Title: FUNCTIONAL SILOXANES AND SILANES AND THEIR VINYL CO-POLYMERS

Abstract: A method for preparing a polymerizable siloxane is provided comprising the steps of (a) synthesizing a redox initiator selected from the group consisting of aldehyde and acetal, wherein said redox initiator comprises an alpha-carbon having either a single hydrogen bond or a single halogen bond; and (b) attaching said redox initiator to a siloxane to form a polymerizable siloxane.
FUNCTIONAL SILOXANES AND SILANES AND THEIR VINYL CO-POLYMERS

FIELD OF INVENTION

This invention relates generally to methods for producing silane and siloxane compositions. More specifically, this invention relates to methods of producing polymerizable silane and siloxane compositions having a polymerization site that is prepared prior to being attached to a silane or siloxane.

BACKGROUND

Silane and siloxane compounds constitute an important class of industrial chemicals that are commonly found in organic copolymers of various forms including fluids, gels, elastomers, and resins. By modifying a silane or siloxane with certain organofunctional groups and then linking these compounds to an organic polymer, polymers and copolymers can be formed having a wide variety of desirable physical and chemical properties such as improved impact resistance, flame resistance, heat stability, lubricity, and flow properties. Many of these compounds have use in such diverse applications as wetting agents, manufacturing processing aides, surfactants, foam control additives, pressure sensitive adhesives, thermoplastic elastomers, compatibilizing agents, water repellant materials, dry cleaning fluids, textile aids, personal and household care, preservatives, pesticides, and electronic circuits. In addition, many of these polymers and copolymers are non-toxic and environmentally compatible.

Of particular interest for the above-mentioned applications are silane-vinyl and siloxane-vinyl block and graft copolymers. Methods of producing such polymers and

Preparation of silane- or siloxane-vinyl copolymers typically involves a polymerization reaction wherein a vinyl is reacted with a functional silane or siloxane, respectively. Particularly desirable functional silanes and siloxanes for these processes are those having aldehyde functionality because of the aldehyde’s ability to readily participate in polymerization reactions. Methods of preparing aldehyde-functional siloxanes are known in the art. For example, U.S. Patent No. 5,739,246 (Graiver, et al.) discloses a method of preparing carbonyl functional polysiloxanes and U.S. Patent No. 5,880,304 (Graiver, et al.) discloses a method of preparing organosilicon carbonyl compounds. In addition, U.S. Patent No. 4,609,574 (Keryk, et al.) discloses a method of hydrolyzing a chlorosilane to produce a polysiloxane having an aldehyde group.

However, methods known in the art for preparing silanes and siloxanes having aldehyde functionality lack precise control of both the architectural design of the molecule and molecule’s molecular weight. In general, these methods are not used in commercial applications because of the process’s poor yield, occurrence of extensive side reactions, and/or significant cost associated with starting materials or the process itself.
For example, the process described by Graiver involves the formation of an aldehyde-functional siloxane wherein a siloxane having terminal olefin moieties is first subject to ozonolysis to form an intermediate ozonide and then the resulting ozonide is reacted with acetic acid in the presence of a zinc catalyst to form an aldehyde-functional siloxane having the following formula (I):

\[
\begin{align*}
\text{H} & \quad \text{H'} \\
\text{\text{C}}_{\text{alpha}} & \quad \left[ \text{CH}_2 \right]_n \\
\text{COH} & \quad \text{Siloxane}
\end{align*}
\]

wherein \( n \) is 2 or 3.

Aldehyde-functional siloxanes synthesized by the Graiver process incur a serious limitation in that both hydrogen bonds on the alpha-carbon function indiscriminately as active polymerization sites which in turn leads to a proliferation of side-chain products when the siloxane is copolymerized. These unwanted side-reactions cause this process to be unstable. (As used herein, the term “stability” refers to the speed and selectivity of the reaction and not to the tendency to readily participate in reactions.)

The lack of control over the copolymerization reaction leads to the formation of many high viscosity, cross-linked polymers, and thus a copolymer product having a high variance in molecular weights instead of the more advantageous narrow molecular weight distribution. Inherently, this also results in low yield of the targeted product.

Moreover, the alkene reactant in the Graiver process determines the nature of the aldehyde functionality. This reactivity cannot be tailored to modify the performance of the
resulting polymer or polymerization reaction. In addition, compounds formed by this process are limited to those having only aldehyde functionality (i.e. this process cannot synthesize compounds having multiple functional groups). Thus, the flexibility of aldehyde-functional siloxanes prepared by processes known in the art is limited.

SUMMARY OF THE INVENTION

The Applicants have discovered that the aforementioned problems, among others, can be solved by synthesis methods wherein a redox initiator having a specific functionality is formed prior to attaching it to a silane or siloxane to produce a polymerizable silane or siloxane, respectively. This redox initiator can then serve as a customized polymerization site for the compound. Customizing the copolymerization site allows for greater control over the kinetics of the copolymerization reaction and substantially reduces unwanted side chain reactions. For example, the redox initiator can be designed to limit the availability and accessibility of the silane’s or siloxane’s copolymerization sites. In general, fewer copolymerization sites lead to fewer unwanted side-chain reactions. In addition, a stabilizing substituent, such as a resonance radical stabilizing functional group, can be added to the redox initiator proximal to the copolymerization site to stabilize the site during a copolymerization reaction, thus leading to better control over the reaction.

Accordingly, one aspect of the present invention is a method for preparing a polymerizable silane or siloxane having a first step of synthesizing a redox initiator and a second step of attaching the redox initiator to the silane or siloxane to produce a polymerizable compound. Since the redox initiator can be chosen so as to control the
copolymerization reaction, the particular redox initiator synthesized will depend on the
desired polymer or copolymer product, but will generally have the following formula (II):

\[
\begin{array}{c}
\text{X} \\
\text{R}_1 - \text{C}_\text{alpha} - \text{A} \\
\text{Z} \\
\end{array}
\]

(II)

5

wherein:

- \text{Z} is a free radical initiator;
- \text{C}_\text{alpha} is the first carbon adjacent to \text{Z};
- \text{X} is an abstraction moiety;
- \text{R}_1 is a stabilizing constituent; and
- \text{A} is a group capable of being hydrosilylated, preferably alkene or alkyne.

Another aspect of the present invention are polymerizable siloxanes and silanes
formed by the method described above. In certain preferred embodiments, the
polymerizable silane or siloxane has the formula (III):

\[
\left( \begin{array}{c}
\text{X} \\
\text{R}_1 - \text{C}_\text{alpha} - \text{A}' \\
\text{Z} \\
\end{array} \right)^d \text{Sil}
\]

(III)

wherein \text{R}_1, \text{X}, \text{C}_\text{alpha}, and \text{Z} are defined as above, \text{A}' is a linking group formed by
hydrosilylation, \text{d} is an integer from about 1 to about 40, and "\text{Sil}" is a silane or siloxane
moiety.
According to yet another aspect of the present invention, provided are methods for forming silane and siloxane copolymers wherein at least one vinyl monomer or polymer is reacted with at least one polymerizable silane or siloxane as described above to form a block or graft copolymer.

