United States Patent

Tapsak et al.

[54] SILALKYLENESILOXANE COPOLYMER MATERIALS AND METHODS FOR THEIR PREPARATION

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[58] Field of Search ............................... 556/434, 435; 528/35, 37, 14, 18, 12

[56] References Cited

U.S. PATENT DOCUMENTS

3,452,071 6/1969 Sperck ............................. 556/434
5,229,034 8/1993 Takago et al.
5,241,034 8/1993 Herzog et al.
5,366,087 1/1995 Herzog et al.
5,386,049 1/1995 Kishita et al.
5,422,083 8/1995 Kobayashi
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5,516,832 5/1996 Kuanan et al.
5,525,696 6/1996 Herzog et al.
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5,696,211 12/1997 Chung et al.
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FOREIGN PATENT DOCUMENTS

2686610 7/1993 France.
WO 96/20964 7/1996 WIPO.
WO 96/35732 11/1996 WIPO.

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Primary Examiner—Robert Dawson
Assistant Examiner—Jeffrey B. Robertson
Attorney, Agent, or Firm—Thomas F. Woods; Harold R. Patton

[57] ABSTRACT

Symmetric and asymmetric cyclic silalkylkenesiloxane monomers and copolymers thereof are disclosed, as well as crosslinked and/or reinforced silalkylkenesiloxane copolymers, medical devices containing such materials, and methods of preparation.

15 Claims, No Drawings
SILALKYLENESIOXANO COPOLYMER MATERIALS AND METHODS FOR THEIR PREPARATION

BACKGROUND OF THE INVENTION

Silicones (i.e., organosiloxanes) are polymers containing alternating silicon and oxygen atoms in the backbone with various organic groups attached to the silicon atoms. Silalkylenesioxane copolymers include alkylene backbone units without unsaturation and also include monovalent hydrocarbon groups attached to silicone atoms. Both silicones and silalkylenesioxanes are useful materials for a wide variety of applications (e.g., rubbers, adhesives, sealing agents, release coatings, antifoam agents). Because of their biocompatibility, silicones present a low risk of unfavorable biological reactions and have therefore gained the medical industry's recognition. Such materials are useful in a wide variety of medical devices. There are, however, limited materials available for medical device applications. In addition, there is a need for improved silicone materials that can be used in the medical industry, particularly those with good strength and tear resistance.

Prior to the present invention, silalkylenesioxane copolymers have been prepared by three methods. Ring opening polymerization of cyclic silalkylenesioxane is disclosed in U.S. Pat. No. 5,117,025 (Takago et al.). Condensation polymerization of silanol terminated silalkylene oligomers is disclosed in U.S. Pat. No. 5,386,049 (Kishita et al.). Step growth hydroisilylation polymerization between a hydride terminated organosiloxane and an unsaturated aliphatic hydrocarbon that contains 2 carbon-double bonds or one carbon-double bond and one carbon-carbon triple bond is disclosed in U.S. Pat. No. 5,442,083 (Kobayashi).

U.S. Pat. No. 5,442,083 (Kobayashi) states that the ring opening polymerization of cyclic silalkylenesioxane is not advantageous for producing silalkylenesioxane copolymers. As reported in Andrianov et al., *Inst. Of Heteroorganic Cpd.,* p. 661, translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 739–44 (1971), a partial depolymerization occurs in this method, which therefore leads to reduced yields of the silalkylenesioxane copolymer.

Step growth condensation polymerization of silanol terminated fluids yields copolymers that have silanol end groups. To make the copolymer end-functional, for example, vinylidemethylsilyl terminated, another synthetic step is required. This is a disadvantage. In addition, degrees of polymerization (Dp) from step growth silanol condensation polymerizations of disilanolalkylenes compounds have been reported to be no greater than 180. See, U.S. Pat. No. 5,386,049 (Kishita et al.) and Benouragha et al., *Eur. Polym. J.*, 33, p. 1117 (1997). This is a disadvantage.

Hydroisilylation step growth polymerization as a method of silalkylenesioxane copolymer synthesis also contains inherent disadvantages. In order to produce high Dp copolymer, the stoichiometry of the silylehydride and unsaturated hydrocarbon moieties must be as close to 1:1 as possible. Side reactions which disturb this balance limit the Dp of said copolymer by creating terminating groups on unsaturated hydrocarbon monomers. For example, it is known in the art that transition metal catalysts typically used for hydroisilylation reactions can cause the isomerization of a terminal carbon-carbon double bond to an internal position. See, Harrod et al., *Organic Synthesis via Metal Carbonyls,* 2, John Wiley & Sons, New York, p. 673 (1977), and Speier, *Adv. Organometallic Chem.,* 17, p. 407 (1979). This is a disadvantage. This isomerization renders the monomers less susceptible to hydroisilylation.

Silalkylenesioxane copolymers having a Dp as high as 10,000 are disclosed in U.S. Pat. No. 5,484,868 (Kobayashi). However, step growth hydroisilylation polymerization was the method used to produce the copolymers and no examples were provided which would circumvent the disadvantages outlined above.

The following lists of documents disclose information regarding siloxane compounds.

### TABLE 1a

<table>
<thead>
<tr>
<th>Patents</th>
<th>Inventor(s)</th>
<th>Issue Date</th>
</tr>
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<tbody>
<tr>
<td>5,117,025</td>
<td>Takago et al.</td>
<td>05/26/92</td>
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<td>5,299,034</td>
<td>Takago et al.</td>
<td>08/24/93</td>
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<td>5,386,049</td>
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<td>5,442,083</td>
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<td>5,484,868</td>
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<td>5,516,832</td>
<td>Kamin et al.</td>
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<td>5,703,150</td>
<td>Dush et al.</td>
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### TABLE 1b

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<tr>
<th>Patent No.</th>
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<td>EP 0 709 403 A1</td>
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<td>W0 9635732</td>
<td>PCT</td>
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### TABLE 1c

Nonpatent Documents


All patents, patent applications, and publications listed above are incorporated by reference in their respective documents.
entireties. As those of ordinary skill in the art will appreciate readily upon reading the application, certain of the information disclosed in the above-listed documents may be utilized in the monomers, polymers, their preparation methods, and the devices disclosed and claimed herein.

SUMMARY OF THE INVENTION

The present invention has certain objects. That is, various embodiments of the present invention provide solutions and advantages to one or more of the problems existing in the prior art with respect to the preparation and properties of siloxanes, and particularly, silalkylenesiloxanes. Certain of these problems are discussed above. The materials and methods of the present invention address one or more of these problems.

The present invention provides symmetric cyclic soxane monomers having the following formula:

$$\text{R}_1^1 \text{O} \text{R}_2^2 \ (\text{CH}_3 \text{O})_p \text{R}_3^3$$

wherein p is at least 6, and v is at least 1, and each R\(^1\) and R\(^2\) group is independently a monovalent organic group. Alternatively, the present invention provides such monomers wherein p is at least 2 and v is at least 2. Such symmetric monomers include the same value for p in each repeat unit.

The present invention also provides asymmetric cyclic silalkylenesiloxane monomers having the following formula:

$$\text{R}_1^1 \text{O} \text{R}_2^2 \ \text{S} \text{O} \text{R}_3^3 \ (\text{CH}_3 \text{O})_p \text{R}_4^4 \text{O} \text{R}_5^5$$

wherein p and q are each at least 2, v and w are each at least 1, with the proviso that q does not equal p for at least one set of silalkylenesiloxane repeat units, and each R\(^1\) and R\(^2\) group is independently a monovalent organic group. Such asymmetric monomers can include values for p that are the same or different in the various repeat units, and values for q that are the same or different in the various repeat units.

The present invention also provides silalkylenesiloxane copolymers of the formula:

$$\text{R}_1^1 \text{O} \text{R}_2^2 \ (\text{CH}_3 \text{O})_p \text{R}_3^3$$

wherein p is at least 2, and c is greater than 300, and each R group is independently a monovalent organic group. These copolymers can be crosslinked and/or reinforced with a silica filler. Preferably, they are both crosslinked and reinforced.

