Serial No. 748,584

Filing Date 13 November 1996

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OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
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ARLINGTON VA 22217-5660

Docket No.: N.C. 77,112
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PATENT APPLICATION

THERMOSET POLYMERS MADE BY BLENDING POLY (CARBORANE-SILOXANE/SILANE-ACETYLENE) AND POLY (SILOXANE/SILANE-ACETYLENE)

Background of the Invention

1. Field of the Invention

The invention relates to high temperature, oxidatively stable thermosets and ceramics. In particular, the invention relates to thermosets and ceramics made by blending a polymer having repeating units of carboranyl, silyl or siloxyl and acetylenic groups with a polymer having repeating units of only silyl or siloxyl and acetylenic groups.

2. Background of the Related Art

The search for high temperature oxidatively stable materials has led to the development of organoboron polymers, particularly silyl or silanoxyl polymers containing carboranyl and acetylenic groups incorporated into the polymer backbone.

Polymers that include carboranyl, silyl or siloxyl and acetylenic groups in the same polymeric chain combine the desirable features of both inorganics and organics: the carborane groups provide thermal and oxidative stability, the silane or siloxane groups provide chain flexibility and the acetylenic groups allow cross-linking of adjacent polymer strands to form thermosets. The acetylene groups remain inactive during processing at lower temperatures and react either thermally or photochemically to form conjugated polymeric cross-links without the evolution of volatiles. Carborane-silane/siloxane-acetylene polymers have the advantage of being extremely easy to process and convert into thermosets or ceramics since they are either liquids at room temperature or low melting solids and are soluble in most organic solvents. The polymers are thus well-suited to serve as ceramic or thermoset polymeric precursors.

Thermoset polymers that include carborane, siloxane or silane and acetylene units are disclosed in U.S. Pat. No. 5,272,237; 5,292,779; 5,348,917 and 5,483,017, each incorporated herein by reference in its entirety and for all purposes. The thermoset polymers described in U.S. Pat. Nos. 5,272,237; 5,292,779 and 5,348,917 are made from linear polymer precursors that include repeating units containing carborane-siloxane/silane-acetylene or related groups. The thermoset polymers described in 5,483,017 are made from linear polymer precursors that include, on each strand, both repeating units of carborane-siloxane/silane-acetylene or related groups and repeating units of siloxane/silane-acetylene or related groups. U.S. Pat Nos. 5,348,917 and 5,483,017 further disclose boron-carbon-silicon ceramics made by pyrolyzing carborane-silane/siloxyl-acetylene thermoset polymers.

The chemical properties of carborane-siloxane/silane-acetylene thermoset polymers, and the corresponding ceramics formed at elevated temperatures, vary according to the relative amount of carborane, silane or siloxane and acetylene incorporated into the thermoset. It would be desirable to be able to control and vary the relative amount of each of these groups in a thermoset polymer so that polymers with different properties could be made for different purposes. The incorporation of carborane into a polymer is costly, and it would be especially desirable to be able to control and, in some circumstances, reduce the amount of carborane in the thermoset polymer. In the carborane-siloxane/silane-acetylene thermoset polymers described in U.S. Pat. Nos. 5,272,237; 5,292,779; and 5,348,917, each repeating unit of each linear polymer precursor must include a carborane group and there is no way to vary or control the amount of carborane in the polymer. U.S. Pat No. 5,483,017 discloses one possible method of varying the carborane content of a thermoset polymer precursor: A linear polymer precursor is formed by reacting repeating units of carborane-silane/siloxane-acetylene and silane/siloxane-acetylene so that the units are joined end-to-end. The carborane content of the polymer precursor can be varied by controlling the relative amount of carborane-silane/siloxane-acetylene and silane/siloxane-acetylene repeating units added to the coupling reaction that forms the linear polymer precursor. However, this method has the disadvantage that once the linear polymer precursor is made, the amount of carborane relative to the amount of other groups is fixed and cannot be changed. The only way to alter the amount of carborane in the linear polymer precursor is to repeat the coupling reaction using a different proportion of carborane-silane/siloxane-acetylene and silane/siloxane-acetylene.

Accordingly, it is therefore an object of the present invention to provide for oxidatively stable materials that have thermosetting properties for making rigid components therefrom, such as engine parts, turbine blades and matrices. These components must withstand high temperatures and be oxidatively stable and have sufficient strength to withstand the stress put on such components.

It is therefore a further object of the present invention to provide carborane-silane-acetylene and/or carborane-siloxane-acetylene thermosetting materials and ceramics wherein the carborane content within the thermosets or ceramics can be varied to provide greater thermal stability or a lower cost.

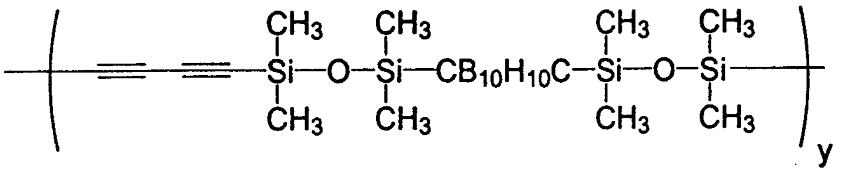
A further object of the present invention is to provide carborane-silane-acetylene and/or carborane-siloxane-acetylene cross-linked thermoset materials and ceramics made from easily processed linear polymer precursors wherein the carborane content within the thermosets or ceramics can be varied after the synthesis, and before the cross-linking or pyrolysis, of the linear polymer precursors.

These and other objects are accomplished by forming an organoboron thermoset polymer precursor composition made up of a mixture of a first linear polymer having a repeating unit comprising at least one carboranyl group, at least one silyl or siloxyl groups, and at least one acetylenic group, and a second linear polymer having a repeating unit comprising at least one silyl or siloxyl groups and at least one acetylenic moiety and wherein the second linear polymer does not contain a carboranyl group. The amount of carborane in the thermoset can be controlled by varying the relative amount of the carborane-containing polymer and the non-carborane-containing polymer in the precursor composition. The amount of carborane can be adjusted up until the time that the thermoset or ceramic is actually formed by adding more carborane-containing polymer or non-carborane-containing polymer to the precursor composition. The precursor composition can be heated at temperatures up to about 450° C to form a thermoset or pyrolyzed at temperatures above about 450° C to form a ceramic.

Brief Description of the Drawings

A more complete appreciation of the present invention and several of the accompanying advantages thereof will be readily obtained by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

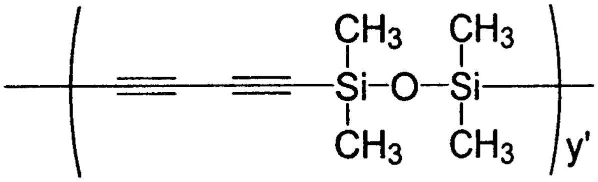
FIG. 1 (a comparative example) shows the superimposed differential scanning calorimetry (DSC) plots of heat flow versus temperature in nitrogen for a polymer of the formula



$$-\left(-C\equiv C-C\equiv C-\mathrm{Si}(CH_3)_2-O-\mathrm{Si}(CH_3)_2-CB_{10}H_{10}C-\mathrm{Si}(CH_3)_2-O-\mathrm{Si}(CH_3)_2-\right)_y-$$

(1')

and for a polymer of the formula



$$-\left(-C\equiv C-C\equiv C-\mathrm{Si}(CH_3)_2-O-\mathrm{Si}(CH_3)_2-\right)_{y'}-$$

(2')

where y and y' are integers.

FIG. 2 shows the superimposed differential scanning calorimetry (DSC) plots of heat flow versus temperature in nitrogen for mixtures of the polymers of formulas **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (Composition C), 1:3 (Composition B) and 1:9 (Composition A).

FIG. 3 shows the superimposed thermogravimetric analytical (TGA) plots of weight % versus temperature in an oxidizing environment during a second heating cycle for the chars obtained from mixtures of the polymers of formulas **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (Composition C), 1:3 (Composition B) and 1:9 (Composition A) that were subjected to a first heating cycle in nitrogen to 1000° C.

FIG. 4 shows the superimposed thermogravimetric analytical (TGA) plots of weight % versus temperature in an oxidizing environment during a second heating cycle for the char obtained from mixtures of the polymers of formulas **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (Composition C), 1:3 (Composition B) and 1:9 (Composition A) that were subjected to a first heating cycle in nitrogen to 1500° C.

FIG. 5 shows the superimposed thermogravimetric analytical (TGA) plot of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for a thermoset made from composition A (molar ratio of **1'** to **2'** of 1:9) and for a thermoset (D) made from copolymer of formula **20'** of U.S. Patent No. 5,483,017. The thermoset polymers were heated in air for 5 hours in sequence at 250, 300, 350 and 400° C and then for 15 hours at 450° C.

FIG. 6 shows the superimposed thermogravimetric analytical (TGA) plots of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for mixtures of the polymers of formulas **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (Composition C), 1:3 (Composition B) and 1:9 (Composition A). The thermoset polymers were heated in air for 5 hours in sequence at 250, 300, 350 and 400° C and then for 15 hours at 450° C.

FIG. 7 shows the thermogravimetric analytical (TGA) plot of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for the long-term oxidative study of the a ceramic char obtained by heating composition A (molar ratio of **1'** to **2'** of 1:9) to 1000° C under nitrogen. The char was aged in sequence at 400, 500, 600 and 700° C in a flow of air for 5 hours at each temperature.

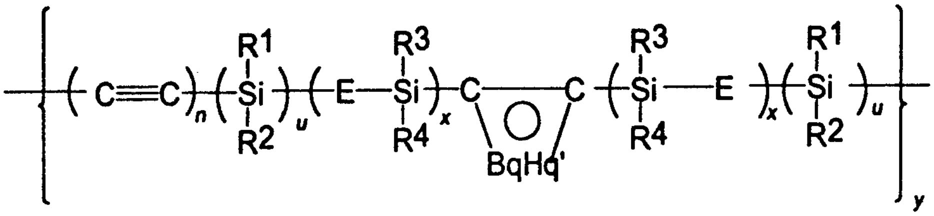
FIG. 8 is a thermogravimetric analytical (TGA) plot of weight % versus temperature in nitrogen obtained on the first heating cycle of composition A (molar ratio of 1' to 2' of 1:9) to 1000° C.