Still another aspect of the present invention are siloxane-vinyl block and graft copolymers formed by the method described above. A preferred embodiment of this aspect of the invention is a block siloxane-vinyl copolymer having the formula (V):

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{R}_{11} & \quad \text{R}_{12} \\
\text{OSi} & \quad \text{Si} \\
\text{R}_{13} & \quad \text{R}_{14} \\
\text{R}_{15} & \quad \text{R}_{15}
\end{align*}
\]

wherein \( R_{11} \) is independently methyl, ethyl, phenyl, and the like;

\( R_{12}, R_{13}, R_{14}, \text{and } R_{15} \) are independently H, alkyl, aryl, heterocyclic, fluoro, fluoroalkyl, acetate, acrylic, anhydride, and the like;

\( R_{21} \) is independently methyl, ethyl, phenyl, and the like;

\( b \) is an integer from 10 to 200; and

\( c \) is an integer from 10 to 200.

**DETAILED DESCRIPTION OF THE INVENTION**

Provided are methods for producing a polymerizable silanes and siloxanes having a polymerization site or copolymerization site, respectively, that can be customized to
efficiently produce a wide variety of block and graft copolymers. Specifically, methods are provided for producing polymerizable silanes and siloxanes wherein a redox initiator having functionality tailored to favor a specific copolymer is first synthesized and is then attached to a silane or siloxane to form the polymerizable silane or siloxane product. During a copolymerization reaction, copolymer linkages form at the redox initiator and, since the functionality of the redox initiator can be tailored to favor a particular copolymer product, the redox initiator functions as a customized copolymerization site.

According to a first aspect of the invention, methods of synthesizing polymerizable silanes and siloxanes are provided comprising the steps of (a) synthesizing a redox initiator functionality engineered to favor a specific copolymer; and (b) attaching the engineered redox initiator to a silane or siloxane to form a polymerizable silane or siloxane, respectively.

The term "redox initiator", as used herein, refers to a system which effects the radical polymerization of the monomers. Specifically, a redox initiator, when attached to a silane or siloxane, promotes oxidative coupling between the silane or siloxane and one or more vinyl monomers or polymers to form silane polymers or block or graft siloxane copolymers. This process of oxidative coupling, which is also known in the art as "redox polymerization", generally involves the transfer of electrons between the redox initiator attached to the silane or siloxane and at least one other monomer or polymer during the polymerization or copolymerization reaction. Without being bound to any particular theory, it is believed that redox initiators suitable for the present invention accept an electron during a redox reaction, thereby creating a polymeric silane or siloxane radical. This polymeric
radical, in turn, reacts with vinylic monomers and/or polymers to form, for example, a siloxane-vinyl block or graft copolymer.

Several redox initiators are known in the art. Those suitable for use with the present invention comprise (1) a free radical initiator which serves to facilitate reduction of a silane monomer or polymeric siloxane, (2) an abstraction moiety which is removable from the redox initiator providing a pair of free electrons, (3) a tertiary alpha-carbon which functions as a copolymerization site, (4) a stabilizing constituent for controlling the copolymerization kinetics, and (5) a group capable of being hydrosilylated which serves to attach the redox initiator to the silane or siloxane. Generally, redox initiators of the present invention will be of Formula (II):

\[
\begin{align*}
X & \quad | \quad C_{\alpha} \quad | \quad A \\
\big/ & \quad Z & \quad R_1 \\
\end{align*}
\]

wherein:

- \(Z\) is a free radical initiator, preferably aldehyde;
- \(C_{\alpha}\) is the first carbon adjacent to \(Z\);
- \(X\) is an abstraction moiety;
- \(R_1\) is a stabilizing constituent; and
- \(A\) is a group capable of being hydrosilylated, preferably alkene or alkyne.

With respect to the free radical initiator, \(Z\), it is an agent used to start the redox copolymerization reaction involving the polymerizable silane or siloxane. The redox initiator, when attached to the siloxane, must be reducible so as to readily form a polymeric free radical. This polymeric free radical has one unpaired electron that is produced upon the
splitting of a molecular bond. That is, the free radical has at least one of the bonding orbitals occupied by a single electron. Once the polymeric radical is formed, it can then undergo oxidative coupling with another monomer and/or polymer. This action starts a chain reaction wherein the radicals that are consumed by the formation of a polymer or copolymer bond are regenerated, thereby leading to the formation a polymer or copolymer. Examples of preferred free radical initiators include, but are not limited to, aldehydes.

With respect to the abstraction moiety, X, it is the moiety that leaves the molecule in order to create the polymeric free radical. Generally, the abstraction site becomes the location of polymeric linkage. According to the present invention, these abstraction moieties are a hydrogen or a highly electronegative atom, such as a halogen. Examples of preferred abstraction moieties include, but are not limited to, hydrogen, chlorine, bromine, and iodine.

With respect to the stabilizing constituent, \( R_1 \), it is a moiety that stabilizes the free radical formed during the polymerization reaction, preferably by resonance forces. It is known that more stable free radicals form more easily. That is, the ease at which radical formation occurs (i.e. the acceptance of an electron and corresponding abstraction of hydrogen or halogen) increases as the stability of the resulting free radical increases. The dissociation energy of the abstraction moiety bond generally provides a measurement of the relative inherent stability of the free radical. With respect to carbon-based free radicals, stability order is as follows:

\[
\text{Tertiary} \quad > \quad \text{Secondary} \quad > \quad \text{Primary} \quad > \quad \text{CH}_4 \quad > \quad \text{Vinyllic}
\]
Increasing the number of alkyl substituent on the radical center generally leads to an increase in stability, which is thought to be caused by hyperconjugation. Thus, redox initiators having a radical on a tertiary carbon (i.e. a carbon having only one abstraction moiety) are preferred to redox initiators having a radical on a secondary carbon because the tertiary carbon-centered radical is more stable due to more distinct resonance stabilization. Such tertiary carbon-centered radicals are formed, for example, by $R_1$ being an alkyl or a phenyl.

The stability of free radicals of the present invention is also enhanced by the presence at the radical center of either an electron-donating group or an electron withdrawing group. It is believed that this increased stability arises from the further increase in resonance. Examples of $R_1$ as an electron donating group include, but are not limited to, alkylxoy, aryloxy, thioethers, dialkylamines, or an phenyl substituted, preferably at the fourth carbon, with an alkylxoy, aryloxy, thioether, or dialkylamine. Particularly preferred alkylxoxies include those having the formula $-O-R_2$, wherein $R_2$ is a $C_1-C_3$ alkyl. Particular preferred arylxoxies include those having the formula $-O-(C_6H_5)$. Particularly preferred thioethers include those having the formula $-S-R_3$, wherein $R_3$ is a $C_1-C_3$ alkyl or a phenyl. Particularly preferred dialkylamines include those having the formula $-N(R_4)_2$, wherein $R_4$ is methyl, ethyl, or phenyl. Examples of $R_1$ as an electron withdrawing group include, but are not limited to aryls substituted, preferably at the fourth carbon, with nitro, nitrile, aldehyde, $C_1-C_3$ ketone, or $C_1-C_3$ ester.

