

Serial No. 687,880
Filing Date 26 July 1996
Inventor Daniel Bucca
Teddy M. Keller

NOTICE

The above identified patent application is available for licensing. Requests for information should be addressed to:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
CODE OCCC3
ARLINGTON VA 22217-5660

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

DISTRIBUTION STATEMENT A

19961004 179

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

1
2
3 **INORGANIC ARYLACETYLENIC MONOMERS**
4

5 **BACKGROUND OF THE INVENTION**
6

7 Field of the Invention

8 The present invention relates to monomers suitable for polymerization to high temperature
9 thermosets, and more particularly to monomers containing silane and/or siloxane groups, aryl
10 groups, acetylene groups, and optionally carborane groups.
11

12 Description of the Related Art

13 Thermoset polymers that are stable at high temperatures are a goal of the art. A great
14 deal of research has been performed to date on developing precursor oligomers and polymers that
15 may be converted to thermosets, and further pyrolyzed to carbon or ceramics depending upon the
16 starting materials.

17 Monomer precursors for thermosets are desired, due to their improved processibility.
18 Monomer precursors usually will be liquid at room temperature, or will melt at low temperatures
19 (i.e., will be low melting solids), and will have controllable viscosity. Broader processing

1 windows, another goal of the art, may also be found with monomer precursors and blends of
2 these precursors.

3 Other desired features of precursors for thermosets include high char yield and low
4 evolution of volatiles.

5

6 SUMMARY OF THE INVENTION

7 Accordingly, it is an object of this invention to provide monomers that have a large
8 processing window (e.g., in excess of 200°C), are low melting, and are highly soluble in
9 commercially available solvents.

10 It is a further object of this invention to provide such monomers that can be converted to
11 products that are stable at high temperatures.

12 These and additional objects of the invention are accomplished by the structures and
13 processes hereinafter described.

14 The present invention is a compound having the formula:

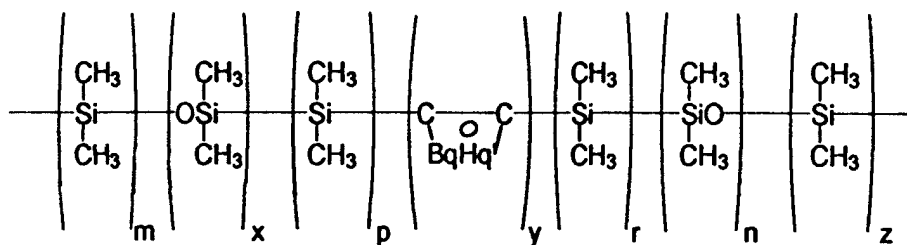


16 where R¹ and R² are independently selected from the group consisting of hydrogen, un-
17 substituted alkyl groups, substituted alkyl groups, unsubstituted aryl groups, and substituted aryl
18 groups,

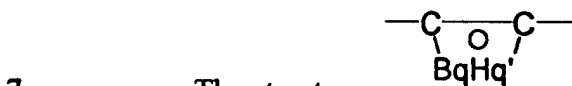
19 where Ac¹ and Ac² are independently selected alkynyl groups having at least 1 carbon-
20 carbon triple bond,

1 where Ar¹ and Ar² are independently selected substituted or unsubstituted aromatic
2 diradicals, and

3 where M has the structure



5 where m is a positive integer (unless otherwise noted, "integer" includes 0), and x, p, y, r, n, and
6 z are independently selected integers.



The structure in the foregoing formula denotes a carboranyl group.

8

1 BRIEF DESCRIPTION OF THE DRAWINGS

2 A more complete appreciation of the invention will be obtained readily by reference to
3 the following Description of the Preferred Embodiments and the accompanying drawings in which
4 like numerals in different figures represent the same structures or elements, wherein:

5 FIG. 1 shows an exemplary synthesis of compounds according to the present invention.

6 FIG. 2 shows another exemplary synthesis of compounds according to the present
7 invention.

8 FIG. 3 shows another exemplary synthesis of compounds according to the present
9 invention.

10 FIG. 4 shows the TGA of three compounds according to the invention.

11 FIGS. 5 through 12 show the ¹H NMR of seven compounds according to the invention.

12
13 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

14 The following are incorporated by reference herein, in their entireties, and for all
15 purposes:

16 (a) U.S. Patent No. 5,483,017, for "High Temperature Thermosets and Ceramics
17 Derived from Linear Carborane-(Siloxane or Silane)-Acetylene Copolymers", issued January 9,
18 1996 to Keller et al (hereinafter Keller '017),