FIG. 9 is a TGA plot of weight versus temperature in an oxidizing environment (air), subsequently obtained on the second heating cycle of the char obtained by heating composition A (molar ratio of 1' to 2' of 1:9) to 1000° C.

Detailed Description of the Preferred Embodiments

The following detailed description of the invention is provided to aid those skilled in the art in practicing the present invention. However, the following detailed description of the invention should not be construed to unduly limit the present invention. Variations and modifications in the embodiments discussed may be made by those of ordinary skill in the art without departing from the scope of the present inventive discovery.

The invention relates to an organoboron thermoset polymer precursor composition made up of a mixture of a first linear polymer having a repeating unit comprising at least one carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group, and a second linear polymer having a repeating unit comprising at least one silyl or siloxyl group and at least one acetylenic group and wherein the second linear polymer does not contain a carboranyl group. More specifically, the invention relates to an organoboron thermoset polymer precursor composition made up of a mixture of a first linear polymer having a repeating unit represented by the formula



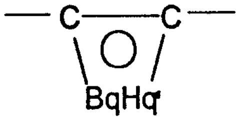
(1)

wherein:

(1) *n* is an integer from 1 to 12 and *u* and *y* are positive integers;

(2) $-\!\left(C\equiv C\right)_n\!-$ represents an unconjugated acetylenic group or conjugated acetylenic groups when *n* is an integer greater than 1;

(3) R^1, R^2, R^3 and R^4 may be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof;

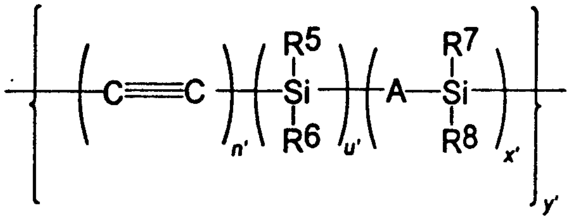
(4)  represents a carboranyl group; and

(5) q and q' are integers from 3 to 16;

(6) *x* represents an integer greater than or equal to zero; and

(7) E is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof;

and a second linear polymer having a repeating unit represented by the formula



$$\left[\left(C\equiv C \right)_{n'} \left(\underset{R6}{\overset{R5}{Si}} \right)_{u'} \left(A-\underset{R8}{\overset{R7}{Si}} \right)_{x'} \right]_{y'}$$

(2)

wherein:

(1) n' is an integer from 1 to 12 and u' and y' are positive integers;

(2) $\left(C\equiv C \right)_{n'}$ represents an unconjugated acetylenic group or conjugated acetylenic groups when n is an integer greater than 1.

(3) R^5, R^6, R^7 and R^8 may be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof;

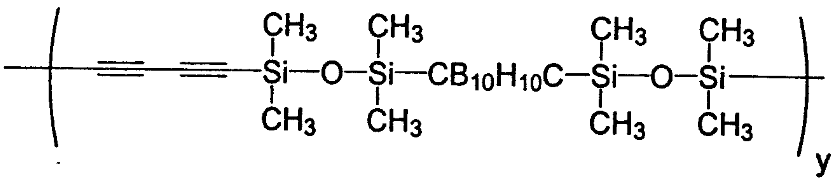
(4) x' represents an integer greater than or equal to zero; and

(5) A is selected from the group consisting of O, an aliphatic bridge, an aryl bridge and mixtures thereof.

Preferably, the carboranyl group represented in formula **(1)** represents a carboranyl group selected from the group consisting of 1,7-dodecacarboranyl; 1,10-octacarboranyl; 1,6-octacarboranyl; 2,4-pentacarboranyl; 1,6-tetracarboranyl; 9-alkyl-1,7-dodecacarboranyl; 9,10-dialkyl-1,7-dodecacarboranyl; 2-alkyl-1,10-octacarboranyl; 8-alkyl-1,6-octacarboranyl; decachloro-1,7-dodecacarboranyl; octachloro-1,10-octacarboranyl; decafluoro-1,7-dodecacarboranyl; octafluoro-1,10-octacarboranyl; *closo*-dodeca-*ortho*-carboranyl; closo-dodeca-*meta*-carboranyl;

closo-dodeca-*para*-carboranyl and mixtures thereof. Preferably, R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 in formulas (1) and (2) represent hydrocarbon groups having up to 20 carbon atoms and are selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof. A and E in formulas (1) and (2) may be the same or different and are preferably selected from the group consisting of O, an aliphatic bridge, and aryl bridge and mixtures thereof. A and E may be further selected from the group consisting of an aliphatic bridge of about 1 to about 20 carbon atoms, an aryl bridge of about 5 to about 40 carbon atoms and mixtures thereof. For example, an aryl bridge may be included in circumstances where more stiffness is desired in the linear polymer precursor.

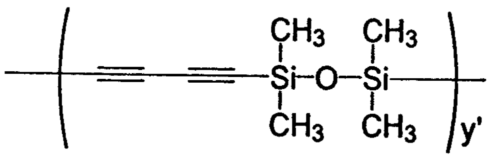
In one specific embodiment, the invention comprises an organoboron thermoset polymer precursor composition made up of a mixture of a first linear polymer having a repeating unit represented by the formula:



$$\left(-C\equiv C-C\equiv C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CB_{10}H_{10}C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}- \right)_y$$

(1')

wherein y is an integer, and a second linear polymer having a repeating unit represented by the formula:

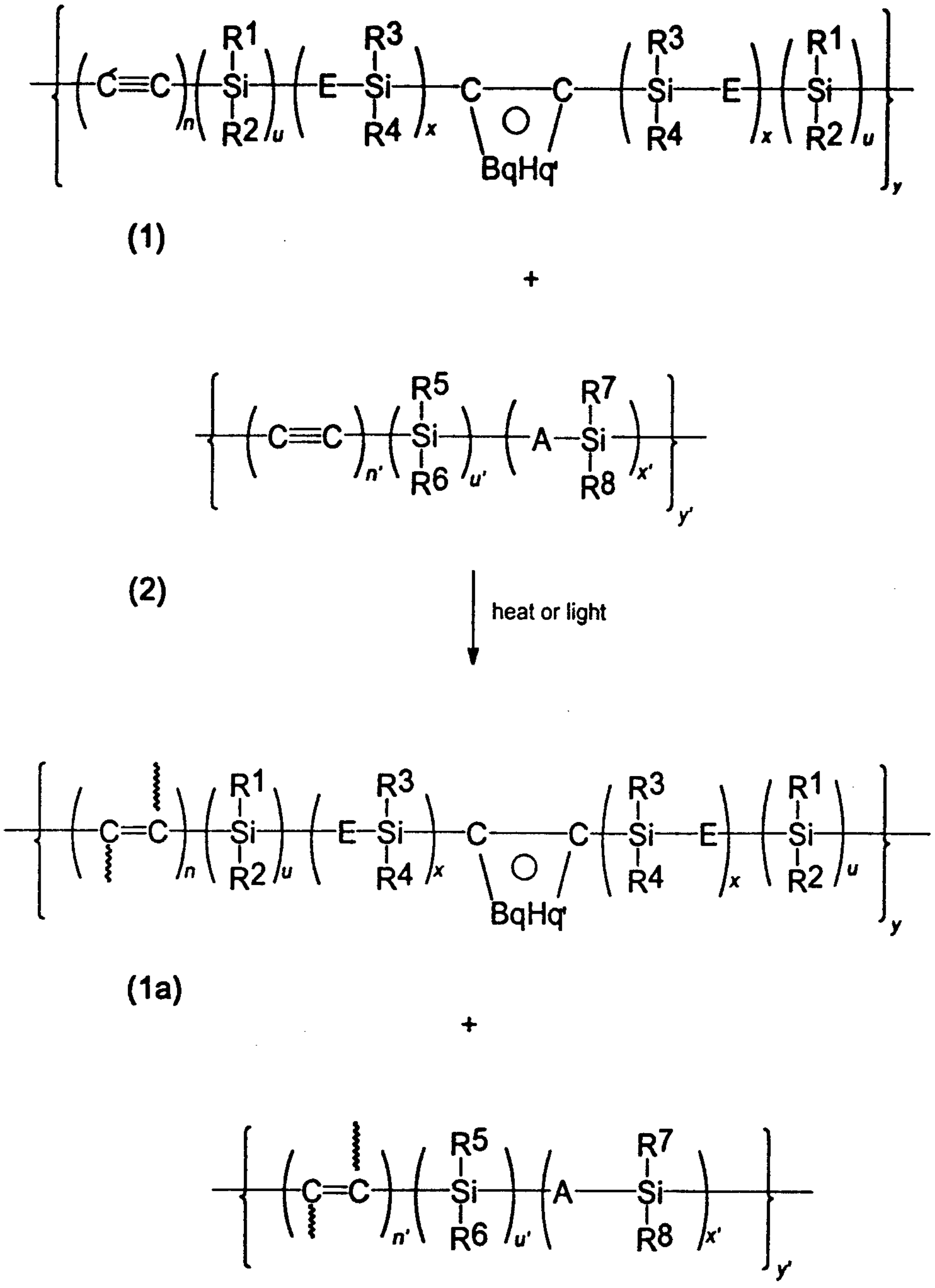


$$\left(-C\equiv C-C\equiv C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}- \right)_{y'}$$

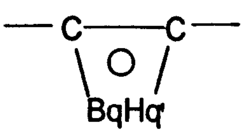
(2')

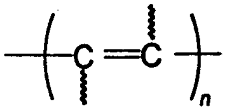
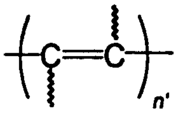
wherein y' is an integer.