The particular $R_1$ substituent incorporated into the redox initiator will depend on the desired reaction kinetics, which can easily be determined by those skilled in the art without undue experimentation. Thus, for copolymerization reactions requiring a decrease in speed
and an increase in selectivity, a redox initiator is synthesized having a substituent capable of resonance stabilizing a free radical, such as aromatic rings. In contrast, for copolymerization reactions requiring an increase in speed and a decrease in selectivity, a redox initiator is synthesized with a group having less resonance stabilizing characteristics, such as methyl. The functionality of the R₁ substituent may also be considered in choosing a particular R₁.

Redox initiators having tertiary carbons are also preferred because polymerization occurs at the site of the hydrogen abstraction and, in the case of tertiary carbons, there is only one abstraction site. Restriction of the polymerization reaction to a single site reduces the uncontrollable side-chain reactions and the resulting undesired cross-linked polymers.

With respect to the group capable of being hydrosilylated, A, it is a functional moiety capable of bonding to a silane or siloxane, preferrably via a hydrosilylation reaction, although any chemical process known in the art may be used. Such a hydrosilylation reaction occurs at a silicon-hydrogen bond of a silane or siloxane and involves the addition of the silane or siloxane across the terminal carbon-carbon double bond or triple bond of the redox initiator. Thus, preferably A is an alkene or alkyne, and more preferably a C₃ alkene or alkyne having its double or triple bond, respectively, at a terminal end of the redox initiator distal to the aldehyde group.

Typcially, the hydrosilylation process is carried out in the presence of a catalyst, such as platinum. In certain preferred embodiments, the redox initiator bearing the carbon-carbon double or triple bond that can be hydrosilylated attaches to the silane, terminally to one or both ends of the siloxane, or pendently to the siloxane backbone. Preferred groups
capable of being hydrosilylated include vinyl moieties, such as 1-propenyl, 1-buteny1, 1-pentenyl, and the like.

In certain preferred embodiments, the redox initiator of Formula (II) can be further defined wherein:

5 A is 3-vinyl or 3-allyl;

X is hydrogen, chlorine, bromine, or iodine;

Z is aldehyde, more preferably methanal, or an aldehyde derived from an acetal such as dimethylacetal; and

R₁ is C₁ – C₃ alkyl, alklyoxy, aryloxy, thioethers, dialkylamines, or an aryl substituted with an alklyoxy, aryloxy, thioether, dialkylamine, nitro, nitrile, aldehyde, C₁ – C₃ ketone, or C₁ – C₃ ester.

In certain preferred embodiments, these redox initiators are pendently or terminally attached to the siloxane.

Particularly preferred redox initiators include 2-methyl-4-pentenal, 2-methyl-2-bromo-4-pentenal, 2-ethyl-4-pentenal, 2-ethyl-2-bromo-4-pentenal, 2-phenyl-4-pentenal, and 2-phenyl-2-bromo-4-pentenal. Particularly preferred redox initiators wherein Z is an aldehyde derived from an acetal include aldehydes derived from 2-methyl-(1,1’-dimethoxy)-4-pentene, 2-ethyl-(1,1’-dimethoxy)-4-pentene, 2-phenyl-(1,1’-dimethoxy)-4-pentene, 2-methyl-2-bromo-(1,1’-dimethoxy)-4-pentene, 2-ethyl-2-bromo-(1,1’-dimethoxy)-4-pentene, or 2-phenyl-2-bromo-(1,1’-dimethoxy)-4-pentene.

Alternatively, these and other aldehydes can be synthesized by methods known in the art. For example, substituted-4-pentenals suitable for the present invention can be
synthesized as described in U.S. Pat. No. 3,928,644, wherein 2-phenyl-4-pentenal is synthesized from phenyl acetaldehyde.

After the redox initiator is synthesized, it is attached to a silane or siloxane as described above.

As used herein, the term “silane” refers to a compound having a single silicon atom bonded to at least one hydrogen, wherein this silicon-hydrogen bond is capable of serving as the attachment site for the redox initiator. Preferable silanes have the formula (VI)

\[
\text{H} - \text{Si} \quad (\text{OR}_5)_{3-q} \\
\quad (\text{R}_6)_q
\]  

(VI)

wherein \( R_5 \) is straight chain or branched, substituted or unsubstituted \( C_1-C_{20} \) alkyl, \( C_6-C_8 \) aryl, or \( C_1-C_{10} \) heterocyclic;

\( R_6 \) is hydrogen, straight chain or branched, substituted or unsubstituted \( C_1-C_{20} \) alkyl, \( C_6-C_8 \) aryl, or \( C_1-C_{10} \) heterocyclic; and

\( q \) is an integer from 0 to 3.

As used herein, the term “siloxane” refers to straight-chain, cyclic, and polycyclic compounds having silicon atoms single-bonded to oxygen atoms and so arranged that each silicon atom is linked to at least one oxygen atom. Preferably, siloxanes of the present invention will be silicones (i.e. siloxane polymers based upon a structure consisting of alternating silicon and oxygen atoms with various organic radicals attached to the silicon atoms). In addition, siloxanes suitable for the present invention have at least one silicon-hydrogen bond which serves as the attachment site for the redox initiator. Thus, preferable siloxanes include hydride end-capped siloxanes, mono hydride terminal siloxanes, and
pendent or “rake” hydride siloxanes. Preferably, siloxanes for use with the present invention will be of the following formula (VII):

![Diagram of siloxane structure](image)

(VII)

wherein $R_7$ is $H$, $C_1 - C_{30}$ straight or branched alkyl, $C_3 - C_{12}$ substituted or unsubstituted cyclic, $C_1 - C_{11}$ heterocyclic, $C_6 - C_8$ aryl, $C_6 - C_8$ arylxy, $C_1 - C_{12}$ alkoxy, $C_2 - C_{12}$ di-alkylamino, $C_1 - C_{12}$ alkylthio, $C_1 - C_{12}$ fluoroalkyl, $C_1 - C_{12}$ epoxy, $C_1 - C_6$ acrylic or methacryoxy, $C_6 - C_{50}$ polyether, or some combination thereof;

$R_8$ is independently $H$, $-O-R_9$, $O$ bonded to Si so as to produce a cyclic or polycyclic form, $C_1 - C_{50}$ straight or branched alkyl, $C_3 - C_{12}$ substituted or unsubstituted cyclic, $C_1 - C_{11}$ heterocyclic, $C_6 - C_8$ aryl, $C_6 - C_8$ aryloxy, $C_1 - C_{12}$ alkoxy, $C_2 - C_{12}$ di-alkylamino, $C_1 - C_{12}$ alkylthio, $C_1 - C_{12}$ fluoroalkyl, $C_1 - C_{12}$ epoxy, $C_1 - C_6$ acrylic or methacryoxy, $C_6 - C_{50}$ polyether, or some combination thereof;

![Diagram of siloxane structure](image)

$R_9$ is $R_8$; and

$p$ is an integer from 3 to 40,
provided that for non-cyclic siloxanes, \( R_7 = H \) and \( R_8 \neq H \) for mono-hydrde terminal siloxanes; \( R_7 = H \) and the terminal \( R_8 = H \) for hydrde end-capped siloxanes; and \( R_7 \neq H \), the terminal \( R_8 \neq H \), and at least one \( R_8 = H \) for rake hydrde siloxanes.