In one embodiment, the reinforced crosslinked material of the present invention is preparable from a silica filler and a crosslinked silalkylenesiloxane copolymer of the formula:

$$\text{R}_1^1 \text{O} \text{R}_2^2 \text{O} \text{CH}_3 \text{O} \text{R}_3^3 \text{O} \text{R}_4^4 \text{O} \text{R}_5^5$$

wherein p is at least 6, b is at least 1, c is zero or greater, and each R group is independently a monovalent organic group.

The present invention also provides a medical device comprising a silalkylenesiloxane copolymer of the formula:

$$\text{R}_1^1 \text{O} \text{R}_2^2 \text{O} \text{R}_3^3 \text{O} \text{R}_4^4 \text{O} \text{R}_5^5$$

wherein p is at least 2, b is at least 1, c is zero or greater, and each R group is independently a monovalent organic group. Preferably, this material is crosslinked, and more preferably, it is crosslinked and compounded with a silica filler.

The present invention also provides methods of making silalkylenesiloxane copolymers of the present invention. In one embodiment, a method involves combining at least one cyclic silalkylenesiloxane monomer with a catalyst. In another embodiment, a method involves combining at least one compound having at least one silalkylenesiloxane unit and at least one compound having at least one siloxane unit with a catalyst. Preferably, the starting compounds (silalkylenesiloxanes and siloxanes) can be linear or cyclic and the catalyst can be acidic or basic.

Herein, the values for the variables in the formulas are integers; however, they can be average values if the formulas represent average structures, such as occurs with polymers.

As used herein, the term “copolymer” refers to polymers having two or more different repeat units and includes copolymers, terpolymers, tetrapolymers, etc.

As used herein, the term “organic group” means a hydrocarbon group that is classified as an aliphatic group, cyclic group, or combination of aliphatic and cyclic groups (e.g., alkaryl and aralkyl groups). In the context of the present invention, the term “aliphatic group” means a saturated linear or branched hydrocarbon group including, for example, methyl, ethyl, isopropyl, t-butyl, heptyl, dodecyl, octadecyl, amyl, 2-ethylhexyl, and the like. The term “alkenyl group” means an unsaturated, linear or branched hydrocarbon group with one or more carbon-carbon double bonds, such as a vinyl group. The term “alkynyl group” means an unsaturated, linear or branched hydrocarbon group with one or more carbon-carbon triple bonds. The term “cyclic group” means a closed ring hydrocarbon group that is classified as an aliphatic group, aromatic group, or heterocyclic group. The term “alkylic group” means a cyclic hydrocarbon group having properties resembling those of aliphatic groups. The term “aromatic group” or “aryl group” means a mono- or polymolecular aromatic.
hydrocarbon group. The term “heterocyclic group” means a closed ring hydrocarbon in which one or more of the atoms in the ring is an element other than carbon (e.g., nitrogen, oxygen, sulfur, etc.).

As is well understood in this technical area, a large degree of substitution is not only tolerated, but is often advisable. Substitution is anticipated on the compounds of the present invention. As a means of simplifying the discussion and recitation of certain terminology used throughout this application, the terms “group” and “moiety” are used to differentiate between chemical species that allow for substitution or that may be substituted and those that do not allow or may not be so substituted. Thus, when the term “group” is used to describe a chemical substituent, the described chemical material includes the unsubstituted group and that group with O, N, or S atoms, for example, in the chain as well as carbonyl groups or other conventional substitution. Where the term “moiety” is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, the phrase “alkyl group” is intended to include not only pure open chain saturated hydrocarbon alkyl substituents, such as methyl, ethyl, propyl, and the like, but also alkyl substituents bearing further substituents known in the art, such as hydroxy, alkoxy, alkylsulfoniloxy, halogen atoms, cyano, nitro, amino, carboxyl, etc. Thus, “alkyl group” includes ether groups, haloalkyls, nitroalkyls, carboxylalkyls, hydroxyalkyls, sulfoalkyls, etc. On the other hand, the phrase “alkyl moiety” is limited to the inclusion of only pure open chain saturated hydrocarbon alkyl substituents, such as methyl, ethyl, propyl, t-butyl, and the like.

**Detailed Description of Preferred Embodiments**

The present invention provides cyclic silalkylenesiloxane monomers that can be preferably polymerized using ring opening polymerization either alone or in the presence of siloxane monomers to yield silalkylenesiloxane random and block copolymers. This methodology facilitates high degrees of polymerization since the cyclic silalkylenesiloxane monomers can be easily purified and the ring opening polymerization is efficient. Alternatively, the polymers of the present invention can be prepared by coequilibrating mixtures of cyclic and linear species.

The copolymerization reactions preferably utilize similar chemistry as that known in the art for silicone materials to yield copolymers having various functionality pendant and/or terminal to the polymer backbone. Pendant and/or terminally functional silalkylenesiloxane copolymers are believed to be useful as elastomers, adhesives, and sealing agents. Such copolymers are capable of being crosslinked. The crosslinked materials are believed to be suitable for a variety of applications, including elastomers, adhesives, sealing agents, and the like. They are believed to be particularly suitable for use in medical devices.

As used herein, medical device refers to a device that has surfaces that contact tissue, blood, or other bodily fluids in the course of their operation, which fluids are subsequently used in patients. This can include, for example, extracorporeal devices for use in surgery such as blood oxygenators, blood pumps, blood sensors, tubing used to carry blood and the like which contact blood which is then returned to the patient. This can also include endoprostheses implanted in blood contact in a human or animal body such as vascular grafts, stents, pacemaker leads, heart valves, and the like that are implanted in blood vessels or in the heart. This can also include devices for temporary intravascular use such as catheters, guide wires, and the like which are placed into the blood vessels or the heart for purposes of monitoring or repair.

**Cyclic Silalkylenesiloxane Monomers**

Silalkylenesiloxane cyclic monomers are made by first preparing a silalkylenesiloxane copolymer via hydroxilation, for example, with these copolymers being generally of a relatively low molecular weight (e.g., having a degree of polymerization (DP) of no greater than about 200) and are not functionalized. Depolymerizing said polymer to cyclosiloxane monomers, then purifying by distillation or recrystallization affords monomers that can be polymerized in the presence of linear and/or cyclosiloxane monomers. By this method, a variety of functionality can be incorporated pendant or terminal to the silalkylenesiloxane copolymers. Also, higher molecular weight silalkylenesiloxane copolymers (e.g., having a DP of greater than about 300) can be prepared.

Specifically, alternating silalkylenesiloxane copolymer starting materials can be prepared by polymerizing a dihydrodisiloxane with an α,ω-alkadienedisiloxane, as represented by the following scheme:

**Scheme 1**

![Scheme 1 Diagram]

wherein s is at least 2, and preferably no greater than 26, and n is at least 1, and preferably no greater than 200. Each R¹ and R² group is independently (i.e., they may be the same or different) a monovalent organic group (preferably, a C₁₋₃₀ organic group). Preferably, R¹ and R² are independently methyl, ethyl, propyl, or other alkyl group; phenyl, tolyl, xylyl, or other aryl group; benzyl, phenethyl, or other aralkyl group. These groups may be substituted in part or in total (i.e., such that all the hydrogen atoms are replaced) with various groups, such as halogen atoms. More preferably, R¹ and R² are C₁₋₄ alkyl groups, and most preferably, methyl moieties.

Alternating silalkylenesiloxane copolymer starting materials may also be prepared by polymerizing a dihydrodisiloxane with an α,ω-alkadienedisiloxane, as represented by the following scheme:

**Scheme 2**

![Scheme 2 Diagram]
wherein R₁, R₂, and n are as described above, t is zero or greater, and preferably, zero to 6, most preferably zero to 1. Transition metal compounds that catalyze hydrosilylation reactions may be used to catalyze the above reactions. Preferred catalysts include, but are not limited to, platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex and platinum 1,3,5,7-tetravinyl-1,3,5,7-tetramethylicyclohexatriene complex. The addition polymerization is preferably carried out at a temperature slightly under the reflux temperature of the reactants in the absence of any solvent. During the course of the reaction, the temperature may be raised since the intermediate silalkylenesiloxanes structures (e.g., dimer, trimer, tetramer, etc.) have a higher boiling point than the starting reactants. The ratio of reactants is typically 1:1 to afford polymer.

