention.

It is highly desirable to have polymer precursors for -Si-B- ceramic materials that are formed from readily available and relatively inexpensive starting materials and in high yield. Additional desirable properties include stability at room temperature for prolonged periods of time, relatively stable to hydrolysis at atmospheric moisture levels, and high yield of ceramic material upon pyrolysis.

SUMMARY OF THE INVENTION

The present invention relates to a polyorganosilazane ceramic precursor polymer comprising a plurality of repeating units of the formula: \( \text{R} - \left(\text{CB}_{10}\text{H}_{10}\text{C}\right) - \left(\text{CH}_{2}\right)_{n} - \text{Si}(\text{X})_{2} - \text{R}' \) with water to form a polysiloxane (-Si-O-) polymer.

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In U.S. Pat. No. 4,298,559, R. H. Baney et al. disclose the preparation of polysilanes having the average formula \([(\text{CH}_{3})_{3}\text{Si}]_{2}[\text{CH}_{3}\text{Si}]\). These polysilanes are prepolymers which produce silicon carbide ceramic materials when pyrolyzed in an inert atmosphere.

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The present invention also relates to a process for preparing a polyorganoborosilane, which process includes:

(a) combining an organic borohalide of the formula: R4-B-(X1)2 with an organohalosilane of the formula: R2(R3)Si(X2)2 wherein R4 is selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; and

(b) heating the reaction mixture for a time and at a temperature up to 160°C effective to produce a polyorganoborosilane; and

(c) recovering the polyorganoborosilane of step (b).

Another aspect of the present invention is the production of silicon-boron-carbon ceramic materials, useful in high temperature applications, by the pyrolysis of the polyorganoborosilane polymers of the present invention. Generally temperatures between about 600° and 1300°C are used.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER I.

FIG. 2 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER II.

FIG. 3 is the Fourier Transform Infrared (FTIR) spectrum of the polyorganoborosilane—POLYMER III.

FIG. 4 is the thermogravimetric analysis (TGA) of POLYMER II.
In a general reaction, about four to six equivalents of the alkali metal is freshly cut and added to the anhydrous aprotic solvent at ambient temperature, then heated to between about 100° and 135° C. The R4—B—(X1)2 compound, such as methylborondibromide, phenylborondichloride, etc. and the R4(R3)Si(X2)2, such as dimethylchlorosilane, in equimolar amounts are combined and slowly added dropwise. The reaction mixture is then refluxed at between about 120° C. and 160° C. for 16 to 24 hours. Methyl iodide or similar alkyl iodide is added and continued to reflux up to an additional 4 hours to remove excess alkali metal and to quench the reaction. After cooling, the alkali halide precipitate has a purple to purple-blue color, and the liquid portion is tan to brown in color. The reaction product is filtered and the solid is washed with additional aprotic solvent. The filtrate is evaporated using reduced pressure to produce a polymer having a molecular weight of between about 800 to 1300 daltons. These polymers are generally soluble in organic solvents and liquid portion is tan to brown in color. The reaction yield is close to the expected theoretical yield. These three-dimension structures are very complex, and both larger and small ring structures are also possible.

These yields from the pyrolysis of Polymers I, II, and III in nitrogen is shown in Table A below.

### TABLE A

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SiC + SiB4 (%)</th>
<th>SiC + SiB6 (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>32.9</td>
<td>33.5</td>
<td>37</td>
</tr>
<tr>
<td>II</td>
<td>53.6</td>
<td>57.1</td>
<td>57</td>
</tr>
<tr>
<td>III</td>
<td>68.7</td>
<td>70.4</td>
<td>64</td>
</tr>
</tbody>
</table>

These ceramic yields are close to the expected theoretical yields.

(The Group A and Group D designations are found in the SUMMARY hereinabove).

In the preparation where R4 is any alkyl or phenyl groups and X1 is halogen, a number of different type of polymers are possible, when combined with (D), e.g.:


(Where the Group A and Group D designations are found in the SUMMARY hereinabove).