In certain preferred embodiments, hydrde end-capped siloxanes, mono hydrde siloxanes, and rake hydrde siloxanes have one of the following formulae:

![Formulae VIII, IX, X](image-url)
wherein \( R_{16} \) and \( R_{17} \) are independently methyl or phenyl,
\[ x \text{ is an integer from } 0 - 80, \]
\[ y \text{ is an integer from } 0 - 80, \]
\[ x + y \neq 0, \]
\[ w + z \text{ is an integer from } 3 - 40, \text{ and} \]
\[ z \text{ is an integer from } 1 - 40. \]

Siloxanes according to the present invention are commercially available from a variety of sources, including for example, dimethylsiloxane - hydrogen terminated (CAS No. 70900-21-9) from Dow Corning, and dimethyl, methylhydrosiloxane – trimethylsiloxyl terminated (CAS No. 68037-59-2) also from Dow Corning.

Alternatively, these and other siloxanes may be prepared by any means known in the art. For example, a polydimethylsiloxane (PDMS) having terminal silicon-hydride
functionality may be formed by reacting octamethylcyclotetrasiloxane with dimethyl silane in the presence of CF₃SO₃H. A polydimethyl siloxane having pendent silicon-hydride functionality may be formed by reacting octamethylcyclotetrasiloxane and 1,3,5,7-tetramethylcyclotetrasiloxane with tetramethyldisiloxane (TMDS) in the presence of CF₃SO₃H.

Once the redox initiator is attached to the silane or siloxane, the compound can participate in a redox copolymerization reaction with vinyl monomers or polymers. The term “polymerizable silane”, as used here, refers to a silane having a functional group capable of transforming the silane monomer into a polymeric radical during a polymerization process. The term “polymerizable siloxane”, as used herein, refers to siloxane polymer having functional group capable of transforming the siloxane compound into a polymeric radical during a copolymerization process. Thus, according to another aspect of the present invention, provided are novel silanes and siloxane having terminal or pendent functionality, preferably aldehyde functionality.

Polymerizable silanes and siloxanes of the present invention may be produced by any chemical process known in the art wherein a redox initiator is attached to a silicon atom of the silane or siloxane. As indicated above, a preferred method of attaching a redox initiator to the silicon atom is via hydrosilylation. Such hydrosilylation reactions occur at a silicon-hydrogen bond and involve the addition of a silane or siloxane across a carbon-carbon double bond of the redox initiator. Typically, the hydrosilylation process is carried out in the presence of a catalyst, such as a platinum catalyst.

In certain preferred embodiments, polymerizable silanes and siloxanes of the present invention will be of Formula III:
wherein $R_1$, $X$, $C_{\text{alpha}}$, and $Z$ are defined as above, $A'$ is a linking group formed via hydrosilylation, $d$ is an integer from about 1 to about 40, and "Sil" is a silane or siloxane moiety. Since hydrosilylation involves the addition of the siloxane across carbon-carbon double bond of the moiety $A$, typically $A'$ will be an alkyl derived from alkene $A$. By way of example, if $A$ is 2-propenyl, the corresponding hydrogenated form $A'$ will be propyl, and so forth.

In certain other preferred embodiments, a hydrosilylation process can also be used to incorporate other functional olefins into the silane or siloxane to produce novel polymerizable silanes and siloxanes. That is, the terminal double carbon bond of functional groups such as ethylene, propylene, styrene, epoxy, acrylic, arcyloxy, and polyether, among others, can undergo hydrosilylation in the presence of a catalyst, such as platinum, wherein the functional group attaches to a silicon atom of the silane or siloxane. For example, multifunctional rake siloxanes can be produced from trimethylsiloxy terminated polyalkylhydrosiloxane as shown below:
wherein $R_{10}$ is, for example, methyl or phenyl;

$R_{18}$ is, for example, alkyl, aryl, alkoxy, aryloxy, di-alkylamino, alkylthio, or fluoralkyl;

$D$ is, for example, ethylene, propylene, $C_2 - C_{50}$ alkyl, styrene, or 1-methyl styrene;

$B$ is, for example,

an epoxy having the formula:

\[
\text{\begin{center}
\begin{array}{c}
\text{\includegraphics[width=1cm]{epoxy.png}}
\end{array}
\end{center}
\]

or

an acrylic or methacryloxy having the formula:

\[
\text{\begin{center}
\begin{array}{c}
\text{\includegraphics[width=1cm]{acrylic.png}}
\end{array}
\end{center}
\]

wherein $R_{19}$ is H or CH$_3$ and $R_{20}$ is CH$_3$, C$_2$H$_5$, or CH$_2$CH$_2$OH, or a polyether having the formula:
wherein \( j \) is an integer from 2 – 20;

\( k \) is an integer from 3 – 40; and

\( i + h + g = k \), wherein \( g \neq 0 \).

5

Other preferred polymerizable siloxanes according to the present invention, include, but are not limited to, those having one of the formulas (XII) – (XIV):

(XII)

(XIII)

(XIV)
wherein \( R_{16}, R_{17}, x, y, \) and \( z \) are defined as above; and \( R_{20} \) is methyl, ethyl, or phenyl.

It is understood that the polymerizable siloxanes mentioned above are merely exemplary and that many other embodiments of the present invention are also contemplated, including but not limited to, cyclic siloxanes, polycyclic siloxanes, and siloxanes having different functional groups attached to the silicon atoms.

According to another aspect of the present invention, methods for preparing block and graft copolymers are provided wherein a polymerizable silane or siloxane, such as those described above, is reacted with a vinyl monomer and/or polymer in the presence of a catalyst to produce a silane- or siloxane-vinyl copolymer.

As used herein, the term “vinyl” refers to a moiety having, or being derived from, at least the functional group \( \text{CH}_2\text{==CH}− \). The term “vinyl monomer”, as used herein, generally refers to vinyl compounds (i.e. compounds having a vinyl functional group), which includes, but is not limited to vinyl chloride, vinyl acetate and similar esters, styrenes, methacrylates, acrylonitriles, and the like. Preferably, the copolymerization reaction involves the formation of a polymeric siloxane radical which is reacted with a vinyl monomer or polymer to yield the siloxane-vinyl copolymer.
In a particularly preferred embodiment, the copolymerization process includes the step of mixing aldehyde-functional polymerizable siloxanes with a vinyl monomer and a copper (II) redox catalyst system in a suitable solvent such as benzene, toluene, xylene, glycol, or the like, and heated to 60°C - 125°C for from about 5 to about 24 hours. For preparation of siloxane-polyfluoroolefins, a fluorinated solvent can be used. Once the polymerization reaction is complete, the reaction mixture is cooled to room temperature and mixed with a protic solvent, such as methanol, and the like, to precipitate the copolymer product. The solid product is then washed with a solvent, dried, and purified using typical polymerization techniques known in the art.