The invention further relates to an organoboron thermoset polymer made by the process of forming an organoboron thermoset polymer precursor composition made up of carborane containing and non-carborane-containing linear polymers as described above, and then curing the precursor composition, that is, heating it or exposing it to light to effect cross-linking of the polymers through the acetylenic groups contained therein, as in the following reaction scheme:



wherein: n, n', u, u', y, y′, $-\!(\mathrm{C{\equiv}C})\!-_{n}$, $-\!(\mathrm{C{\equiv}C})\!-_{n'}$, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8

,  , *q*, *q'*, *x*, *x'*, A and E are as defined above, and

wherein  and 

in formulas **(1a)** and **(2b)** represent alkenyl groups formed by the crosslinking of acetylenic groups in the compounds of formulas **(1)** and **(2)** wherein the alkenyl carbon atoms are directly bonded to alkenyl carbon atoms of other polymers represented by formulas **(1a)** and **(2b)**. Because the organoboron thermoset polymer precursor composition is made up of a mixture of a first (carborane-containing) linear polymer and a second (non-carborane-containing) linear polymer, any particular alkenyl carbon atom may crosslink to another first linear polymer or another second linear polymer. The crosslinking creates an extended conjugated network that includes both the first and the second linear polymers. Typically, the organoboron thermoset polymer precursor composition will be poured into a mold of a desired shape before conversion into a thermoset polymer.

The amount of carborane in the thermoset can be varied and controlled by varying the amount of the first (carborane-containing) linear polymer and the second (non -carborane containing) linear polymer that are mixed together to form the organoboron thermoset polymer precursor composition before the crosslinking step. Preferably, the molar ratio of the first (carborane-containing) linear polymer and the second (non -carborane containing) linear polymer is from about 99:1 to about 1:99 More preferably, the molar ratio of the first (carborane-containing) linear polymer and the second (non -carborane containing) linear polymer is from about 1:1 to about 1:25. Even more preferably, the molar ratio is between about 1:1 and about 1:9.

In forming the organoboron thermoset polymer precursor composition, the first (carborane-containing) linear polymer and the second (non-carborane containing) linear polymer can be combined by any conventional means. Typically, both the first and the second linear polymer and the mixture of the two polymers will be either liquid at room temperature or solid with a low melting temperature and will be soluble in most organic solvents.

The conversion of the mixture of the first (carborane-containing) linear polymer and the second (non -carborane containing) linear polymer into the cross-linked organoboron thermoset polymer is accomplished by exposing the mixture of linear polymers to either heat or light. Thermal conversion of the carbon-to-carbon triple bonds in the mixture of linear polymers to form the thermoset polymer is dependent on both the curing temperature and the curing time. The heating of the precursor composition is carried out over a curing temperature range and curing time sufficient for the reaction (cross-linking) of the carbon-to-carbon triple bonds of the individual linear polymers to occur, resulting in the formation of a single mass of cross-linked thermoset polymer. In general, the curing time is inversely related to the curing temperature. The typical temperature range, the preferred temperature range, the more preferred temperature range and the most preferred temperature range for the thermal conversion of the precursor composition to the cross-linked thermoset polymer are, typically, 150-450° C, 200-400° C, 225-375° C and 250-350° C, respectively. The typical curing time, the preferred curing time, the more preferred curing time, and the most preferred curing time are, typically, 1-48 hours, 2-24 hours, 8-12 hours and 1-8 hours, respectively.

Photocrosslinking of the carbon-to-carbon triple bonds in the mixture of linear polymers to form the thermoset polymer by exposing the mixture to light is dependent on both the exposure time and the intensity of the light used during the photocrosslinking process. Ultraviolet (UV) light is the most preferred wavelength of light used during the photocrosslinking process, but other wavelengths can be used. The exposure time is inversely related to the intensity of the UV light used. The exposure time, the intensity, and the wavelength of the light used are that time, intensity and wavelength which are sufficient to cause the carbon-to-carbon triple bonds in the precursor composition to be crosslinked to form the thermoset polymer. The typical exposure time, the preferred exposure time, the more preferred exposure time and the most preferred exposure time are, typically, 1-100 hours, 24-36 hours, 12-24 hours and 4-8 hours, respectively. Because of the limited penetration of light into a polymer composition, the use of photocrosslinking to form thermoset polymers in according to the present invention will be generally limited to films or coatings formed from the precursor composition.

The invention further relates to a method of making a boron-carbon-silicon ceramic comprising the steps of forming an organoboron thermoset polymer precursor composition as described above, and pyrolyzing the precursor composition to form a boron-carbon-silicon ceramic. The pyrolysis is accomplished typically by heating the precursor composition in an inert atmosphere such as N_2 at a temperature between about 450° C and about 2750° C, or by heating the precursor composition in an oxidizing atmosphere such as air at a temperature between about 450° C and about 1650° C. The boron content of the boron-carbon-silicon ceramic can be varied and controlled by varying the relative amount of the carborane containing and non-carborane-containing linear polymers in the precursor composition prior to the pyrolysis step.

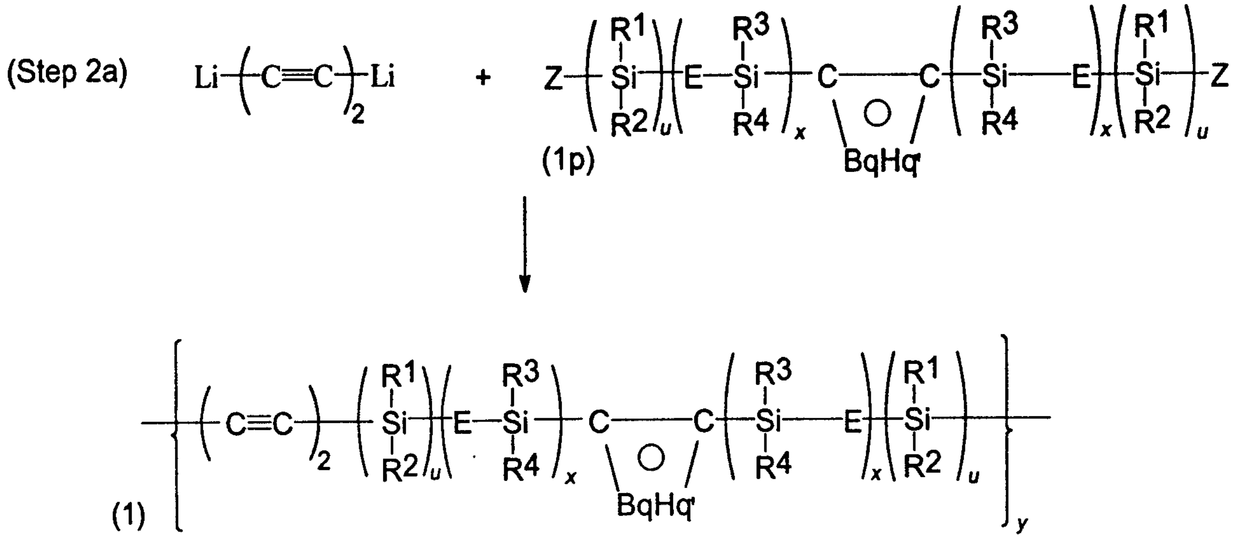
Alternatively, a boron-carbon-silicon ceramic can be made by the steps of forming an organoboron thermoset polymer precursor composition as described above, converting the precursor composition to an organoboron thermoset polymer by heating, as described above, and then pyrolyzing the organoboron thermoset polymer under the same conditions as described above.

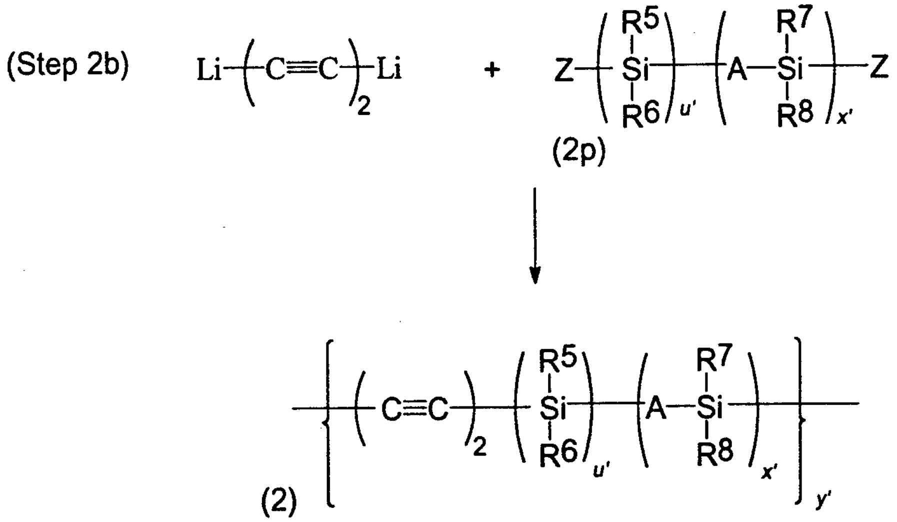
The first linear polymer of the present invention, and, in particular, the polymers represented by formulas (1) and (1') above, can be made by any method known in the art for synthesizing and polymerizing a repeating unit having at least one carboranyl group, at least one silyl or siloxyl group and at least one acetylenic group. The second linear polymer, and in particular, the polymers represented by formulas (2) and (2') above, can be made by any method known in the art for synthesizing and polymerizing a repeating unit having at least one silyl or siloxyl group and at least one acetylenic group and not containing a carboranyl group. Methods for making the first and second linear polymers are described in U.S. Pat. Nos. 5,272,237; 5,292,779; 5,348,917 and 5,483,017, each incorporated by reference above. In particular, U.S. Pat No. 5,483,017 provides guidance for making polymers of formulas (1) and (2) where A and E are aliphatic or aryl bridges. Additional guidance may be found in U.S. Patent Application Serial No. 08/337012 entitled LINEAR CARBORANE-SILOXANE-ACETYLENE COPOLYMERS, filed on November 7, 1994 by named inventors Teddy M. Keller and David Y. Son, in U.S. Patent Application Serial No. 08/437742 entitled SILOXANE-ACETYLENIC

POLYMERS AND BLENDS, filed on May 9, 1995, also by named inventors Teddy M. Keller and David Y. Son, in Son D.Y. and Keller T.M. "Linear Siloxane-Acetylene Polymers as Precursors to High-Temperature Materials" *Fire and Polymers II*; Gordon L. Nelson; ACS Symposium Series 599, American Chemical Society, 1995 edition, Chapter 19, p. 280, in Son, D. Y and Keller, T. M. "Synthesis and Characterization of Linear Siloxane-Diacetylene Polymers" *Macromolecules* **1995**, *28*, 399., in Henderson, L. J. and Keller, T. M. "Synthesis and Characterization of Poly(Carborane-siloxane-acetylene)" *Macromolecules* **1994**, *27*, 1660, and in Keller, T. M. and Son, D. Y., "Inorganic/Organic Hybrid Polymers (High Temperature, Oxidatively Stable)", *Polymeric Materials Encyclopedia*; Joseph C. Salamone; CRC Press: New York 1996; Vol. 5(H-L), p. 3262. These applications and articles are incorporated herein by reference.

