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Inventor Teddy M. Keller
David Y. Son

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NAVY CASE NO.: 77,160

1 MACROMOLECULES 3528-30 (1988), incorporated herein by reference. The recent literature
2 reflects continuing major research efforts to advance fundamental knowledge in high
3 temperature material design. See K.J. Wynne and R.W. Rice, Ceramics Via Polymer
4 Pyrolysis 14 ANN. REV. MAT. SCI. 297 (1984) incorporated herein by reference in its
5 entirety and for all purposes. In the search for high temperature oxidatively stable
6 materials considerable attention has been given to polymers containing boron within the
7 polymer. It has been known that the addition of a carborane within a siloxane polymer
8 significantly increases the thermal stability of such siloxane polymers.

9 The thermal properties of various siloxane polymers are given by PETAR DVORNIC ET
10 AL. in HIGH TEMPERATURE SILOXANE ELASTOMERS published by Huthig & Wepf Verlag Basel,
11 New York (1990) on pp. 277 in Fig. 5.7 and on pp.282 in Fig. 5.12 and by Edward N.
12 Peters in Poly(dodecacarborane-siloxanes) published in J. MACROMOL. SCI.-REV. MACROMOL.
13 CHEM., C17(2) on pp. 190-199 in Figs. 3,4,5,6,7,10 and 12, each reference being
14 incorporated herein by reference in its entirety and for all purposes.
15 See also Maghsoodi et al. in Synthesis and Study of Silylene-Diacetylene Polymers published
16 in 23 MACROMOLECULES pp. 4486 (1990), incorporated herein by reference in its entirety
17 and for all purposes.

18 Many of the carborane polymers manufactured are cited in various U.S. patents.
19 See, for instance, the following U.S. Pat. Nos.: 5,348,917; 5,292,779; 5,272,237; 4,946,919;
20 4,269,757; 4,235,987; 4,208,492; 4,145,504; 3,661,847; 3,542,730; 3,457,222; and 3,234,288,
21 each patent being incorporated herein by reference in its entirety and for all purposes.

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1 There is a need for oxidatively stable ceramic materials suitable for making rigid
2 components therefrom (e.g. by combining with fiberglass or carbon matrix or other
3 matrix fibers, respectively), such as engine parts, turbine blades and matrices. These
4 components must withstand high temperatures and be oxidatively stable and have
5 sufficient strength to withstand the stress put on such components.

6 There is a need for carborane-silane and/or carborane-siloxane ceramic materials
7 wherein the carborane content of the ceramics can be varied by varying the carborane
8 content of the precursor thermosetting polymers. Weight percentage loss of the ceramic
9 materials is limited to 50% or less from the original total weight or where the weight
10 percentage loss is limited to 40% or less after formation of the precursor thermoset when
11 heated in excess of 400 to 700 °C in an oxidative environment.

12 There is a need for carborane-silane and/or carborane-siloxane ceramic materials
13 wherein the carborane content of the ceramics can be varied by varying the carborane
14 content of the precursor thermosetting polymers. Weight percentage loss of the ceramic
15 materials is limited to 30% or less from the original total weight or where the weight
16 percentage loss is limited to 15% or less after formation of the precursor thermoset when
17 heated in excess of 400 to 700 °C in an oxidative environment.

18 There is a need for carborane-silane and/or carborane-siloxane ceramic materials
19 wherein the carborane content of the ceramics can be varied by varying the carborane
20 content of the precursor thermosetting polymers. Weight percentage loss of the ceramic
21 materials is limited to 20% or less from the original total weight or where the weight

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1 percentage loss is limited to 10% or less after formation of the precursor thermoset when
2 heated in excess of 400 to 700 °C in an oxidative environment.

3 In addition, there is a need for carborane-silane and/or carborane-siloxane ceramic
4 materials that behave more as rigid materials and less as elastomeric materials and
5 wherein the carborane content of the ceramics can be varied.

6 There is a further need to provide carborane-silane and/or carborane-siloxane
7 ceramic materials wherein the carborane content within the ceramics can be varied to
8 provide maximum thermal stability and minimum cost.

9 In addition, a majority of the carborane-siloxane and/or carborane-silane polymers
10 made by others show elastomeric properties rather than properties of more rigid
11 products like ceramics. Thus, in addition to thermal stability, there is also a need for
12 materials that behave more as ceramics, upon further polymerization, and less like
13 elastomeric polymers.

14 **SUMMARY OF THE INVENTION**

15 It is therefore an object of the present invention to provide carborane-silane-
16 alkenyl and/or carborane-siloxane-alkenyl containing ceramic materials that show high
17 temperature stability where weight percentage loss is limited to 50% or less from the
18 original total weight or where the weight percentage loss is limited to 40% or less after
19 formation of the precursor thermoset when heated in excess of 400 to 700 °C in an
20 oxidative environment and wherein the content of carborane within the ceramic (and the
21 precursor thermoset) can be varied.

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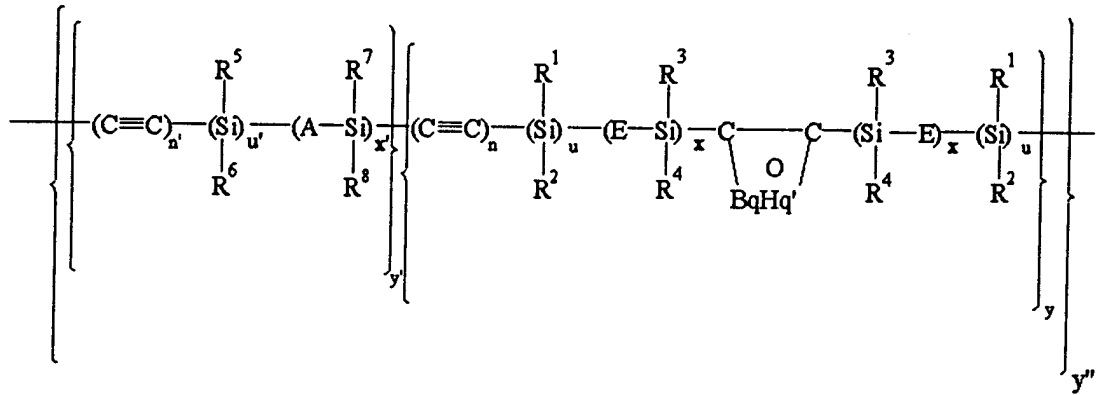
1 It is therefore an object of the present invention to provide carborane-silane-
2 alkenyl and/or carborane-siloxane-alkenyl containing ceramic materials that show high
3 temperature stability where weight percentage loss is limited to 30% or less from the
4 original total weight or where the weight percentage loss is limited to 15% or less after
5 formation of the precursor thermoset when heated in excess of 400 to 700 °C in an
6 oxidative environment and wherein the content of carborane within the ceramic (and the
7 precursor thermoset) can be varied.

8 It is therefore an object of the present invention to provide carborane-silane-
9 alkenyl and/or carborane-siloxane-alkenyl containing ceramic materials that show high
10 temperature stability where weight percentage loss is limited to 20% or less from the
11 original total weight or where the weight percentage loss is limited to 10% or less after
12 formation of the precursor thermoset when heated in excess of 400 to 700 °C in an
13 oxidative environment and wherein the content of carborane within the ceramic (and the
14 precursor thermoset) can be varied.

15 It is therefore yet another object of the present invention to provide carborane-
16 silane-alkenyl and/or carborane-siloxane-alkenyl containing ceramic materials wherein the
17 carborane content within the ceramic materials can be varied to provide maximum
18 thermal stability and minimum cost.

19 These and other objects are accomplished by forming linear polymers having the
20 composition:

21



wherein $n, n', u, u', x, x', y, y'$ and y'' are integers, wherein the ratio $y'/y \neq 0$, wherein A is selected from the group consisting of O, an aliphatic bridge, an aryl bridge or mixtures thereof and E is selected from the group consisting of O, an aliphatic bridge, an aryl bridge or mixtures thereof. In addition, E and/or A may further be selected from the group consisting of an aliphatic bridge of about 1 to about 20 carbon atoms, an aryl bridge of about 5 to 40 carbon atoms, or mixtures thereof. Furthermore, A and E may be the same or different. Further heating or light exposure forms the desired thermosets. Further heating of the thermosets forms the desired ceramics.

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:

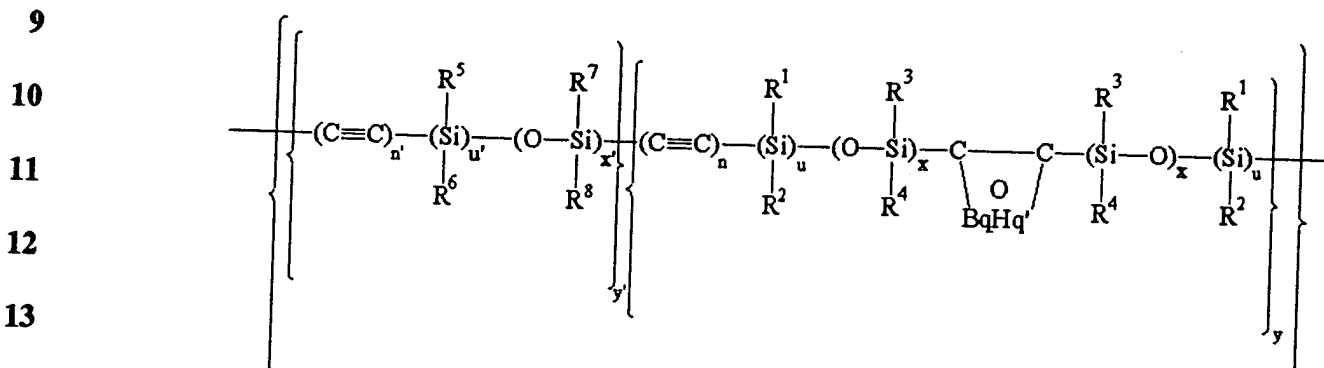
FIG. 1 is a differential scanning calorimetry (DSC) plot of heat flow versus

1 temperature in nitrogen obtained at an exemplary heating rate of 10 °C/minute.

2 FIG. 2 is a thermogravimetric analytical (TGA) plot of weight % versus
 3 temperature in nitrogen obtained on the first heating cycle (e.g. heating from 50 °C to
 4 1000 °C at 10 °C/minute).

5 FIG. 3 is a TGA plot of weight versus temperature in an oxidizing environment
 6 (air), subsequently obtained on the second heating cycle (e.g. heating from 100 °C to
 7 1000 °C at 10 °C/minute).

8 FIGS. 1, 2, and 3 are for the polymer having the formula:



14 where $n' = n = 2$, $q = q' = 10$, $u = u' = x = x' = 1$, $R^1 = R^2 = R^3 = R^4 = R^5 = R^{6y''} =$
 15 $R^7 = R^8 = \text{CH}_3$ and the ratio y'/y on average is equal to about 1.0.

16 FIG. 4 is a differential scanning calorimetry (DSC) plot of heat flow versus
 17 temperature in nitrogen obtained at an exemplary heating rate of 10 °C/minute.

18 FIG. 5 is a thermogravimetric analytical (TGA) plot of weight % versus
 19 temperature in nitrogen obtained on the first heating cycle (e.g. heating from 50 °C to
 20 1000 °C at 10 °C/minute).

21 FIG. 6 is a TGA plot of weight versus temperature in an oxidizing environment

1 (air), subsequently obtained on the second heating cycle (e.g. heating from 100 °C to
2 1000 °C at 10 °C/minute).

3 FIGS. 4, 5, and 6 are for the polymer having the formula:

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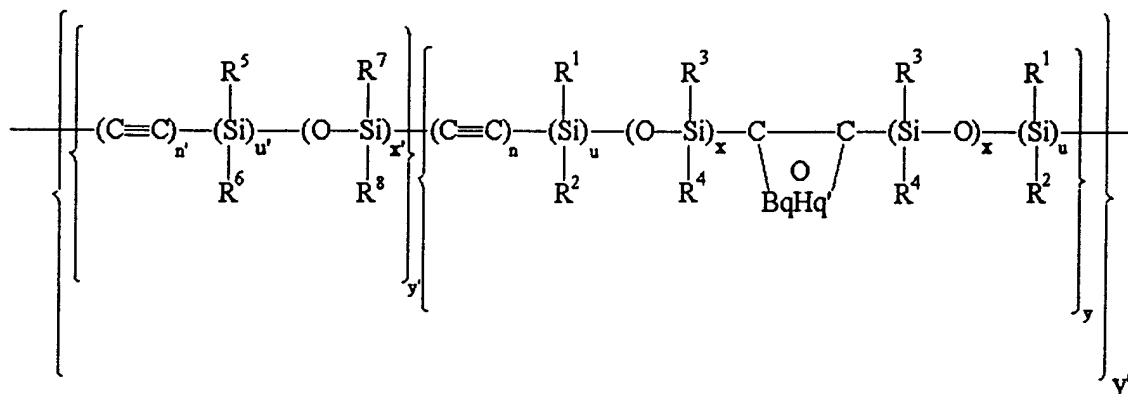
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10 where $n' = n = 2$, $q = q' = 10$, $u = u' = x = x' = 1$, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 =$
11 $R^7 = R^8 = \text{CH}_3$, and the ratio y'/y on average is equal to about 3.0.

12 FIG. 7 is a differential scanning calorimetry (DSC) plot of heat flow versus
13 temperature in nitrogen obtained at an exemplary heating rate of 10 °C/minute.

14 FIG. 8 is a thermogravimetric analytical (TGA) plot of weight % versus
15 temperature in nitrogen obtained on the first heating cycle (e.g. heating from 50 °C to
16 1000 °C at 10 °C/minute).

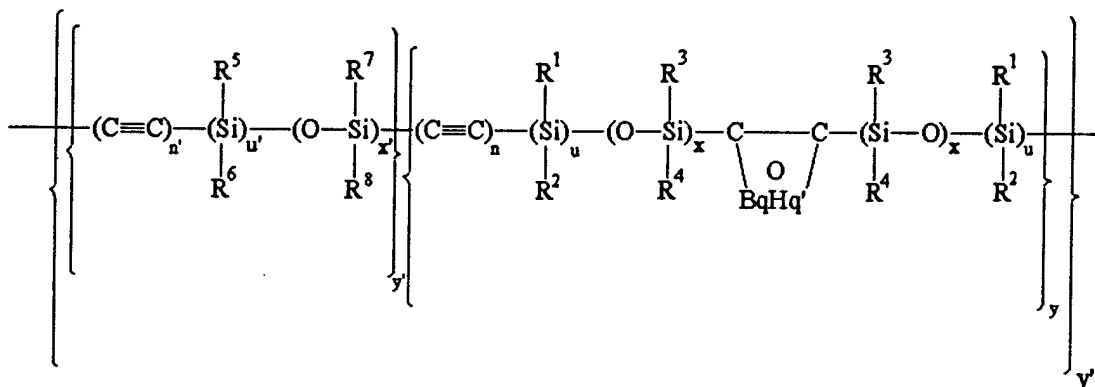
17 FIG. 9 is a TGA plot of weight versus temperature in an oxidizing environment
18 (air), subsequently obtained on the second heating cycle (e.g. heating from 100 °C to
19 1000 °C at 10 °C/minute).

20 FIGS. 7, 8, and 9 are for the polymer having the formula:

21

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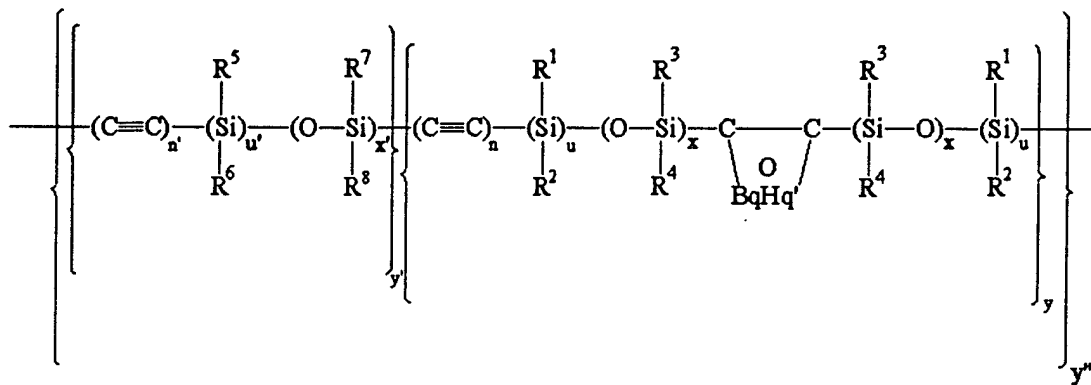
7 where $n' = n = 2$, $q = q' = 10$, $u = u' = x = x' = 1$, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 =$
8 $R^7 = R^8 = CH_3$, and the ratio y'/y on average is equal to about 9.0.

9 FIG. 10 is a differential scanning calorimetry (DSC) plot of heat flow versus
10 temperature in nitrogen obtained at an exemplary heating rate of 10 °C/minute.

11 FIG. 11 is a thermogravimetric analytical (TGA) plot of weight % versus
12 temperature in nitrogen obtained on the first heating cycle (e.g. heating from 50 °C to
13 1000 °C at 10 °C/minute).

