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3 HIGH TEMPERATURE ELASTOMERS FROM LINEAR POLY(SILARYLENE-SILOXANE-
4 ACETYLENE)
5

6 **Background of the Invention**

7 **1. Field of the Invention**

8 The invention relates generally to linear polymers that can be cured to form high temperature
9 elastomers and plastics, and in particular to a high temperature elastomer made by curing linear
10 poly(silarylene-siloxane-acetylene).

11 **2. Description of the Related Art**

12 The aerospace industry has a continuing demand for high performance materials that can
13 withstand extreme variations of temperatures. In particular, there is a need for materials that have
14 elastomeric properties, that have thermal, thermo-oxidative and hydrolytic stability at high
15 temperatures (as high as 300 - 350 °C) and that maintain their flexibility below ambient
16 temperatures. For example, fuel tanks of high flying airplanes and space vehicles require sealants
17 that maintain elasticity for up to 10,000 hours of use at temperatures that range from -60 °C to 400
18 °C. Further, the material must resist swelling when coming into contact with jet fuel and must have
19 excellent adhesion to and inertness toward metallic substrates.

20 Linear polymers and crosslinked polymers that have repeating units made up of diacetylene
21 groups and siloxane groups are disclosed in, for example, U.S. Patent No. 5,563,181 to Keller et al

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and U.S. Patent No. 5,874,514 to Keller et al, both incorporated herein by reference.

Linear polymers and crosslinked polymers and copolymers made up of silarylene and siloxane units are disclosed in, for example, U.S. Patent No. 5,578,380 to Babu, U.S. SIR No. H1612 to Rhein et al, and U.S. Patent No. 5,346,980 to Babu, all incorporated herein by reference.

Summary of the Invention

It is therefore an object of the present invention to provide a linear polymer that can be crosslinked to form a polymer that has elastomeric properties, that is thermally and oxidatively stable at high temperatures and that maintains its elastomeric properties at low temperatures.

Another object of the present invention is to provide a crosslinked polymer that has elastomeric properties.

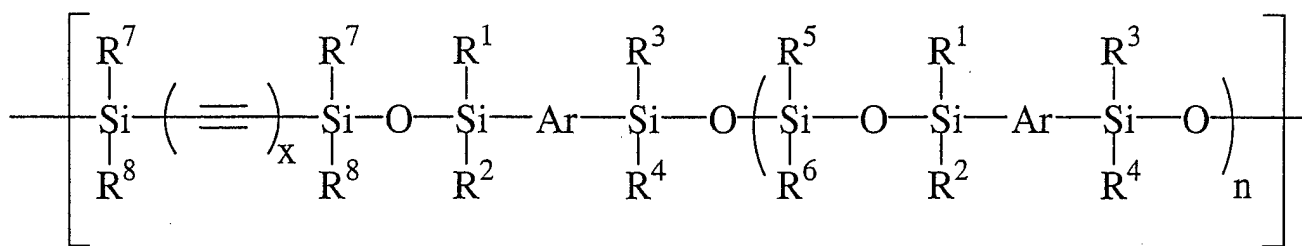
Another object of the present invention is to provide a crosslinked polymer that is thermally and oxidatively stable at temperatures as high as 300 - 350 °C.

Another object of the present invention is to provide a crosslinked polymer that maintains its elastomeric properties at temperatures as low as -50 °C.

Another object of the present invention is to provide a linear polymer made by a method of synthesis wherein the mechanical properties of the linear polymer and of a crosslinked polymer obtained from curing the linear polymer can be controlled.

These and other objects are obtained by a linear polymer that has repeating units represented by the formula

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wherein

(a) n is an integer greater than or equal to 0,

(b) x is an integer greater than or equal to 1, and $\left(\equiv \right)_x$ represents an unconjugated

acetylenic group when x is equal to 1 or conjugated acetylenic groups when x is greater than 1;

(c) Ar is an aromatic group, and

(d) $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7$ and R^8 are independently selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof.

The invention is further directed to crosslinked polymers by curing a linear polymer as described above.

In the linear polymers and crosslinked polymers of the present invention, the acetylenic groups in the backbone of the polymer provide for crosslinking in comparison to polymers that only have silarylene-siloxane groups. The aromatic groups in the backbone of the polymer provide for improved thermal stability and rigidity, in comparison to polymers that only have siloxane and acetylene groups.