In the preparation where R4 is a halogen e.g. chloro and X1 is halogen, e.g. chloro (Group A) and

\[ R^2-Si-R^3 \]

is for example dimethylsilyl (Group D) a number of two and three dimensional polymers [including Group (E)] are possible, e.g.:

- \[ D-A-A-D-D-E- \]
- \[ D-D-D-E-D-D-E- \]; OR
- \[ E-D-E- \]
- \[ E-D-E \]

The polyorganoborosilanes yield ceramic materials up to 64% upon thermal decomposition (pyrolysis) in nitrogen at temperatures up to 1,100° C. The ceramic yields from the pyrolysis of Polymers I, II, or III are close to those expected from the theoretical yield as is shown above in Table A.

In FIG. 4 is shown the thermogravimetric analysis (TGA) curve for the decomposition of POLYMER II to produce a ceramic material in nitrogen between ambient and 1,100° C. (line 42). The polymer residue/ceramic material showed no weight gain or loss up to 1,100° C in an air environment (line 41). From this experiment, it can be concluded that once the organic portions of the polymer precursors are pyrolyzed the remaining ceramic materials obtained; e.g., SiC, SiB4, Si—B2 and the like, are very thermally oxidatively stable and do not react further up to about 1,100° C.

The following Examples are to be construed as being illustrative and are not to be considered limiting in any way.

**GENERAL**

Boron trichloride was obtained from Matheson Gas Products. Phenyl boron dichloride and methyl boron dibromide were obtained from Alpha Products. All other chemicals were from Aldrich Chemical Co. infrared spectra were recorded on a Nicolet MX-1 Fourier Transfer InfraRed (FTIR). A Varian EM360 Nuclear Magnetic Resonance (NMR) spectrometer was used for NMR spectra. A DuPont 1090 thermal analyzer was used for thermogravimetric analysis. Molecular weights of the polymers were measured by the conventional vapor-pressure-osmometry method in chloroform, using Wescan Molecular Apparatus Model 233-200. Electron Spectroscopy for Chemical Analysis (ESCA) was used to measure the surface properties, a Hewlett-Packard Model 5950 ESCA instrument was used. X-Ray diffractometer (X-RD) measurements were obtained using a conventional General Electric Company X-Ray diffractometer.
EXAMPLE 1
Phenyloborondichloride and Dimethyldichlorosilane to Produce Polymer I

(a) A mixture of phenyloborondichloride (5 g, 0.03 mole) and dimethyldichlorosilane (3.9 g, 0.03 mole) in 10 ml of xylene is placed in a dropping funnel and added dropwise into a 3-neck round-bottom flask, containing xylene (30 ml) and sodium (2.8 g, 0.12 mole), equipped with a nitrogen gas inlet. The reaction is carried out at 130°C. to 140°C. (refluxing temperature of xylene) for 18 hrs. Upon cooling, a purple precipitate is filtered and washed with xylene or toluene. This precipitate is further treated with methanol and water. A small quantity of an insoluble, black solid is obtained, but not identified. The xylene filtrate is evaporated to dryness yielding a solid material, Polymer I, which has a molecular weight of 900-1,000. The FTIR spectrum as found in FIG. 1 shows phenyl and methyl peaks at 3000-3100 cm⁻¹ (peak 11) and 2850-2980 cm⁻¹ (peak 12) respectively. The NMR spectrum also shows phenyl and methyl peaks. Additional Polymer I is isolated from the methanol solution on evaporation of the solvent; the polymer is washed with xylene to remove any sodium methoxide. The ratio of Si-B for this polymer appears to be about 2:5. Total yield of Polymer I is 2 g (46%).

(b) Similarly, the reaction is repeated as is described in Subpart 1(a) above except that a stoichiometrically equivalent amount of p-methylphenylborondichloride is used instead of phenyloborondichloride and a stoichiometrically equivalent amount of dimethyldichlorosilane is used instead of dimethyldichlorosilane. A good yield of a polymer of the structure:

$$[-p\text{CH}_3\text{C}_6\text{H}_4\text{B}]-[\text{Si}(\text{C}_6\text{H}_5)_2]_n$$

where p and q are each integers between 1 and 12 is expected to be obtained.