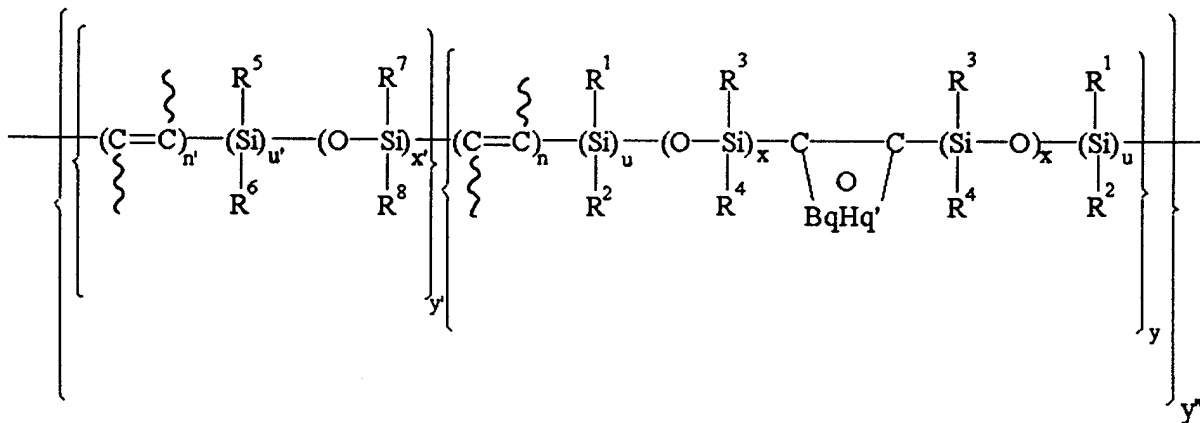
14 FIG. 12 is a TGA plot of weight versus temperature in an oxidizing environment
15 (air), subsequently obtained on the second heating cycle (e.g. heating from 100 °C to
16 1000 °C at 10 °C/minute).

FIGS. 10, 11, and 12 are for the polymer having the formula:



where $n' = n = 2$, $q = q' = 10$, $u = u' = x = x' = 1$, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = \text{CH}_3$, and the ratio y'/y on average is equal to about 19.0.

FIGURE 13 is a TGA of the thermoset made from the linear polymer of FIGURES 1, 2, and 3. FIGURE 14 is a TGA of the thermoset made from the linear polymer of FIGURES 4, 5, and 6. FIGURE 15 is a TGA of the thermoset made from the linear polymer of FIGURES 7, 8, and 9. FIGURE 16 is a TGA of the thermoset made from the linear polymer of FIGURES 10, 11, and 12. The thermosets of FIGS. 13, 14, 15 and 16 have the formula:



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1 wherein the values of n, n', q, q', x, x', y, y' and y'' are unchanged and the identities of R¹
2 = R² = R³ = R⁴ = R⁵ = R⁶ = R⁷ = R⁸ = CH₃ as previously indicated and the ratio y'/y
3 is also unchanged, respectively.

4 **Detailed Description of the Preferred Embodiments**

5 The following detailed description of the invention is provided to aid those skilled
6 in the art in practicing the present invention. However, the following detailed description
7 of the invention should not be construed to unduly limit the present invention.

8 Variations and modifications in the embodiments discussed may be made by those of
9 ordinary skill in the art without departing from the scope of the present inventive
10 discovery.

11 This invention relates to a new class of novel cross-linked thermosetting polymers
12 (35) made by the following general reaction scheme:

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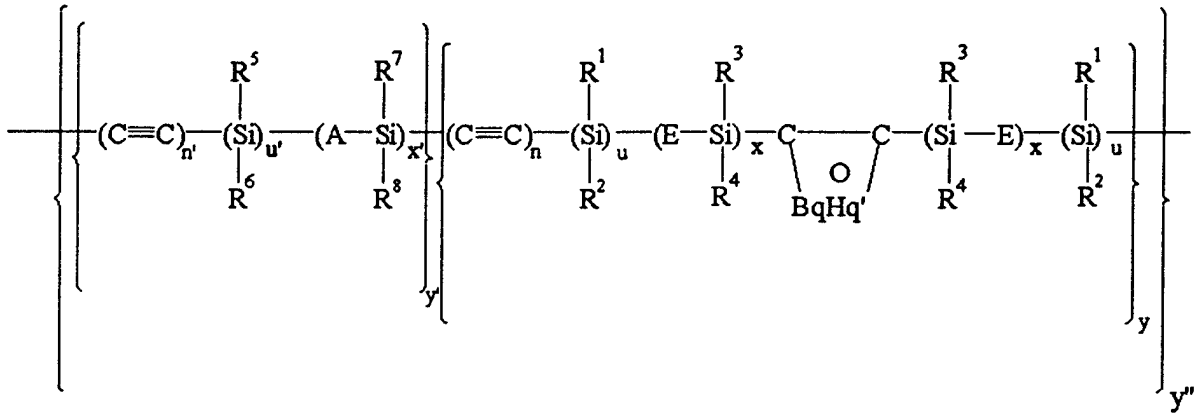
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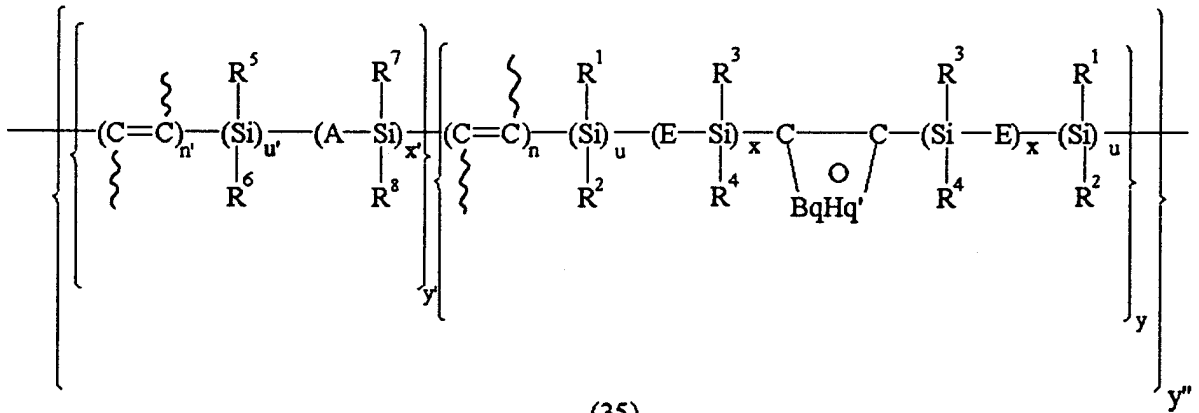
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1



(20)

heat or light



(35)

2 wherein

3 (1) n and n' are integers from 1 to 12 and u, u', y, y' and y'' are positive

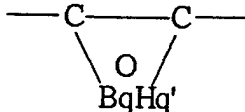
1 integers;

2

3 (2) $\text{---}(\text{C}\equiv\text{C})_n\text{---}$ and $\text{---}(\text{C}\equiv\text{C})_{n'}\text{---}$ represent unconjugated
4 acetylenic moieties or conjugated acetylenic moieties when n and n' are
5 integers greater than 1, respectively;

6 (3) $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7$ and R^8 are selected from the group consisting of
7 saturated aliphatic, unsaturated aliphatic, aromatic, fluorocarbon moieties
8 and mixtures thereof;

9

10 (4)  represents said carboranyl group;

11

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

13 (6) x and x' represent integers greater than or equal to zero ($x \geq 0; x' \geq 0$);

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

16 (8) E is selected from the group consisting of O, an aliphatic bridge, an aryl
17 bridge or mixtures thereof;

18 (9) wherein E and A may be the same or different;

19 (10) wherein said carboranyl group represents a carboranyl group selected from
20 the group consisting of 1,7-dodecacarboranyl; 1,10-octacarboranyl; 1,6-octacarboranyl;
21 2,4-pentacarboranyl; 1,6-tetracarboranyl; 9-alkyl-1,7-dodecacarboranyl; 9,10-dialkyl-1,7-

1 dodecacarboranyl; 2-alkyl-1,10-octacarboranyl; 8-alkyl-1,6-octacarboranyl; decachloro-1,7-
2 dodecacarboranyl; octachloro-1,10-octacarboranyl; decafluoro-1,7-dodecacarboranyl;
3 octafluoro-1,10-octacarboranyl; closo-dodeca-ortho-carboranyl; closo-dodeca-meta-
4 carboranyl; closo-dodeca-para-carboranyl and mixtures thereof; and

5 (11) wherein $\text{---}(\overset{\zeta}{\text{C}}=\overset{\zeta}{\text{C}})_{n'}$ and $\text{---}(\overset{\zeta}{\text{C}}=\overset{\zeta}{\text{C}})_{n}$ represent cross-linked
6 alkenyl moieties and wherein n and n' are as previously indicated.

7 The conversion of the linear polymers (20) to the cross-linked polymers (35) is
8 accomplished either by exposing the linear polymers (20) to heat or light. Thermal
9 conversion of the carbon-to-carbon triple bonds in polymers (20) to form the
10 thermosetting polymers (35) is dependent on both the curing temperature and the curing
11 time. The heating of the linear polymers (20) is carried out over a curing temperature
12 range sufficient for the cross-linking of the carbon-to-carbon triple bonds of the individual
13 linear polymers (20) to occur resulting in the formation of a single mass of cross-linked
14 polymers (35). The heating of the linear polymers (20) is carried out over a curing time
15 sufficient for the cross linking of the carbon-to-carbon triple bonds of the individual
16 linear polymers (20) to occur resulting in the formation of the cross-linked polymers (35).
17 In general, the curing time is inversely related to the curing temperature. The typical
18 temperature range, the preferred temperature range, the more preferred temperature
19 range and the most preferred temperature range for the thermal conversion of linear
20 polymers (20) to the cross-linked thermoset polymers (35) are, typically, 150-450°C, 200-
21 400°C, 225-375°C and 250-350°C, respectively. The typical curing time, the preferred

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1 curing time, the more preferred curing time, and the most preferred curing time for the
2 thermal conversion of linear polymers (20) to the cross-linked thermoset polymers (35)
3 are, typically, 1-48 hours, 2-24 hours, 8-12 hours and 1-8 hours, respectively.

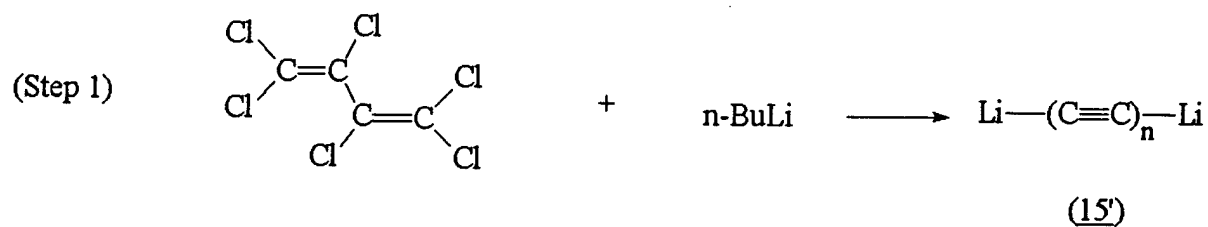
4 The photocrosslinking process, of converting the carbon-to-carbon triple bonds of
5 the linear polymers (20) into unsaturated cross-linked moieties necessary for forming the
6 thermosetting polymers (35), is dependent on both the exposure time and the intensity of
7 the light used during the photocrosslinking process. Ultraviolet (UV) light is the most
8 preferred wavelength of light used during the photocrosslinking process. The exposure
9 time of the linear polymers (20) to the UV light is inversely related to the intensity of the
10 UV light used. The exposure time to the UV or to other light used is that time which is
11 sufficient for the carbon-to-carbon triple bonds of the linear polymers (20) to be cross
12 linked to form the thermosetting polymers (35). The intensity of the light used is that
13 intensity which is sufficient for the carbon-to-carbon triple bonds of the linear polymers
14 (20) to be cross linked to form the thermosetting polymers (35). Furthermore, the
15 wavelength of the light used is not limited to the UV range. The wavelength of light
16 used is that wavelength which is sufficient for the carbon-to-carbon triple bonds of the
17 linear polymers (20) to be cross linked to form the thermosetting polymers (35). The
18 typical exposure time, the preferred exposure time, the more preferred exposure time
19 and the most preferred exposure time are, typically, 1-100 hours, 24-36 hours, 12-24
20 hours and 4-8 hours, respectively. Examples of the conversion of linear polymers (20) to
21 the cross-linked thermosets (35) are given *infra*.

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1 The general chemical scheme for synthesizing these novel linear polymers (20) is
2 represented by the exemplary synthesis of (20') given below:

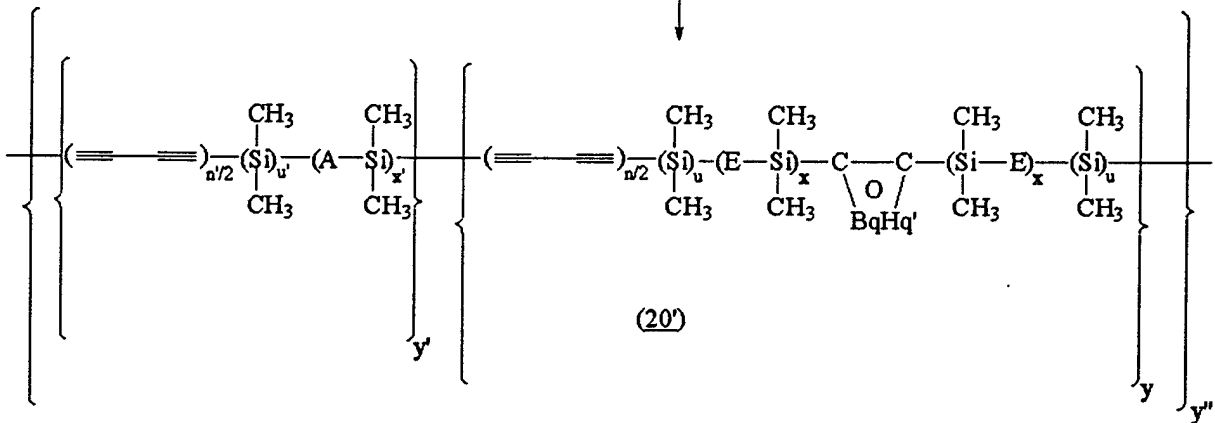
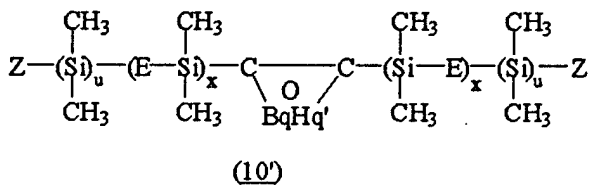
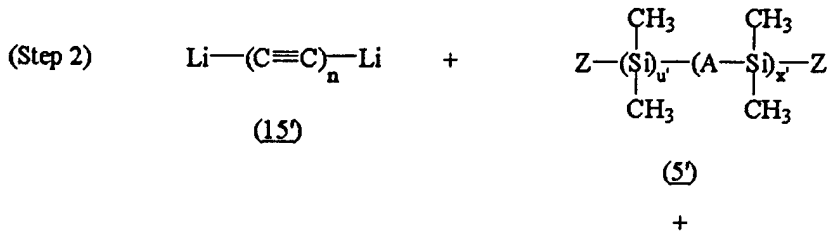
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1 wherein:

2 (1) $n = n' = 2, u = u' = x = x' = 1, y, y'$ and y'' are positive integers;

3 (2) $\text{---}(\text{C}\equiv\text{C})_n\text{---}$ and $\text{---}(\text{C}\equiv\text{C})_{n'}\text{---}$ represents a conjugated
4 acetylenic moiety where $n = n' = 2$;

5 (3) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{R}^6 = \text{R}^7 = \text{R}^8 = \text{CH}_3$;

6 (4)  represents said carboranyl group; and

7
8 (5) $q = q' = 10$;

9 (6) Z is selected from the group consisting of F, Cl, Br and I;

10 (7) $\text{Li---}(\text{C}\equiv\text{C})_n\text{---Li}$ represents a dilithio salt where $n = 2$ or $n' = 2$;

11 (8) n-BuLi represents n-butyllithium;

12 (9) A is an oxygen atom; and

13 (10) E is an oxygen atom.

14 Given the general scheme, step 1 involves forming a salt, for example, the dilithio salt of
15 butadiyne by reacting 4 equivalents of n-BuLi with hexachlorobutadiene. Note that
16 Reagents of the following general formula may be used:



18 wherein M is selected from the group consisting of Li, Na, K and MgX' where X' is

19 selected from the group consisting of F, Cl, Br and I. To form the polymer (20'),

20 wherein $y'/y = 1.0$, step 2 involves reacting the dilithiobutadiyne (15') produced in step 1

21 with compounds (5') and (10') wherein the molar concentration of (5') equals the molar

1 concentration of (10') and wherein the molar concentrations of (5') and (10'),
2 respectively, equal one-half (1/2) the molar concentration of the dilithiobutadiyne (15').

3 In general, the following concentrations are used:

4 (i) molar conc. of (5') + molar conc. of (10') = molar conc. of (15')

5 (ii) the ratio of $y'/y = (\text{molar conc. of } (5'))/(\text{molar conc. of } (10'))$.