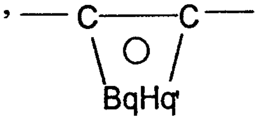
The general chemical scheme for synthesizing linear polymers of formulas **(1)** and **(2)** is represented by the exemplary synthesis of **(1')** and **(2')** given below:

(Step 1)





wherein *u*, *u'*, y, y', $\left(C\equiv C\right)_{n}$, $\left(C\equiv C\right)_{n'}$, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸

,  , *q*, *q'*, *x*, *x'*, A and E are as defined above.

In the general scheme, **step 1** involves forming a salt of the general formula:

$M\left(C\equiv C\right)_{n}M$ wherein M is selected from the group consisting of Li, Na, K and MgX' where X' is selected from the group consisting of F, Cl, Br and I. In the exemplary synthesis outlined above, the dilithio salt of butadiyne is formed by reacting 4 equivalents of n-BuLi with hexachlorobutadiene.

If trichloroethylene is used instead of hexachlorobutadiene in **step 1**, a salt of ethyne or acetylene is formed where n = 1. Consequently, an ethynyl moiety is incorporated into the polymer **(1)** and **(2)** produced in **step 2a** or **step 2b** where n = n' = 1. If hexachlorobutadiene is used in **step 1**, a salt of butadiyne is formed where n = 2. In turn, a butadiyne moiety is incorporated into polymers **(1a)** and **(2a)** where n = n' = 2. To form a polymer where n = 3, a salt of hexatriyne must be formed in **step 1**. The synthesis of the disodium salt of hexatriyne is given in the article by **Bock and Seidl**, ***d-Orbital Effects in Silicon Substituted π-Electron Systems. Part XII. Some Spectroscopic Properties of Alkyl and Silyl Acetylenes and Polyacetylenes***, **J. CHEM. SOC. (B), 1158 (1968)** at **pp. 1159**, incorporated herein by reference in its entirety and for all purposes. Thus, by forming the appropriate alkynyl salt, the length of the alkynyl moiety, represented by the value of n and n', incorporated into the polymer formed in **step 2a** and **step 2b** can be controlled. Typically, the value of n and n' can be varied from 1 to 12. Acetylenic derivatives having the general formula $H(C\equiv C)_nH$ can be readily converted into the dilithio salts by reacting with n-butyllithium. The respective dilithio salts, with values of n varying from 1 to 12, can then be incorporated into the backbone of polymers **(1)** and **(2)** as shown in **step 2a** and **step 2b**. The value of n and n' can be varied, typically, from 1 to 12, more often from 1 to 10 and 1 to 8, most often from 1 to 6 and, in particular, from 1 to 3 and 1 to 2. Acetylenic derivatives having the general formula $H(C\equiv C)_nH$ can be readily formed by the synthesis given by **Eastmond et al.** in **Silylation as a Protective Method for Terminal Alkynes in Oxidative Couplings--A General Synthesis of the Parent Polyynes**, **28 TETRAHEDRON 4601 (1972),** incorporated herein by reference in its entirety and for all purposes.

The reaction parameters (for example, the relative molar amounts of reactants) for the reactions outlined in **step 2a** and **step 2b** can be adjusted to result in carborane-silane/siloxane-acetylene and silane/siloxane-acetylene polymers having an average molecular weight of about 4,000 to more than 10,000. Polymers with average molecular weights much greater than 10,000 can be synthesized and used in the present invention, but these may be less desirable for many purposes because of their greater viscosity. Lower molecular weight species formed by the above reactions may be removed by, for example, heating under vacuum at 150° C.

Examples

The following examples outline preferred embodiments of the present invention.

General Comments

All reactions were carried out in an inert atmosphere unless otherwise noted. Solvents were purified by established procedures. 1,3-Dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were obtained from Silar Laboratories and used as received. n-Butyllithium (*n*-BuLi) (2.5 M in hexane) was obtained from Aldrich and used as received. 1,7-

Bis(chlorotetramethyldisiloxyl)-*m*-carborane was purchased from Dexsil Corporation. Hexachlorobutadiene was obtained from Aldrich and distilled before use. Cure and thermal analysis studies were performed on various mixtures of the compound of formulas **(1')** and **(2')** in milligram quantities. Thermogravimetric analyses (TGA) were performed on a DuPont SDT 2960 Simultaneous DTA-TGA analyzer. Differential scanning calorimetry analyses (DSC) were performed on a DuPont 910 instrument. Unless otherwise noted, all thermal experiments were carried out at a heating rate of 10°C/min and a nitrogen flow rate of 50 cc/min.

EXAMPLE 1

Synthesis of poly (carborane-siloxane-acetylene) (the polymer of formula 1'). In a typical synthesis, a 2.5M hexane solution of *n*-BuLi (34.2 ml, 85.5 mmol) in 12.0 ml of THF was cooled to -78 °C under an argon atmosphere. Hexachlorobutadiene (5.58 g, 21.4 mmol) in 2.0 ml THF was added dropwise by cannula. The reaction was allowed to warm to room temperature and stirred for 2 hours. This reaction forms dilithiobutadiyne. The dilithiobutadiyne in THF was then cooled to -78 °C. At this time, an equimolar amount of 1,7-bis(chlorotetramethyldisiloxyl)-*m*-carborane (10.22 g, 21.4 mmol) in 4.0 ml THF was added dropwise by cannula while stirring. The temperature of the reaction mixture was allowed to slowly rise to room temperature. While stirring the mixture for 1 hour, a copious amount of white solid (LiCl) was formed. The reaction mixture was poured into 100 ml of dilute hydrochloric acid resulting in dissolution of the salt and the separation of a viscous oil. The polymer **1'** was extracted into ether. The ethereal layer was washed several times with water until the washing was neutral, separated, and dried over sodium sulfate. The ether was evaporated at reduced pressure leaving a dark-brown viscous polymer **1'**. A 97% yield (9.50 g) was obtained after drying in vacuo. GPC analysis indicated the presence of low molecular weight species (≈500) as well as higher average molecular weight polymers (Mw≈4900, Mn≈2400). Heating of **1'** under vacuum at 150° C removed lower molecular weight volatiles giving a 92% overall yield. Major FTIR peaks (cm^{-1}): 2963 (C-H); 2600 (B-H); 2175 (C≡C); 1260 (Si-C); and 1080 (Si-O). The polymer was used in preparing mixtures of polymers **1'** and **2'**, as described below and was also used by itself as a comparative example for differential scanning calorimetry analysis (DSC).

Example 2

Synthesis of poly (siloxane-acetylene) (the polymer of formula 2'). A mixture of 1,4-dilithio-1,3-butadiyne (6.3 mmol) in THF/hexane was cooled in a dry ice/acetone bath. To this mixture, 1,3-dichlorotetramethyldisiloxane (1.24 mL, 6.3 mmol) was added dropwise over 15 min. After addition, the cold bath was removed and the mixture was stirred at room temperature for two hours. The tan mixture was poured into 20 mL of ice-cooled saturated aqueous ammonium chloride solution with stirring. The mixture was filtered through a Celite pad and the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic layers were washed twice with distilled water and once with saturated aqueous NaCl solution. The dark brown organic layer was dried over anhydrous magnesium sulfate and filtered. Most of the volatiles were removed at reduced pressure and the residue was heated at 75 °C for three hours at 0.1 torr to give **2'** as a thick, dark brown material (1.04 g, 92%). Polymer **2'** slowly solidifies on standing at room temperature and liquefies at approximately 70 °C. ^1H NMR (ppm) 0.30 (s, 12H, -Si(C*H*$_3$)); ^{13}C NMR (ppm) 1.7, 1.9 (-Si(*C*H$_3$)), 84.9 (-Si-*C*C-), 86.9 (-Si-C*C*-). Anal. Calcd. for $(C_8H_{12}OSi_2)_n$: C, 53.31; H, 6.66; Si, 31.16. Found: C, 55.81; H, 7.61; Si, 27.19. The polymer was used in preparing mixtures of polymers **1'** and **2'**, as described below and was also used by itself as a comparative example for differential scanning calorimetry analysis (DSC).

Example 3

Preparation of Homogeneous Mixtures of 1' and 2'. Mixtures of **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (50:50), 1:3 (25:75) and 1:9 (10:90) were prepared by weighing the appropriate amounts of **1'** and **2'** into a vial, mixing by dissolution in THF, and concentrating at reduced pressure. The resulting mixtures as prepared were viscous compositions. Gummy, semicrystalline compositions formed after several days. Upon heating to 100° C, the mixtures again became viscous liquids. These compositions were used for thermal analysis studies. In the Figures, the 1:1 mixture is composition C, the 1:3 mixture is composition B and the 1:9 mixture is composition A.

Example 4

Differential Scanning Calorimetry Analysis.