Generally, the silalkylenesiloxane copolymer starting materials are of the following formula:

\[
\begin{array}{c}
\text{Formula 1} \\
\end{array}
\]

wherein R₁ and R₂ are as described above, p is at least 2, and n is at least 1. Preferably, p is at least 6 and n is at least 100. More preferably, p is no greater than 30 and n is no greater than 300. Such materials are suitable for preparing cyclic monomers as described below. The repeat unit in formula 1 is referred to herein as a silalkylenesiloxane unit, wherein “alkylene” refers to the hydrocarbon chain in the backbone.

In addition, asymmetric silalkylenesiloxane copolymer starting materials are prepared when mixtures of α,ω-alkadienes and/or α,ω-alkadienedisiloxanes are used in schemes 1 or 2 above. Such silalkylenesiloxane copolymers are of the following general formula:

\[
\begin{array}{c}
\text{Formula 2} \\
\end{array}
\]

wherein R₁, R₂, p, and n are as described above, q is at least 2 and m is at least 1, with the proviso that q does not equal p for at least one set of silalkylenesiloxane repeat units. Preferably, q is at least 6 and m is at least 100. More preferably, q is no greater than 30 and m is no greater than 300. Such materials can include various asymmetric polymers wherein the values for p can be the same or different throughout the various repeat units, and the values for q can be the same or different throughout the various repeat units. Such materials are suitable for preparing cyclic monomers as described below.

The silalkylenesiloxane copolymer starting materials as shown above can be depolymerized under vacuum with heat and a base to produce mixtures of cyclic monomers. Either an alkali metal hydroxide such as potassium hydroxide or alkali metal silanolate such as potassium trimethylsilanolate can be used to perform the copolymer cracking. Sufficient temperature and vacuum are used in order to remove cyclic silalkylenesiloxane monomers by distillation so as to continually drive the depolymerization equilibrium. Pot temperatures as high as 300°C and vacuum as low as 20 mTorr are typically used to distill the large cyclic rings away from the copolymer.

The copolymers described above can be depolymerized without removal of the platinum or transition metal catalyst. However, under the conditions of the depolymerization reaction, such catalysis can promote degradation of the polymer, which leads to copolymer crosslinking. This, therefore, reduces the yield of cyclic monomer produced. Higher yields are obtained when the residual catalyst is removed.

Such symmetric cyclic silalkylenesiloxane monomers of the present invention are of the following general formula:

\[
\begin{array}{c}
\text{Formula 3} \\
\end{array}
\]

wherein R₁, R₂, and p are as defined above, v is at least one. Preferably, v is no greater than 3. For certain preferred embodiments, p is at least 2 when v is at least 2.

Silalkylenesiloxane monomers of the present invention are not limited to symmetrical structures. When a mixture of α,ω-alkadienes having different carbon lengths are used to prepare the silalkylenesiloxane copolymer via hydrosilylation, for example, a copolymer as previously described in formula 2, can be depolymerized to a mixture of asymmetric compounds. Such asymmetric silalkylenesiloxane monomers of the present invention are of the following general formula:

\[
\begin{array}{c}
\text{Formula 4} \\
\end{array}
\]

wherein R₁, R₂, p, q, and v are defined as above, w is at least 1. Preferably, w is no greater than 3. More preferably, the sum of v and w is no greater than 3. Such materials can include various asymmetric cyclic monomers wherein the values for p can be the same or different in the various repeat units, and the values for q can be the same or different in the
various repeat units. Again, $q$ does not equal $p$ for at least one set of silalkylenesiloxane repeat units.

The cyclic silalkylenesiloxane monomers can be purified by distillation and/or recrystallization from polar solvents, such as ethanol, for example. Preferably, they are purified before preparing the silalkylenesiloxane copolymers of the present invention as described below.

Silalkylenesiloxane Copolymers

Cyclic silalkylenesiloxane monomers can be polymerized using methods that are similar to those used for cyclic siloxanes. For example, depending upon the ring size, the cyclic silalkylenesiloxane monomers can undergo ring opening reactions under either anionic and cationic catalysis. The anionic polymerization of cyclic silalkylenesiloxane monomers can be initiated by alkali metal oxides and hydroxides, silanlates and other bases, preferably potassium hydroxide and potassium trimethylsilylate. Alternatively, cationic polymerization can be initiated by protonic and Lewis acids, preferably triflic acid and strongly acidic ion-exchange resins.

Typically, both anionic and cationic ring opening polymerizations (ROP) may be performed without the use of solvents. However, in order to deliver well-controlled amounts of catalyst to reaction mixtures, solvents such as toluene may be used to dilute said catalyst. Both the anionic and cationic catalyzed equilibration reaction conditions (e.g., time and temperature) are similar to those known in the art for ROP of cyclic organosiloxanes. For example, the triflic acid catalyzed ROP of cyclic silalkylenesiloxane monomers typically requires a catalyst concentration of about $[7 \times 10^{-4}]$ to about $[5 \times 10^{-3}]$ and, once added to the cyclic monomer mixture, the equilibration reaction is complete within about 30 minutes to several hours.

The ability to prepare highly pure cyclic silalkylenesiloxane monomers enables the invention herein to produce much higher degrees of polymerization (e.g., $D_p$ values of greater than about 300) than step growth silalkylenesiloxane copolymers previously known in the art. Such silalkylenesiloxane copolymers contain the same structure as defined in formula 1, with the proviso that $n$ is preferably greater than 300. Preferably, $n$ is no greater than 10,000.

The utility of the present invention is particularly appreciated when cyclic silalkylenesiloxane monomers (including mixtures of symmetric and asymmetric cyclic monomers) are copolymerized in the presence of cyclic and/or linear siloxane compounds. A representative synthesis of such copolymers are described, for example, by scheme 3 as follows:

![Scheme 3](image)

wherein $R_1$, $R_2$, $p$, and $v$ are as defined above. The value of $x$ is at least 3 and preferably no greater than 3. The value of $c$ can be zero or greater, although, preferably, it is at least 1, more preferably, at least 3, and most preferably, at least 50. The value of $b$ is at least 1, preferably, at least 50, although more preferably, it is at least equal to $c$. Preferably, the sum of $b$ and $c$ is no greater than 10,000. Each $R^2$ and $R^4$ group is independently a monovalent organic group (preferably, a C$_1$-C$_3$ organic group). Preferably, $R^2$ and $R^4$ are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, or other alkyl group; vinyl or other alkenyl group; phenyl, tolyl, xylyl, or other aryl group; benzyl, phenethyl, or other aralkyl group. These groups may be substituted in part or in total (i.e., such that all the hydrogen atoms are replaced) with various groups, such as halogen atoms, cyano groups, and amino groups. More preferably, $R^2$ and $R^4$ are methyl, phenyl, and vinyl moieties. The resultant copolymers can be random or block copolymers with the value of $p$ being the same or different in the repeat units. Herein, the structural unit containing $R^2$ and $R^4$ groups in the above scheme is referred to as a siloxane unit and the structural unit containing the $R^1$ and $R^2$ groups is referred to as a silalkylenesiloxane unit.

Furthermore, silalkylenesiloxane copolymers containing terminal and/or pendant functional groups can be produced, for example, as shown in scheme 4:
wherein $R^1$, $R^2$, $R^3$, $R^4$, $p$, $v$, $x$, $b$, and $c$ are as defined above, each $R^5$ group is independently a monovalent organic group (preferably, a C$_3$-C$_{20}$ organic group). Preferably, each $R^5$ is independently methyl, ethyl, propyl, butyl, pentyl, hexyl, or other alkyl group; vinyl, allyl, or other alkenyl group; phenyl, tolyl, xylyl, or other aryl group; benzyl, phenethyl, or other aralkyl group. These groups may be substituted in part or in total (i.e., such that all the hydrogen atoms are replaced) with various groups, such as halogen atoms, cyano groups, amino groups. More preferably, each terminal silyl group includes at least one $R^5$ which is a vinyl moiety. The resultant copolymers can be random or block copolymers with the value of $p$ being the same or different in the repeat units.