EXAMPLE 2
Methylborondibromide and Dimethyldichlorosilane to Produce Polymer II

Sodium (13 g; 0.565 mole) and 100 ml of octane are placed in a 500-ml three-neck flask equipped with condenser, nitrogen inlet tube, magnetic stirrer, and dropping funnel. The flask is heated to the reflux temperature of the solvent. Dimethyldichlorosilane (17.4 g; 0.135 mole) and 25 g of methylborondibromide (0.135 mole) in 50 ml of octane are added dropwise to the reaction flask through the dropping funnel over a period of 30 min. The reaction mixture is refluxed for 20 hrs. After cooling, the mixture is filtered and the purple solid is washed with xylene. A brown solid (Polymer III; 4.2 g; 41% yield) is isolated from the xylene filtrate after evaporation of the solvent under reduced pressure. Polymer III has a melting point of about 100°C and a molecular weight of about 1200.

The purple solid is washed with methanol and water to give a white-yellowish solid. Some white solid, isolated from the methanol solution after evaporation of the solvent, is washed with water. Both solids were considered to be high-molecular-weight forms of Polymer III.

The NMR spectrum of POLYMER I has a broad peak at about 7 ppm (aromatic protons) to an internal reference (tetramethylsilane) and broad peaks at about 0.2 ppm (methyl groups). The NMR spectra of Polymer II and Polymer III showed only methyl protons about 0.2 ppm, as expected.

The Fourier Transform infrared (FTIR) spectrum of Polymer I (FIG. 1) showed both aromatic and aliphatic C—H absorption peaks at 3000-3100 (band 11) and 2850-2980 cm⁻¹ (band 12), respectively. The FTIR spectra of Polymer I, Polymer II and Polymer III also indicated the presence of the Si—B bond. Although small Si—H (2100 cm⁻¹, band 13, band 24 and band 34) and B—H (2500 cm⁻¹, band 14, band 25 and band 35) are present in the polymers, the major structure of the polymers is a polymer and/or a block copolymer as is described herein.

FIG. 2 and FIG. 3 show only aliphatic C—H absorption (peak 21 and peak 31) due to the aliphatic methyl groups. A new band which appear at 1310 cm⁻¹ is assigned to the Si—B stretching absorption (band 16, band 23 and band 33). From the literature a weak absorption band was also observed in the region of 440-510 cm⁻¹, which was assigned the Si—B bending absorption (band 22 and band 32).
The IR spectra obtained for these —B—Si— polymers described above show the presence of some —B—H and Si—H groups in the polymeric material. The quantity of these —B—H and Si—H groups, if present, is always very low, of the order of 1–5 percent. It is suggested that the Si—H and —B—H bonds are observed because the very reactive Si and B groups during the reaction remove a hydrogen atom from the solvent medium and therefore terminate that Si—B unit as a further polymer addition group. It is, therefore, contemplated within the present invention that some small amount of R1, R2 and R3 groups in the organic polymer may be hydrogen.

**EXAMPLE 4**

Ceramic Products by Pyrolysis

(a) The boron-silicon polymers were pyrolyzed at 1300°C in flowing nitrogen for 1 hr. (Argon can also be used.) Table B shows the atom ratio in the resulting ceramic as measured by electron spectroscopy for chemical analysis (ESCA).

<table>
<thead>
<tr>
<th>Element</th>
<th>Polymer II Atom Ratio</th>
<th>Polymer III Atom Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.5 Carbide</td>
<td>5.5 Carbide</td>
</tr>
<tr>
<td>Si</td>
<td>10 (2.8 SiC)</td>
<td>7.8 (3 SiC)</td>
</tr>
<tr>
<td>B</td>
<td>14</td>
<td>13</td>
</tr>
</tbody>
</table>

It is seen that in Polymer II carbon is present as 4.5 atom ratio as carbide. Of that carbide 2.8 atom ratio is present as silicon carbide. A portion of the remainder of the silicon is combined as boron carbides, and the remainder of the carbide is combined as boron carbides.

Silicon, carbon, and boron were found in the ceramic products derived from the pyrolysis of the organoborosilicon polymer. The ratio of Si, C, and B indicate the presence of mixtures of SiC and SiB2, where X is between 2 and 6 or a combination. B4C may also be present in the ceramic product, but was not identified. X-Ray diffraction (X-RD) analysis confirmed the presence of SiC. Elemental analysis of the ceramic product from the pyrolysis of Polymer III showed a trace of carbon present as free carbon.

While a few embodiments of the present invention have been shown and described herein, it will be apparent to those skilled in the art that various modifications and changes can be made in the polyanorganoborosilanes, without departing from the spirit and scope of the present invention. All such modifications and changes coming within the scope of the appended claim are intended to be covered thereby.