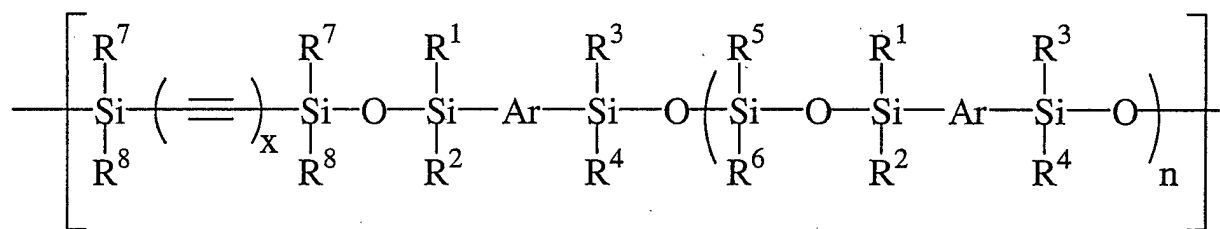
Detailed Description of the Preferred Embodiment

The following detailed description of the invention is provided to aid those skilled in the art

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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 a linear inorganic-organic hybrid polymer and a crosslinked polymer derived therefrom. The linear polymer is made up of repeating units represented by the formula



wherein

(a) n is an integer greater than or equal to 0,

(b) x is an integer greater than or equal to 1, and $\left(\text{---} \right)_x$ represents an unconjugated

acetylenic group when x is equal to 1 or conjugated acetylenic groups when x is greater than 1;

(c) Ar is an aromatic group, and

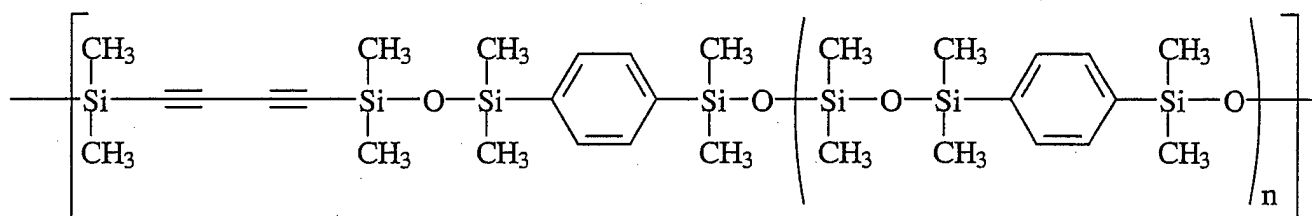
(d) $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7$ and R^8 are independently selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof.

Particular values for n and x, particular choices for the side chains $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8$, and the aromatic group Ar may be selected according to particular properties desired for the

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linear polymer and for elastomers and plastics made using the compound. For example, increasing the relative number of silarylene and siloxane units (increasing n) increases the chain flexibility. As discussed in more detail below, the relative amount of silarylene-siloxane units and acetylene units in the repeating unit (as represented by the value of n in the formula) can be controlled by selecting the relative molar amounts of reactants in one of the steps of the synthesis of the polymer. Using larger alkyl groups for the side chains R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ increases the solubility of the linear polymer in organic solvents and increases the hydrophobicity and decreases the thermo-oxidative stability of elastomers and plastics made using the compound. Using aryl groups for the side chains R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ increases the stiffness and slightly increases the thermo-oxidative stability of polymers made using the compound. Using larger aryl linking groups for Ar adds stiffness to elastomers and plastics made from the compound. Linear polymers with larger conjugated acetylenic groups (x greater than 2) are more easily cured, but are more expensive to produce.

In the most preferred embodiment, the acetylenic group is butadiyne (x = 2), the aromatic group is phenylene, and all the R groups are methyl. The repeating units of this embodiment may thus be represented by the following formula:



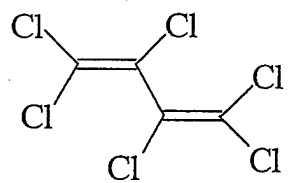
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1 The linear polymer of the present invention has the advantage of being extremely easy to
2 process and convert into elastomers and plastics since it is , depending on the selection of variables
3 and substituents, either a liquid at room temperature or a low melting solid and is soluble in most
4 organic solvents. The linear polymer is thus well-suited to serve as a thermoset polymeric precursor.