Differential Scanning Calorimetry Analyses (DSC) were performed on polymers **1'** and **2'** and on the 1:1, 1:3 and 1:9 mixtures described above. The superimposed DSC thermograms of polymer **1'** and **2'** are shown in Figure 1. The superimposed DSC thermograms of the 1:1, 1:3 and 1:9 mixtures (C, B, and A, respectively) are shown in Figure 2. The DSC analyses of the mixtures show a homogeneous reaction initially to a thermoset. The DSC scans to 400 °C of the blends exhibit only one cure exotherm for each of the compositions studied. For example, mixtures A (1:9), B (1:3) and C (1:1) display exotherms (polymerization reaction) peaking at 296, 298 and 328 °C, respectively. It is apparent from the observed cure temperature for the blends that **2'** being more reactive initially forms radicals that are not selective in the chain propagation reaction with the acetylenic units of both **1'** and **2'**. Samples that have been heat treated to 400 °C do not exhibit characteristic exothermic transitions. The copolymer of formula **20'** of U.S. Patent No. 5,483,017 shows a similar DSC thermogram with a strong exotherm at approximately 300 °C (see Figs. 1, 4, and 7 of U.S. Pat No. 5,483,017).

Example 5

Oxidative Aging Studies of Thermoset from Composition A (molar ratio of 1' to 2' of 1:9)

A 10/90 molar mixture (18.39 mg) of **1'** and **2'** was weighed into a TGA platinum sample pan and cured by heating under an inert atmosphere at 200, 250, 350, and 450 °C for 4 hours at each temperature. Upon cooling the cured thermoset was aged in sequence in a flow of air (50 cc/min) at 200, 250, 300, 350, and 400 °C for 5 hours at each temperature. Additional oxidative heating at 450 °C was performed up to 15 hours. During the heat treatment, the thermoset gained about 6 % weight while being annealed between 200 and 300 °C. Further heat treatment at 350 °C resulted in a slow weight loss of 3 % weight. While heating at 400 °C, the sample lost about 7 % weight. Additional annealing at 450 °C caused initially an enhancement in the weight loss, a stabilizing affect after 15 hours and a char yield of approximately 79 %. Figure 5 shows the superimposed thermogravimetric analytical (TGA) plot of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for composition A and also for the copolymer of formula **20'** of U.S. Patent No. 5,483,017. Figure 6 shows the superimposed thermogravimetric analytical (TGA) plots of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for compositions A, B and C.

Example 6

Oxidative Aging Studies of Thermoset from Composition B (molar ratio of 1' to 2' of 1:3)

A 25/75 molar mixture (18.39 mg) of **1'** and **2'** was weighed into a TGA platinum sample pan and cured by heating under an inert atmosphere at 200, 250, 350, and 450 °C for 4 hours at each temperature. Upon cooling the cured thermoset was aged in sequence in a flow of air (50 cc/min) at 200, 250, 300, 350, and 400 °C for 5 hours at each temperature. Additional oxidative heating at 450 °C was performed up to 15 hours. During the heat treatment, the thermoset gained about 6 % weight while being annealed between 200 and 300 °C. Further heat treatment at 350 °C resulted in a weight loss of less than 2 %. While heating at 400 °C, the sample lost slightly greater than 3 % weight. Additional annealing at 450 °C caused initially an enhancement in the weight loss and a stabilizing affect after 15 hours. After 15 hours, the thermoset had a char yield of almost 90 %. Figure 6 shows the superimposed thermogravimetric analytical (TGA) plots of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for compositions A, B and C.

Example 7

Oxidative Aging Studies of Thermoset from Composition C (molar ratio of 1' to 2' of 1:1)

A 50/50 molar mixture (18.39 mg) of **1'** and **2'** was weighed into a TGA platinum sample pan and cured by heating under an inert atmosphere at 200, 250, 350, and 450 °C for 4 hours at each temperature. Upon cooling the cured thermoset was aged in sequence in a flow of air (50 cc/min) at 200, 250, 300, 350, and 400 °C for 5 hours at each temperature. Additional oxidative heating at 450 °C was performed up to 15 hours. During the heat treatment, the thermoset gained about 4 % weight while being annealed between 200 and 300 °C. Further heat treatment at 350 and 400 °C resulted in a weight loss of less than 1 %. Additional annealing at 450 °C resulted in a weight loss of less than 1 %. After 15 hours at 450 °C, the thermoset had a total weight gain of 2 %. Figure 6 shows the superimposed thermogravimetric analytical (TGA) plots of weight % (y-axis, left scale) versus temperature (y-axis, right scale) and time (x-axis) for compositions A, B and C.

Example 8

Conversion of Homogeneous Mixtures of 1' and 2' to Ceramics.

Mixtures of **1'** and **2'** having molar ratios of **1'** to **2'** of 1:1 (50:50), 1:3 (25:75) and 1:9 (10:90) were weighed into a alumina TGA sample pan and heated to either 1000 °C or 1500 °C under inert conditions resulting in char yields of 77-80 %. During the heat treatment, similar exothermic transitions (DTA) as found during the DSC scans were observed. Moreover, above 1000 °C, an exothermic transition is observed which is attributed to the formation of crystalline ceramic components such as SiC and B_4C. The TGA plot of composition A heated to 1000° C is shown in Figure 8.

Example 9

Exposure of Ceramics to Extreme Oxidizing Environments.

Upon cooling the ceramic chars from Example 8 were reheated to 1500 °C under a flow of air to determine the oxidative stability. The oxidative stability of the charred mass was found to be a function of the amount of **1'** present and the initial heat treatment. Charred samples obtained from heat treatment to 1000 °C and 1500 °C of mixtures of **1'** and **2'** having molar ratios of **1'** to **2'** of 1:9 (composition A), 1:3 (composition B) and 1:1 (composition C) showed chars of 98, 98, 99% and 90, 97, 98% respectively, when reheated in air. The superimposed TGA plots of compositions A, B, and C that were originally heated to 1000° C are shown in Figure 3. The superimposed TGA plots of compositions A, B, and C that were originally heated to 1500° C is shown in Figure 4. The major difference observed was in the chars formed from the 10/90 mixtures (composition A). The crystalline-containing compositions lost most of their weight between 700 and 800 °C. For the amorphous compositions, weight losses occurred between 600 and 700 °C and above 1000 °C. As the temperature was further increased, an acceleration in the weight loss was observed. These results indicate that the oxidative stability of the carbon/ceramic mass depends on the morphology.

FIG. 9 shows the TGA plot of weight versus temperature in an oxidizing environment (air) of the char obtained from first heating composition A (molar ratio of 1' to 2' of 1:9) to 1000° C and then allowing the char to cool. The maximum temperature for the second heating cycle was also 1000° C.

Example 10

Oxidative Aging Studies on Ceramics Formed from Molar Mixtures of 1' and 2'

Long-term oxidative studies were also performed on the chars obtained from mixtures of **1' and 2'**. A ceramic composition prepared from the 10/90 mixture (composition A) was initially processed to 1000 °C under a nitrogen atmosphere. Upon cooling, the char was aged in sequence at 400, 500, 600, and 700 °C in a flow of air for 5 hours at each temperature. While at 500 °C the char gained about 0.3% weight. During the entire heat treatment, the ceramic sample lost less than 1% weight. This weight loss occurred between 500 and 600 °C. At 700 °C, no weight changes were observed. These observations indicate that a protective outer layer forms and insulates the interior against further oxidation. A charred sample that had been processed from poly (siloxane-acetylene) in an identical manner as the blended mixture showed a 28% weight loss after 15 hours in air at 500 °C. The outer surface of the sample was coated with a white flaky residue attributed to silicon oxide. The outer surface of the chars formed from the blended mixtures upon exposure to air at elevated temperatures remained black. This observation indicating that a different outer oxidized surface forms with structural integrity when boron is present. Figure 7 shows the thermogravimetric analytical (TGA) plot of weight % (y-axis left scale) versus temperature (y-axis, right scale) and time (x-axis) for the long-term oxidative study of the composition A.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that

the invention may be practiced otherwise than as specifically described.

Docket No.: N.C. 77,112
Inventor's Name: Teddy M. Keller and David Y. Son

PATENT APPLICATION

ABSTRACT

An organoboron thermoset polymer precursor composition is made up of a mixture of a first linear polymer having a repeating unit comprising at least one carboranyl group, at least one silyl or siloxyl groups, and at least one acetylenic group, and a second linear polymer having a repeating unit comprising at least one silyl or siloxyl groups and at least one acetylenic moiety and wherein the second linear polymer does not contain a carboranyl group. The amount of carborane in the thermoset can be controlled by varying the relative amount of the carborane-containing polymer and the non-carborane-containing polymer in the precursor composition. The organoboron thermoset polymer precursor is used to make a thermoset by curing the precursor composition with heat or light, and to make a ceramic by pyrolyzing the precursor composition or a thermoset made from the precursor composition.