6 For the formation of polymer (20), the present invention makes the ratio of y'/y
7 variable by the use of appropriate molar ratios of compounds having the formula (5) and
8 (10), *infra*. In general, the ratio of y'/y is equal to the molar concentration of (5) used
9 divided by the molar concentration of (10) used in forming (20). Thus, if equimolar
10 amounts of (5) and (10), *infra*, are used, then the ratio of y'/y is about 1.0. If the molar
11 ratios of (5) and (10), *infra*, used are 1 to 99, respectively, then the ratio of y'/y is about
12 0.01 in the formed product (20). Typically, the ratio y'/y is between about 0.01 to about
13 50. More typically, the ratio y'/y is between about 1 to about 25. Most typically, the
14 ratio y'/y is between about 5 to about 15. Preferably, the ratio y'/y is between about 8 to
15 about 12. Most preferably, the ratio y'/y is about 9.

16 It should be noted that if trichloroethylene is used in step 1 instead of
17 hexachlorobutadiene, a salt of ethyne or acetylene is formed in step 1 where $n = 1$.
18 Consequently, an ethynyl moiety is incorporated into the polymer (20) produced in step 2
19 where $n = n' = 1$. By using hexachlorobutadiene in step 1, the salt of butadiyne is
20 formed where $n = 2$. In turn, a butadiyne moiety is incorporated into polymer (20')
21 where $n = n' = 2$. In order to form a polymer where $n = 3$, a salt of hexatriyne needs

1 to be formed in step 1. The synthesis of the disodium salt of hexatriyne is given in the
2 article by Bock and Seidl, *d-Orbital Effects in Silicon Substituted π -Electron Systems. Part*
3 *XII. Some Spectroscopic Properties of Alkyl and Silyl Acetylenes and Polyacetylenes*, J. CHEM.
4 SOC. (B), 1158 (1968) at pp. 1159, incorporated herein by reference in its entirety and for
5 all purposes. Thus, by forming the appropriate alkynyl salt, the length of the alkynyl
6 moiety, represented by the value of n and n', incorporated into the polymer formed in
7 step 2 can be controlled. Typically, the value of n and n' can be varied from 1 to 12.
8 Acetylenic derivatives having the general formula $H(C\equiv C)_nH$ can be readily converted
9 into the dilithio salts by reacting with n-butyllithium. The respective dilithio salts, with
10 values of n varying from 1 to 12, can then be incorporated into the backbone of polymers
11 (20) as shown in the aforementioned step 2. The value of n and n' can be varied,
12 typically, from 1 to 12, more often from 1 to 10 and 1 to 8, most often from 1 to 6 and,
13 in particular, from 1 to 3 and 1 to 2. Acetylenic derivatives having the general formula
14 $H(C\equiv C)_nH$ can be readily formed by the synthesis given by Eastmond et al. in *Silylation*
15 *as a Protective Method for Terminal Alkynes in Oxidative Couplings--A General*
16 *Synthesis of the Parent Polyynes*, 28 TETRAHEDRON 4601 (1972), incorporated herein by
17 reference in its entirety and for all purposes.

18 Furthermore, a variety of compounds can be produced that have structures similar
19 to that of compound (10') shown in step 1. One variation includes replacing the methyl
20 groups attached to the Si with other hydrocarbon or aromatic moieties. Typical reactions
21 synthesizing disubstituted dichloro silanes of varying size (varying values of u) and having

1 different R groups are known in the art:

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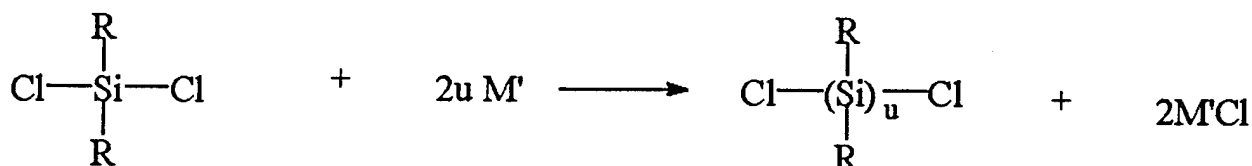
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8 where M' is a group I metal or alloy. The above reaction is cited by ZELDIN ET AL.

9 (EDITORS) in INORGANIC AND ORGANOMETALLIC POLYMERS, published by American Chemical

10 Society, Washington, DC (1988) at 44 and 90. The value of u can be varied, typically,

11 from 1 to 1000, more often from 1 to 500 and 1 to 250, most often from 1 to 100 and 1

12 to 10, and, in particular, from 1 to 6. Another variation includes controlling the values of

13 x in addition to that of u.

14 Synthesis of a variation of compound (10') where u = 1 and

15 x = 0 and E = O and Z = Cl is given by Papetti et al. in A New Series of Organoboranes.

16 VI. The Synthesis and Reactions of Some Silyl Neocarboranes, 3 INORG. CHEM. 1448 (1964)

17 at 1449 under the caption "C,C'-Bis(methyldichlorosilyl)neocarborane (IV)", incorporated

18 herein by reference in its entirety and for all purposes. The synthesis of compound (10')

19 where u = 1 and x = 1 and E = O and Z = Cl is given by Papetti et al. in A New Series

20 of Organoboranes. VII. The Preparation of Poly-m-carboranylenesiloxanes, 4 JOURNAL OF

21 POLYMER SCIENCE: PART A-1, 1623 (1966) at 1630 under the caption "Compound (VII)",

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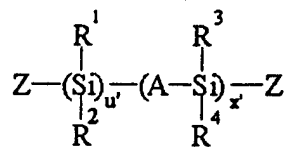
1 incorporated herein by reference in its entirety and for all purposes. Synthesis of a
2 variation of compound (10') where $u = 1$ and $x = 2$ and $E = O$ and $Z = Cl$ is given by
3 Scott et al. in *Icosahedral Carboranes. XV. Monomeric Carboranylenesiloxanes*, 9 INORG.
4 CHEM. 2597 (1970) at 2599 under the caption "1,7-Bis(5-chlorohexamethyltrisiloxanyl)-m-
5 carborane (IV)", incorporated herein by reference in its entirety and for all purposes.

6 While leaving $u = 1$, the value of x can be varied, typically, from 0 to 1000, more
7 often from 0 to 500 and 0 to 250, most often from 0 to 10, and, in particular, from 0 to 2
8 by the following proposed reaction scheme (i.e. the length of the polymer chain within
9 compound (10) is varied according to the following reaction):

10

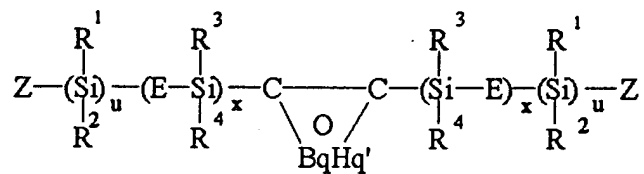
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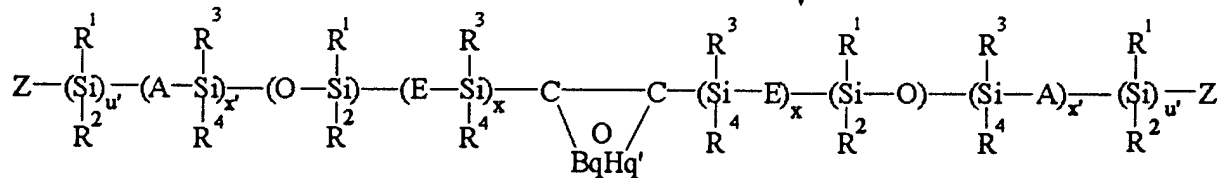
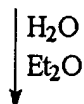


(5)

+



(10)



(10'')

1

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1 where x and x' are integers greater than or equal to 0 ($x \geq 0$; $x' \geq 0$), u' is a positive integer
2 and A is an oxygen atom and E is an oxygen atom.

3 The value of x can be iteratively increased by reacting compounds (5) and (10)
4 wherein $u = u' = 1$ until the desired integral value of x is obtained; thereafter, further
5 reacting the reaction product (10^u) with compound (5) wherein u' is an integer greater
6 than 1 thereby forming product (10) wherein the value of u can be varied to integral
7 values greater than 1 and wherein the value of x has been adjusted to a desired integral
8 value greater than 1. Note that reaction product (10^u) is analogous to reactant (10)
9 wherein the values of integrals u and x have been varied.

10 However, A may be selected from the group consisting of O, an aliphatic bridge,
11 an aryl bridge or mixtures thereof. A may further be selected from the group consisting
12 of an aliphatic bridge of about 1 to about 20 carbon atoms, an aryl bridge of about 5 to
13 about 40 carbon atoms, or mixtures thereof. Furthermore, E may be selected from the
14 group consisting of O, an aliphatic bridge, an aryl bridge or mixtures thereof. E may
15 further be selected from the group consisting of an aliphatic bridge of about 1 to about
16 20 carbon atoms, an aryl bridge of about 5 to about 40 carbon atoms, or mixtures
17 thereof. In addition, A and E may be the same or different. An exemplary synthesis of
18 compound (10) is shown by the synthesis of exemplary compound (100). Synthesis of
19 exemplary compound (100) wherein R^1 , R^2 , R^3 and R^4 are $-\text{CH}_3$, wherein E is
20 $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, wherein $x = 2$, $u = 1$, and $q = q' = 10$ is given in EXAMPLE 10,
21 *infra*.

1 The synthesis of (5) is given below:

2

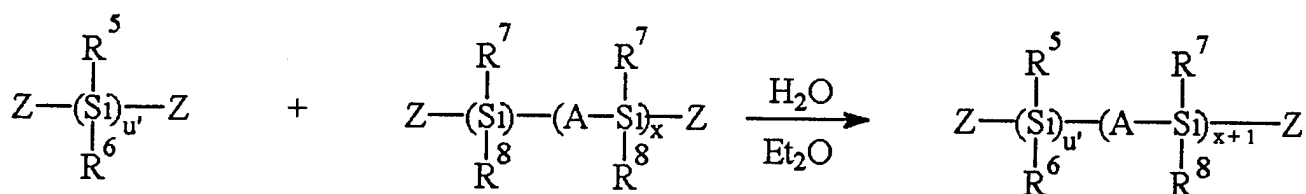
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8 wherein $x' = x + 1$ and A is an oxygen atom and wherein R^5 , R^6 , R^7 , and R^8 may be the
 9 same or different.

10 For the case where A is not an oxygen atom, the synthesis of (5) is given below:

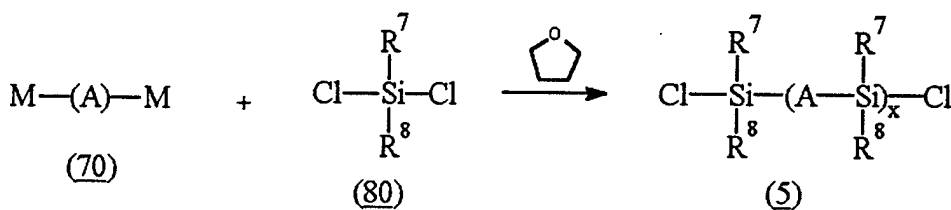
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16 wherein M is selected from the group consisting of Li, Na, K and MgX' where X' is
 17 selected from the group consisting of F, Cl, Br and I, wherein R^7 and R^8 may be the
 18 same or different and x is a positive integer. Where the ratio of the molar concentration
 19 of (70) to the molar concentration of (80) is equal to about one-half, the value of x is
 20 about 1. Where the ratio of the molar concentration of (70) to the molar concentration
 21 of (80) is greater than one-half but less than 1, the value of x is greater than 1. When

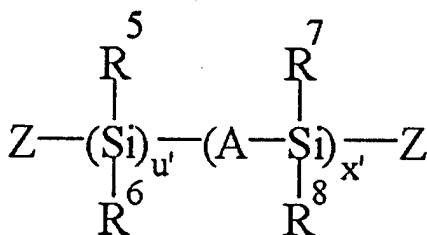
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1 A is not an oxygen atom, to form compound (5), the value of x can be controlled by
2 selecting the appropriate ratio of the molar concentration of (70) to the molar
3 concentration of (80). If the ratio is selected according to
4 $\frac{1}{2} \leq (\text{molar concentration of (70)} / \text{molar concentration of (80)}) < 1$, then the integral
5 value of x obtained in compound (5) is proportional to the ratio of the molar
6 concentration of (70) to the molar concentration of (80).

7 A may be selected from the group consisting of O, an aliphatic bridge, an aryl
8 bridge or mixtures thereof. A may further be selected from the group consisting of an
9 aliphatic bridge of about 1 to about 20 carbon atoms, an aryl bridge of about 5 to about
10 40 carbon atoms, or mixtures thereof.

11 Following the scheme in the aforementioned steps 1 and 2, the novel linear
12 polymers (20) can be formed by reacting a salt of an alkyne or a respective Grignard
13 reagent with compounds (5) and (10):

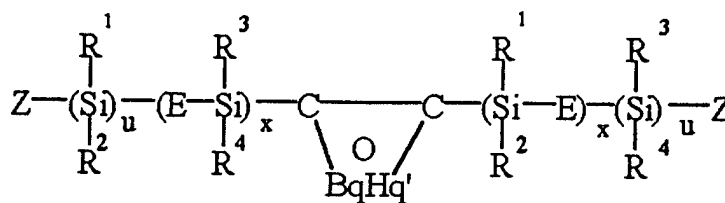


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(10)

wherein E is selected from the group consisting of O, an aliphatic bridge, an aryl bridge or mixtures thereof and wherein A is selected from the group consisting of O, an aliphatic bridge, an aryl bridge or mixtures thereof.

These novel linear polymers (20) exhibit sufficiently low viscosities either at room temperature or at their respective melting points (i.e. 20 - 70 °C) to readily fill complex dies or shapes for forming parts therefrom. In addition, these polymers (20) can be further polymerized into thermosets and ceramics that form rigid shapes which are oxidatively stable at high temperatures above 600 °C.

The following examples outline preferred embodiments of the present invention.

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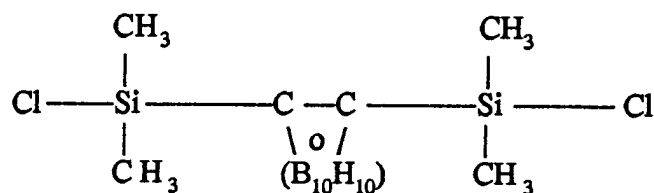
EXAMPLE 1

3

4 Compound (30) is synthesized according to the method of Papetti & Heying. See

5 S. Papetti et al. 3 INORG CHEM 1448 (1964). The structure of compound (30) is given

6 below:



7

(30)

8 According to the method of Papetti et al., a 100ml round bottom 3-neck flask was fitted

9 with an addition funnel and septa, flushed with argon, and flamed. The reaction was

10 carried out under an inert atmosphere (argon). Butyllithium (18.0 ml/ 2.5M in hexanes,

11 44.9 mmol) was cooled to -78°C. *Meta*-carborane (2.5902 g, 18.0 mmol) in 10 ml THF

12 was added dropwise. A white solid (dilithiocarborane) formed and the reaction was

13 allowed to warm to ambient temperature. After cooling the reaction mixture back to -

14 78°C, dichlorodimethylsilane (5.5 ml, 43.5 mmol) was added dropwise.

15

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EXAMPLE 2

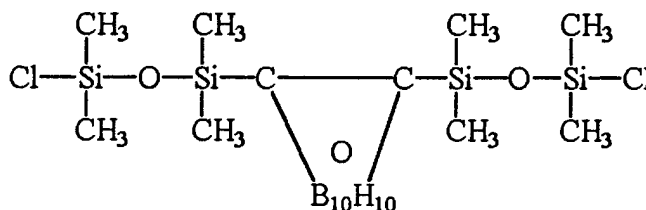
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4 EXPERIMENTAL SECTION

5 General Comments apply to Examples 2 - 8:

6 All reactions were carried out in an inert atmosphere unless otherwise noted. Solvents
7 were purified by established procedures. 1,7-Bis(chlorotetramethyldisiloxy)-*m*-carborane
8 (40) was obtained from Dexsil and used as received. 1,7-Bis(chlorotetramethyldisiloxy)-
9 *m*-carborane (40) has the following structure:

10



11

12

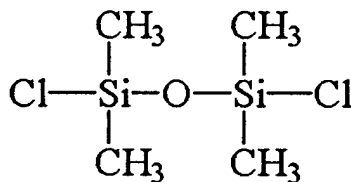
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(40)

15 1,3-Dichlorotetramethyldisiloxane (50) was obtained from Silar Laboratories or United
16 Chemical Technologies and used as received. 1,3-Dichlorotetramethyldisiloxane (50) has
17 the following structure:

18



19

20

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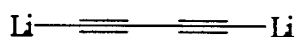
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1 n-Butyllithium (2.5 M in hexane), and hexachlorobutadiene were obtained from Aldrich
2 and used as received. Thermogravimetric analyses (TGA) were performed on a DuPont
3 951 thermogravimetric analyzer. Differential scanning calorimetry analyses (DSC) were
4 performed on a DuPont 910 instrument. Unless otherwise noted, all thermal
5 experiments were carried out with a heating rate of 10 C/min and a nitrogen flow rate
6 of 50 mL/min.