5 The linear polymer may be easily produced by the method exemplified in the following
6 reaction scheme, which illustrates the synthesis of the most preferred embodiment, compound 1,
7 wherein the acetylenic group is butadiyne ($x = 2$), the aromatic group is phenylene, and all the R
8 groups are methyl. The synthesis may be carried out in a one pot, two step reaction.
9 Hexachlorobutadiene, 2, is reacted with four equivalents of n-butyllithium to get 1,4-dilithio-1,3-
10 butadiyne, 3. Dimethylaminochlorodimethylsilane, 4, is added to the solution to get 1,4-
11 bis(dimethylamino-dimethylsilyl)butadiyne, 5.

12 Meanwhile, compound 6 is formed by reacting an excess amount of 1,4-
13 bis(hydroxydimethylsilyl)benzene, 7, (weak acid) with bis(dimethylamino)dimethylsilane 8 in
14 refluxing toluene. Despite the relative stability of Si-N bonds, they are readily cleaved by acids and
15 various organic and inorganic nucleophiles and/or electrophiles.

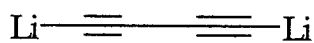
16 Compound 1, the linear polymer, is produced by reacting compound 5 and compound 6.
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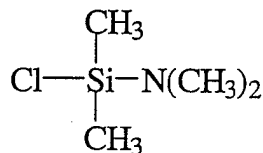
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4 n-BuLi

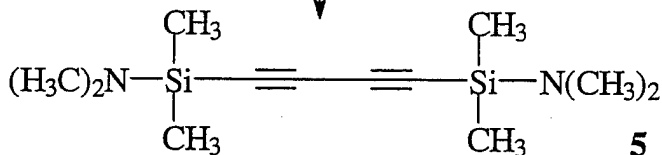


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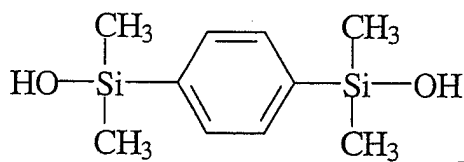
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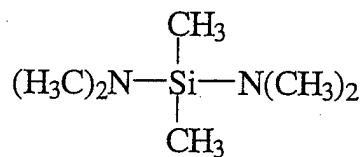


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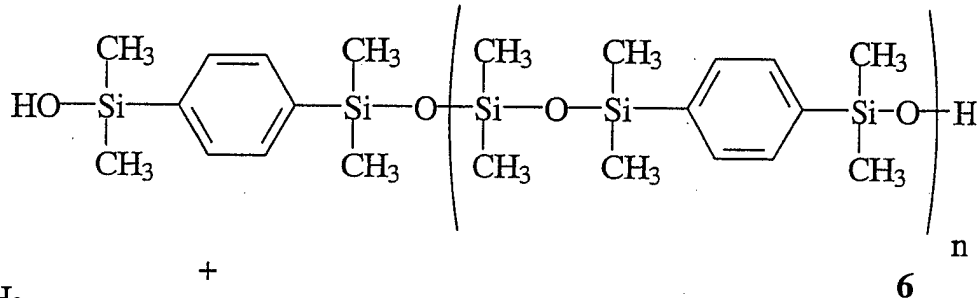


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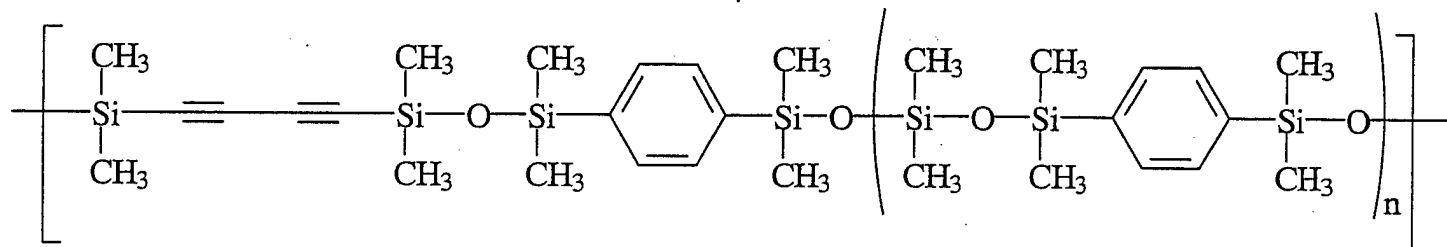


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1 Different linear polymers represented by compound **1** may be created by varying the relative
2 amount of compound **7** and compound **8** used in the creation of compound **6** (thereby changing the
3 value of *n*, which represents the length of the aromatic disiloxy/trisiloxy group in compounds **1** and
4 **6**). In this manner, linear polymers having different properties and processing parameters tailored
5 to specific needs can be easily created.