The selection of a vinyl monomer for the copolymerization reaction is dependent upon the desired copolymer product. Examples of vinyl monomers that may be used in the present invention include, but are not limited to, ethylene, propylene, styrene, N-vinyl pyrrolidone, vinylidene fluoride, chlorotrifluoroethylene, methyl methacrylate, ethyl methacrylate, acrylonitrile, hydroxyethyl methacrylate, vinyl acetate, and maleic anhydride.

Other examples of vinyl monomers include fluoro olefin monomers such as 3,3,3-trifluoro-1-propene; 2,3,3,3-tetrafluoro-1-propene; 1,3,3,3-tetrafluoro-1-propene; 1-chloro-1,3,3,3-tetrafluoro-1-propene; 2,2,3,3,3-pentafluoro-1-propene; 4-vinyl-pyridine; and the like.

Depending on the starting materials selected for use in the above-described process, a wide range of novel siloxane-vinyl block and graft copolymers can be efficiently obtained.

As used herein, the term “block copolymer” refers to a linear copolymer wherein several monomers of a single first species are proximally connected and then sequentially connected to another chain of proximally connected monomers of another single species that is different than the first species. The term “graft copolymer”, as used herein, refers to
a non-linear copolymer wherein one or more chains consisting of a single species of monomer are connected to a main polymer chain of a different species as side-chains. Thus, according to yet another aspect of the present invention, provided are novel siloxane-vinyl block and graft copolymers. In certain preferred embodiments, the siloxane-vinyl block polymer will be of Formula (V):

![Image of chemical structure]

(V)

wherein $R_{11}$ is methyl, ethyl, phenyl, and the like;

$R_{12}$, $R_{13}$, $R_{14}$, and $R_{15}$ are independently H, alkyl, aryl, heterocyclic, fluoro, fluoroalkyl, acetate, acrylic, anhydride, and the like;

$b$ is an integer from 10 to 200; and

c is an integer from 10 to 200.

In certain other preferred embodiments, the siloxane-vinyl is a graft copolymer. It is understood that graft copolymers according to the present invention may utilize the siloxane moieties either as the backbone portion of the copolymer, such as for example, the structure:
or as the pendent portion of the copolymer, such as for example, the structure:

Additionally, by engineering the redox initiator, the copolymerization reactions which occur are more selective thereby leading to a higher yield and better process control of, and less side products in, the desired product stream. As used herein, the term “product stream” refers to a process wherein siloxane and vinyl monomers are reacted to form a product of block or graft copolymers. Although the term “stream” is used, it should be understood that the present invention can be applied to batch or continuous processes. The term “product yield” refers to the weight percentage of targeted copolymer that is formed via a product stream based upon the weight of the reactants.

EXAMPLES

The present invention is further described in light of the following examples which are intended to be illustrative but not limiting in any manner.
Example 1:
Hydrosilylation of 2-phenyl-pentenal with tetramethyldimethylsiloxane (TMDS):

\[
\begin{align*}
H-Si-O-Si-H & + 2 \text{Ph} & \xrightarrow{\text{Pt-cat.}} & \text{Ph} \quad \text{OHC} \quad \text{Si-O-Si} & \text{Ph} \\
& & & \text{Si} & \text{CHO} \\
\end{align*}
\]

Reagents:
1.4 g tetramethyldimethylsiloxane (TMDS) (0.01 mol)
60 ppm (Pt) Karstedt-catalyst in xylene
3.5 g 2-phenyl-4-pentenal (appr. 92%, 0.02 mol), CAS Number: [24401-36-3]
The reagents are mixed, degassed with nitrogen and heated to 85°C for 24 hours.

The mixture turns dark. After filtration over active charcoal, IR shows complete
disappearance of the Si-H-group, GC shows now TMDS, some residual pentenal and the di-
substituted product which is also analyzed by GC-MS. The excess 2-phenyl-4-pentenal can
be removed by distillation.

Example 2:
Hydrosilylation of 2-phenyl-pentenal with Polydimethylsiloxane (PDMS):

\[
\begin{align*}
\text{HSi} & \quad \text{Si-O-Si} & \quad \text{SiH} & + 2 \text{Ph} & \xrightarrow{\text{Pt-cat.}} & \text{Ph} \quad \text{OHC} \quad \text{Si-O-Si} & \quad \text{Si} & \quad \text{CHO} \\
& & & \text{Si} & \quad \text{Si} & & \text{Si} & \quad \text{Si} & \quad \text{Si} \\
\end{align*}
\]

Reagents:
5 g Polydimethylsiloxane (PDMS) (Gelest, MW 400-500, active H 0.5%)
60 ppm (Pt) Karstedt-catalyst in xylene
3.5 g 2-phenyl-4-pentenal

The reagents are mixed, degassed with nitrogen and heated to 85°C for 24 hours.

After filtration over active charcoal, IR shows complete disappearance of the Si-H-group, 1H-NMR shows complete disappearance of the Si-H-group, some residual 2-phenyl-4-pentenal and a group of signals concurrent to the new compound. The excess 2-phenyl-4-pentenal can be removed by distillation.

Example 3:

Cu(II)-catalyzed copolymerization of styrene with 2-phenylpentanal-modified PDMS:
Reagents:

10 ml chlorobenzene (dry)

0.1 g (2.68 x 10^-4 mol) copper(II)-ethylhexanoate

0.5 g pyridine

0.3 g triphenylphosphine (0.3 g, 1.14 x 10^-3 mol)

0.1 g triethylamine (1 x 10^-3 mol)

5 mL styrene

2-phenylpentanal-modified PDMS (3.1 x 10^-4 mol aldehyde functions), Copper(II)-ethylhexanoate, pyridine, triphenylphosphine and triethylamine are added to chlorobenzene, the mixture turns green. Styrene and 2-phenylpentanal-modified PDMS are added and the mixture is degassed for 5 minutes with N₂. The mixture is heated at 70°C for about 20-24 hours. The colour is a less intensive green, the mixture is more viscous. After cooling the mixture to room temperature, it is quenched into 20 mL MeOH under vigorous stirring. A polymer precipitate forms. The precipitate is filtered and washed with MeOH, then dried under vacuum at room temperature.

Example 4:

This example demonstrates the hydrosilylation of H-terminated PDMS MW 1100 and 2-phenyl-4-pentenal.
250 g (0.238 mol) DMS-H11 (Gelest, Inc., Morrisville, PA19067, USA) and 83 g 2-phenyl-4-pentenal (0.5 mol) are heated to 85°C with stirring and under inert atmosphere. A total of 0.96 mL Karstedt catalyst (Aldrich, 0.1m in xylenes) are added in 4 portions, with a reaction time of 2 hours between each addition. After the first catalyst addition, the temperature rises from 85°C to 110°C. After completed catalyst addition, the mixture is stirred at 85°C overnight. A sample shows complete conversion of the Si-H in the IR. The mixture is filtered over a carbon filter and the excess 2-phenyl-4-pentenal is distilled off.

**Example 5:**

This example demonstrates the hydrosilylation of H-terminated PDMS MW 6000 and 2-phenyl-4-pentenal.