8 EXAMPLE 3

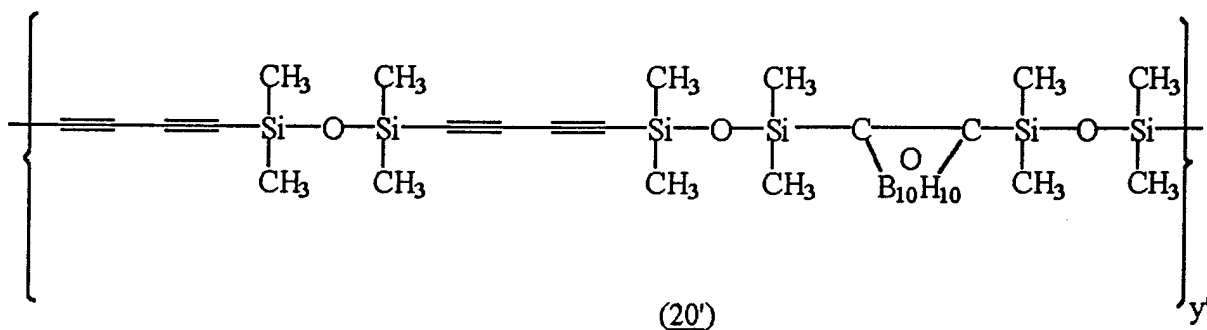
9
10 Preparation of 1,4-dilithio-1,3-butadiyne:



13
14 A 50 mL three-necked round-bottomed flask was equipped with a stir bar, glass
15 stopper, septum, and gas inlet tube. After the flask was flame-dried, THF (5 mL) was
16 injected and the flask was placed in a dry ice/acetone bath. n-BuLi (10.6 mL of a 2.5M
17 solution, 26.5 mmol) was then added and the mixture was stirred for 5 min.
18 Subsequently, hexachlorobutadiene (0.99 mL, 6.3 mmol) was added dropwise via syringe.
19 After completion of addition, the cold bath was removed and the mixture was stirred at
20 room temperature for two hours. The resulting dark brown mixture was used without
21 further treatment.

EXAMPLE 4

Preparation of polymer (20') from 50/50 of (40)/(50), respectively ($y'/y \approx 1.0$):



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 a homogeneous solution of (40) (1.43 mL, 3.15 mmol) and (50) (0.62 mL, 3.15 mmol) was added dropwise over a period of 15 min. After addition, the cold bath was removed and the mixture was stirred at room temperature for two hours. The tan mixture was then poured into an ice-cooled solution of saturated aqueous ammonium chloride (30 mL) with stirring. The resulting two-phased mixture was filtered through a Celite pad and the layers were separated. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with distilled water and once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and filtered. Most of the volatiles were removed under reduced pressure at room temperature and the residue was

1 heated at 75 °C for three hours at 0.1 mm Hg pressure to leave a viscous dark brown
2 material (1.76 g). ¹H NMR spectroscopy shows large peaks at δ (ppm) 0.2-0.4
3 corresponding to the -SiCH₃ protons, and a broad resonance from δ (ppm) 1.2-2.8
4 corresponding to the carborane protons in the polymer. ¹³C NMR spectroscopy shows
5 two peaks at δ (ppm) 0.30 and δ (ppm) 1.9 corresponding to the -SiCH₃ carbons, a peak
6 at δ (ppm) 68.1 corresponding to the carborane carbons, and two peaks at δ (ppm) 84.8
7 and δ (ppm) 87.0 corresponding to the two acetylenic carbons in the polymer. Infrared
8 spectroscopic (IR) analysis confirms the presence of the acetylenic groups with a strong
9 peak at 2071 cm⁻¹. Other prominent peaks are present at (cm⁻¹): 2962 (C-H), 2596 (B-
10 H), and 1077 (Si-O). DSC analysis showed the principal exotherm at 321 °C (figure 1).
11 Char yield (TGA) = 82% (figure 2). Reheating the char to 1000 °C in air resulted in
12 only ~0.3% weight loss (figure 3). Holding the sample at 1000 °C in air for one hour
13 resulted in an additional ~0.3% weight loss. The weight loss leveled off after
14 approximately 40 minutes.

16 EXAMPLE 5

17
18 Preparation of polymer (20) from 25/75 of (40)/(50), respectively ($y'/y \approx 3.0$):

19 In the same manner outlined above, 1,4-dilithio-1,3-butadiyne (6.3 mmol) was reacted
20 with a homogeneous mixture of (40) (0.71 mL, 1.58 mmol) and (50) (0.92 mL, 4.72
21 mmol). The usual workup gave a viscous dark brown material (1.3 g) which slowly

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1 solidified into a sticky solid. DSC analysis showed the principal exotherm at 299 °C
2 (figure 4). Char yield (TGA) = 76% (figure 5). Reheating the char to 1000 °C in air
3 showed minimal weight loss (figure 6). Holding the sample at 1000 °C in air for one
4 hour resulted in ~0.3% weight loss.

5

6

EXAMPLE 6

7

8 Preparation of polymer (20) from 10/90 of (40)/(50), respectively ($y'/y \approx 9.0$):

9 In the usual manner, 1,4-dilithio-1,3-butadiyne (6.3 mmol) was reacted with a
10 homogeneous mixture of (40) (0.29 mL, 0.63 mmol) and (50) (1.1 mL, 5.67 mmol). The
11 usual workup gave a very viscous dark brown material (1.22 g) which slowly solidified
12 into a sticky solid. DSC analysis showed the principal exotherm at 289 °C (figure 7).
13 Char yield (TGA) = 73% (figure 8). Reheating the char to 1000 °C in air resulted in
14 1% weight loss (figure 9). Holding the sample at 1000 °C in air for one hour resulted in
15 no additional weight loss.

16

17

EXAMPLE 7

18

19 Preparation of polymer (20') from 50/50 of (40)/(50), respectively ($y'/y \approx 1.0$) using the
20 stepwise method:

21 A mixture of 1,4-dilithio-1,3-butadiyne (6.3 mmol) in THF/hexane was cooled in a dry

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1 ice/acetone bath. To this mixture compound (40) (1.43 mL, 3.15 mmol) was added
2 dropwise. After addition and without delay, compound (50) (0.62 mL, 3.15 mmol) was
3 added dropwise. The addition of both components lasted approximately 15 min. Usual
4 workup gave a material whose properties were virtually identical to those of the material
5 described in the 50/50 homogeneous approach. Reversing the order of addition (i.e.
6 adding (50) followed by (40) also gave similar material (20') wherein $y'/y \approx 1.0$.

7

8

EXAMPLE 8

9

10 Preparation of polymer (20) from 5/95 of (40)/(50), respectively ($y'/y \approx 19.0$) using the
11 stepwise method:

12 In the usual manner, compounds (40) (0.14 mL, 0.31 mmol) and (50) (1.17 mL, 5.98
13 mmol) were added sequentially to a mixture of 1,4-dilithio-1,3-butadiyne (6.3 mmol) in
14 THF/hexane cooled in a dry ice/acetone bath. The usual workup gave a viscous, dark
15 brown material (1.2 g) which slowly solidified into a sticky solid. DSC analysis showed
16 the principal exotherm at 290 °C (figure 10). Char yield (TGA) = 66% (figure 11).
17 Reheating the char to 1000 °C in air resulted in 16% weight loss (figure 12). Holding the
18 sample at 700 °C in air for one hour resulted in an additional 13% weight loss after two
19 hours.

20

EXAMPLE 9

21 Preparation of Polymer (20) Where A = phenyl and E = oxygen and $y'/y = 1$

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1
2 Cool a mixture of 1,4-dilithio-1,3-butadiyne in THF/hexane using a dry ice/acetone bath.
3 To this mixture add a homogeneous solution of 1,4-bis-dimethylchlorosilylbenzene and 40
4 (equal molar amounts) dropwise over a period of 15 min. After addition, remove the
5 cold bath and stir the reaction mixture at room temperature for two hours. Pour the
6 reaction mixture into an ice-cooled solution of saturated aqueous ammonium chloride
7 with stirring. Filter the suspension through a Celite pad and separate the layers. Extract
8 the aqueous layer twice with diethyl ether and wash the combined organic layers twice
9 with distilled water and once with saturated aqueous sodium chloride solution. Dry the
10 organic layer over anhydrous magnesium sulfate and filter. Remove volatiles by heating
11 (no higher than 75 °C) under reduced pressure to leave the polymer. Note that in the
12 final polymer of this example, $x = x' = 1$, $n = n' = 2$, $u = 1$, $q = q' = 10$, and $R^1, R^2,$
13 R^3, R^4, R^5, R^6, R^7 and R^8 are $-CH_3$. Additional details for preparation of 1,4-bis-
14 dimethylchlorosilylbenzene are given by Sveda et al., in U.S. Patent Nos. 2,561,429 (1951)
15 and 2,562,000 (1951), each patent incorporated herein by reference in its entirety and for
16 all purposes. Additional details are given in U.S. Patent Nos. 5,272,237; 5,292,779 and
17 5,348,917, each patent incorporated herein by reference in its entirety and for all
18 purposes.

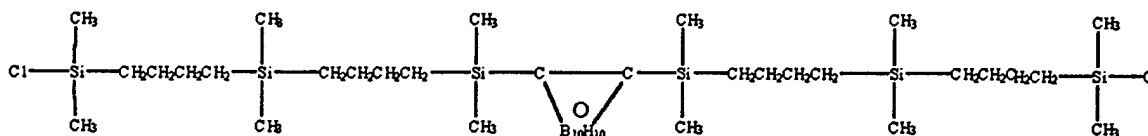
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EXAMPLE 10

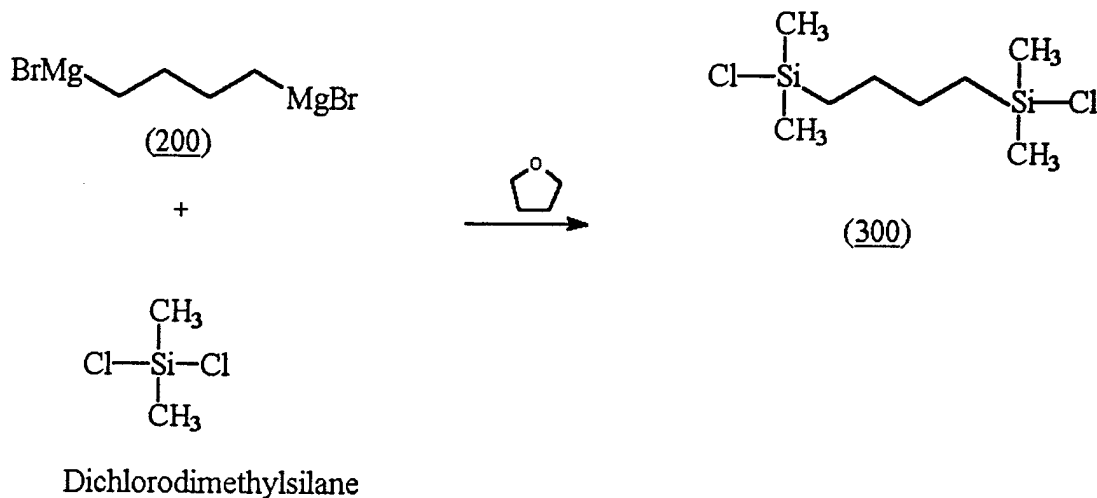
Preparation of the polymer (100) having the formula given below--

$(\text{ClSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2)_2\text{CB}_{10}\text{H}_{10}\text{C}$ (100)



Prepare a THF solution of $\text{BrMgCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr}$ (200) from 1,4-dibromobutane and two equivalents of magnesium. Add two equivalents of dimethylchlorosilane to form $\text{HSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{H}$. Treat this compound with catalytic amounts of benzoyl peroxide in refluxing carbon tetrachloride to form $\text{ClSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (300). Treat a solution of (200) with one equivalent of (300) and one-half equivalent of $\text{ClSi}(\text{CH}_3)_2\text{CB}_{10}\text{H}_{10}\text{CSi}(\text{CH}_3)_2\text{Cl}$ to form the target material (100).

1 Alternatively, exemplary compound (300) may be formed according to the
2 reaction:



11 EXAMPLE 11

12

13 Preparation of Polymer (20) Where E = A = $-(CH_2CH_2CH_2CH_2)-$ and $y'/y = 1$

14

15 Cool a mixture of 1,4-dilithio-1,3-butadiyne in THF/hexane using a dry ice/acetone bath.

16 To this mixture add a homogeneous solution of 300 and 100 (equal molar amounts)

17 dropwise over a period of 15 min. After addition, remove the cold bath and stir the

18 reaction mixture at room temperature for two hours. Pour the reaction mixture into an

19 ice-cooled solution of saturated aqueous ammonium chloride with stirring. Filter the

20 suspension through a Celite pad and separate the layers. Extract the aqueous layer twice

21 with diethyl ether and wash the combined organic layers twice with distilled water and

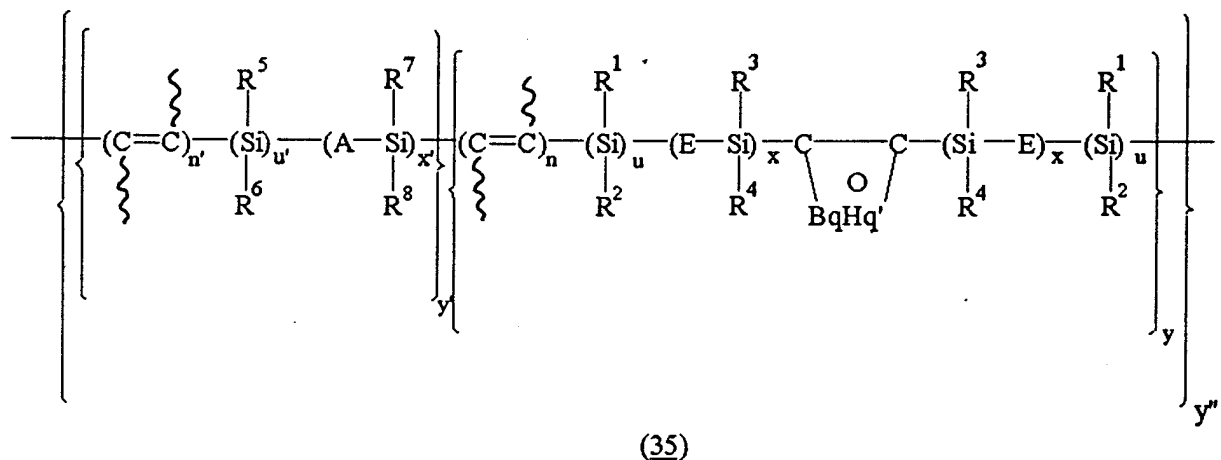
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1 once with saturated aqueous sodium chloride solution. Dry the organic layer over
 2 anhydrous magnesium sulfate and filter. Remove volatiles by heating (no higher than 75
 3 °C) under reduced pressure to leave the polymer. Note that in the final polymer of this
 4 example, $x = 2$, $x' = 1$, $n = n' = 2$, $u = 1$, $q = q' = 10$, and $R^1, R^2, R^3, R^4, R^5, R^6, R^7$
 5 and R^8 are $-CH_3$.

7 EXAMPLE 12

9 Preparation of thermoset (35) having the formula wherein $y'/y = 1.0$:



17 wherein $n = n' = 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, and
 18 $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$. To obtain the thermoset (35) wherein the
 19 ratio y'/y is varied as desired, the corresponding linear polymer of the structure (20) is
 20 used as the starting material subjected to either heat or light.

21 To form the compound of EXAMPLE 12, the linear polymer (20) wherein $n = n'$

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1 = 2, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, $y'/y = 1.0$ and R^1 ,
2 $R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$, was heated in nitrogen at $300\text{ }^\circ\text{C}$ for 2 hours
3 then at $350\text{ }^\circ\text{C}$ for 2 hours and finally at $400\text{ }^\circ\text{C}$, for 2 hours. Between each isotherm, the
4 linear polymer (20) was subjected to a temperature heating gradient of $5\text{ }^\circ\text{C}/\text{minute}$. The
5 thermoset (35) of EXAMPLE 12 was formed in this manner. Approximately, 15 mg of
6 linear polymer (20) was converted to the thermoset (35) by the isothermic heating
7 described above wherein about 13.50 mg of thermoset (35) was formed. The TGA of the
8 thermoset of this example in air is shown in FIGURE 13.

EXAMPLE 13

12 Preparation of thermoset (35), *supra*, having the formula wherein $y'/y = 3.0$:

13 wherein $n = n' = 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, and
14 $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$. To obtain the thermoset (35) wherein the
15 ratio y'/y is varied as desired, the corresponding linear polymer of the structure (20) is
16 used as the starting material subjected to either heat or light.

17 To form the compound of EXAMPLE 13, the linear polymer (20) wherein $n = n'$
18 $= 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, $y'/y = 3.0$ and R^1 ,
19 $R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$, was heated in nitrogen at $300\text{ }^\circ\text{C}$ for 2 hours
20 then at $350\text{ }^\circ\text{C}$ for 2 hours and finally at $400\text{ }^\circ\text{C}$, for 2 hours. Between each isotherm, the
21 linear polymer (20) was subjected to a temperature heating gradient of $5\text{ }^\circ\text{C}/\text{minute}$. The

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1 thermoset (35) of EXAMPLE 13 was formed in this manner. Approximately, 15 mg of
2 linear polymer (20) was converted to the thermoset (35) by the isothermic heating
3 described above wherein about 13.50 mg of thermoset (35) was formed. The TGA of the
4 thermoset of this example in air is shown in FIGURE 14.