6 The crosslinked polymer is made by thermally curing the linear polymer **1**. Typically, the
7 curing is carried out for a sufficient time and at a sufficient temperature to allow at least some of the
8 acetylene groups of the linear polymer to react intermolecularly with each other to form a crosslinked
9 network.

10 EXAMPLES

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

14 Example #1. Synthesis of 1,4-Bis(Dimethylaminodimethylsilyl)butadiyne.

15 A flame dried 250 ml Schlenk flask containing THF (20 ml) was cooled to -78 °C and *n*-butyl
16 lithium (20 ml of 2.4 M in hexane, 48.0 mmol) was added by syringe. After several minutes
17 hexachlorobutadiene (1.88 ml, 12.0 mmol) was added dropwise via syringe over a 10 minute period.
18 After completion of addition, the cold bath was removed and the mixture stirred at room temperature
19 for 3 hours. The resulting 1,4-dilithio-1,3-butadiyne was used without further purification. The flask
20 was then re-cooled to -78 °C, and dimethylaminodimethylchlorosilane (3.6 ml, 24 mmol) was added
21 by syringe. The flask was removed from the cold bath and the reaction mixture stirred at room

1 temperature for 16 hours. At this time ^1H NMR analysis indicated complete disappearance of
2 dimethylaminodimethylchlorosilane and formation of 1,4-bis(dimethylaminodimethylsilyl)-
3 butadiyne. The THF was removed in vacuo, and the mixture was taken up in a minimum amount of
4 pentane and filtered. The pentane was removed in vacuo to give 2.91 g (96%) of 1,4-
5 bis(dimethylaminodimethylsilyl)butadiyne.

6 **Example #2. Synthesis of Silarylene-Siloxane Prepolymer Terminated by Hydroxyl Moieties,**
7 **where $n = 1$.**

8 A three-necked flask was equipped with a stir bar, reflux condenser, inlet and outlet adapters
9 for argon gas. The entire assembly was flame dried. 1,4-Bis(hydroxydimethylsilyl)benzene (5.20 g,
10 23 mmol) was added and toluene (15 ml) was injected by syringe followed by the addition of
11 bis(dimethylamino)dimethylsilane (2.07 ml, 11.5 mmol). The resulting solution was brought to
12 reflux temperature and maintained until there was no further evidence of dimethylamine evolution,
13 as determined by a moist litmus paper test on the exhaust stream of the argon outlet. The reaction
14 mixture was refluxed an additional hour. ^1H NMR analysis showed complete disappearance of the
15 starting materials and formation of the silarylene-siloxane prepolymer. The prepolymer was used as
16 prepared and then chain extended with 1,4-bis(dimethylaminodimethylsilyl)butadiyne (see example
17 #6).

18 **Example #3. Synthesis of Silarylene-Siloxane Prepolymer Terminated by Hydroxyl Moieties,**
19 **where $n = 2$.**

20 A three-necked flask was equipped with a stir bar, reflux condenser, inlet and outlet adapters
21 for argon gas. The entire assembly was flame dried. 1,4-Bis(hydroxydimethylsilyl)benzene (5.65 g,

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24.9 mmol) was added and toluene (15 ml) was injected by syringe followed by the addition of bis(dimethylamino)dimethylsilane (3.00 ml, 16.6 mmol). The resulting solution was brought to reflux temperature and maintained until there was no further evidence of dimethylamine evolution, as determined by a moist litmus paper test on the exhaust stream of the argon outlet. The reaction mixture was refluxed an additional hour. ^1H NMR analysis showed complete disappearance of the starting materials and formation of the silarylene-siloxane prepolymer. The prepolymer was used as prepared and then chain extended with 1,4-bis(dimethylaminodimethylsilyl)butadiyne (see example #7).

Example #4. Synthesis of Silarylene-Siloxane Prepolymer Terminated by Hydroxyl Moieties, where $n = 3$.