Interestingly, the alternating silaklylenesiloxane copolymers containing the structures described by formulas 1 and 2, when crosslinked, do not exhibit reinforcement by treated fumed silica. However, reinforcement and enhanced physical properties are obtained when treated fumed silica is compounded with copolymers containing a siloxane block length of greater than 2 (e.g., wherein $c$ is equal to or greater than $b$ in scheme 4). These preferred functionalized copolymers can be compounded with a silica filler (e.g., fumed silica) and/or crosslinked using similar chemistry as known in the art for silicone rubber.

Preferably, silaklylenesiloxane copolymers of the present invention have the following general formula:

$$\text{Formula 5}$$

wherein $R^1$, $R^2$, $R^3$, $R^4$, $p$, $b$, and $c$ are as defined above. As used herein, this formula represents both random and block copolymers. Such materials can include symmetric polymers and various asymmetric polymers wherein the values for $p$ can be the same or different in the various repeat units.

For certain embodiments of the copolymers in the above formula, $p$ is at least 2 when $b$ is at least 1 and the sum of $b$ and $c$ (which can be referred to as the degree of polymerization or Dp) is greater than 300. For other embodiments of the copolymers, $p$ is at least 2, preferably, at least 6, when $b$ is at least 1 and $c$ is zero or greater.

For certain embodiments of the copolymers in the above formula, one or more of the $R$ groups ($R^1$, $R^2$, $R^3$, $R^4$, and/or $R^5$) include crosslinkable functionalities, such as vinyl, alkoxy, acetoxy, enoxy, oxime, amino, hydroxyl, cyano, halo, acrylate, epoxide, isocyanate groups, etc. For particularly preferred embodiments, copolymers, whether crosslinked or not, are compounded with a silica filler, which typically provides reinforcement and better physical properties for certain applications. For such materials, the sum of $b$ and $c$ (Dp) is preferably 1000 to 5000.

Cyclic silaklylenesiloxane monomers can be polymerized using methods that are similar to those used for cyclic siloxanes, as described above. Alternatively, the above silaklylenesiloxane copolymers may be prepared by coequilibrating mixtures of cyclic and/or linear species. Coequilibrations can be performed under the same anionic or cationic reaction conditions as described above for ROP of silaklylenesiloxane copolymers. For example, a cyclic silaklylenesiloxane monomer as described in formula 3 can be equilibrated with a linear siloxane polymer to yield a silaklylenesiloxane copolymer. In addition, a cyclic siloxane monomer can be equilibrated with a silaklylenesiloxane copolymer to afford a silaklylenesiloxane copolymer having incorporated additional siloxane units. Alternatively, a linear silaklylenesiloxane copolymer and linear siloxane polymer may be equilibrated together to afford a copolymer which contains a summation of both linear starting reagent units.

Thus, the present invention provides methods for the preparation of silaklylenesiloxane copolymers, which involve the use of cyclic silaklylenesiloxane monomers, particularly those described above. Preferably, the present invention provides a method that involves combining at least one compound having at least one silaklylenesiloxane unit and at least one compound having at least one siloxane unit with a catalyst. The compounds having at least one silaklylenesiloxane unit can be cyclic or linear, preferably, they are cyclic silaklylenesiloxane monomers. The compounds having at least one siloxane unit can be cyclic or linear, preferably, they are cyclic siloxane monomers. The catalysts can be acidic or basic compounds as described above. Thus, as discussed above, the reaction conditions can involve cationic or anionic polymerization.

In order to prepare crosslinked silaklylenesiloxane materials, it is preferred for the copolymers to be functionalized and miscible with the crosslinker. When the alkylene content of a silaklylenesiloxane copolymer is greater than about 15% by weight, the copolymer is not miscible with
conventional polysiloxane crosslinking materials. However, if both crosslinking functionalities reside terminal and/or pendant to silalkylenesiloxane copolymers, the materials are typically miscible and will react. For example, the vinyldimethylylsil terminated silalkylene prepared in Example 4.1 and used within the compounded rubber in Example 5.3 contains 10.6% alkylene by weight. This facilitated the use of a conventional poly(dimethylsiloxane-co-dimethylsiloxane) crosslinker. However, the vinyldimethylsil terminated silalkylenesiloxane copolymers used in Examples 5.1 and 5.2 contained 39% and 29% alkylene by weight, respectively. These copolymers are not miscible with conventional poly(dimethylsiloxane-co-dimethylsiloxane) crosslinker. Therefore, a silalkylenesiloxane copolymer containing hydroxethylsiloxane units and containing 30% by weight alkylene units was used to crosslink said materials.

Advantages of the invention are illustrated by the following examples. However, the particular materials and amounts thereof recited in these examples, as well as other conditions and details, are to be interpreted to apply broadly in the art and should not be construed to unduly limit the invention.

EXAMPLES

Materials: Hexadecane, octadecane, and decadecane were purchased from Aldrich, Milwaukee, Wis., were distilled prior to use. 1,1,3,3-Tetramethyldisiloxane was purchased from Gelest, Tullytown, Pa., and was distilled before use. Distillations were performed at ambient pressure through a 90 cm3x3 cm mirrored vacuum-jacketed column packed with stainless steel mesh. Hexanes, xylenes, tricic acid, neutral alumina and DOWEX-50W-hydrogen were purchased from Aldrich and were used without further purification. The platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex and the 1,3,5,7-tetravinyl-1,3,5,7-tetramethyl cyclotetrasiloxane inhibitor were purchased from Gelest and were used without further purification.

Instrumentation: Size exclusion chromatography was performed on a WATERS 150CV and calibrated using narrow molecular weight polydimethylsiloxane standards. Samples were run in toluene at 0.8 ml/min and at 50 °C. Differential scanning calorimetry was performed on a PERKIN ELMER DSC7. Infrared spectra were taken on a PERKIN-ELMER 1720 Fourier-Transform Infrared spectrometer running in transmission mode. Samples were placed between potassium bromide windows. Nuclear Magnetic Resonance spectra were performed on a BRUKER 300 MHz/52MM instrument.

Example 1

Procedure for Preparation of Silalkylenesiloxane

Starting Materials for Synthesis of Cyclic Monomers

1.1 Preparation of Copoly(1,3-disiloxanylene-alt-1,6-hexanylene): 1,5-hexadiene (550 g, 6.7 mol) was added to a three-necked 3 L round-bottomed flask. The flask was fitted with a mechanical stirrer, a thermometer and a 1 L pressure-equalizing dropper funnel. The funnel was charged with 1,1,3,3-tetramethyldisiloxane (900 g, 6.7 mol). In a test tube was mixed xylene (2 ml) and platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (5 drops neat), this solution was added to the reaction flask. The 1,1,3,3-tetramethyldisiloxane was then added to the reaction flask dropwise, the addition rate was adjusted to maintain a pot temperature of 70 °C. After ¼ of the 1,5-hexadiene was added, the pot temperature was maintained at 100°C by the use of a heat mantle. The reaction was allowed to run for 24 hours at 100°C. The crude copolymer was diluted 1:1 (v:v) with hexanes, then flashed through a column (9 cm dia.x15 cm) of neutral alumina. An additional litter of hexanes was used to wash the column of any remaining copolymer.

Solvants were removed by evaporation under reduced pressure. In this way, 1430 g of crude copolymer Mw/Mn=52, 000/23,600, Tg=-93 °C, was obtained. 1H NMR (CDCl3, 300 MHz) δ: 0.01(s, 12H), 0.46-0.51(m, 4H), 1.28(s, 8H). 13C NMR (CDCl3, 75.5 MHz) δ: 0.38, 18.46, 23.24, 33.21. 29Si NMR (CDCl3, 60.0 MHz) δ: 7.30. IR v: 2957, 2921, 2855, 2796, 1588, 1461, 1410, 1342, 1300, 1253, 1191, 1156, 1057, 967, 802, 839, 794, 704, 631, 537 cm⁻¹.