5

6

EXAMPLE 14

7

8 Preparation of thermoset (35), supra, having the formula wherein $y'/y = 9.0$:

9 wherein $n = n' = 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, and
10 $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$. To obtain the thermoset (35) wherein the
11 ratio y'/y is varied as desired, the corresponding linear polymer of the structure (20) is
12 used as the starting material subjected to either heat or light.

13 To form the compound of EXAMPLE 14, the linear polymer (20) wherein $n = n'$
14 $= 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, $y'/y = 9.0$ and $R^1,$
15 $R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$, was heated in nitrogen at 300 °C for 2 hours
16 then at 350°C for 2 hours and finally at 400 °C, for 2 hours. Between each isotherm, the
17 linear polymer (20) was subjected to a temperature heating gradient of 5 °C/minute. The
18 thermoset (35) of EXAMPLE 14 was formed in this manner. Approximately, 15 mg of
19 linear polymer (20) was converted to the thermoset (35) by the isothermic heating
20 described above wherein about 12.75 mg of thermoset (35) was formed. The TGA of the
21 thermoset of this example in air is shown in FIGURE 15.

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1 heating the thermosets to about 1000 °C at a rate of about 10 °C / minute either in a
2 nitrogen or oxidizing atmosphere (e.g. air). The ceramics of each of the thermosets of
3 **EXAMPLES 12, 13, 14 and 15** were made during the heating process entailed in
4 obtaining the TGA plots shown in **FIGURES 13, 14, 15 and 16**, respectively.

5 Patent application entitled **LINEAR CARBORANE-(SILOXANE or SILANE)**
6 **ACETYLENE BASED COPOLYMERS** with named inventors Teddy M. Keller and David
7 Y. Son having the docket Navy Case No. **76,339** filed on 07 November 1994 is
8 incorporated herein by reference in its entirety and for all purposes.

9 **EXAMPLE 17**

10 Formation of Ceramics from linear polymer (20) wherein $y'/y = 9.0$:

11 wherein $n = n' = 2$, $u = u' = 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, and
12 $R^1, R^2, R^3, R^4, R^5, R^6, R^7$ and R^8 are $-CH_3$. Four circular pans were coated with a
13 fluorinated mold release agent and loaded with polymer (20) wherein $n = n' = 2$, $u = u'$
14 $= 1$, $x = x' = 1$, $q = q' = 10$, $A = E =$ an oxygen atom, and $R^1, R^2, R^3, R^4, R^5, R^6, R^7$
15 and R^8 are $-CH_3$. The samples were degassed at 110°C in a vacuum oven. Total mass
16 of samples was equal to about 6.28g. The samples were then placed in a furnace under
17 argon and cured to a maximum temperature of 300°C as in previous examples. Four
18 hard thermosets were obtained (6.07g total). The thermosets were sanded down. Total
19 mass of the thermosets was about 5.15g. The thermoset samples so formed were placed
20 in the furnace again and heated to 1000°C at a rate of 1°/min and held at 1000°C for one
21 hour before cooling to room temperature. Hard, black ceramic chars were obtained with

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- 1 a total mass of about 3.84g. Two of these chars were heated to 600°C in air and held at
- 2 that temperature for 100 hours. After this heating period, the char samples so formed
- 3 exhibited no weight loss and appeared visibly the same as prior the heat treatment.

Sample: DSI-46A DSC

Size: 1.4500 mg

Method: DYS DSC PROGRAM

Comment: 50/50 BLEND OF CARBORANE/SILOXYL

File: C:DDSI-46A

Operator: DYS

Run Date: 13-Apr-94 03:16

DSC

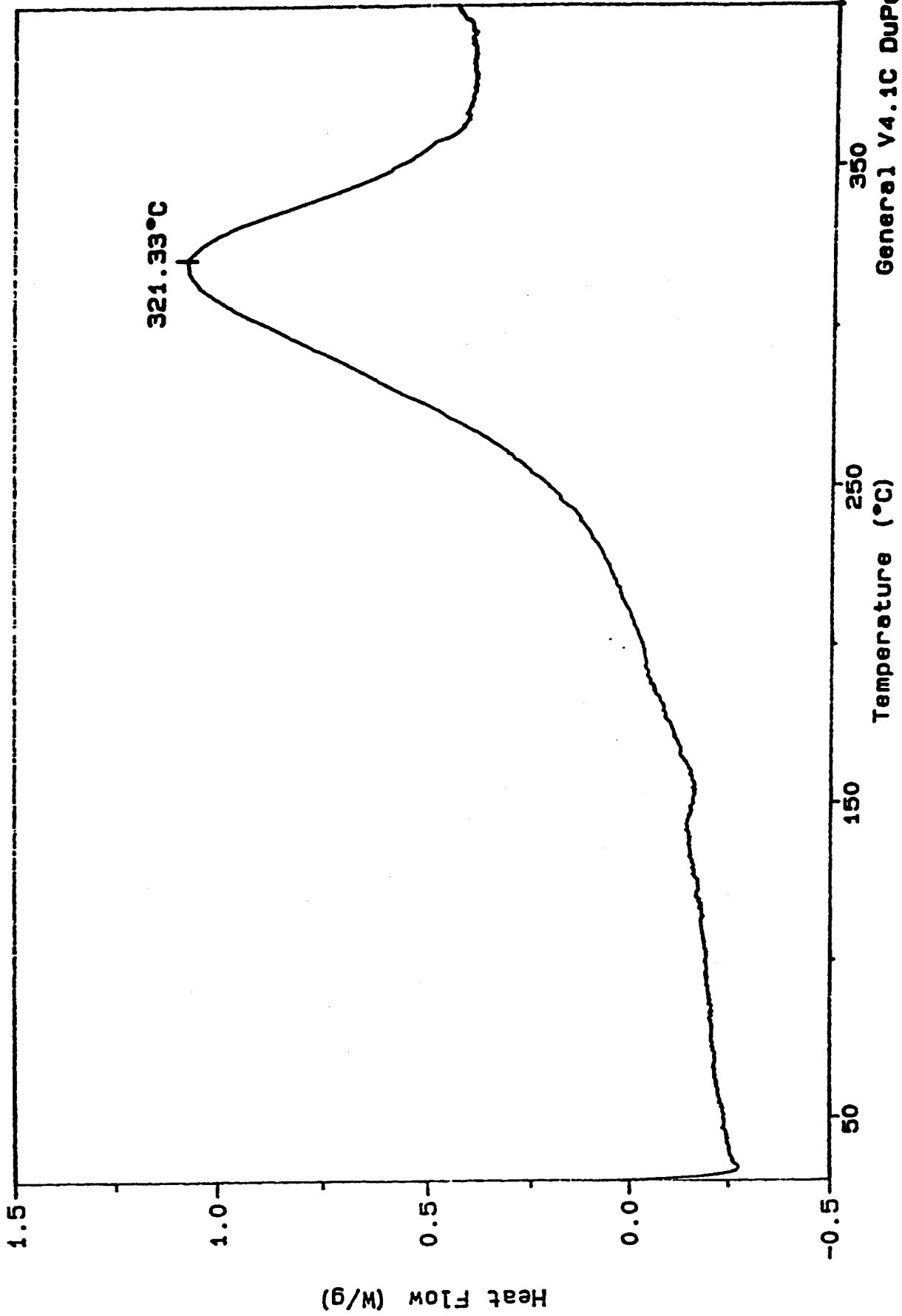


FIGURE 1

Sample: DSI-46A TGA

Size: 13.1540 mg

Method: 50-1000C AT 10C/MIN

Comment: 50/50 BLEND OF CARBORANE/SILOXYL

TGA

File: C: TDSI-46A

Operator: DYS

Run Date: 12-Apr-94 07:21

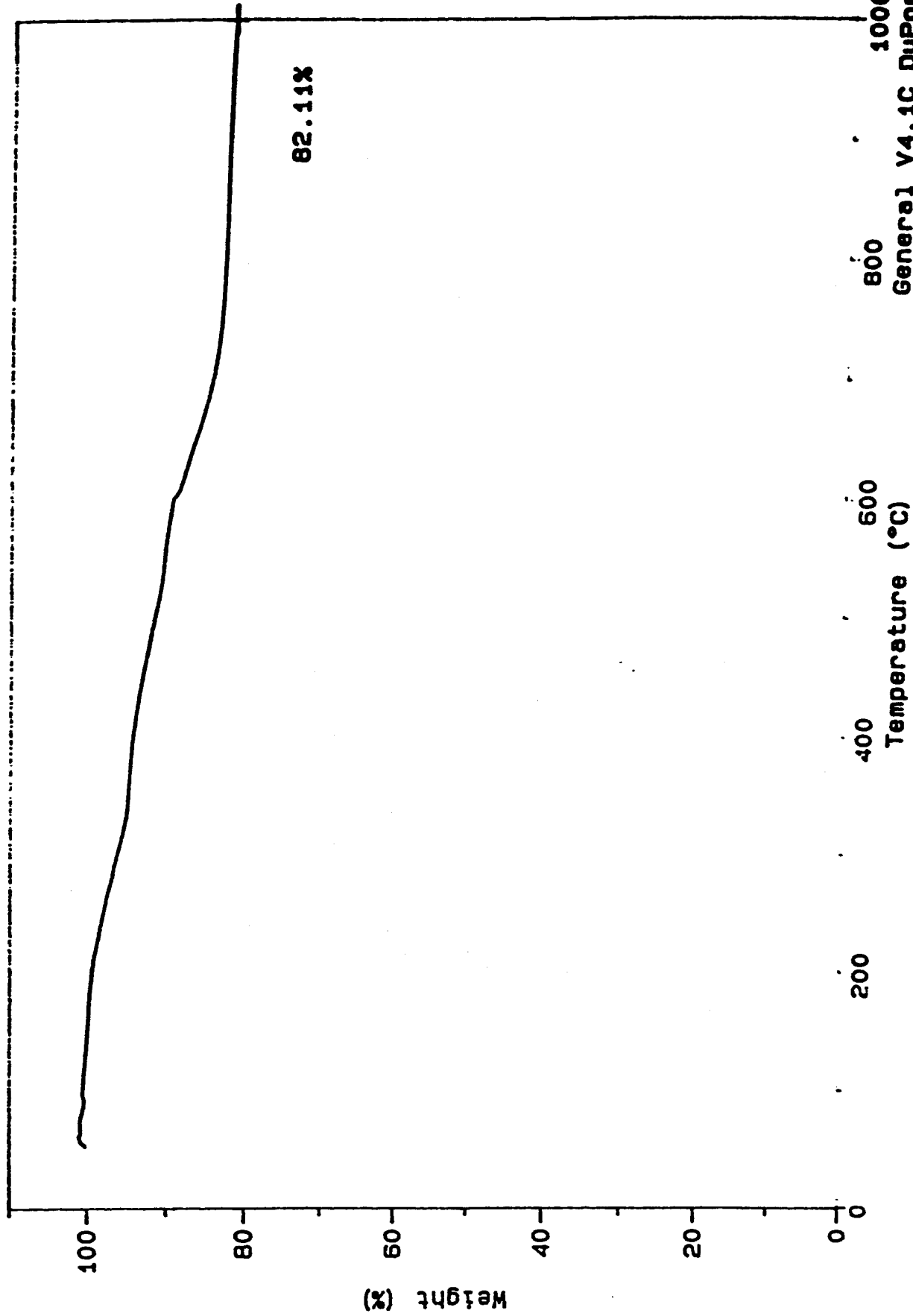


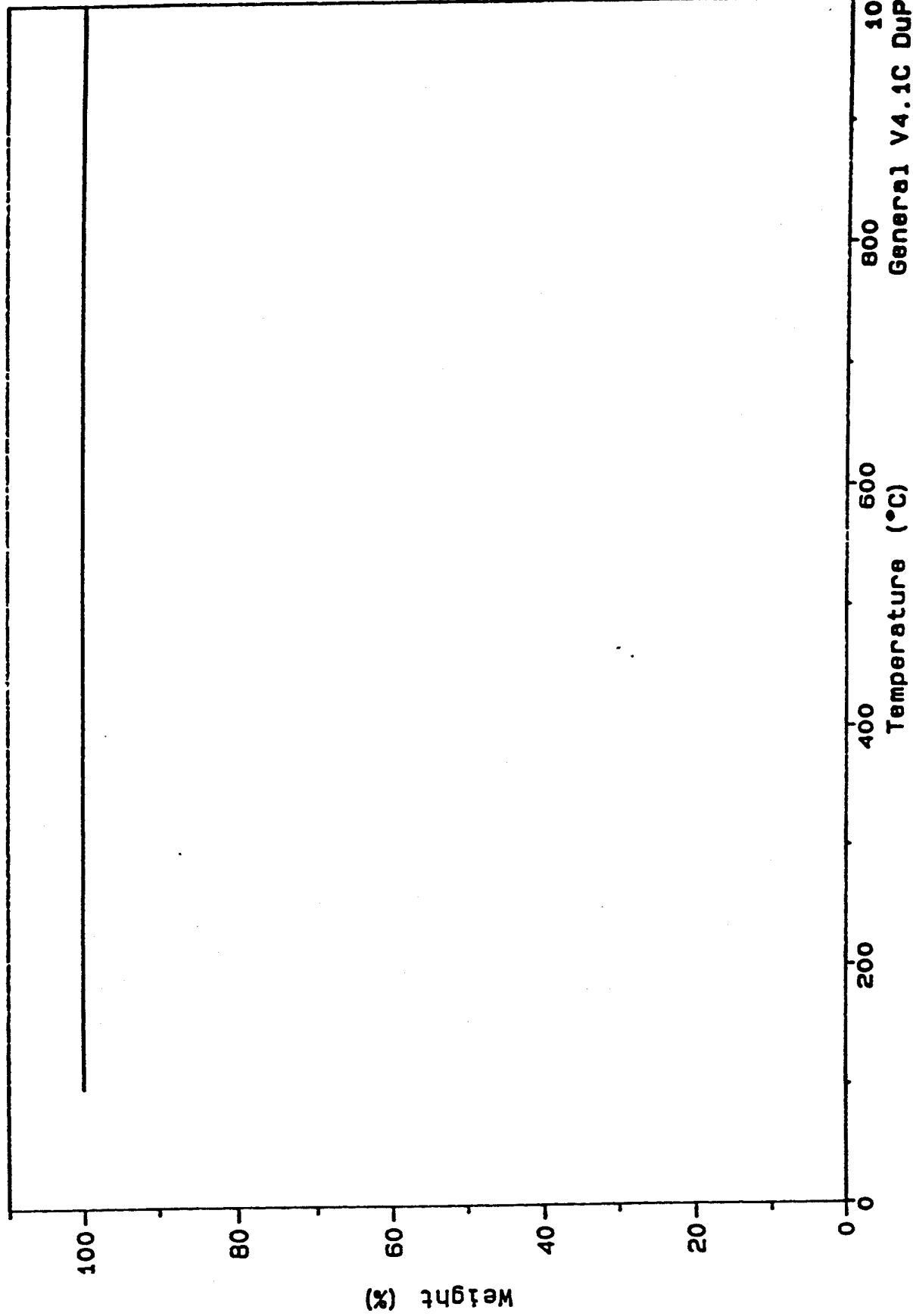
FIGURE 2

General V4.1C DuPont 21

Sample: DSI-46A CHAR TGA IN AIR
Size: 10.8030 mg
Method: 100-1000C AT 10C/MIN
Comment: 50/50 BLEND OF CARBORANE/SILOXYL

TGA

File: C:TDSI-46A.2
Operator: DYS
Run Date: 12-Apr-94 09:42



Sample: DSI-47A DSC
Size: 1.4000 mg
Method: DYS DSC PROGRAM
Comment: 75/25 SILOXYL/CARBORANE