A three-necked flask was equipped with a stir bar, reflux condenser, inlet and outlet adapters for argon gas. The entire assembly was flame dried. 1,4-Bis(hydroxydimethylsilyl) benzene (2.66 g, 11.7 mmol) was added and toluene (10 ml) was injected by syringe followed by the addition of bis(dimethylamino)dimethylsilane (1.59 ml, 8.81 mmol). The resulting solution was brought to reflux temperature and maintained until there was no further evidence of dimethylamine evolution, as determined by a moist litmus paper test on the exhaust stream of the argon outlet. The reaction mixture was refluxed an additional hour. ^1H NMR analysis showed complete disappearance of the starting materials and formation of the silarylene-siloxane prepolymer. The prepolymer was used as prepared and then chain extended with 1,4-bis(dimethylaminodimethylsilyl)butadiyne (see example #8).

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Example #5. Synthesis of Linear Poly(Silarylene-Siloxane-Acetylene) where, $n = 0$ as a Precursor to a High Temperature Plastic.

A three-necked flask was equipped with a stir bar, reflux condenser, inlet and outlet adapters for argon gas. The entire assembly was flame dried. 1,4-Bis(hydroxydimethylsilyl)benzene (2.43 g, 10.7 mmol) was added. A previously prepared sample of 1,4-bis-(dimethylaminodimethylsilyl)butadiyne (2.71 g, 10.7 mmol) was dissolved in 20 ml of toluene. Part of this solution (16 ml) was added to the three-necked flask containing the 1,4-bis(hydroxydimethylsilyl)benzene. The remaining 4 ml was diluted to 20 ml with toluene. After refluxing the reaction mixture for 1 hour, an additional amount of the 1,4-bis(dimethylaminodimethylsilyl)butadiyne solution (4 ml) was added at time intervals of 30 to 60 minutes until dimethylamine evolution had ceased. Toluene was removed at reduced pressure and excess ether was added. The ether solution was washed with a saturated solution of aqueous NH_4Cl (2 x 100 ml). After aqueous workup and extraction with diethyl ether, the polymeric solution was dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo* to give 2.71 g, (65%) of the linear poly(silarylene-siloxane-acetylene) as a viscous brown liquid.

Example #6. Synthesis of Linear Poly(Silarylene-Siloxane-Acetylene) where, $n = 1$ as a Precursor to a High Temperature Elastomer.

To a three-necked flask containing the previously prepared silarylene-siloxane prepolymer terminated by hydroxyl moieties (see example #2) was added a 19.5 ml aliquot of a 20 ml toluene solution containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (2.91 g, 11.5 mmol). After refluxing the reaction mixture for 1 to 2 hours, an additional amount of the toluene solution

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1 containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (200-500 μ l) was added at time intervals
2 of 30 to 60 minutes until the viscosity of the solution visibly increased and dimethylamine evolution
3 had ceased. Toluene was removed at reduced pressure and excess ether was added. The ether
4 solution was washed with a saturated solution of aqueous NH_4Cl (2 x 100 ml). After aqueous workup
5 and extraction with diethyl ether, the polymer solution was dried over Na_2SO_4 and filtered. The
6 solvent was removed *in vacuo* to give 4.31 g, (56%), of the linear poly(silarylene-siloxane-acetylene)
7 as a brown viscous liquid. IR (cm^{-1}) 2080 (m), ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 1059 (vs, broad), (Si-O). ^1H NMR
8 (CDCl_3 , ppm) 7.51 (s), (C_6H_4), 0.35 (s), 0.30 (s), 0.29 (s), 0.22 (s), 0.03 (s), ($\text{Si}(\text{CH}_3)_2$). ^{13}C NMR
9 (CDCl_3 , ppm) 140.8, 140.7, 132.3, 132.25, 132.21, (C_6H_4), 86.9, 85.4, ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 2.09, 1.36,
10 0.92, 0.74, 0.59, ($\text{Si}(\text{CH}_3)_2$).

11 **Example #7.Synthesis of Linear Poly(Silarylene-Siloxane-Acetylene) where, n = 2 as a**
12 **Precursor to a High Temperature Elastomer.**

13 To a three-necked flask containing the previously prepared silarylene-siloxane prepolymer
14 terminated by hydroxyl moieties (see example #3) was added a 19.5 mL aliquot of a 20 ml toluene
15 solution containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (2.10 g, 8.32 mmol). After
16 refluxing the reaction mixture for 1 to 2 hours, an additional amount of the toluene solution
17 containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (200-500 μ l) was added at time intervals
18 of 30 to 60 minutes until the viscosity of the solution visibly increased and dimethylamine evolution
19 had ceased. Toluene was removed at reduced pressure and excess ether was added. The ether
20 solution was washed with a saturated solution of aqueous NH_4Cl (2 x 100 mL). After aqueous
21 workup and extraction with diethyl ether, the polymeric solution was dried over Na_2SO_4 and filtered.