9 g (1.5 mmol) DMS-H21 (Gelest, Inc), 1.88 μl Karstedt catalyst solution (Johnson Matthey, 4% in isopropanol) and 0.53 g 2-phenyl-4-pentenal (3.3 mmol) are stirred in 45 mL isopropanol and heated to 83°C under inert atmosphere for 48h. IR analysis shows complete turnover of the SiH band.

**Example 6:**

This example demonstrates the hydrosilylation of H-terminated PDMS MW 550 and 2-phenyl-4-pentenal.

The procedure of example 4 is conducted, except replacing DMS-H11 (Gelest, Inc) with the same molar amount of DMS-H03 (Gelest, Inc). IR analysis shows complete turnover of the SiH band.
Example 7:

This example demonstrates the copolymerization of styrene with 2-phenyl-4-
pentanal-modified PDMS-H03.

5 mL styrene, 5 mL of copper-catalyst solution (44 mL chlorobenzene, 5 mL
pyridine, 1 g copper (II)-ethylhexanoate, 1.36 mL triethylamine and 1.5 g
triphenylphosphine) and 150 mg of hydrosilylation product (as macroinitiator) from
Example 6 are degassed with nitrogen and heated to 80°C with stirring under nitrogen-
atmosphere for 21h. The thick mixture is diluted with another 15 mL chlorobenzene and
added to 150 mL of methanol while stirring with an Ultraturrax homogenizer. The white
solid is filtered and washed with 75 mL methanol, then dried. The yield is 2.3 g, GPC
determination of average molecular weight is 300000.

Example 8:

This example demonstrates the copolymerization of 4-vinylpyridine with 2-phenyl-
4-pentanal-modified PDMS-H03.

5 mL 4-Vinylpyridine, 5 mL of copper-catalyst solution (44 mL chlorobenzene, 5 mL
pyridine, 1 g copper (II)-ethylhexanoate, 1.36 mL triethylamine and 1.5 g
triphenylphosphine) and 150 mg of hydrosilylation product (as macroinitiator) from
Example 6 are degassed with nitrogen and heated to 70°C with stirring under nitrogen-
atmosphere for 21h. The result is a completely polymerized product, which forms a gum-
like plug.
Example 9:

This example demonstrates the copolymerization of methacrylic acid ethyl ester with 2-phenyl-4-pentanal-modified PDMS-H03.

5 mL (4.6 g) methacrylic acid ethyl ester, 5 mL of copper-catalyst solution (44 mL chlorobenzene, 5 mL pyridine, 1 g copper (II)-ethylhexanoate, 1.36 mL triethylamine and 1.5 g triphenylphosphine) and 150 mg of hydrosilylation product (as macroinitiator) from Example 6 are degassed with nitrogen and heated to 70°C with stirring under nitrogen-atmosphere for 21h. The thick mixture is diluted with 3 5mL-portions of chlorobenzene and added to 150 mL methanol at 15-20°C whilst stirring with an Ultraturrax homogenizer.

After stirring for another 15 minutes, the wax-like product is decanted, 100 mL methanol are added and the mixture is stirred with an Ultraturrax homogenizer at -5 to 0°C. The product is then filtered, washed with methanol and dried at 30 mbar and 30°C. Yield is 3.1 g white, slightly sticky solid, GPC determination of average molecular weight is 295000.

Example 10.

The procedure in Example 9 is repeated, but leaving out the hydrosilylation product from Example 6 as macroinitiator. No polymerization is observed.

Having thus described a few particular embodiments of the invention, various alterations, modifications, and improvements will readily occur to those skilled in the art. Such alterations, modifications, and improvements, as are made obvious by this disclosure, are intended to be part of this description though not expressly stated herein, and are
intended to be within the spirit and scope of the invention. Accordingly, the foregoing
description is by way of example only, and not limiting. The invention is limited only as
defined in the following claims and equivalents thereto.
CLAIMS

What is claimed is:

1. A method for preparing polymerizable silanes and siloxanes comprising the steps of:
   (a) providing a redox initiator; and
   (b) attaching said redox initiator to a silane or siloxane to form a polymerizable compound.

2. The method of claim 1, wherein said redox initiator has the formula:

   \[
   X \\
   \bigg\downarrow \text{C}_{\alpha} \\
   R_1 - \text{C}_{\alpha} - A \\
   \bigg\downarrow \\
   Z \\
   \bigg(\text{II}\bigg)
   \]

   wherein:

   Z is a free radical initiator;

   \(\text{C}_{\alpha}\) is the first carbon adjacent to Z;

   X is an abstraction moiety;

   \(R_1\) is a stabilizing constituent; and

   A is a \(C_2-C_6\) alkene or a \(C_2-C_6\) alkyne.

3. The method of claim 2, wherein Z is aldehyde.
4. The method of claim 2, wherein A is selected from the group consisting of 2-vinyl, 3-allyl, or 4-butenyl.

5. The method of claim 2, wherein X is selected from the group consisting of hydrogen, chloride, bromide, and iodide.

6. The method of claim 2, wherein R₁ is selected from the group consisting of \( C_1 - C_3 \) alkyl, \( C_6 \) aryl, \( C_1 - C_3 \) alklyoxy, \( C_1 - C_3 \) thioethers, diphenyl thioether, nitro, nitrile, \( C_1 - C_3 \) ketone, \( C_1 - C_3 \) ester, dimethylamine, diethylamine, diphenylamine, \( C_6 \) arlyoxy, and \( C_6 \) aryl having a substitution at the fourth carbon ring selected from nitro, nitrile, aldehyde, \( C_1 - C_3 \) ketone, \( C_1 - C_3 \) ester, \( C_1 - C_3 \) alkyl, \( C_6 \) aryl, \( C_1 - C_3 \) alklyoxy, \( C_1 - C_3 \) thioethers, diphenyl thioether, dimethylamine, diethylamine, diphenylamine, and \( C_6 \) arlyoxy.

7. The method of claim 6, wherein R₁ is selected from the group consisting of methyl, ethyl, propyl, and phenyl.

8. The method of claim 2, wherein said redox initiator is selected from the group consisting of 2-methyl-4-pentenal, 2-methyl-2-bromo-4-pentenal, 2-ethyl-4-pentenal, 2-ethyl-2-bromo-4-pentenal, 2-phenyl-4-pentenal, and 2-phenyl-2-bromo-4-pentenal.

9. The method of claim 2, wherein said redox initiator is an aldehyde derived from 2-methyl-(1,1'-dimethoxy)-4-pentene, 2-ethyl-(1,1'-dimethoxy)-4-pentene, 2-phenyl-(1,1'-
dimethoxy)-4-pentene, 2-methyl-2-bromo-(1,1’-dimethoxy)-4- pentene, 2-ethyl-2-bromo-
(1,1’-dimethoxy)-4-pentene, or 2-phenyl-2-bromo-(1,1’-dimethoxy)-4-pentene.

10. The method of claim 2, wherein said redox initiator has the formula:

```
R₁  H
|    |
CH₂= CH – (CH₂)ₓ – C – C =O
|    |  X
```

wherein  
R₁ is methyl or phenyl;  
X is hydrogen; and  
x is 1 or 2.