1.2 Preparation of Copoly(1,3-disiloxanylene-alt-1,8-octanylene): 1,7-octadiene (740 g, 6.7 mol) was added to a three-necked 3 L round-bottomed flask. The flask was fitted with a mechanical stirrer, a thermometer and a 1 L pressure-equalizing dropper funnel. The funnel was charged with 1,1,3,3-tetramethyldisiloxane (900 g, 6.7 mol). In a test tube was mixed xylene (2 ml) and platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (5 drops neat), this solution was added to the reaction flask. The 1,1,3,3-tetramethyldisiloxane was then added to the reaction flask dropwise, the addition rate was adjusted to maintain a pot temperature of 70 °C. After ¼ of the 1,7-octadiene was added, the pot temperature was maintained at 100°C by the use of a heat mantle. The reaction was allowed to run for 24 hours at 100°C. The crude copolymer was diluted 1:1 (v:v) with hexanes, then flashed through a column (9 cm dia.x15 cm) of neutral alumina. An additional litter of hexanes was used to wash the column of any remaining copolymer.

Solvants were removed by evaporation under reduced pressure. In this way, 1610 g of crude copolymer Mw/Mn=46, 500/21,400, Tg=-15 °C, Tσ=-90 °C, was obtained. 1H NMR (CDCl3, 300 MHz) δ: 0.01(s, 12H), 0.45-0.50(m, 4H), 1.26(s, 12H). 13C NMR (CDCl3, 75.5 MHz) δ: 0.40, 18.44, 23.31, 29.38, 33.53. 29Si NMR (CDCl3, 60.0 MHz) δ: 7.30. IR v: 2956, 2921, 2854, 2796, 1585, 1463, 1410, 1341, 1253, 1218, 1184, 1158, 1060, 959, 909, 840, 795, 704, 631 cm⁻¹.

1.3 Preparation of Copoly(1,3-disiloxanylene-alt-1,10-decanylene): 1,9-decadiene (926 g, 6.7 mol) was added to a three-necked 3 L round-bottomed flask. The flask was fitted with a mechanical stirrer, a thermometer and a 1 L pressure-equalizing dropper funnel. The funnel was charged with 1,1,3,3-tetramethyldisiloxane (900 g, 6.7 mol). In a test tube was mixed xylene (2 ml) and platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (5 drops neat), this solution was added to the reaction flask. The 1,1,3,3-tetramethyldisiloxane was then added to the reaction flask dropwise, the addition rate was adjusted to maintain a pot temperature of 70 °C. After ¼ of the 1,9-decadiene was added, the pot temperature was maintained at 100°C by the use of a heat mantle. The reaction was allowed to run for 24 hours at 100°C. The crude copolymer was diluted 1:1 (v:v) with hexanes, then flashed through a column (9 cm dia.x18 cm) of neutral alumina. An additional litter of hexanes was used to wash the column of any remaining copolymer.

Solvants were removed by evaporation under reduced pressure. In this way, 1790 g of crude copolymer Mw/Mn=54, 600/25,600, Tg=-10 °C, Tσ=-70 °C, was obtained. 1H NMR (CDCl3, 300 MHz) δ: 0.01(s, 12H), 0.50-0.46(m, 4H), 1.25-1.27(m, 16H). 13C NMR (CDCl3, 75.5 MHz) δ: 0.40,
1.4 Preparation of Copoly(1,3-disiloxanylene-alt-1,4-tetradecaneylene): 

1,1,3-tetradecadiene (56 g, 0.29 mol) was added to a three-necked 250 ml round-bottomed flask. The flask was fitted with a TEFILON-coated magnetic stir bar, a thermometer and a 125 ml pressure-equalizing dropper funnel. The funnel was charged with 1,1,3,3-tetramethyldiisiloxane (39 g, 0.29 mol). 

Platinum(II) divinyl-1,1,3,3-tetramethyldisiloxane complex (2 drops neat) was added directly to the reaction flask. The 1,1,3,3-tetramethyldiisiloxane was then added to the reaction flask dropwise, the addition rate was adjusted to maintain a pot temperature of 100°C. After all of the 1,1,3-tetradecadiene was added, the pot temperature was maintained at 85°C by a heat mantle. The reaction was allowed to run for 24 hours at 85°C. In this way, 95 g of crude copolymer M_n = 32,200/14,400, T_g = 24°C (T_g not observed) was obtained. 

1H NMR (CDCl_3, 300 MHz) δ = 0.01 (s, 12H), 0.50-0.45 (m, 4H), 1.23-1.29 (m, 24H). 

13C NMR (CDCl_3, 75.5 MHz) δ = 0.40, 18.43, 23.31, 29.32-29.77 (m), 33.49. 

29Si NMR (CDCl_3, 60.0 MHz) δ = 7.35. IR ν: 2955, 2923, 2854, 1584, 1465, 1410, 1342, 1253, 1173, 1059, 967, 840, 796, 705, 631, 539 cm⁻¹. 

1.5 Preparation of Copoly(1,3-disiloxanylene-random-1,4-tetradecaneylene-random-1,2-ethylenylene): 

1,1,3-tetradecadiene (56 g, 0.29 mol) and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (20 g, 0.11 mol) is added to a three-necked 250 ml round-bottomed flask. The flask is fitted with a TEFILON-coated magnetic stir bar, a thermometer and a 125 ml pressure-equalizing dropper funnel. The funnel is charged with 1,1,3,3-tetramethyldisiloxane (53.6 g, 0.40 mol). Pt complex (2 drops neat) is then added directly to the reaction flask. The 1,1,3,3-tetramethyldisiloxane is added to the reaction flask dropwise, the addition rate is adjusted to maintain a pot temperature of 100°C. After all of the 1,1,3-tetradecadiene is added, the pot temperature is held at 85°C by a heat mantle. The reaction is allowed to run for 24 hours. The xylene is removed by evaporation under reduced pressure. No analytical information is available. 

Example 2 

Procedure for Preparation of Cyclic Monomers 

2.1 Depolymerization of Copoly(1,3-disiloxanylene-alt-1,6-hexaneylene): 

Copoly(1,3-disiloxanylene-alt-1,6-hexaneylene) (380 g), KOH (1.4 g) and a TEFILON-coated magnetic stir bar was charged to a three-necked 1 L round-bottomed flask. The flask was fitted with a thermometer, a distillation adapter, a glass stopcock and a heat mantle. The distillation adapter was also fitted to a three-necked 1 L round-bottomed receiving flask. A ice water bath is placed under the receiver flask and the distillation adapter is wrapped with heat tape in order to provide more efficient collection of monomers. Cracking was performed under vacuum using both a mechanical and oil diffusion pump. The reaction flask contents were heated to 200°C and the cracking continued until the remaining copolymer cross-linked. In this way, 130 g, 13.36 (100%). 

13C NMR (CDCl_3, 75.5 MHz) δ = 0.45-0.51 (m, 4H), 1.26-1.33 (m, 8H). 

1H NMR (CDCl_3, 300 MHz) δ = 0.04-0.19 (m, 4H), 0.44-0.49 (m, 4H), 1.33 (m, 8H). 

13C NMR (CDCl_3, 75.5 MHz) δ = 0.51, 18.48, 23.28, 29.43, 33.49. 

29Si NMR (CDCl_3, 60.0 MHz) δ = 7.12. IR ν: 2958, 2877, 2853, 1719, 1586, 1467, 1410, 1321, 1252, 1186, 1147, 1067, 1005, 989, 940, 842, 791, 747, 710, 684, 653, 632, 507, 470 cm⁻¹. 

Elemental Analysis calculated for C_3H_8O_3Si_3: C, 55.49; H, 11.17; Si, 25.95. Found: C, 55.30; H, 11.34; Si, 25.47. 