DSC

File: C: DSI-47A
Operator: DYS
Run Date: 20-Apr-94 03:57

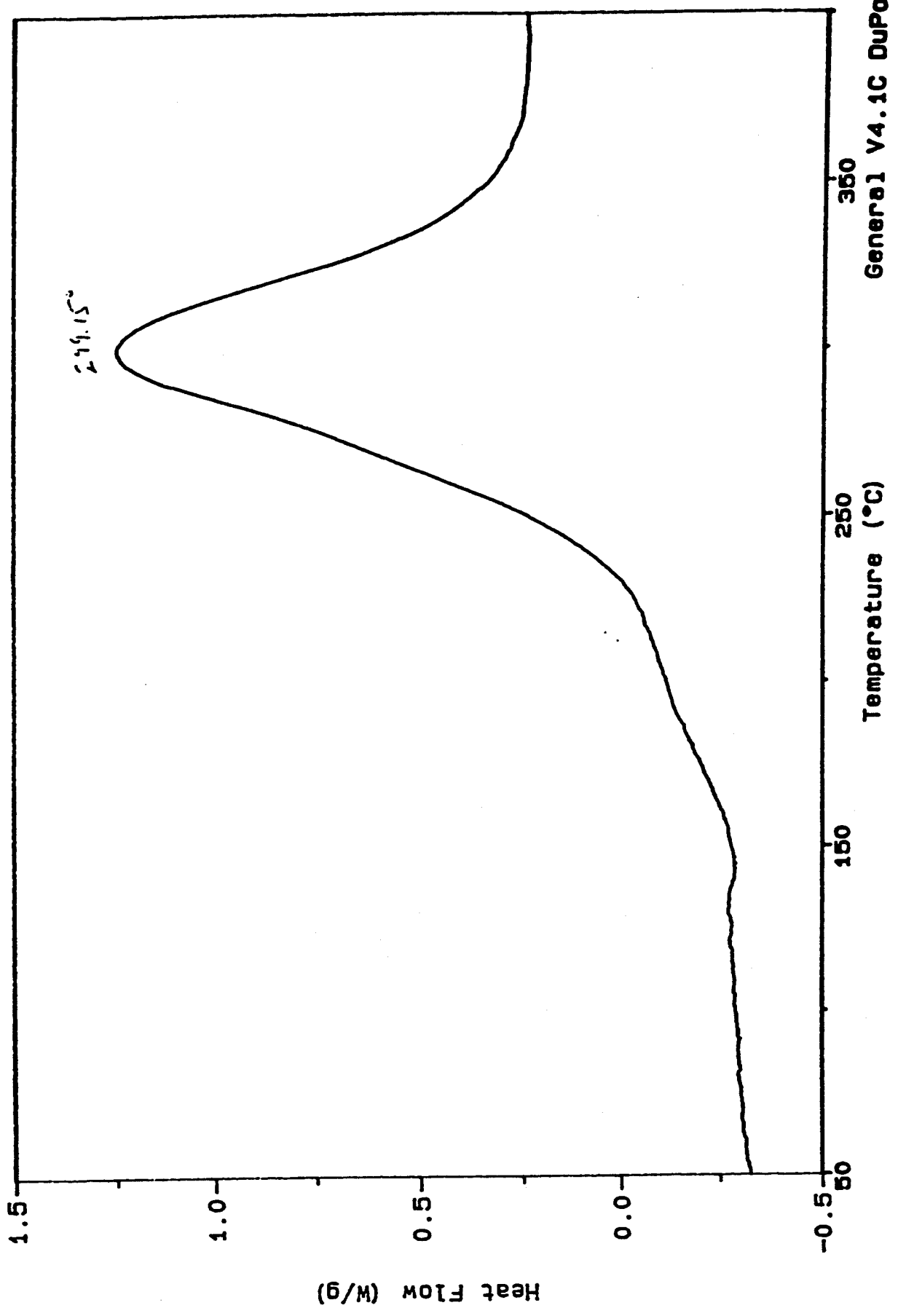


FIGURE 4

Sample: DSI-47A TGA

Size: 11.2400 mg

Method: 50-1000C AT 10C/MIN

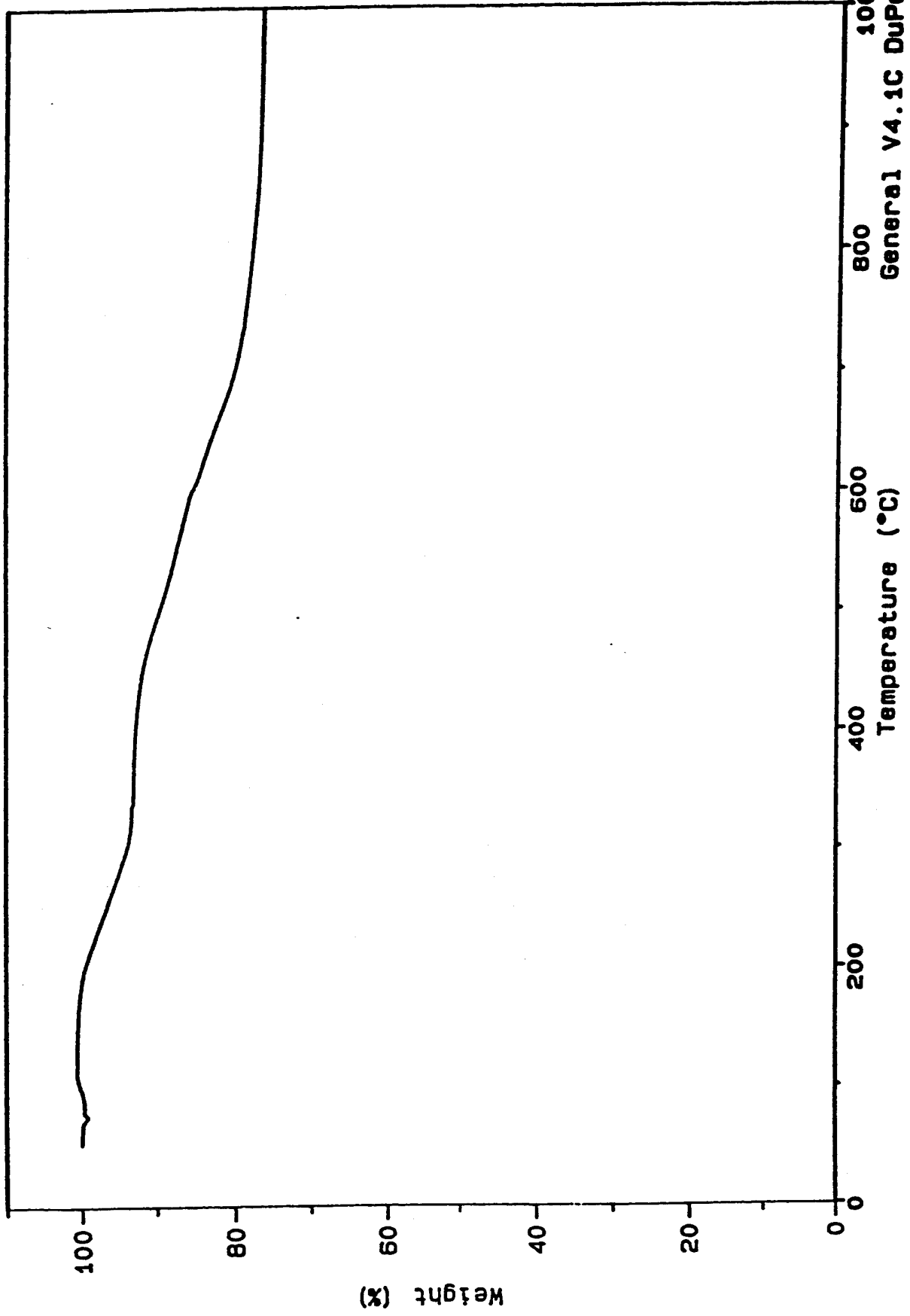
Comment: 75/25 SILOXYL/CARBORANE

TGA

File: C:TDSI-47A

Operator: DYS

Run Date: 19-Apr-94 04:30



Weight (%)

Temperature (°C)

1000

800

600

400

200

0

General V4.1C DuPont 21

FIGURE 5

7645*

Sample: DSI-47A CHAR TGA IN AIR
Size: 8.6750 mg
Method: 50-1000C AT 10C/MIN
Comment: 75/25 SILOXYL/CARBORANE IN AIR

TGA

File: C:TDSI-47A.2
Operator: DYS
Run Date: 22-Apr-94 01:22

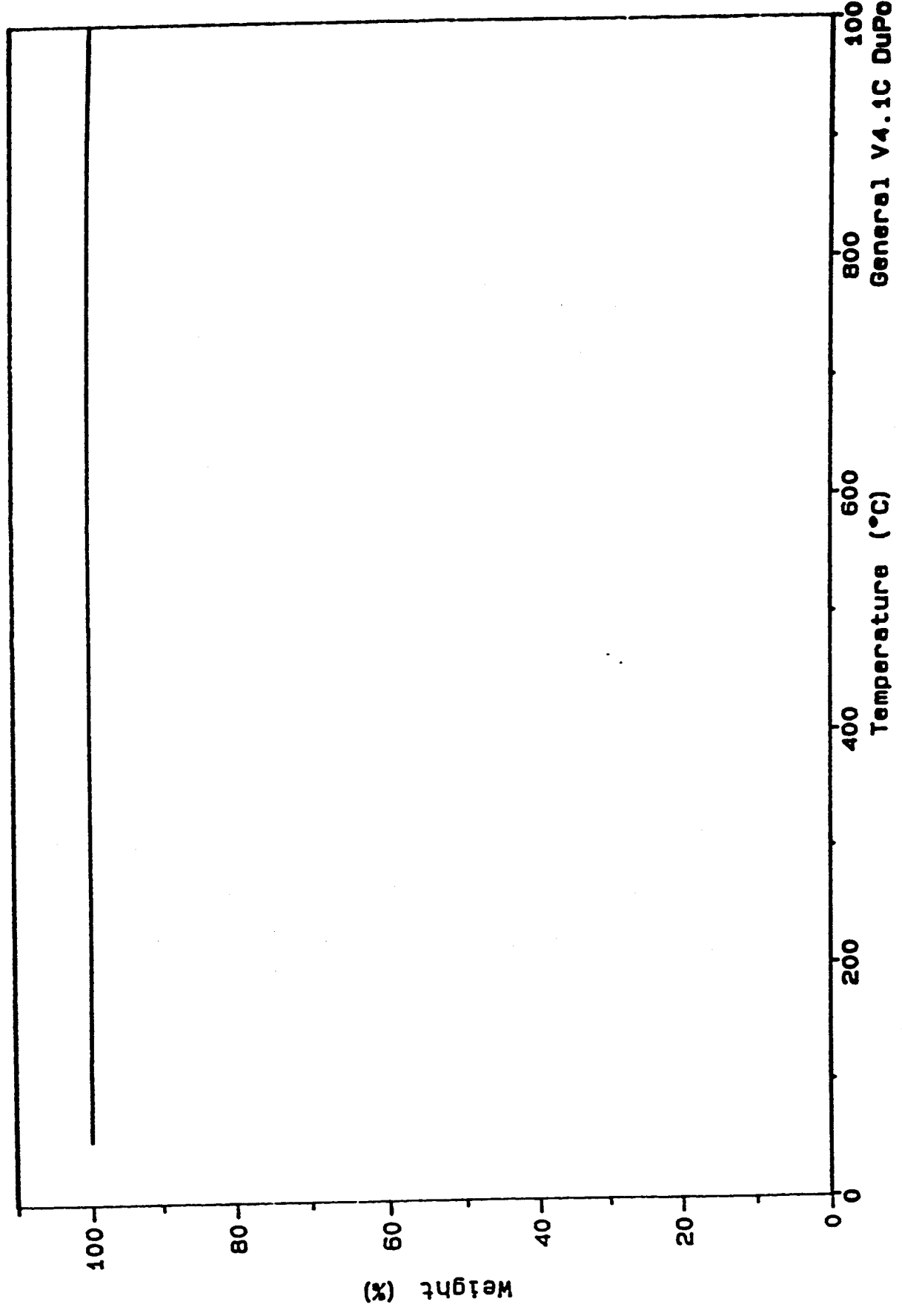


FIGURE 6

Sample: DSI-57E DSC

Size: 4.6660 mg

Method: DYS DSC PROGRAM

Comment: 10/90 CARBORANE/SILOXYL

DSC

File: C:DDSI-57E

Operator: DYS

Run Date: 19-May-94 23:08

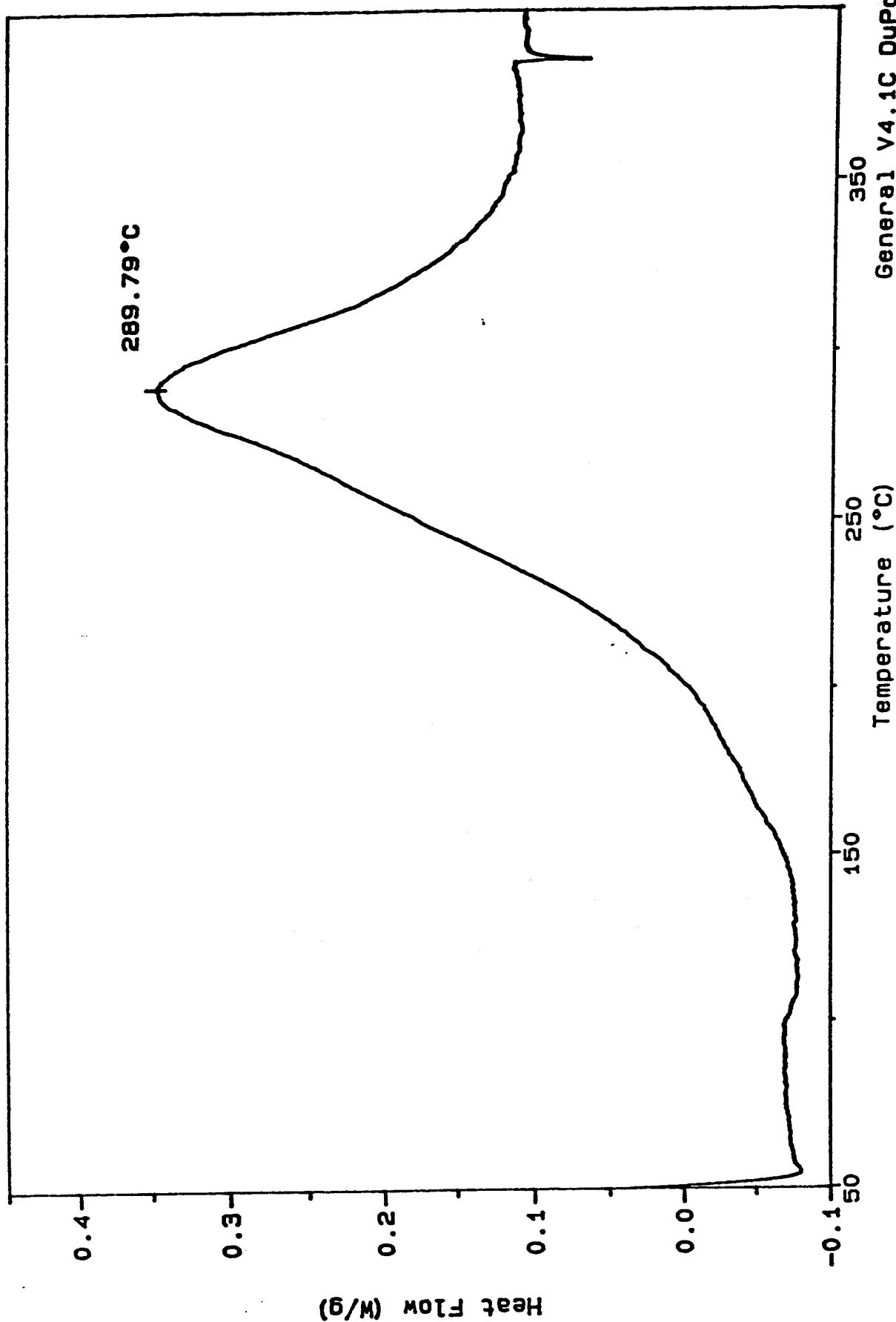


FIGURE 7

Sample: DSI-57E TGA

Size: 9.9780 mg

Method: 50--1000C AT 10C/MIN

Comment: 10/90 CARBORANE/SILOXYL

TGA

File: C:TDSI-57E

Operator: DYS

Run Date: 19-May-94 23:59

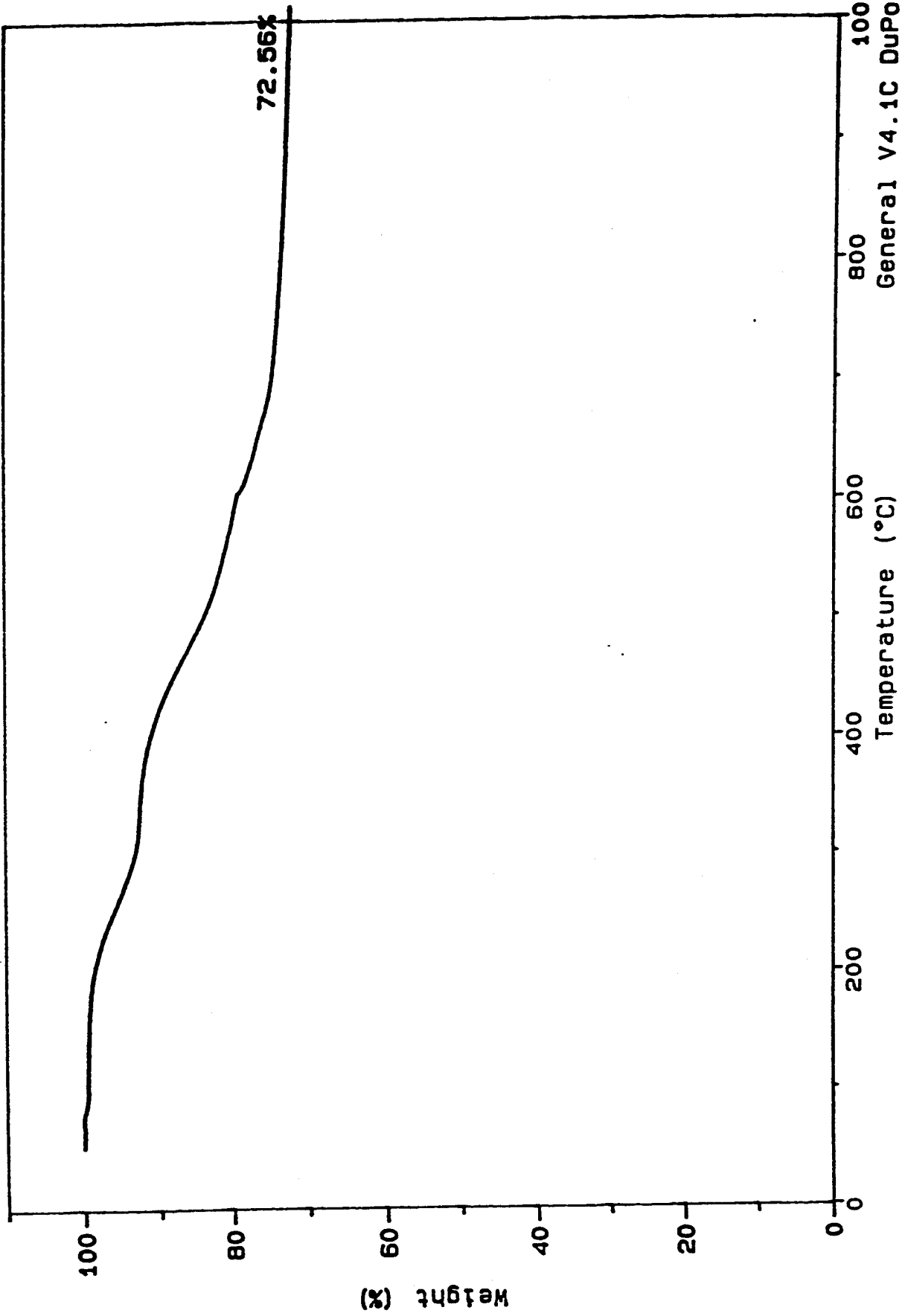


FIGURE 8

Sample: DSI-57E TGA
Size: 8.0060 mg
Method: 50-1000C AT 10C/MIN
Comment: 10/90 CARBORANE/SILOXYL CHAR IN AIR