11. The method of claim 1, wherein said silane has the formula:

```
H—Si—(OR₅)₃₋₉  (R₆)ₙ
```

wherein  
R₅ is straight chain or branched, substituted or unsubstituted C₁-C₂₀ alkyl,  
C₆-C₈ aryl, or C₁ – C₁₀ heterocyclic;  
R₆ is hydrogen, straight chain or branched, substituted or unsubstituted C₁-
C₂₀ alkyl, C₆-C₈ aryl, or C₁ – C₁₀ heterocyclic; and  
q is an integer from 0 to 3.
12. The method of claim 1, wherein said siloxane has the formula:

\[
\begin{array}{c}
R_7 \quad \text{Si} \quad O \quad R_9 \\
\end{array}
\]

wherein

- \( R_7 \) is selected from the group consisting of \( H, C_1 - C_{50} \) straight or branched alkyl, \( C_3 - C_{12} \) substituted or unsubstituted cyclic, \( C_1 - C_{11} \) heterocyclic, \( C_6 - C_8 \) aryl, \( C_6 - C_8 \) arylx, \( C_1 - C_{12} \) alkoxy, \( C_2 - C_{12} \) di-alkylamino, \( C_1 - C_{12} \) alkylthio, \( C_1 - C_{12} \) fluoroalkyl, \( C_1 - C_{12} \) epoxy, \( C_1 - C_6 \) acrylic or methacryoxy, \( C_6 - C_{50} \) polyether, and some combination thereof;

- \( R_8 \) is independently selected from the group consisting of \( H, -O-R_9, O \) bonded to Si wherein a cyclic or polycyclic structure is produced, \( C_1 - C_{50} \) straight or branched alkyl, \( C_3 - C_{12} \) substituted or unsubstituted cyclic, \( C_1 - C_{11} \) heterocyclic, \( C_6 - C_8 \) aryl, \( C_6 - C_8 \) arylx, \( C_1 - C_{12} \) alkoxy, \( C_2 - C_{12} \) di-alkylamino, \( C_1 - C_{12} \) alkylthio, \( C_1 - C_{12} \) fluoroalkyl, \( C_1 - C_{12} \) epoxy, \( C_1 - C_6 \) acrylic or methacryoxy, \( C_6 - C_{50} \) polyether, or some combination thereof;

\[
\begin{array}{c}
R_8 \\
\text{Si} \\
R_8
\end{array}
\]

\( R_9 \) is \( R_8 \); and

\( p \) is an integer from 3 to 40,
provided that for non-cyclic siloxanes, $R_7 = H$ and $R_8 \neq H$ for mono-hydride terminal siloxanes; $R_7 = H$ and the terminal $R_8 = H$ for hydride end-capped siloxanes; and $R_7 \neq H$, the terminal $R_8 \neq H$, and at least one $R_8 = H$ for rake hydride siloxanes.

13. The method of claim 12, wherein said siloxane has a formula selected from the group consisting of:

\[
\begin{align*}
\text{Me} & \quad \text{Si} \quad \text{O} \quad \text{Si}_x \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si}_y \quad \text{H} \\
\text{Me} & \quad \text{O} \quad \text{Si}_x \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si}_y \quad \text{H} \\
\text{Me} & \quad \text{Si} \quad \text{O} \quad \text{Si}_x \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Me} \\
\text{Me} & \quad \text{O} \quad \text{Si}_x \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Me} \\
\text{Me} & \quad \text{Si} \quad \text{O} \quad \text{Si}_x \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{Me} \\
\end{align*}
\]
wherein $R_{16}$ and $R_{17}$ are independently methyl or phenyl,

$x$ is an integer from $0 - 80$,

$y$ is an integer from $0 - 80$,

$x + y \neq 0$,

$w + z$ is an integer from $3 - 40$, and

$z$ is an integer from $1 - 40$.

14. The method of claim 1, wherein said attaching step comprises a hydrosilylation process.

15. The method of claim 14, wherein said hydrosilylation process occurs in the presence of a platinum catalyst.
16. The method of claim 14, further comprising the step of:

(c) attaching a vinyl compound to said polymerizable silane or siloxane,

wherein said vinyl compound is selected from the group consisting of $C_2 - C_{20}$ alkene, styrene, epoxy, acrylic, arcyloxy, and $C_4 - C_{20}$ polyether.

17. The method of claim 16, wherein said polymerizable siloxane has the formula:
wherein

- $R_{10}$ is methyl or phenyl;
- $R_{16}$ and $R_{17}$ are independently methyl or phenyl,
- $R_{18}$ is selected from the group consisting of $C_1 - C_3$ alkyl, $C_6$ aryl, $C_1 - C_3$ alkoxy, $C_1 - C_3$ thioethers, diphenyl thioether, nitro, nitrile, $C_1 - C_3$ ketone, $C_1 - C_3$ ester, dimethylamine, diethylamine, diphenylamine, $C_6$ aryloxy, and $C_6$ aryl having a substitution at the fourth carbon ring selected from nitro, nitrile, aldehyde, $C_1 - C_3$ ketone, $C_1 - C_3$ ester, $C_1 - C_3$ alkyl, $C_6$ aryl, $C_1 - C_3$ alkoxy, $C_1 - C_3$ thioethers, diphenyl thioether, dimethylamine, diethylamine, diphenylamine, and $C_6$ aryloxy.

- $R_{20}$ is methyl, ethyl, or phenyl;
D is selected from the group consisting of ethylene, propylene, C₂ – C₁₀ alkyl, styrene, or 1-methyl styrene;

B is selected from the group consisting of epoxy having the formula:

\[
\begin{align*}
&\text{acrylic,} \\
&\text{methacryloxy having the formula:} \\
&\text{wherein } R_{19} \text{ is H or CH₃, and} \\
&R_{20} \text{ is selected from the group consisting of CH₃, C₂H₅, and CH₂CH₂OH,} \\
&\text{and polyether having the formula:} \\
&\text{wherein } j \text{ is an integer from } 2 – 20; \\
&x \text{ is an integer from } 0 – 80, \\
y \text{ is an integer from } 0 – 80, \\
x + y \neq 0, \text{ and} \\
z \text{ is an integer from } 1 – 40. \\
k \text{ is an integer from } 3 – 40; \text{ and} \\
i + h + g = k, \text{ wherein } g \neq 0.
\end{align*}
\]
18. The method of claim 24, wherein said polymerizable siloxane has a cyclic or polycyclic structure.

19. A method of producing a copolymers comprising the steps of:
   (a) providing a polymerizable silane or siloxane according to claim 1,
   (b) providing a vinylic compound, and
   (c) reacting said polymerizable siloxane with said vinyl compound to produce a copolymer.

20. The method of claim 19, wherein said vinyl compound is a monomer or polymer having a vinyl functional group.

21. The method of claim 20, wherein said vinyl compound is selected from the group consisting of ethylene, propylene, styrene, N-vinyl pyrrolidone, vinylidene fluoride, chlorofluoroethylene, methyl methacrylate, ethyl methacrylate, acrylonitrile, hydroxyethyl methacrylate, vinyl acetate, maleic anhydride, 3,3,3-trifluoro-1-propene, 2,3,3,3-tetrafluoro-1-propene, 1,3,3,3-tetrafluoro-1-propene, 1-chloro-1,3,3,3-tetrafluoro-1-propene, 2,2,3,3,3-pentafluoro-1-propene, and 4-vinyl-pyridine.