1 (b) U.S. Patent Application Serial No. 08/540,148, for "High Temperature Ceramics
2 Derived from Linear Carborane-(Siloxane or Silane)-Acetylene Copolymers", filed October 6,
3 1995 by Keller et al. (hereinafter Keller '148 application), and

4 (c) U.S. Patent Application Serial No. 08/_____ for "Thermoset Polymers From
5 Inorganic Arylacetylenic Monomers", filed on date even herewith by Bucca et al., and designated
6 Navy Case No. 77,459.

7 The monomers of the present invention contain a group near the center of the molecule
8 (designated "M" in the formula above), where this group contains at least a silane moiety, and
9 optionally also any of the following: additional silane moieties, siloxane moieties, carborane
10 moieties, and combinations thereof. The monomers of the present invention also contain two
11 aromatic groups (designated Ar¹ and Ar² in the formula above) on either side of the "M" group,
12 two alkynyl groups (designated Ac¹ and Ac² in the formula above) bonded to the aromatic
13 groups, and two terminal groups (designated R¹ and R² in the formula above).

14

15 Preferred "M" Groups

16 Depending on the particular properties desired, skilled practitioners will select appropriate
17 values for m, n, p, q, r, x, y, and z.

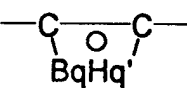
18 Preferably, m is a positive integer between 1 and 15, inclusive. Preferably, x is an integer
19 between 0 and 10, inclusive. Preferably, p is an integer between 0 and 10, inclusive. Preferably,
20 y is an integer between 0 and 10, inclusive. Preferably, r is an integer between 0 and 10, inclu-

1 sive. Preferably, n is an integer between 0 and 10, inclusive. Preferably, z is an integer between
2 0 and 10, inclusive.

3 Varying the ratio of carborane to silane groups can vary the properties of the monomer.
4 More siloxane groups will lead to a lower melting point and therefore a broader processing
5 window. More carboranyl groups will lead to better oxidative resistance. See Keller '148
6 application.

7 Preferred "M" groups include one or more silane moieties, one or more siloxane moieties,
8 and one or more carboranyl moieties, and combinations thereof.

9 In some circumstances it will be preferred to have M consist only of silane (and optionally
10 siloxane) moieties. For such embodiments, y = 0, and the proportions of m, x, and p (or
11 equivalently r, n, and z) are adjusted to give the desired proportions of silane to siloxane.

12 In the structure  , q and q' are independently selected integers from 3 to

13 16, inclusive. Suitable carboranyl groups are 1,7-dodecacarboranyl, 1,10-octacarboranyl, 1,6-octa-
14 carboranyl, 2,4-pentacarboranyl, 1,6-tetracarboranyl, 9-alkyl-1,7-dodecacarboranyl, 9,10-di-
15 alkyl-1,7-dodecacarboranyl, 2-alkyl-1,10-octacarboranyl, 8-alkyl-1,6-octacarboranyl, deca-
16 chloro-1,7-dodecacarboranyl, octachloro-1,10-octacarboranyl, decafluoro-1,7-dodecacarboranyl,
17 octafluoro-1,10-octacarboranyl, closo-dodeca-ortho-carboranyl, closo-dodeca-meta-carboranyl,
18 closo-dodeca-para-carboranyl, and combinations thereof.


1 Good results have been obtained with compounds having $m = x = y = z = n = 1$ and
2 $p = r = 0$ (designated herein as M moiety **a**), having $m = x = 1$ and $y = z = n = p = r = 0$
3 (designated herein as M moiety **b**), and having $m = 1$ and $x = y = z = n = p = r = 0$ (designated
4 herein as M moiety **c**).