TGA

File: C:TDSI-57E.3
Operator: DYS
Run Date: 22-May-94 21:36

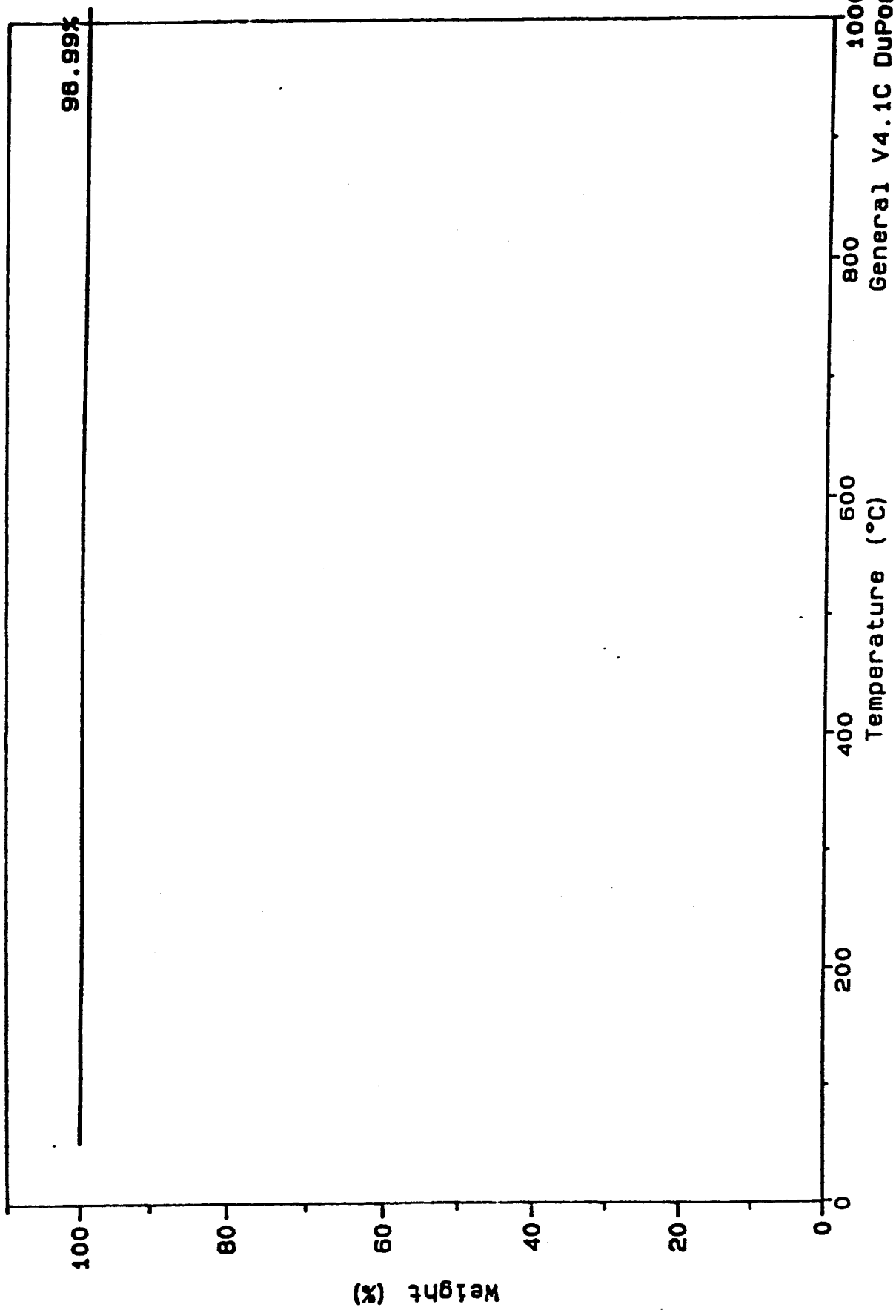


FIGURE 9

Sample: DSI-67A DSC
Size: 1.0000 mg
Method: 50-400C 10C/MIN DSC
Comment: 5/95 CARBORANE/SILOXYL POLYMER

DSC

File: C:DDSI-67A
Operator: DYS
Run Date: 11-Jul-94 14:11

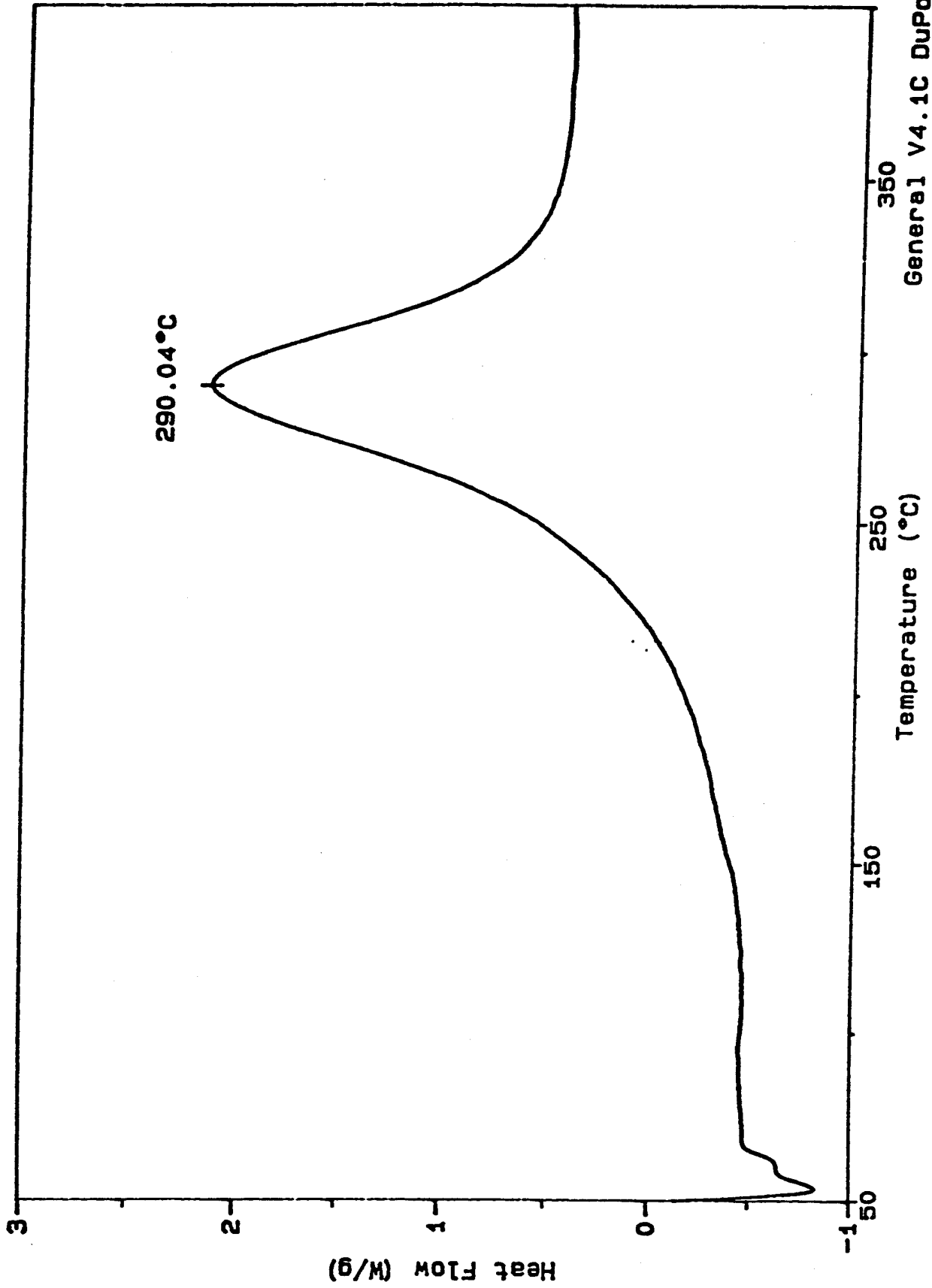


FIGURE 10

Temperature (°C)

350

250

150

50

General V4.1C DuPont 210

Sample: DSI-67A TGA
Size: 10.1930 mg
Method: 50-1000C 10C/MIN
Comment: 5/95 STEPWISE CARBORANE/SILOXYL BLEND

TGA

File: C:TDSI-67A
Operator: DYS
Run Date: 30-Jun-94 13:39

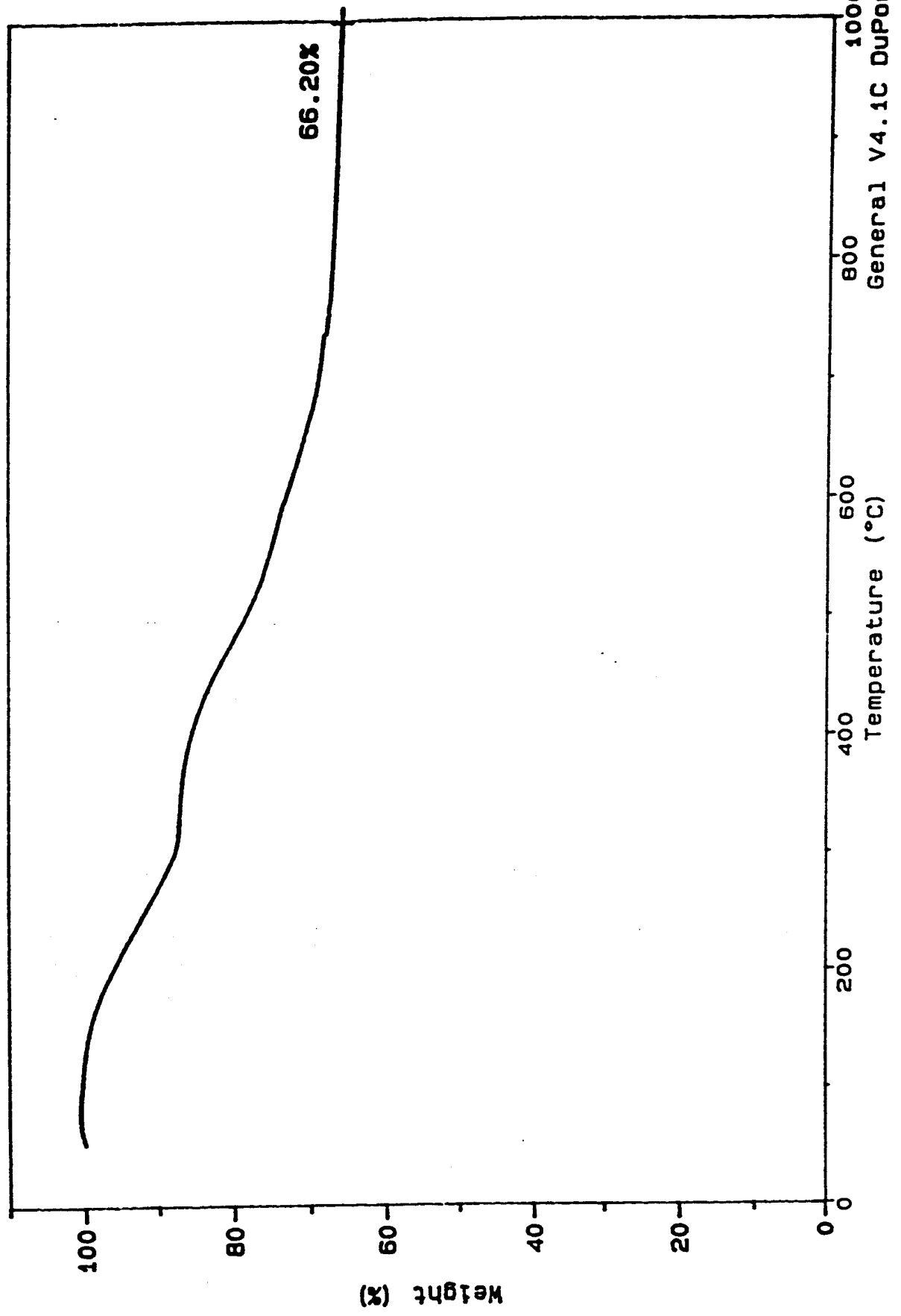


FIGURE 11

Sample: DSI-67A CHAR TGA
Size: 6.7410 mg
Method: 200-1000C WITH ISOTHERM
Comment: 5/95 STEPWISE CARBORANE/SILOXYL BLEND CHAR IN AIR