22. The method of claim 20, wherein said reacting step occurs in the presence of a copper catalyst and in a solvent selected from the group consisting of benzene, toluene, xylene, and glycol.
23. The method of claim 19, wherein said copolymer is a block copolymer or a graft copolymer.

24. The method of claim 23, wherein said block copolymer comprises repeating units having the formula:

\[ \text{Diagram image} \]

wherein \( R_{11} \) is selected from the group consisting of methyl, ethyl, and phenyl;

\( R_{12}, R_{13}, R_{14}, \) and \( R_{15} \) are independently selected from the group consisting of \( H, \text{C}_1-\text{C}_6 \) alkyl, \( \text{C}_6 - \text{C}_8 \) aryl, \( \text{Cl} - \text{C}_{10} \) heterocyclic, fluoro, \( \text{C}_1 - \text{C}_6 \) fluoroalkyl, acetate, acrylic, anhydride, and the like;

\( b \) is an integer from 10 to 200; and

\( c \) is an integer from 10 to 200.

25. A polymerizable composition having the formula:
wherein

- $Z$ is a free radical initiator;
- $C_{\alpha}$ is the first carbon adjacent to $Z$;
- $X$ is an abstraction moiety;
- $R_1$ is a stabilizing constituent;
- $A'$ is an alkyl derived from an alkene substituent;
- Sil is silane or siloxane moiety; and
- $d$ is an integer from about 1 to about 40.

26. The composition of claim 25, wherein $Z$ is aldehyde.

27. The composition of claim 25, wherein $A'$ is selected from the group consisting of propyl, butyl, or pentyl.

28. The composition of claim 25, wherein $X$ is selected from the group consisting of hydrogen, chloride, bromide, and iodide.

29. The composition of claim 25, wherein $R_1$ is selected from the group consisting of $C_1$ – $C_3$ alkyl, $C_6$ aryl, $C_1$ – $C_3$ alkoxy, $C_1$ – $C_3$ thioethers, diphenyl thioether, nitro, nitrile, $C_1$ – $C_3$ ketone, $C_1$ – $C_3$ ester, dimethylamine, diethylamine, diphenylamine, $C_6$ aryloxy, and $C_6$ aryl having a substitution at the fourth carbon ring selected from nitro, nitrile, aldehyde, $C_1$ –
C₃ ketone, C₁ – C₃ ester, C₁ – C₃ alkyl, C₆ aryl, C₁ – C₃ alkoxy, C₁ – C₃ thioethers, diphenyl thioether, dimethylamine, diethylamine, diphenylamine, and C₆ aryloxy.

30. The composition of claim 29, wherein R₁ is selected from the group consisting of methyl, ethyl, propyl, and phenyl.

31. The composition of claim 25, wherein said composition has a formula selected from the group consisting of:
wherein $R_{10}$ is methyl or phenyl,

$R_{16}$ and $R_{17}$ are independently methyl or phenyl,

$R_{18}$ is selected from the group consisting of $C_1 - C_3$ alkyl, $C_6$ aryl, $C_1 - C_3$ alkoxy, $C_1 - C_3$ thioethers, diphenyl thioether, nitro, nitrile, $C_1 - C_3$ ketone, $C_1 - C_3$ ester, dimethylamine, diethylamine, diphenylamine, $C_6$ aryl, and $C_6$ aryloxy, and $C_6$ aryl having a substitution at the fourth carbon ring selected from nitro, nitrile, aldehyde, $C_1 - C_3$ ketone, $C_1 - C_3$ ester, $C_1 - C_3$ alkyl, $C_6$ aryl, $C_1 - C_3$ alkoxy, $C_1 - C_3$ thioethers, diphenyl thioether, dimethylamine, diethylamine, diphenylamine, and $C_6$ aryloxy.

$R_{20}$ is methyl, ethyl, or phenyl;
D is selected from the group consisting of ethylene, propylene, \( C_2 - C_{50} \) alkyl, styrene, or 1-methyl styrene;

B is selected from the group consisting of epoxy having the formula:

\[
\begin{align*}
\text{or } & \quad \begin{array}{c}
\text{acrylic,}
\end{array} \\
\text{methacryloxy having the formula:}
\end{align*}
\]

wherein \( R_{19} \) is H or CH\(_3\), and

\( R_{20} \) is selected from the group consisting of \( \text{CH}_3, \text{C}_2\text{H}_5, \text{and CH}_2\text{CH}_2\text{OH}, \)

and polyether having the formula:

\[
\begin{align*}
\text{wherein } j \text{ is an integer from } 2 - 20; \\
x \text{ is an integer from } 0 - 80, \\
y \text{ is an integer from } 0 - 80, \\
x + y \neq 0, \text{ and} \\
z \text{ is an integer from } 1 - 40. \\
k \text{ is an integer from } 3 - 40; \text{ and} \\
i + h + g = k, \text{ wherein } g \neq 0.
\end{align*}
\]
32. A polymeric composition comprising repeating units derived from the polymerizable composition of claim 25.

33. The polymeric composition of claim 32 comprising a block or graph copolymer.

34. The polymeric composition of claim 33 wherein said repeating unit has the formula:

\[ \text{Diagram of polymer structure} \]

wherein \( R_{11} \) is selected from the group consisting of methyl, ethyl, and phenyl;

\( R_{12}, R_{13}, R_{14}, \) and \( R_{15} \) are independently selected from the group consisting of H, C\(_1\) – C\(_6\) alkyl, C\(_6\) – C\(_8\) aryl, C\(_1\) – C\(_{10}\) heterocyclic, fluoro, C\(_1\) – C\(_6\) fluoroalkyl, acetate, acrylic, anhydride, and the like;

\( b \) is an integer from 10 to 200; and

\( c \) is an integer from 10 to 200.

35. A method of producing a functionalized silane or siloxane comprising the steps of:

(a) preparing a compound comprising an aldehyde moiety; and

(b) attaching said compound to said silane or siloxane via a hydrosilation reaction.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
<thead>
<tr>
<th>IPC(T)</th>
<th>US CL</th>
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<tbody>
<tr>
<td>C08F 283/12, C08G 77/06, 77/14, 77/442</td>
<td>525/474, 529/15,31,32</td>
</tr>
</tbody>
</table>

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S.: 525/474; 529/15,31,32

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Please See Continuation Sheet

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

- **X**: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **E**: document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- **L**: document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- **O**: document referring to an oral disclosure, use, exhibition or other means
- **P**: document published prior to the international filing date but later than the priority date claimed
- **&**: document member of the same patent family

[Box checked] Further documents are listed in the continuation of Box C. [Box checked] See patent family annex.

Date of the actual completion of the international search: 28 October 2005 (28.10.2005)

Date of mailing of the international search report: 1 DEC 2009

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