Figure 1

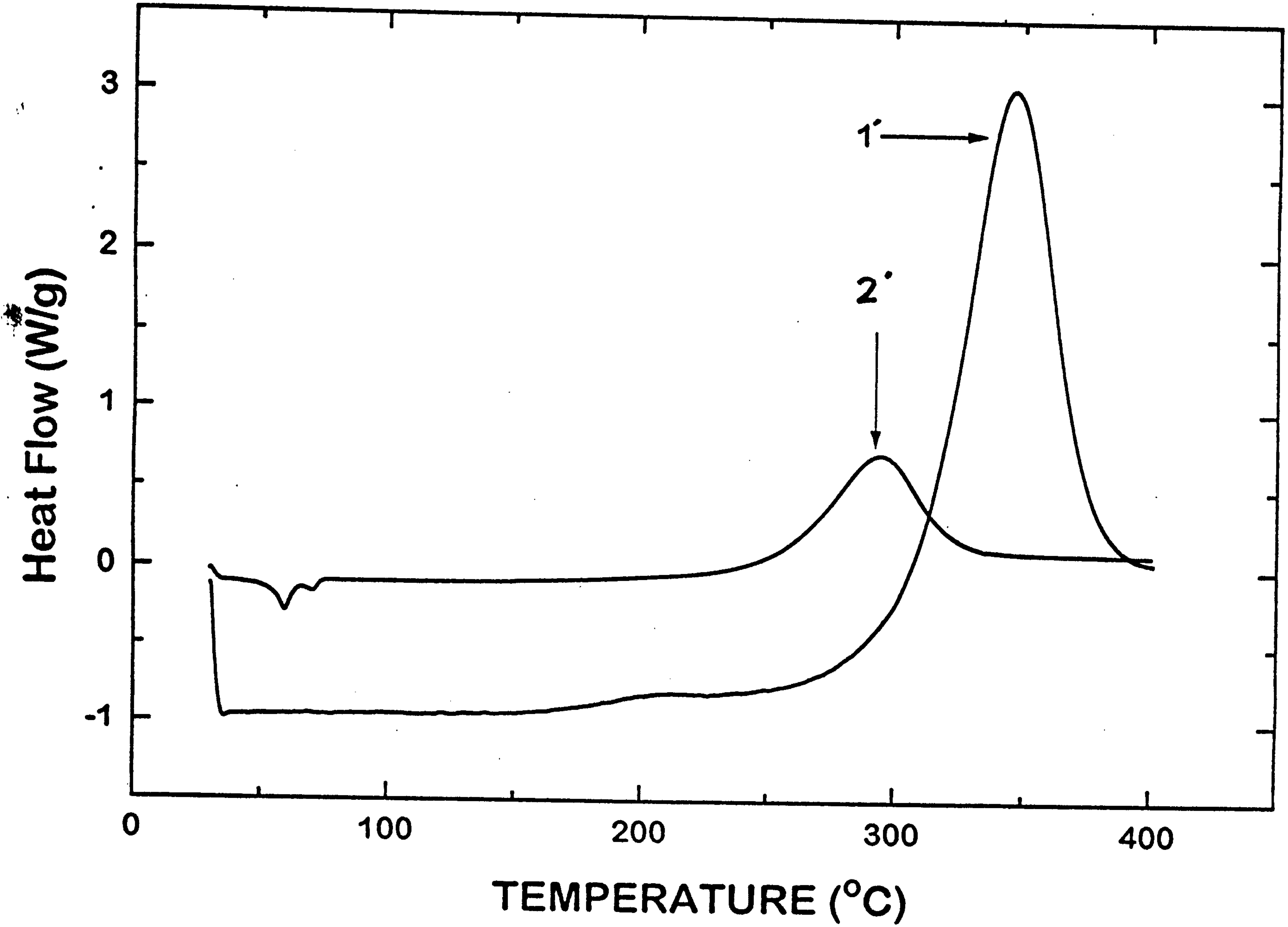


Figure 2

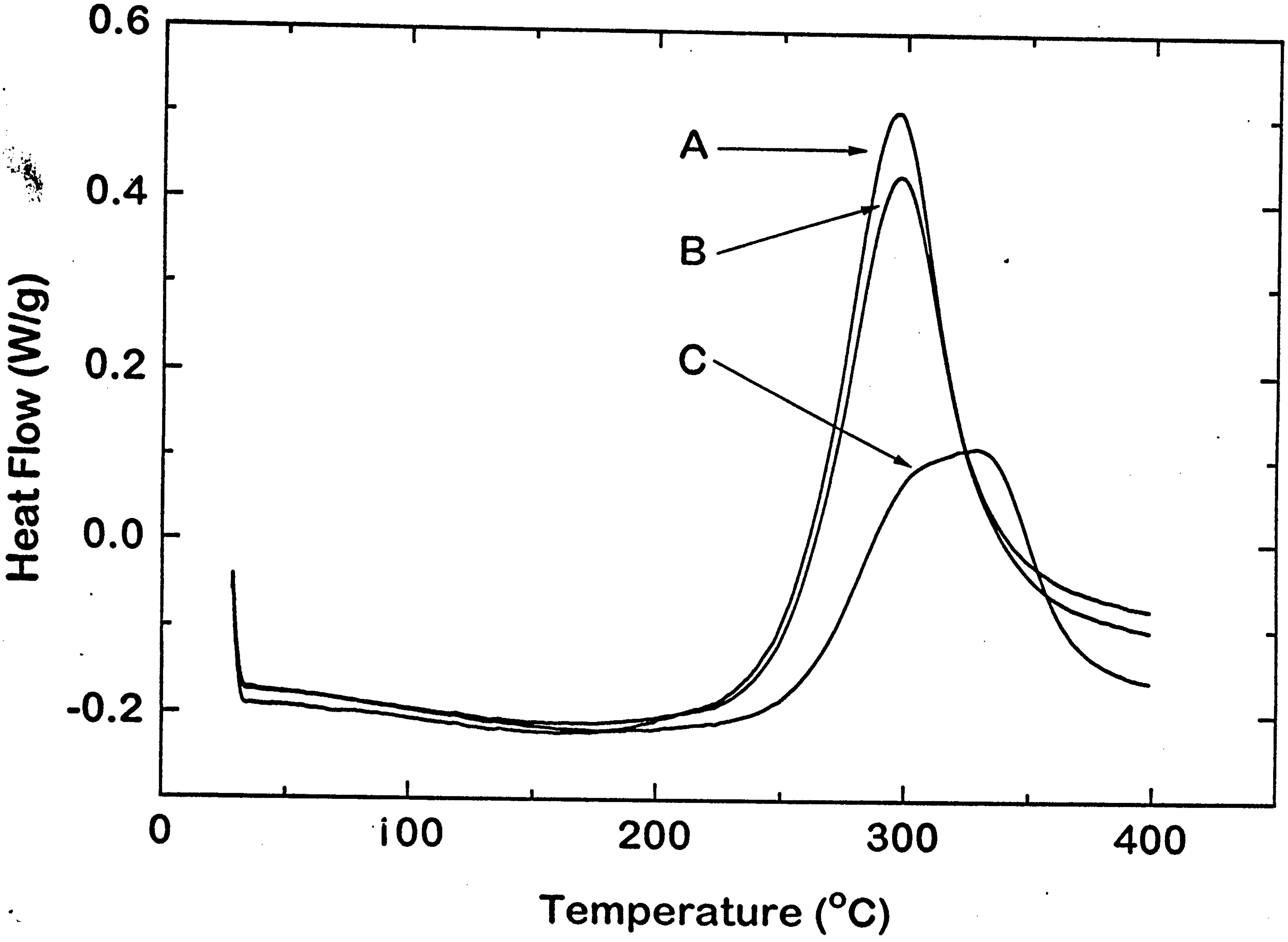
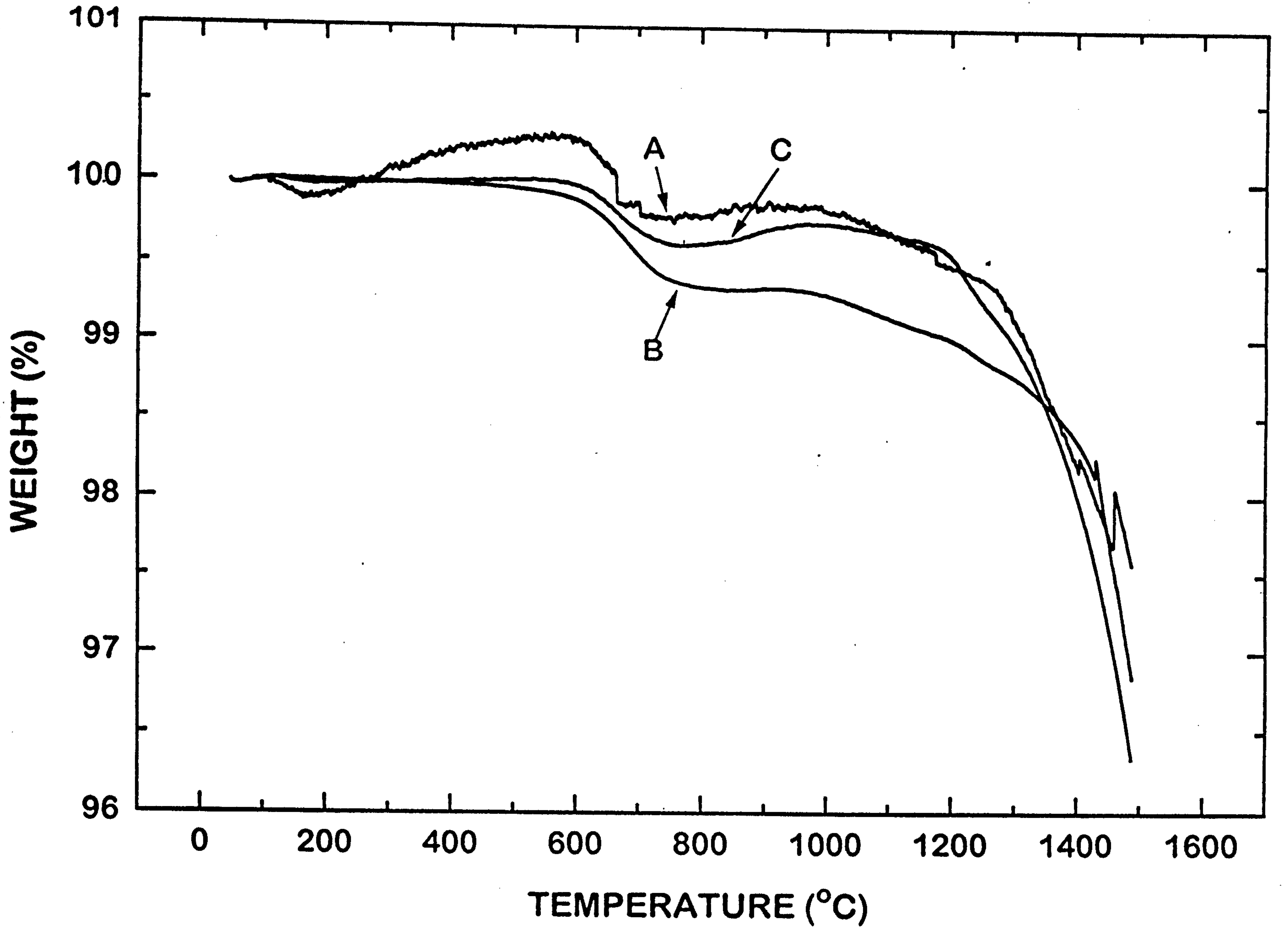