TGA

File: C:TDSI-67A.2
Operator: DYS
Run Date: 30-Jun-94 15:48

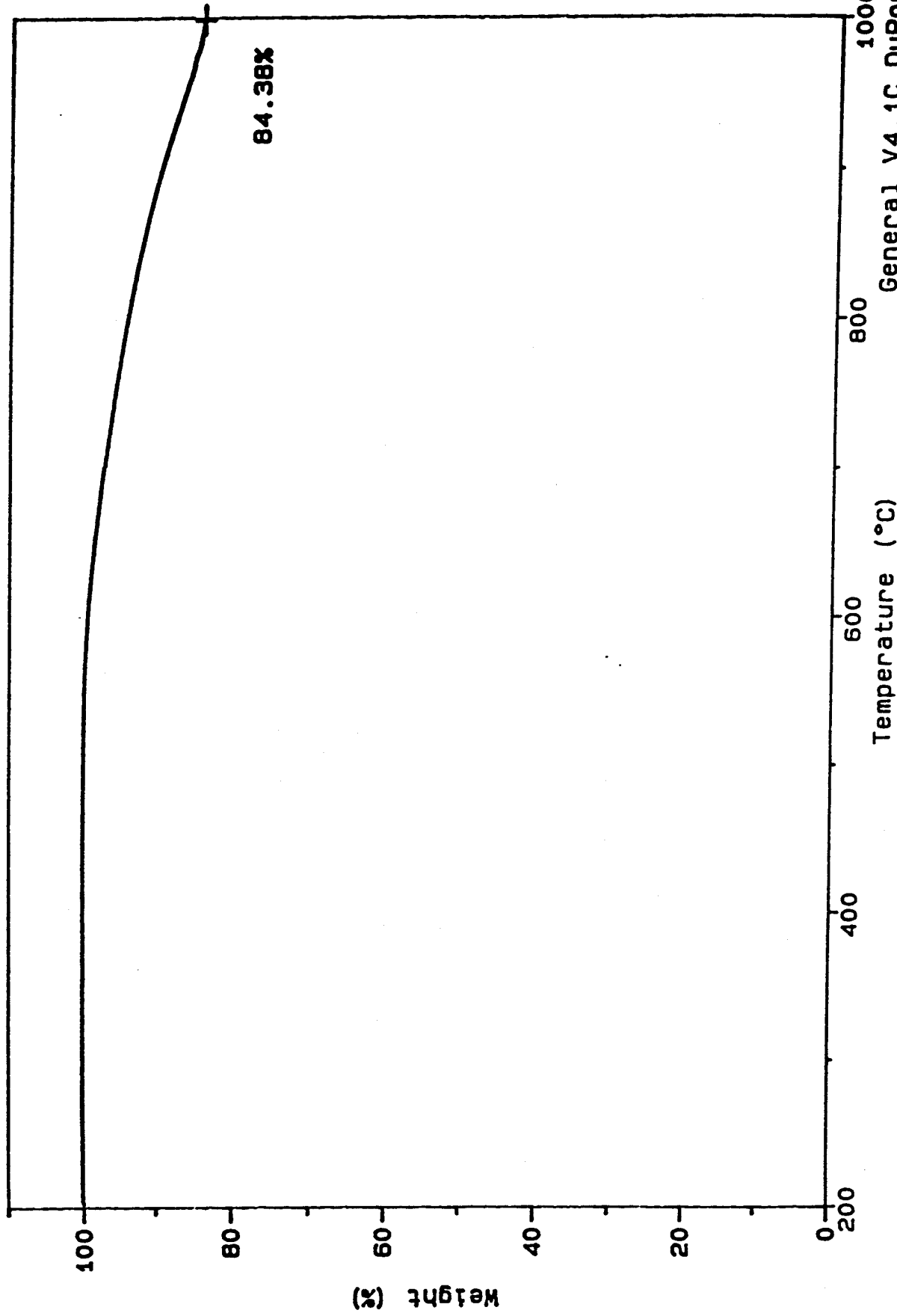
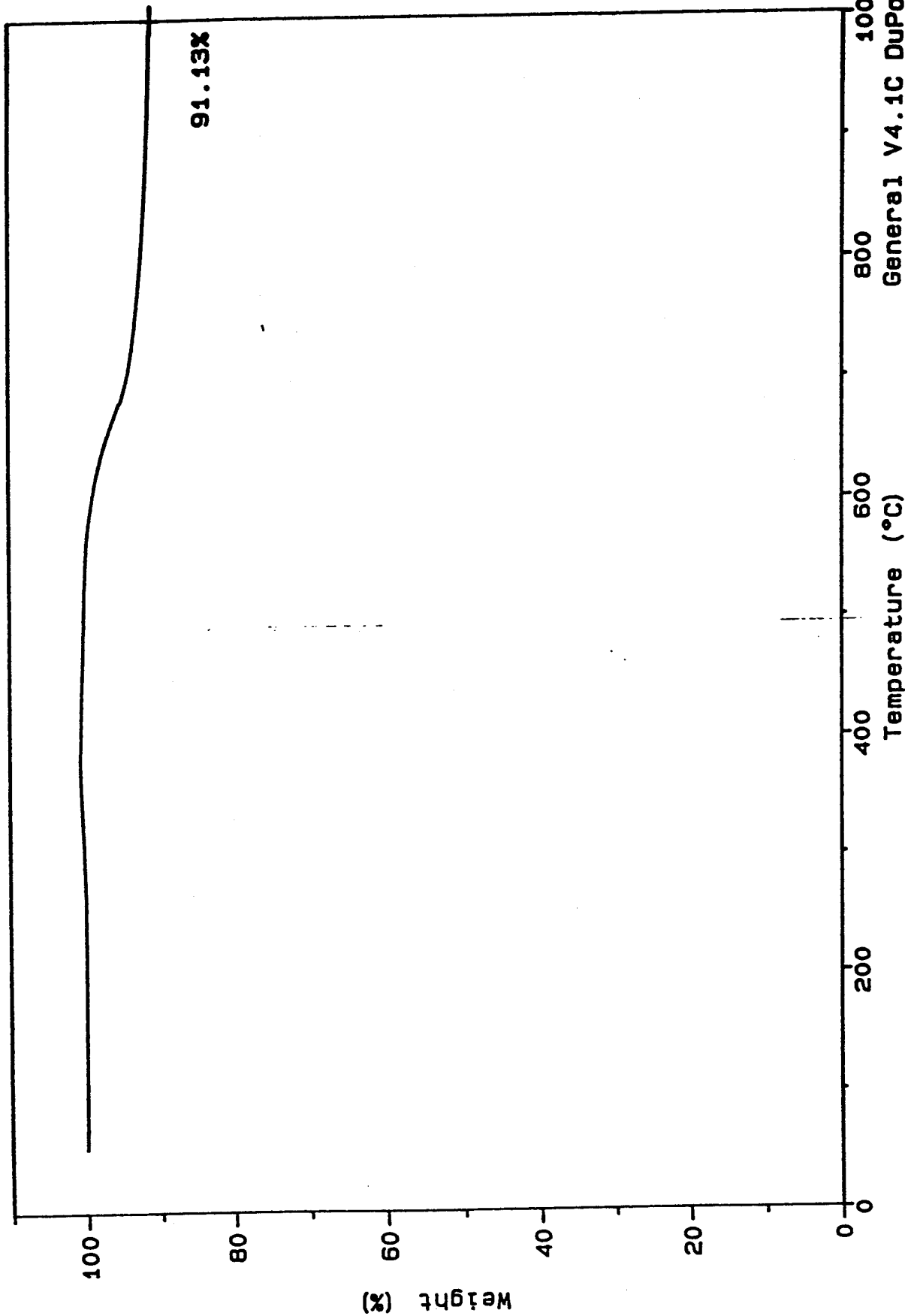


FIGURE 12

Sample: DSI-56A
Size: 19.8730 mg
Method: 50-1000C AT 10C/MIN
Comment: 50/50 COPOLYMER CURED TGA IN AIR

TGA

File: A: TDSI-56A.2
Operator: DYS
Run Date: 9-May-94 23:00



Sample: DSI-568 THERMOSET TGA IN AIR TGA
Size: 12.8080 mg
Method: 50-1000C 10C/MIN
Comment: CURE OF 25/75 CARBORANE/SILOXYL POLYMER
File: C: TDSI-568.2
Operator: DYS
Run Date: 5-JUL-94 09:15

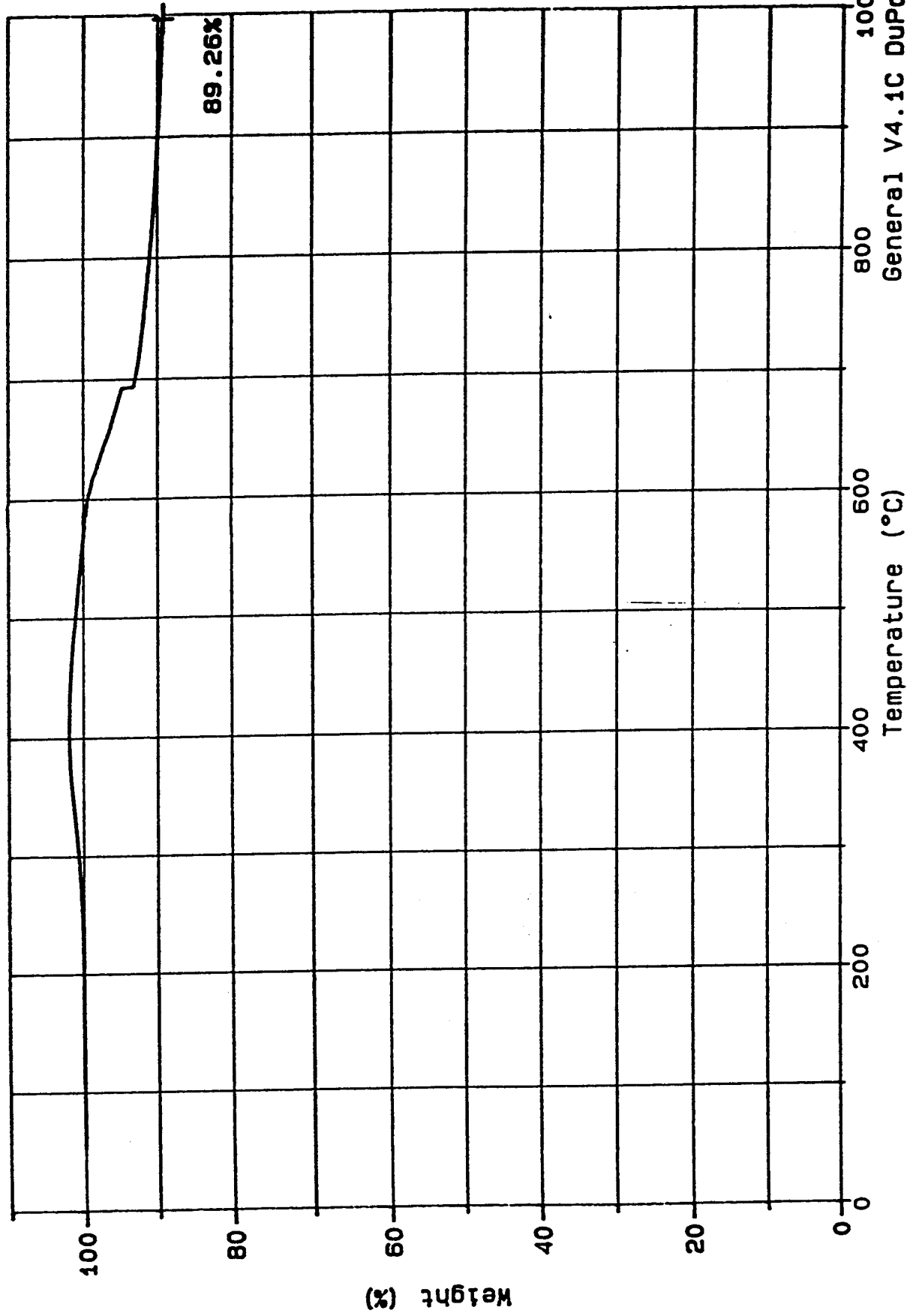
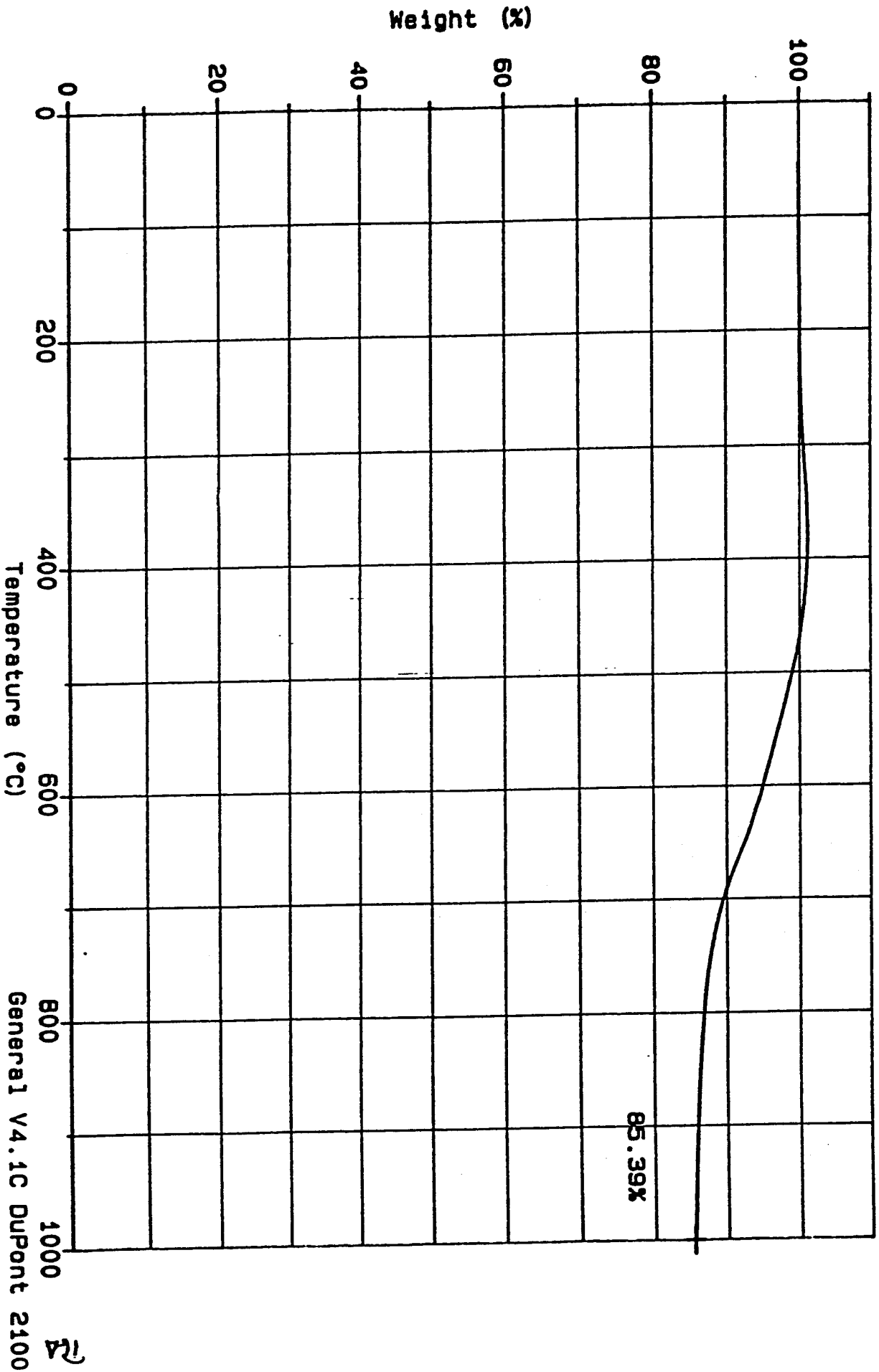


FIGURE 15

Sample: DSI-56C CURED SAMPLE TGA
Size: 15.4160 mg
Method: 50-1000C 10C/MIN
Comment: 10/90 CARBORANE/SILOXYL CURE

TGA

File: C:TDISI-56C.2
Operator: DYS
Run Date: 7-JUL-94 09:17



Sample: DSI-560 CURED TGA
Size: 11.9960 mg
Method: 50-1000C 10C/MIN
Comment: 5/95 CARBORANE/SILOXYL POLYMER CURE

TGA

File: C:TDSI-560.2
Operator: DYS
Run Date: 12-Jul-94 07:37

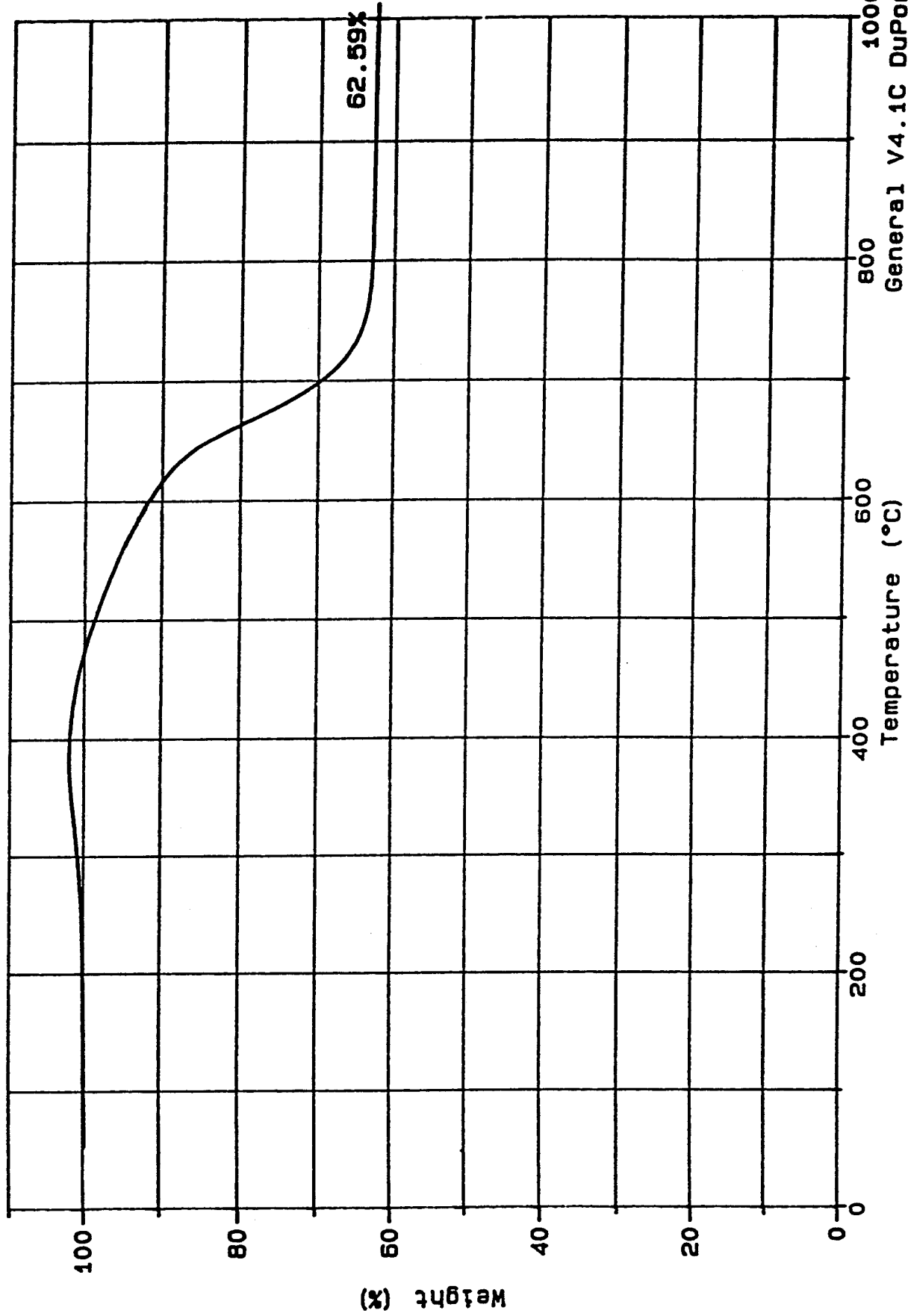


FIGURE 16