2.2 Depolymerization of Copoly(1,3-disiloxanylene-alt-1,8-octaneylene): 

Copoly(1,3-disiloxanylene-alt-1,8-octaneylene) (380 g), KOH (1.4 g) and a TEFILON-coated magnetic stir bar was charged to a three-necked 1 L round-bottomed flask. The flask was fitted with a thermometer, a distillation adapter, a glass stopcock and a heat mantle. The distillation adapter was also fitted to a three-necked 1 L round-bottomed receiving flask. A ice water bath is placed under the receiver flask and the distillation adapter is wrapped with heat tape in order to provide more efficient collection of monomers. Cracking was performed under vacuum using both a mechanical and oil diffusion pump. The reaction flask contents were heated to 200°C and the cracking continued until the remaining copolymer cross-linked. In this way, 130 g, 13.36 (100%). 

13C NMR (CDCl_3, 75.5 MHz) δ = 0.45-0.51 (m, 4H), 1.26-1.33 (m, 8H). 

1H NMR (CDCl_3, 300 MHz) δ = 0.04-0.19 (m, 4H), 0.44-0.49 (m, 4H), 1.33 (m, 8H). 

13C NMR (CDCl_3, 75.5 MHz) δ = 0.51, 18.48, 23.28, 29.43, 33.49. 

29Si NMR (CDCl_3, 60.0 MHz) δ = 7.12. IR ν: 2958, 2877, 2853, 1719, 1586, 1467, 1410, 1321, 1252, 1186, 1147, 1067, 1005, 989, 940, 842, 791, 747, 710, 684, 653, 632, 507, 470 cm⁻¹. 

Elemental Analysis calculated for C_3H_8O_3Si_3: C, 55.49; H, 11.17; Si, 25.95. Found: C, 55.30; H, 11.34; Si, 25.47.
was performed under vacuum using both a mechanical and oil diffusion pump. The reaction flask contents were heated to 200°C and the cracking continued until the remaining copolymer crosslinked. In this way, 200 g, 53% combined yield of 1,1,3,3-tetramethyl-1,3-disila-2-oxacyclooctadecane and 1,1,3,3,14,16,16-octamethyl-1,3,14,16-tetrasila-2,15-dioxacyclohexacosane was obtained.

1,1,3-tetramethyl-1,3-disila-2-oxacyclooctadecane was distilled under vacuum to yield a colorless liquid. 1H NMR (CDCl3, 300 MHz) δ: 0.04(s, 12H), 0.47–0.52(m, 4H), 1.32–1.42(m, 8H). 13C NMR (CDCl3, 75.5 MHz) δ: 88.17, 20.99, 24.74, 25.77, 30.04. 15Si NMR (CDCl3, 60.0 MHz) δ: 7.04. IR v: 2924, 2861, 1460, 1409, 1345, 1253, 1196, 1173,1059,842,797,785,707 cm⁻¹. Elemental Analysis calculated for C15H27O1Si: C, 61.69; H, 11.83; Si, 20.61. Found: C, 61.41; H, 12.04; Si, 20.14.

1,1,3,3,14,16,16-octamethyl-1,3,14,16-tetrasila-2,15-dioxacyclohexacosane was recrystallized from hot ethanol to yield white crystals, m.p. 90°C. 1H NMR (CDCl3, 300 MHz) δ: 0.016(s, 12H), 0.45–0.50(m, 4H), 1.26–1.35(m, 8H). 13C NMR (CDCl3, 75.5 MHz) δ: 50.81, 24.33, 29.54, 29.74, 33.44. 15Si NMR (CDCl3, 60.0 MHz) δ: 7.13. IR v: 2958, 2920, 2853, 1596, 1468, 1405, 1252, 1221, 1160, 1072, 1050, 998, 799, 702, 622, 507 cm⁻¹. Elemental Analysis calculated for C18H33O3Si: C, 61.69; H, 11.83; Si, 20.61. Found: C, 61.60; H, 11.86; Si, 19.96.

2.4 Depolymerization of Copoly(1,3-disiloxanylene-alt-1,14-tetradecacylene):

Copoly(1,3-disiloxanylene-alt-1,10-tetradecacylene) (95 g), KOH (0.2 g) and a TEFLO-coated magnetic stir bar was charged to a three-necked 1 L round-bottomed flask. The flask was filled with a thermometer, a distillation adapter, a glass stopcock and a heat mantle. The distillation adapter was also fitted to a three-necked 1 L round-bottomed receiving flask. An ice water bath was placed under the receiver flask and the distillation adapter is wrapped with heat tape in order to provide more efficient collection of monomers. Cracking was performed under vacuum using both a mechanical and oil diffusion pump. The reaction flask contents were heated to 200°C and the cracking continued until the remaining copolymer crosslinked. In this way, 29 g, 30% combined yield 1,1,3,3-tetramethyl-1,3-disila-2-oxacyclooctadecane and 1,1,3,3,18,19,20,20-octamethyl-1,3,18,20-tetrasila-2,19-dioxacyclooctatetracontane was obtained.

1,1,3-tetramethyl-1,3-disila-2-oxacyclooctadecane was distilled under vacuum to yield a colorless liquid. 1H NMR (CDCl3, 300 MHz) δ: 0.04(s, 12H), 0.48–0.54(m, 4H), 1.27(s, 4H), 1.33(s, 20H). 13C NMR (CDCl3, 75.5 MHz) δ: 41.81, 22.68, 26.36, 27.10, 27.20, 27.52, 32.45. 15Si NMR (CDCl3, 60.0 MHz) δ: 7.10. IR v: cm⁻¹. Elemental Analysis calculated for C15H27O3Si: C, 65.78; H, 12.27; Si, 17.09. Found: C, 65.32; H, 12.58; Si, 17.43. 1,1,3,3,18,19,20-octamyethyl-1,3,18,20-tetrasila-2,19-dioxacyclooctatetracontane was recrystallized from hot ethanol to yield white crystals, m.p. 97°C. 1H NMR (CDCl3, 300 MHz) δ: 0.01(s, 24H), 0.45–0.50(m, 8H), 1.24–1.29(m, 48H). 13C NMR (CDCl3, 75.5 MHz) δ: 0.41, 18.25, 22.71, 26.35, 27.09, 27.22, 27.56, 32.40. 15Si NMR (CDCl3, 60.0 MHz) δ: 7.16. IR v: 2958, 2919, 2852, 1587, 1468, 1410, 1305, 1253, 1202, 1175, 1145, 1065, 985, 919, 835, 794, 746, 717, 654, 632, 554, 504, 435 cm⁻¹. Elemental Analysis calculated for C25H35O3Si: C, 65.78; H, 12.27; Si, 17.09. Found: C, 65.48; H, 12.35; Si, 16.97.

Copoly(1,3-disiloxanylene-alt-1,14-tetradecacylene-alt-1,14-tetradecacylene) (120 g), KOH (0.44 g) and a TEFLO-coated magnetic stir bar is charged to a three-necked 1 L round-bottomed flask. The flask is fitted with a thermometer, a distillation adapter, a glass stopcock and a heat mantle. The distillation adapter is also fitted to a three-necked 1 L round-bottomed receiving flask. An ice water bath is placed under the receiver flask and the distillation adapter is wrapped with heat tape in order to provide more efficient collection of monomers. Cracking is performed under vacuum using both a mechanical and oil diffusion pump. The reaction flask contents are heated to 200°C and the cracking continued until the remaining copolymer crosslinked. In this way, a mixture of asymmetric monomers is obtained. No analytical information is available.

Example 3

Ring Opening Polymerization of Cyclic Silalkylenesiloxane Monomers

3.1 Cationic ROP of Silalkylenesiloxane Monomers: DOWEX-50W-hydrogen acidic ion exchange resin (1.0 g) and a TEFLO coated magnetic stir bar were added to a 50 ml one-necked round-bottomed flask. The flask and its contents were stirred for 4 hours at 200°C. After this time, 1,1,3,3,12,12-octamethyl-1,3,12,14-tetrasila-2,13-dioxacyclooctacosane (8.0 g) was added to the hot flask. The flask was fitted with a drying tube (DRIERITE) and was heated to 70°C. The flasks' contents rose in viscosity until, after 8 hours, the stir bar was no longer effective. The crude product was diluted with THF (2:1 v/v solvent to polymer) and the DOWEX resin removed by filtration. The polymer was precipitated with methanol. The polymer precipitation from THF/methanol was repeated twice. In this way, 6.6 g, 83% yield of colorless copolymer Mw/Mn=180,000/82,000, Tg~90°C was obtained. The analytical data matches that previously described for copoly(1,3-disiloxanylene-alt-1,8-octanylene).