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1 The solvent was removed *in vacuo* to give 5.84 g, (88%) of the linear poly(silarylene-siloxane-
2 acetylene) as a brown viscous liquid. IR (cm^{-1}) 2076 (m), ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 1053 (vs, broad), (Si-O).
3 ^1H NMR (CDCl_3 , ppm) 7.50 (s), (C_6H_4), 0.34 (s), 0.27 (s), 0.21 (s), 0.02 (s), ($\text{Si}(\text{CH}_3)_2$). ^{13}C NMR
4 (CDCl_3 , ppm) 141.5, 132.9, (C_6H_4) 86.0, 83.1, ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 2.08, 1.52, 1.03, 0.88, 0.67,
5 ($\text{Si}(\text{CH}_3)_2$).

6 **Example #8. Synthesis of Linear Poly(Silarylene-Siloxane-Acetylene) where, $n = 3$ as a**
7 **Precursor to a High Temperature Elastomer.**

8 To a three-necked flask containing the previously prepared silarylene-siloxane prepolymer
9 terminated by hydroxyl moieties (see example #4) was added a 4.0 ml aliquot of a 5.0 ml toluene
10 solution containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (0.83 g, 3.28 mmol). After
11 refluxing the reaction mixture for 1 to 2 hours, an additional amount of the toluene solution
12 containing 1,4-bis(dimethylaminodimethylsilyl)butadiyne (50-100 μl) was added at time intervals
13 of 15 to 30 minutes until the viscosity of the solution visibly increased and dimethylamine evolution
14 had ceased. Toluene was removed at reduced pressure and excess ether was added. The ether
15 solution was washed with a saturated solution of aqueous NH_4Cl (2 x 100 ml). After aqueous workup
16 and extraction with diethyl ether, the polymeric solution was dried over Na_2SO_4 and filtered. The
17 solvent was removed *in vacuo* to give 2.45 g, (67%) of the linear poly(silarylene-siloxane-acetylene)
18 as a brown viscous liquid. IR (cm^{-1}) 2074 (w), ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 1052 (vs, broad), (Si-O). ^1H NMR
19 (CDCl_3 , ppm) 7.50 (s), (C_6H_4), 0.35 (s), 0.30 (s), 0.28 (s), 0.22 (s), 0.02 (s), ($\text{Si}(\text{CH}_3)_2$). ^{13}C NMR
20 (CDCl_3 , ppm) 140.7, 140.2, 132.2, (C_6H_4) 86.9, 85.3, ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), 2.11, 1.40, 0.96, 0.77,
21 ($\text{Si}(\text{CH}_3)_2$).

Example #9. Thermal Curing of the Plastic Precursor: Linear Poly(Silarylene-Siloxane-Acetylene) where $n = 0$ (See Example #5 for Synthesis).

To a platinum thermogravimetric analyzer pan was placed 28.7410 mg of the linear poly(silarylene-siloxane-acetylene). The sample was then heated under an atmosphere of dry nitrogen at 150, 200, 350 and 450 °C for 60, 60, 120 and 120 minutes, respectively. After completion of the isothermal curing experiment the sample was void free and exhibited the characteristics of a plastic material.

Example #10. Post Cure Thermo-Oxidative Stability Study on Crosslinked Poly(Silarylene-Siloxane-Acetylene) where $n = 0$ (See Example #5 for Synthesis and Example #9 for Curing).

Following the isothermal curing cycle performed on the linear poly(silarylene-siloxane-acetylene), the sample was allowed to cool to ambient temperature. The sample was then isothermed on a thermogravimetric analyzer for 120 minutes at 200, 250, 300, and 350 °C, respectively, in an air atmosphere at a flow of 50 cc/min. The plastic sample exhibited excellent oxidative stability over the time frame of the experiment, experiencing only a 0.17% weight loss, as determined by thermogravimetric analysis.

Example #11. Bulk Thermal Curing of the Plastic Precursor: Linear Poly(Silarylene-Siloxane-Acetylene) where $n = 0$ (See Example #5 for Synthesis).