5

6 Preferred "Ar" Groups

7 Ar^1 and Ar^2 may be the same or different. Suitable Ar groups include substituted or
8 unsubstituted phenyl, substituted or unsubstituted naphthalene radical, substituted or unsubstituted
9 anthracene radical, substituted or unsubstituted phenanthrene radical, and substituted or unsub-
10 stituted pyrene radical. Other suitable Ar groups include aromatic groups having at least one
11 heterocycle. Appropriate heterocycles include substituted or unsubstituted pyridine, substituted
12 or unsubstituted pyrrole, substituted or unsubstituted furan, and substituted or unsubstituted
13 thiophene.

14 Preferred Ar groups are substituted or (more preferably) unsubstituted aromatic diradicals
15 having 4 or fewer aromatic rings.

16 It is preferred to have the Ar groups bonded to the M groups and the Ac groups at non-
17 adjacent sites, to minimize steric effects. For example, in the case of an Ar group having a
18 single aromatic ring (such as a  group), it is preferred to have the M and Ac groups at meta
19 or para positions to each other. Meta substitution typically provides better polymerizing and/or
20 processing properties, while para substitution typically provides better thermal properties.

1 Preferred "Ac" Groups

2 Ac¹ and Ac² may be the same or different. As shown *infra*, a range of acetylenic groups
3 are within the scope of the present invention. Preferred Ac groups have 10 or fewer carbons.

4 Ac groups may have one carbon-carbon triple bond. Ac groups may have two or more
5 carbon-carbon triple bonds. In the case where the Ac groups have two or more triple bonds, two
6 or more of these bonds may be conjugated. Alternatively, these two or more carbon-carbon triple
7 bonds may be unconjugated. In the case where the adjacent terminal R group is H or phenyl
8 (i.e., R¹ in the case of Ac¹ and R² in the case of Ac²), the preferred Ac group is $-C\equiv C-$. In the
9 case where the adjacent terminal R group is C_6H_5- , the Ac group can be $-C\equiv C-C\equiv C-$.

10

11 Preferred "R" Groups

12 R¹ and R² may be the same or different. Suitable R groups include unsubstituted alkyl
13 groups, hydrogen, and unsubstituted aryl groups. Typical R groups include hydrogen, un-
14 substituted alkyl groups having 10 or fewer carbons, substituted alkyl groups having 10 or fewer
15 carbons, unsubstituted aryl groups having 10 or fewer carbons, and substituted aryl groups having
16 10 or fewer carbons.

17 More typical R groups include alkyl groups and aryl groups, substituted with one or more
18 halide or -OH groups. Preferred R groups include primary, secondary, and tertiary alkyl groups.
19 More preferred R groups are taken from the group consisting of H, phenyl, substituted phenyl,
20 substituted or unsubstituted alkyl having 6 or fewer carbons, substituted or unsubstituted benzyl,

1 substituted or unsubstituted naphthalene radical, substituted or unsubstituted anthracene radical,
2 substituted or unsubstituted phenanthrene radical, and substituted or unsubstituted pyrene radical.

3 H-terminated monomers will tend to react at lower temperatures and therefore provide
4 higher char yields. Aryl-terminated monomers (especially phenyl-terminated monomers) will tend
5 to have broader processing windows.

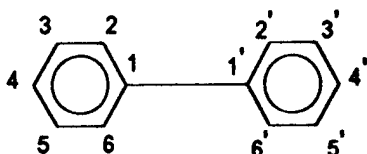
6
7 Synthetic Routes

8 An exemplary synthesis is depicted in FIG. 1. As shown, an aryl dihalide (in this case,
9 *p*-dibromobenzene) 1 undergoes a substitution reaction with *n*-butyllithium 2 to form a lithium
10 aryl halide 3 (in this case, *p*-bromolithium benzene). 1,4-Dichlorinated M 4 (for the desired M
11 group in the final product) reacts with the Li moieties in 3 to produce M with substituted
12 bromoaryl groups in the 4 and 4' positions. The aryl groups correspond to the desired Ar groups
13 in the final product.

14 This dihalide 5 is then reacted (typically with a Pd catalyst) with an acetylenic compound
15 6 containing the desired terminal group R and acetylenic group Ac, to yield the desired monomer
16 7.