3.2 Cationic ROP of Silalkylenesiloxane Monomers: 1,1,3,3,10,10,-12,12-Octamethyl-1,3,10,12-tetrasila-2,11-dioxacyclooctadecane (200 g) and a TEFLO coated magnetic stir bar were added to an oven dried 500 ml three-necked round-bottomed flask. The flask was fitted with two rubber septum, flushed with dry nitrogen and then filled with a water-cooled condenser and drying tube (DRIERITE). Anhydrous toluene (250 ml) was added to the flask via syringe. The reaction mixture was heated to reflux, then trifluoro acid (70 ml) was added via syringe. The solution turned slightly orange. The reaction was let to run for 24 hours after which the polymer product was precipitated once from THF/methanol. In this way, 190 g, 95% yield of colorless polymer Mw/Mn=546,000/346,000, Tg~93°C was obtained. The analytical data matches that previously described for copoly(1,3-disiloxanylene-alt-1,6-hexanylene).

3.3 Anionic ROP of Silalkylenesiloxane Monomers: 1,1,3,3-Tetramethyl-1,3-disila-2-oxacyclododecane (18 g), potassium silanolate/toluene mixture (0.2 ml) and a TEFLO coated magnetic stir bar were added to an oven dried 250 ml two-necked round-bottomed flask. The flask was fitted with a rubber septum, flushed with dry nitrogen and then fitted with a drying tube (DRIERITE). The reaction mixture was heated to 140°C and was let to run for 28 hours. After this time, the polymer product was precipitated twice from THF/methanol. In this way, 16.9 g, 94% yield of colorless polymer Mw/Mn=88,700/35,500, Tg~93°C was obtained. The analytical data matches that previously described for copoly(1,3-disiloxanylene-alt-1,6-hexanylene).
Example 4

Ring Opening Polymerization of Cyclic Silalkylenesiloxane Monomers In the Presence of Silicone Monomers

4.1 Cationic ROP of Monomer and Polymer Mixtures:

1,1,3,3-tetramethyl-1,3-disila-2-oxacyclocotridecane (80 g), vinyldimethylsilyle terminated polidimethyloxylole (320 g, DP 2400), anhydrous hexanes (800 ml) and a TEFLO coated magnetic stir bar were added to an oven dried 2 L two-necked round-bottomed flask. The flask was fitted with a rubber septum, flushed with dry nitrogen and then fitted with a drying tube (DIERITE). Triflic acid (90 µl) was added via syringe. The solution turned slightly orange. The reaction was let to run for 24 hours. After this time, 1,3-divinyltetramethylsiloxane (100 µl) was added via syringe and this removed the color within 2 minutes. The mixture was allowed to stand for 1 hour, then the crude product was precipitated once from THF (1200 ml)/ethanol (3000 ml). The remaining solvent in the precipitate was removed under reduced pressure. In this way, 328 g, 82 % yield of colorless polymer M<sub>3</sub>M<sub>4</sub> = 200,000/130,000, T<sub>p</sub> = 123°C was obtained.

1<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 0.05(s), 2.61(d, 60), 1.43(s, 121), 1.35(s, 4H). 1<sup>3</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ: 0.54, 1.02, 1.53, 17.25, 20.81, 23.14, 24.56, 25.60, 29.32, 29.56, 29.85, 33.38. 25Si NMR (CDCl<sub>3</sub>, 60.0 MHz) δ: -22.09, -21.84, -21.41, -21.14, 7.06, 7.32, 7.66. IR v: 2964, 2927, 2857, 1412, 1260, 1095, 1019, 865, 797, 703, 665, 506 cm<sup>-1</sup>. 4.2 Cationic ROP of Polymer/Polymer Mixtures:

Copoly (1,3-disiloxanylene-alt-1,10-decane) (190 g), poly(hydromethylsiloxane) (184 g, DP 40), octamethylcycloptoversiloxane (240 g), anhydrous toluene (240 ml) and a TEFLO coated magnetic stir bar were added to an oven dried 2 L two-necked round-bottomed flask. The flask was fitted with a rubber septum, flushed with dry nitrogen and then fitted with a drying tube (DIERITE). Triflic acid (100 µl) was added via syringe. The slightly orange and cloudy solution turned clear within 10 minutes. The reaction was let to run for 24 hours. After this time, hexamethyldisiloxane (200 µl) was added via syringe and this removed the color within 2 minutes. The mixture was allowed to stand for one hour, then the crude product was precipitated once from THF (1500 ml)/ethanol (3800 ml). The remaining solvent in the precipitate was removed under reduced pressure. In this way, 510 g, 83 % yield of colorless polymer, T<sub>p</sub> = 123°C, was obtained.

1<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 0.00–0.18 (m, 28.6H), 0.49–0.57 (m, 2H), 1.25–1.27 (m, 10H), 4.64–4.71 (m, 2H). 1<sup>3</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ: 0.08, 0.21, 0.99, 18.08, 18.27, 23.15, 23.23, 29.43, 29.69, 33.49. 25Si NMR (CDCl<sub>3</sub>, 60.0 MHz) δ: -38.24 to -34.22 (m, -22.07 to -21.26 (m), -20.65 to -19.95 (m), -19.27 to -18.47 (m), 6.98–8.17 (m), 9.28–10.38 (m). IR v: 2962, 2924, 2856, 2159, 1459, 1411, 1260, 1093, 1037, 912, 879, 828, 800, 762, 705, 509 cm<sup>-1</sup>.

4.3 Anionic ROP of Monomers:

1,1,3,3-Tetramethyl-1,3-disila-2-oxacyclocotridecane (94 g, 0.44 mol), octamethylcycloptoversiloxane (332 g, 1.11 mol), 1,3-divinyltetramethylsiloxane (15 g, 0.08 mol) and a TEFLO coated magnetic stir bar were added to an oven dried 250 ml two-necked round-bottomed flask. The flask was fitted with a rubber septum, flushed with dry nitrogen and then fitted with a drying tube (DIERITE). Potassium silanolate/toluene mixture (0.2 ml) was added to the mixture and the flask’s contents were heated to 140°C and was let to run for 28 hours. After this time, residual cyclic material was extracted from the polymer using hot ethanol. In this way, 330 g, 75 % yield of colorless polymer M<sub>3</sub>M<sub>4</sub> = 15,800/6,100, T<sub>p</sub> = 123°C, was obtained. 1<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 0.05(s), 0.06(s), 0.08(s), 0.10(s), 0.51–0.56(m), 0.61–0.65(m), 1.31(bs), 1.43–1.47(m), 1.55–1.61(m), 5.74 (dd, J=4 and 20 Hz), 5.94(dd, J=4 and 15 Hz), 6.14(dd, J=15 and 20 Hz). 1<sup>3</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz) δ: 0.26, 0.78, 15.02, 16.12, 18.33, 21.41, 23.20, 25.22, 27.04, 33.25, 111.40, 131.62. 25Si NMR (CDCl<sub>3</sub>, 60.0 MHz) δ: -21.86, -21.40, 6.83–7.04(m). IR v: 2963, 2925, 2907, 2858, 1446, 1411, 1261, 1095, 1020, 864, 805, 701, 665, 507 cm<sup>-1</sup).