To a circular aluminum pan pretreated with a teflon mold release was weighed 1.2015 g of the linear poly(silarylene-siloxane-acetylene). In order to remove any volatile material, the sample

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1 was placed on a hot plate and isothermed at 125 °C under dynamic vacuum conditions. Following
2 the degassing procedure, the sample was placed in a tube furnace and heated sequentially under an
3 atmosphere of dry argon for 120 minutes at 200, 250, 300 and 350 °C, respectively. After completion
4 of the isothermal curing cycle, the liquid linear poly(silarylene-siloxane-acetylene) had been
5 transformed to a void free, hard plastic material.

6 **Example #12. Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-Siloxane-**
7 **Acetylene) where $n = 1$ (See Example #6 for Synthesis).**

8 To a platinum thermogravimetric analyzer pan was placed 53.6410 mg of the liquid linear
9 poly(silarylene-siloxane-acetylene). The sample was then converted to an elastomer by heating
10 sequentially under an atmosphere of dry nitrogen for 120 minutes at 200, 250, 300, 350 and 400 °C,
11 respectively. After completion of the isothermal curing experiment, the sample was void free and
12 exhibited the characteristics of an elastomeric material, i.e., soft and flexible.

13 **Example #13. Post Cure Thermo-Oxidative Stability Study on Crosslinked Poly(Silarylene-**
14 **Siloxane-Acetylene) where $n = 1$ (See Example #6 for Synthesis and Example #12 for Curing).**

15 Following the isothermal curing cycle performed on the elastomeric precursor linear
16 poly(silarylene-siloxane-acetylene), the sample was allowed to cool to ambient temperature. The
17 sample was then isothermed in a thermogravimetric analyzer for 60 minutes at 200 and 250 °C and
18 for 120 minutes at 300 and 330 °C, respectively, in an air atmosphere at a flow rate of 50 cc/min.
19 The sample exhibited excellent oxidative stability over the time frame of the experiment,
20 experiencing only a 3.26% weight loss. After completion of the thermo-oxidative study, the sample
21 was visibly void free and still retained flexibility as determined by bending the sample.

Example #14. Bulk Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-Siloxane-Acetylene) where $n = 1$ (See Example #6 for Synthesis).

To a circular aluminum pan pretreated with a teflon mold release was weighed 1.6182 g of the linear poly(silarylene-siloxane-acetylene). In order to remove any volatile material, the sample was placed on a hot plate and isothermed at 125 °C under dynamic vacuum conditions. Following the degassing procedure, the sample was placed in a tube furnace and converted to an elastomer by heating sequentially under an atmosphere of dry argon for 120 minutes at 200, 250, 300 and 350 °C, respectively. After completion of the isothermal curing cycle, the liquid linear poly(silarylene-siloxane-acetylene) had been transformed to a tough, void-free, flexible material.

Example #15. Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-Siloxane-Acetylene) where $n = 2$ (See Example #7 for Synthesis).

To a platinum thermogravimetric analyzer pan was placed 28.9990 mg of the liquid linear poly(silarylene-siloxane-acetylene). The sample was then heated sequentially under an atmosphere of dry nitrogen for 120 minutes at 200, 250, 300, 350 and 400 °C, respectively. After completion of the isothermal curing experiment, the sample was void free and exhibited the characteristics of an elastomeric material, i.e., soft and flexible.

Example #16. Post Cure Thermo-Oxidative Stability Study on Crosslinked Poly(Silarylene-Siloxane-Acetylene) where $n = 2$ (See Example #7 for Synthesis and Example #15 for Curing).

Following the isothermal curing cycle performed on the liquid precursor linear poly(silarylene-siloxane-acetylene), the elastomeric sample was allowed to cool to ambient temperature.

1 The sample was then isothermed in a thermogravimetric analyzer for 60 minutes at 200 and 250 °C
2 and for 120 minutes at 300 and 330 °C, respectively, in an air atmosphere at a flow rate of 50
3 cc/min. The sample exhibited excellent oxidative stability over the time frame of the experiment,
4 experiencing only a 7.69% weight loss. After completion of the thermo-oxidative study, the sample
5 was visibly void-free and still retained flexibility, as determined by bending the sample.