Figure 3



A
C
B
101
100
99
98
97
96
0
200
400
600
800
1000
1200
1400
1600
WEIGHT (%)
TEMPERATURE (°C)

Figure 4

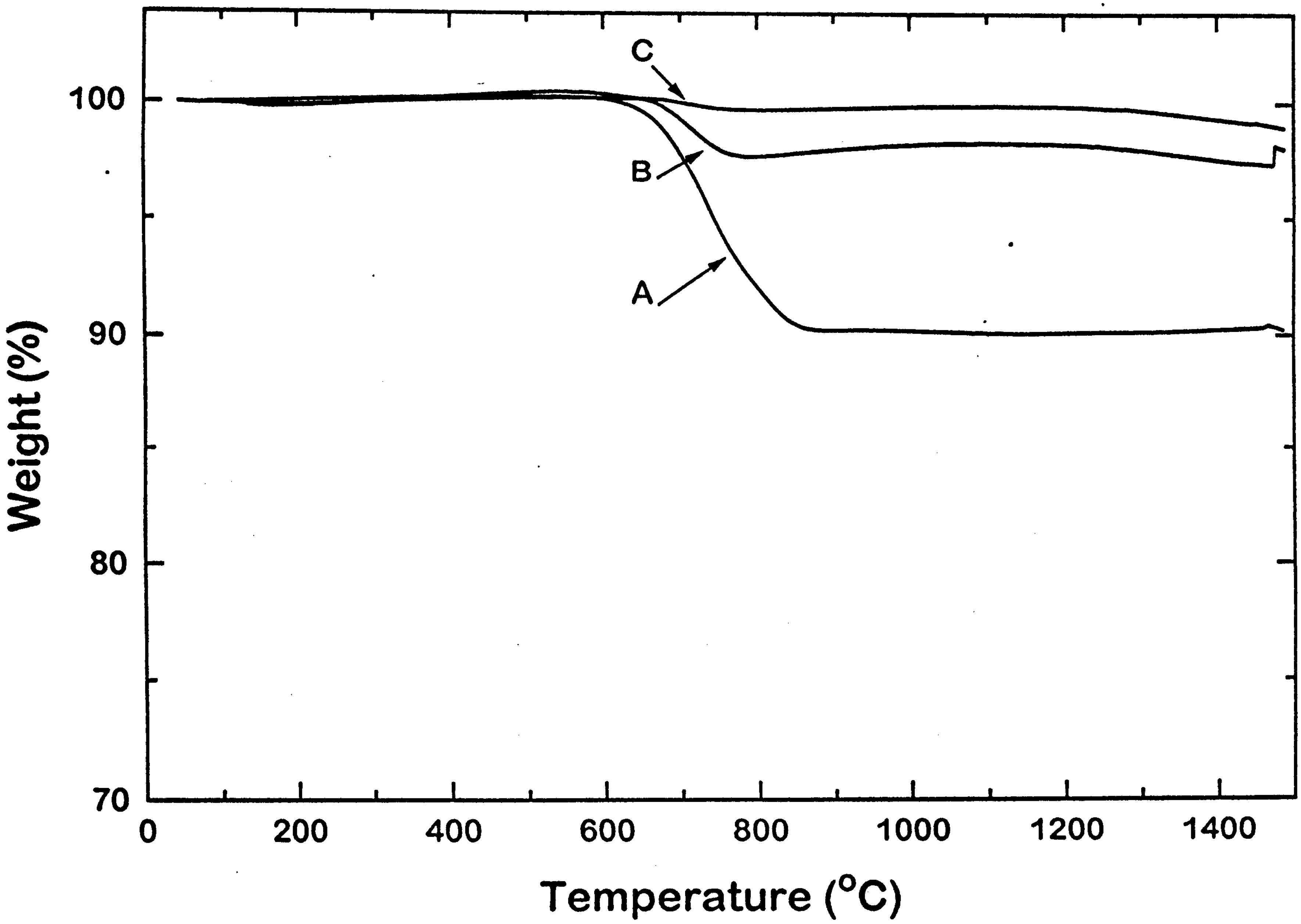

C
B
A
100
90
80
70
Weight (%)
0
200
400
600
800
1000
1200
1400
Temperature (°C)

Figure 6

Figure 5

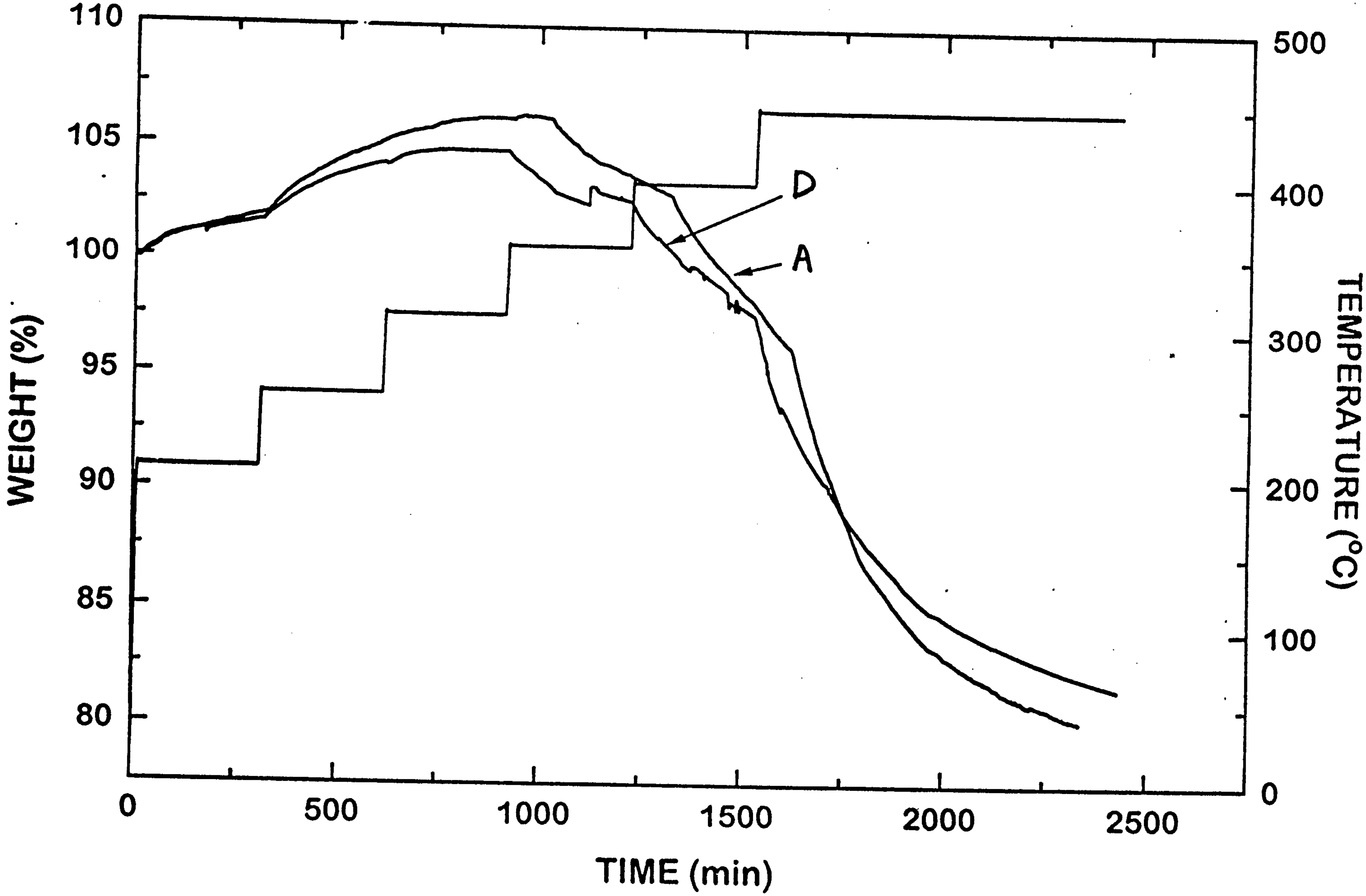
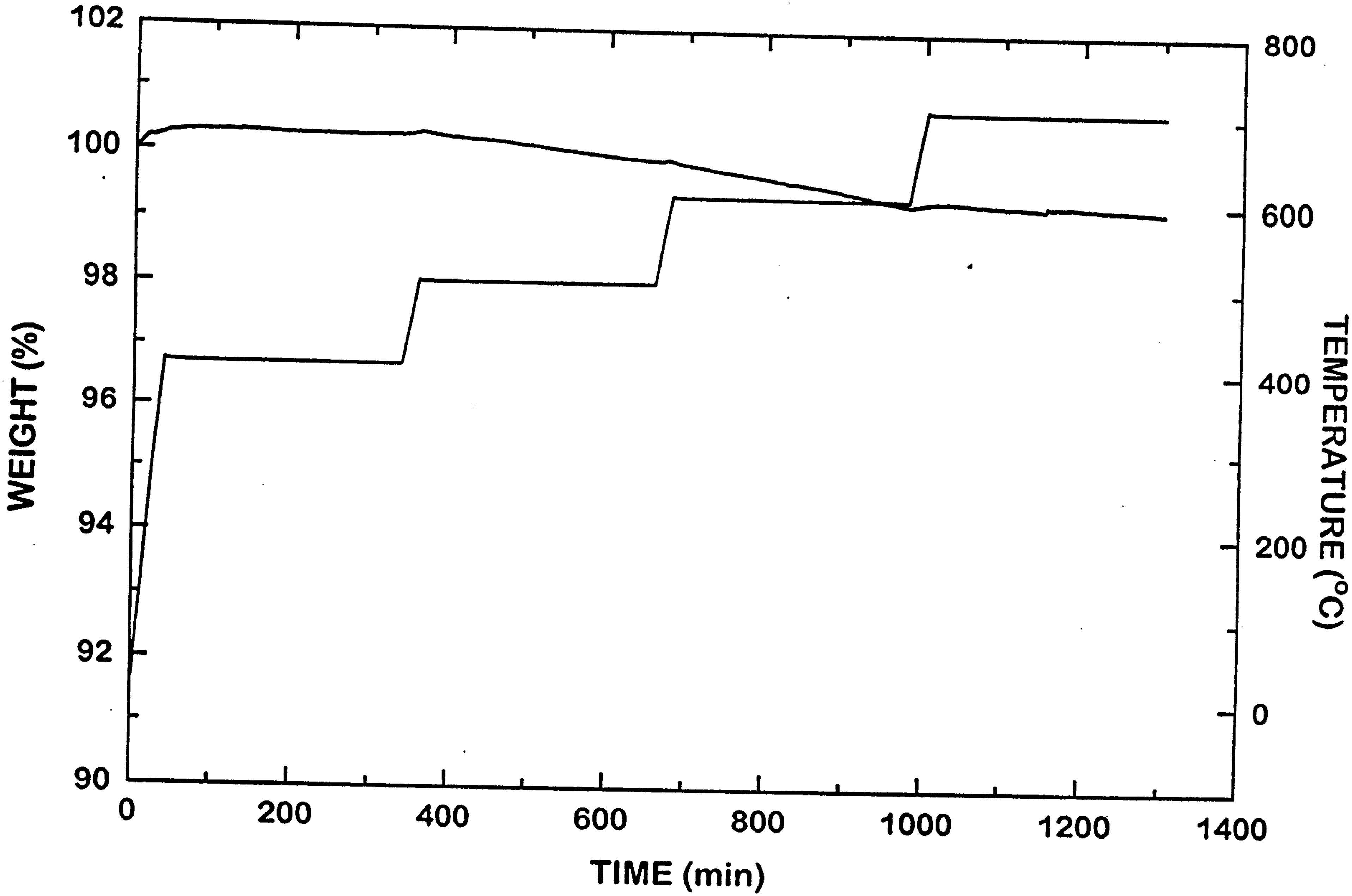