17 To vary the aryl halide groups, e.g., to put a bromophenyl group in the 4 position, and
18 a bromonaphthalenyl group in the 4' position, and in turn vary the Ar groups in the monomer so
19 that $Ar^1 \neq Ar^2$, one would first add one equivalent of lithium bromobenzyl to the 4,4' dichlorin-
20 ated M4 to produce a monochlorinated M4 with an aryl halide group in the 4 position. Then the

1 addition of the second lithium aryl halide (lithium bromonaphthalenyl) would yield the desired 4-
2 bromobenzyl,4'-bromonaphthalenyl M4. The notations "4" and "4'" in the foregoing example
3 represent the substituent positions at opposite ends of the molecule or group. For example:



4

5 This is notation is adopted as a convenience, for illustrative purposes.

6 To vary the terminal R groups, mixtures of various substituted primary acetylenic
7 compounds can be used in the above synthesis.

8 To make H-terminated monomers, heating a dibromide precursor inside a bomb, with
9 acetylene and a catalyst is an effective synthetic route.

10 If more than one $-C\equiv C-$ moiety is desired in the monomer of the invention, different
11 synthetic routes may be employed. For example, as shown in FIG. 2, monomers with multiple
12 acetylene groups and multiple aromatic rings can be synthesized. Another synthetic route is
13 shown in FIG. 3. Of course, skilled practitioners will be able to modify the foregoing synthetic
14 routes, using the knowledge of a person of ordinary skill in the art.

15

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

EXAMPLES

Having described the invention, the following examples are given to illustrate specific applications of the invention, including the best mode now known to perform the invention. These specific examples are not intended to limit the scope of the invention described in this application.

Example 1. 1,7-Bis(4-bromophenyltetramethyldisiloxy)-*m*-carborane (5a).

A 100-mL three-necked round bottomed flask was equipped with two addition funnels and a stir bar and was charged with 1.75g (7.42 mmol) of 1,4-dibromobenzene and 30 mL of dry THF. The flask was equilibrated at -78°C and 3.0 mL (7.5 mmol) of *n*-butyllithium in hexane was added dropwise through the first addition funnel, which caused the formation of a white precipitate. After the mixture had been stirred for 45 min, 1.6 mL (3.5 mmol) of 1,7-bis(chloro-tetramethyldisiloxy)-*m*-carborane (4a) was added through the second addition funnel causing the milky white mixture to change to a clear yellow solution. This solution was warmed to room temperature, then poured into cold aqueous ammonium chloride and extracted with ether. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, and the solvent removed by rotary evaporation. The product (5a, 2.37 g, 93% yield) was a clear-colorless-viscous liquid and appeared pure by ¹H NMR. ¹H NMR (in CDCl₃): 7.48 (doublet of doublets, 2H, aromatic); 7.35 (doublet of doublets, 2H, aromatic); 3.1 (broad, 10H, BH); 0.34 (s,

1 12H, CH₃); 0.12 (s, 12H, CH₃). ¹³C NMR (CDCl₃): 137.7, 135.7, 134.5, 131.0 (aromatic); 68.27
2 (Si-C-B); 0.52 (Si-C).

3
4 Example 2. Synthesis of 1,7-Bis(4phenylethynylphenyltetramethyldisiloxy)-*m*-carborane (7a).

5 A 100-mL three-necked, round bottomed flask was equipped with a condenser and stir bar
6 and charged with 60 mL of degassed triethylamine, 2.37 g (3.30 mmol) of 1,7-bis(4-bromo-
7 phenyl-tetramethyldisiloxy)-*m*-carborane (5a), 1.1 mL (10 mmol) of phenylacetylene, 66 mg
8 (0.094 mmol) of bis(triphenylphosphine)palladium(II) chloride, 250 mg (0.954 mmol) of tri-
9 phenylphosphine, and 96 mg (0.502 mmol) of copper (I) iodide. The mixture was stirred and
10 heated at reflux for 12 h, resulting in the formation of a white precipitate. The reaction mixture
11 was then cooled to room temperature, the precipitate filtered and the solvent removed by rotary
12 evaporation. The resulting solid was taken up in ether, washed with dilute aqueous HCl, dried
13 over anhydrous sodium sulfate and the solvent removed by rotary evaporation to afford an orange
14 solid (7a). The solid was recrystallized from isopropanol yielding a light yellow powder (1.92
15 g, 58% yield). ¹H NMR (in CDCl₃): 7.49 (m, 12H, aromatic); 7.31 (m, 6H, aromatic); 3.1-1.2
16 (b, 10H, BH); 0.34 (s, 12H, CH₃); 0.13 (s, 12H, CH₃). ¹³C NMR (CDCl₃): 39.3, 132.8, 131.6,
17 130.8, 128.3, 124.3, 123.2 (aromatic); 90.1, 89.4 (acetylene); 68.39 (Si-C-B); 0.46 (Si-C).