6 **Example #17. Bulk Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-**
7 **Siloxane-Acetylene) where $n = 2$ (See Example #7 for Synthesis).**

8 To a circular aluminum pan pretreated with a teflon mold release was weighed 1.6203g of
9 the liquid linear poly(silarylene-siloxane-acetylene). In order to remove any volatile material, the
10 sample was placed on a hot plate and heated at 125 °C under dynamic vacuum conditions. Following
11 the degassing procedure, the sample was placed in a tube furnace and converted to an elastomer by
12 heating sequentially under an atmosphere of dry argon for 120 minutes at 200, 250, 300 and 350 °C,
13 respectively. After completion of the isothermal curing cycle, the liquid linear poly(silarylene-
14 siloxane-acetylene) had been transformed to a tough, void-free, flexible material.

15 **Example #18. Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-Siloxane-**
16 **Acetylene) where $n = 3$ (See Example #8 for Synthesis).**

17 To a platinum thermogravimetric analyzer pan was placed 41.6950 mg of the liquid linear
18 poly(silarylene-siloxane-acetylene). The sample was then converted to an elastomer by heating
19 sequentially under an atmosphere of dry nitrogen for 120 minutes at 200, 250, 300, 350 and 400 °C,
20 respectively. After completion of the isothermal curing experiment, the sample was void-free and
21 exhibited the characteristics of an elastomeric material, i.e., soft and flexible.

Example #19. Post Cure Thermo-Oxidative Stability Study on Crosslinked Poly(Silarylene-Siloxane-Acetylene) where $n = 3$ (See Example #8 for Synthesis and Example #18 for Curing).

Following the isothermal curing cycle performed on the elastomeric precursor linear poly(silarylene-siloxane-acetylene), the sample was allowed to cool to ambient temperature. The elastomeric sample was then isothermed in a thermogravimetric analyzer for 60 minutes at 200 and 250 °C and for 120 minutes at 300 and 330 °C, respectively in an air atmosphere at a flow rate of 50 cc/min. The sample exhibited excellent oxidative stability over the time frame of the experiment, experiencing only a 3.96% weight loss. After completion of the thermo-oxidative study, the sample was visibly void-free and still retained flexibility, as determined by bending the sample.

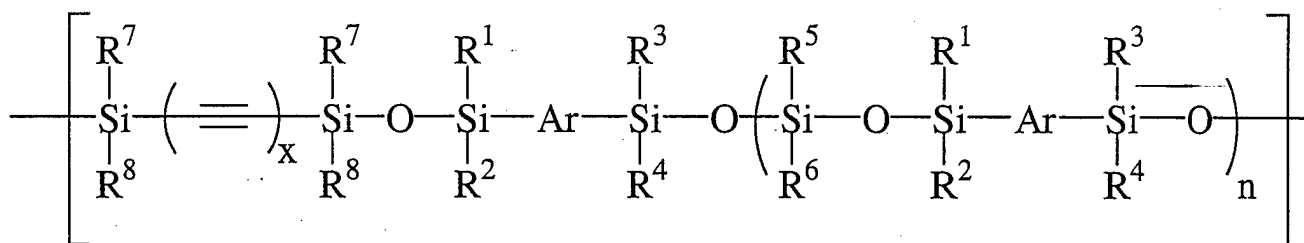
Example #20. Bulk Thermal Curing of the Elastomeric Precursor: Linear Poly(Silarylene-Siloxane-Acetylene) where $n = 3$ (See Example #8 for Synthesis).

To a circular aluminum pan pretreated with a teflon mold release was weighed 1.6053g of the linear poly(silarylene-siloxane-acetylene). In order to remove any volatile material, the sample was placed on a hot plate and isothermed at 125 °C under dynamic vacuum conditions. Following the degassing procedure, the sample was placed in a tube furnace and converted to an elastomer by heating sequentially under an atmosphere of dry argon for 120 minutes at 200, 250, 300 and 350 °C, respectively. After completion of the isothermal curing cycle, the liquid linear poly(silarylene-siloxane-acetylene) had been transformed to a tough, void-free, flexible material.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

ABSTRACT

A linear polymer has repeating units represented by the formula



wherein

(a) n is an integer greater than or equal to 0,

(b) x is an integer greater than or equal to 1, and $\text{---} \left(\text{---} \right)_x \text{---}$ represents an unconjugated

acetylenic group when x is equal to 1 or conjugated acetylenic groups when x is greater than 1;

(c) Ar is an aromatic group, and

(c) $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7$ and R^8 are independently selected from the group consisting of alkyl, aryl, alkylaryl, haloalkyl, haloaryl and mixtures thereof.

The linear polymer may be thermally cured to form a crosslinked polymer.