Figure 7


WEIGHT (%)
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100
98
96
94
92
90
TEMPERATURE (°C)
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600
400
200
0
TIME (min)
0
200
400
600
800
1000
1200
1400

Figure 8

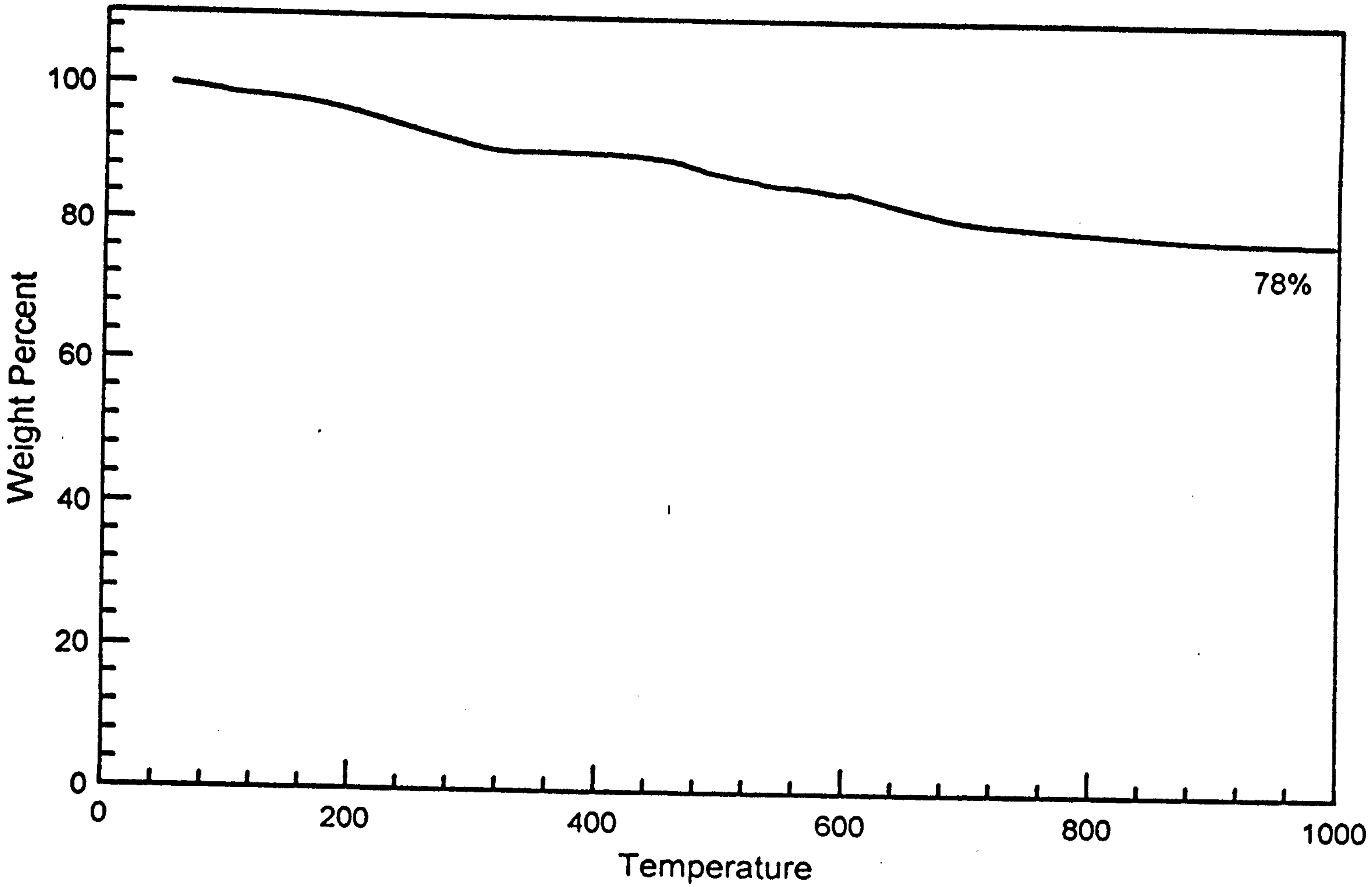
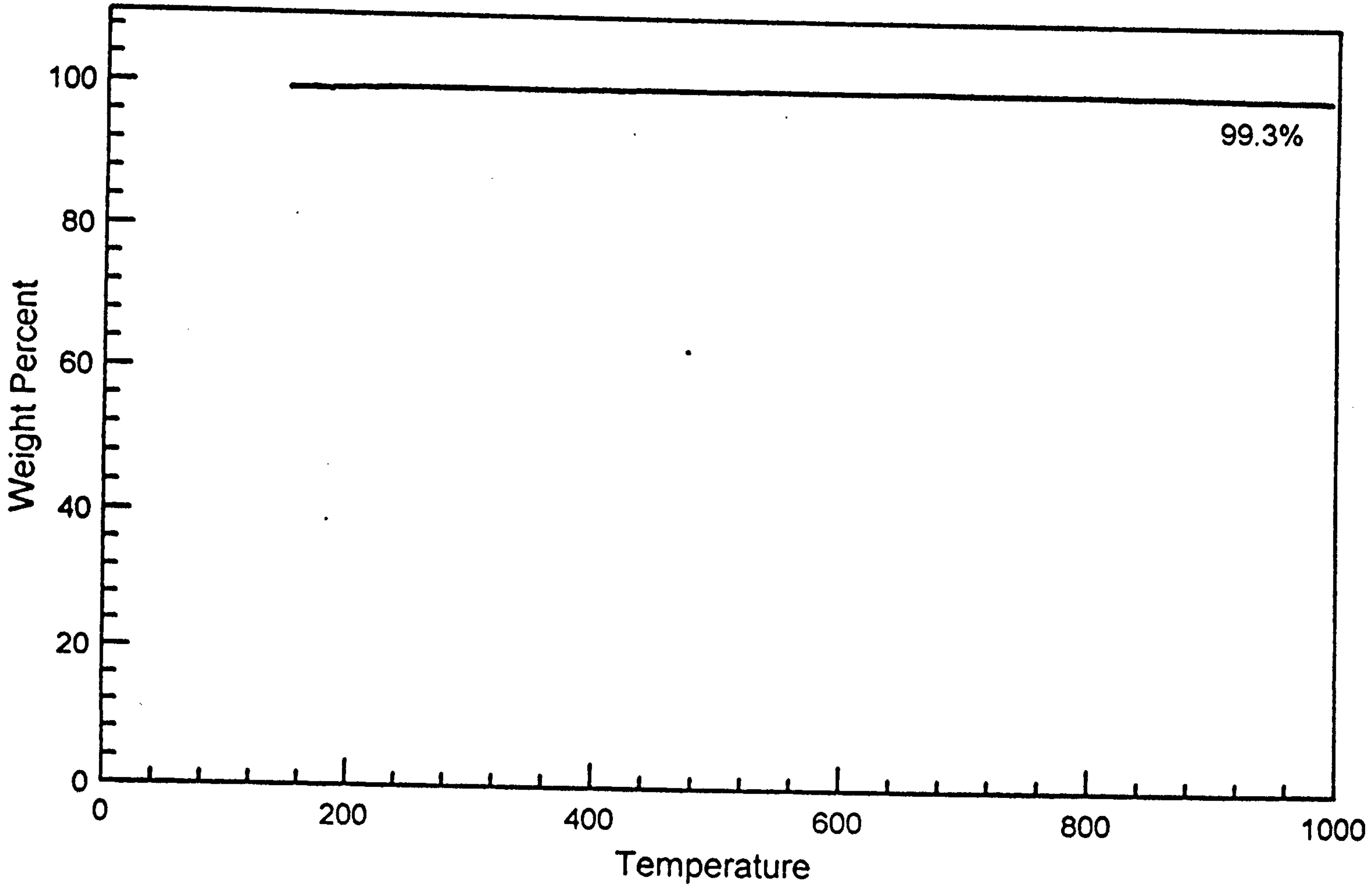

100
80
60
40
20
0
Weight Percent
0
200
400
600
800
1000
Temperature
78%

Figure 9


99.3%
Weight Percent
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20
40
60
80
100
0
200
400
600
800
1000
Temperature