18

1 Example 3. Bis(4-bromophenyl)tetramethyldisiloxane (**5b**).

2 This compound was prepared in a similar manner as **5a** by combining 1,4-dibromobenzene
3 (10 g, 42 mmol) with *n*-butyllithium (20 mL, 50 mmol) and 1,3-dichlorotetramethyldisiloxane
4 (4.6 mL, 22 mmol). Purification of **5b** was achieved by vacuum distillation to afford a colorless-
5 viscous liquid (60% yield). ¹H NMR (CDCl₃): 7.52 (doublet of doublets, 8H, aromatic), 0.34 (s,
6 12H, CH₃).

7
8 Example 4. Bis(4-phenylethynylphenyl)tetramethyldisiloxane (**7b**).

9 This compound was prepared in a similar manner as **7a** by combining compound **5b** (3.0
10 g, 6.8 mmol) with phenylacetylene (2.3 g, 23 mmol) and the catalyst combination: bis(triphenyl-
11 phosphine)palladium(II) chloride (200 mg 0.3 mmol), triphenylphosphine (400 mg, 1.6 mmol),
12 and copper (I) iodide (100 mg, 0.6 mmol). Purification of **7b** was achieved by dissolution in
13 methylene chloride and passing the concentrated solution through a column of silica. A light
14 brown solid (**7b**, 1.33 g, 56% yield) was recovered. ¹H NMR (CDCl₃): 7.53 (m, 12H, aromatic);
15 7.35 (m, 6H, aromatic); 0.36 (s, 12H, CH₃).

16
17 Example 5. Bis(*p*-bromophenyl)dimethylsilane (**5c**).

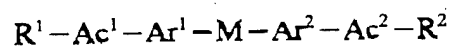
18 A 100 mL three-neck flask was equipped with an addition funnel, condenser, and stir bar.
19 The flask was flame dried, flushed with argon and charged with magnesium (1.04g, 42.8 mmol)
20 and 5 mL of dry ether. A few drops of 1,2-dibromoethane was added to activate the magnesium

Navy Case No. 77,458
 Inventor(s): Bucca et al.

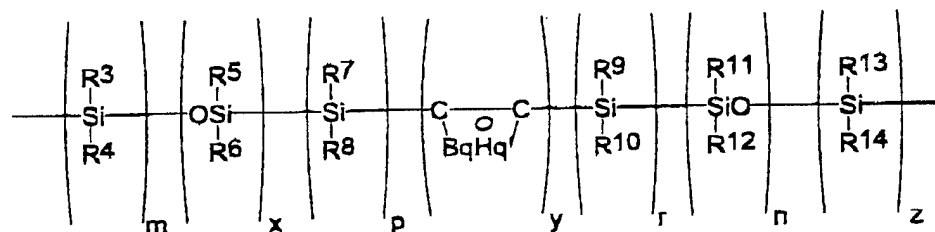
PATENT APPLICATION

ABSTRACT OF THE DISCLOSURE

The present invention is a compound having the formula:



where R^1 and R^2 are independently selected from the group consisting of hydrogen, unsubstituted alkyl groups, substituted alkyl groups, unsubstituted aryl groups, and substituted aryl groups, where Ac^1 and Ac^2 are independently selected alkynyl groups having at least 1 carbon-carbon triple bond, where Ar^1 and Ar^2 are independently selected substituted or unsubstituted aromatic diradicals, and where M has the structure



where m is a positive integer, wherein x , p , y , r , n , and z are independently selected integers, where $z \neq 0$ when $n \neq 0$, and where R^3 through R^{14} are independently selected from the group consisting of hydrogen, unsubstituted alkyl groups, substituted alkyl groups, unsubstituted aryl groups, and substituted aryl groups.