We claim:

1. A polyanorganoborosilane ceramic precursor polymer consisting essentially of a plurality of repeating units of the formula:

   \[ \text{Polym} = \left( \frac{\text{R}_1}{\text{B}} \right)_n \]

   where the polymer unit being linked together by second units of the formula:

   \[ \text{Polym} = \left( \frac{\text{R}_2}{\text{Si}} \right)_n \]

   wherein R1 and R2 are each independently selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; n is an integer between 1 and 100; p is an integer between 1 and 100; and q is an integer between 1 and 100, wherein the precursor polymer has a linear block, linear alternating, linear random structure, or a random three-dimensional structure.

2. The polyanorganoborosilane of claim 1 wherein R1 is lower alkyl.

3. The polyanorganoborosilane of claim 1 wherein R1 is methyl.

4. The polyanorganoborosilane of claim 1 wherein R1 is phenyl.

5. The polyanorganoborosilane of claim 1 wherein R2 and R3 are identical.

6. The polyanorganoborosilane of claim 5 wherein R2 and R3 are each lower alkyl.

7. The polyanorganoborosilane of claim 5 wherein R2 and R3 are each methyl.

8. The polyanorganoborosilane of claim 4 wherein R2 and R3 are each phenyl.

9. The polyanorganoborosilane of claim 2 wherein R2 and R3 are each lower alkyl.

10. The polyanorganoborosilane of claim 4 wherein R3 and R4 are each free carbon.

11. The polyanorganoborosilane of claim 1 wherein R1 is free carbon.

12. The polyanorganoborosilane of claim 11 wherein R2 and R3 are each lower alkyl.

13. A process for preparing a polyanorganoborosilane, which process comprises:

(a) combining an organoborohalide of the formula R1—B—(X1)2 and an organohalosilane of the formula R7R8Si(X2)2 wherein R1 and R7 are selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; R2 and R3 are each independently selected from lower alkyl, vinyl, cycloalkyl, aryl, or substituted aryl; and X1 and X2 are each independently selected from chloro or bromo, in an anhydrous aprotic solvent having a boiling point at ambient pressure.
of not greater than 160° C., with at least four equivalents of a alkali metal;

(b) heating the reaction mixture for a time and at a temperature up to about 160° C. effective to produce a polyorgano-borosilane; and

(c) recovering the polyorganoborosilane produced in step (b) which consists essentially of a plurality of repeating units of the formula:

\[
\begin{align*}
&\text{(A)} \\
&\begin{cases}
R_1 \\
B
\end{cases}_p
\end{align*}
\]

the polymer unit being linked together by second units of the formula:

\[
\begin{align*}
&\text{(D)} \\
&\begin{cases}
R_2 \\
S \\
R_3
\end{cases}_q
\end{align*}
\]

wherein \(R_1\) is lower alkyl, vinyl, cycloalkyl, phenyl, or

wherein \(R_2^2\) and \(R_3^3\) are each independently selected from halogen, lower alkyl, vinyl, cycloalkyl, or phenyl; \(n\) is an integer between 1 and 100; \(p\) is an integer between 1 and 100; and \(q\) is an integer between 1 and 100 wherein the polymer has a linear block, linear alternating, linear random structure or a random three dimensional structure.

14. The process of claim 13 wherein \(R^4\) and \(X^1\) are each chloro or bromo.

15. The process of claim 13 wherein \(R^4\) is lower alkyl and \(X^1\) is halogen.

16. The process of claim 13 wherein \(R^4\) is phenyl and \(X^1\) is chloro.

17. The process of claim 13 wherein \(R^2\) and \(R^3\) are each selected from lower alkyl or phenyl and \(X^2\) is chloro.

18. The process of claim 15 wherein \(R^2\) and \(R^3\) are each methyl.

19. The process of claim 16 wherein \(R^2\) and \(R^3\) are each lower alkyl and \(X^2\) is chloro.

20. The process of claim 17 wherein \(R^2\) and \(R^3\) are each lower alkyl and \(X^2\) is chloro.

21. The process of claim 13 wherein the aprotic solvent is selected from hydrocarbons or aromatic hydrocarbons.

22. The process of claim 21 wherein the alkali metal is selected from sodium, potassium, or mixtures thereof.