Example 5

Compounding Functional Silalkylenesiloxane Copolymers with Silica and Poly(hydromethylsiloxane-co-dimethylsiloxane) Crosslinkers

Treated fumed silica (DeGussa R812 S or Cabot TS-530) was compounded into vinylidimethylsilyle terminated silalkylenesiloxane copolymers using a tangential sigma blade mixer. Throughout mixing, the mixer’s bowl was heated to 140°C with circulating oil. After all of the silica had been added incrementally to the copolymer fluids, the gum was mixed for at least 2 hours. All other ingredients were added to the base rubber using a three roller mill. Test slabs were cured in a heated press at 150°C for five minutes, and post cured in a circulating air oven at 150°C for 2 hours. Before mechanical testing, the slabs were allowed to relax at room temperature for at least 24 hours. The following Table 2 gives three formulation examples and mechanical results for each.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Example 5.1</th>
<th>Example 5.2</th>
<th>Example 5.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total wt. % HC in final crosslinked elastomer</td>
<td>26%</td>
<td>19%</td>
<td>5%</td>
</tr>
<tr>
<td>M&lt;sub&gt;3&lt;/sub&gt; of first vinyl terminated silalkylenesiloxane copolymer</td>
<td>M&lt;sub&gt;4&lt;/sub&gt; 40,000 (93 parts) M&lt;sub&gt;4&lt;/sub&gt; 60,000 (95 parts) M&lt;sub&gt;4&lt;/sub&gt; 90,000 (96 parts)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wt. % HC in first copolymer</td>
<td>39%</td>
<td>29%</td>
<td>0</td>
</tr>
<tr>
<td>M&lt;sub&gt;4&lt;/sub&gt; of second (silanol) terminated silalkylenesiloxane copolymer</td>
<td>M&lt;sub&gt;4&lt;/sub&gt; 180 (3 parts) M&lt;sub&gt;4&lt;/sub&gt; 180 —</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wt. % HC in second copolymer</td>
<td>39%</td>
<td>29%</td>
<td>10.6%</td>
</tr>
<tr>
<td>Silica type</td>
<td>Cabot</td>
<td>Cabot</td>
<td>DeGussa R812 S</td>
</tr>
<tr>
<td>Silica loading, phr</td>
<td>52</td>
<td>52</td>
<td>41</td>
</tr>
<tr>
<td>Poly(hydromethylsiloxane-co-dimethylsiloxane) (Si-H crosslinker)</td>
<td>4 parts</td>
<td>2 parts</td>
<td>4 parts</td>
</tr>
<tr>
<td>Crosslinker Equiv. Wt.</td>
<td>3.5,5-tetrahydro-1,1,3,3,5,5-hexamethyldimethylsiloxane (Inhibitor)</td>
<td>2 ppm</td>
<td>2 ppm</td>
</tr>
<tr>
<td>5% Pt complex (platinum 1,3-divinyl-1,1,3,3-tetramethylsiloxane) in xylenes</td>
<td>Ultimate Tensile Strength (psi) per ASTM D-412</td>
<td>1220</td>
<td>1516</td>
</tr>
<tr>
<td>Elongation at break (%) per ASTM D-412</td>
<td>526</td>
<td>1038</td>
<td></td>
</tr>
<tr>
<td>Tensile (psi) per ASTM D-412</td>
<td>231</td>
<td>248</td>
<td></td>
</tr>
</tbody>
</table>
The interaction between the copolymers and the fumed silica is important to the reinforcement of the cured elastomer. Example 5.1 utilized a copolymer as shown in formula 6:

\[
\text{H}_2\text{C} = \text{CH} - \text{O} - \text{Si} - \text{O} - \text{Si} - \left( \text{CH}_3 \right)_7 \text{O} - \text{Si} - \text{CH} = \text{CH}_2
\]

which contained only one disiloxane unit (1.51D) per hexaylene unit. This material provided little to no interaction with the fumed silica filler. Thus, this material had poorer mechanical properties. Example 5.2 used a copolymer shown formula 7 below:

\[
\text{H}_2\text{C} = \text{CH} - \text{O} - \text{Si} - \text{O} - \text{Si} - \left( \text{CH}_3 \right)_7 \text{O} - \text{Si} - \text{CH} = \text{CH}_2
\]

which had an average dimethylsiloxane unit length of 2.51D. The mechanical strength of Example 5.2 is comparable to added cured silicone rubber known in the art. This demonstrates that there exists a minimum dimethylsiloxane unit block length which will facilitate reinforcement of the cured rubber by treated fumed silica. Example 5 shows that minimum to be an average of 2.51D units, as shown in formula 8 below:

\[
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si}
\]

The complete disclosure of all patents, patent documents, and publications cited herein are incorporated by reference. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims. It is to be understood, therefore, that other expedites known to those skilled in the art or disclosed herein, may be employed without departing from the invention or the scope of the appended claims.

What is claimed is:

1. A symmetric cyclic silalkyleneasiloxane monomer having the following formula:

\[
\text{R}^1 - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \text{R}^2
\]

wherein \( p \) is at least 6, \( v \) is at least 1, and each \( R^1 \) and \( R^2 \) group is independently a monovalent organic group.

2. The cyclic silalkyleneasiloxane monomer of claim 1 wherein each \( R^1 \) and \( R^2 \) group is independently a \( C_1-C_4 \) alkyl group.

3. The cyclic silalkyleneasiloxane monomer of claim 2 wherein each \( R^1 \) and \( R^2 \) group is a methyl moiety.

4. The cyclic silalkyleneasiloxane monomer of claim 1 wherein \( p \) is 6 to 30.

5. The cyclic silalkyleneasiloxane monomer of claim 1 wherein \( v \) is 1 to 3.

6. A symmetric cyclic silalkyleneasiloxane monomer having the following formula:

\[
\text{R}^1 - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \text{R}^2
\]

wherein \( p \) is at least 2, \( v \) is at least 2, and each \( R^1 \) and \( R^2 \) group is independently a monovalent organic group.

7. An asymmetric cyclic silalkyleneasiloxane monomer having the following formula:

\[
\text{R}^1 - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \left( \text{CH}_2 \right)_p - \text{O} - \text{Si} - \text{R}^2
\]

wherein \( p \) and \( q \) are each at least 2, \( v \) and \( w \) are each at least 1, with the proviso that \( q \) does not equal \( p \) for at least one set of silalkyleneasiloxane repeat units, and each \( R^1 \) and \( R^2 \) group is independently a monovalent organic group.

8. The asymmetric cyclic silalkyleneasiloxane monomer of claim 7 wherein each \( R^1 \) and \( R^2 \) group is independently a \( C_1-C_4 \) alkyl group.
9. The asymmetric cyclic silalkylenesiloxane monomer of claim 8 wherein each R¹ and R² group is a methyl moiety.

10. The asymmetric cyclic silalkylenesiloxane monomer of claim 7 wherein q is 2 to 30.

11. The asymmetric cyclic silalkylenesiloxane monomer of claim 7 wherein w is 1 to 3.

12. A silalkylenesiloxane copolymer of the formula:

\[ R^5 - \begin{array}{c} \vdots \\ \vdots \\ \vdots \\ \vdots \end{array} \begin{array}{c} O - S - O - S - \left( \overset{\ldots}{CH_2} \right)_p \end{array} - \begin{array}{c} \vdots \\ \vdots \\ \vdots \\ \vdots \end{array} - R^3 \]

wherein p is at least 2, b is at least 1, the sum of b and c is greater than 1000, and each of R¹, R², R³, R⁴ and R⁵ is independently a monovalent organic group, wherein said copolymer is crosslinked.

13. A medical device comprising a silalkylenesiloxane copolymer of the formula:

\[ \begin{array}{c} R^5 \\ R^5 \end{array} - \begin{array}{c} O - S - O - S - \left( \overset{\ldots}{CH_2} \right)_p \end{array} - \begin{array}{c} O - S - O - S - R^3 \end{array} \]

wherein p is at least 2, b is at least 1, c is zero or greater, the sum of b and c is greater than 1000, and each of R¹, R², R³, R⁴ and R⁵ is independently a monovalent organic group.

14. The medical device of claim 13 wherein the copolymer is crosslinked.

15. The medical device of claim 14 wherein the crosslinked copolymer is compounded with a silica filler.

* * * * *