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(54) Title: CERTAIN SILICONE POLYETHERS, METHODS FOR MAKING THEM AND USES

(57) Abstract: There are disclosed silicone polyether compositions, methods for making them and their uses. The compositions are based on polyethers initiated by non-isomerizing alkenyl or alkynyl alcohols.



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**CERTAIN SILICONE POLYETHERS, METHODS
FOR MAKING THEM AND USES**

CROSS-REFERENCE

[0001] This application is a continuation-in-part of U.S. Patent Application Serial No.
10 09/756,440 filed January 8, 2001 currently pending.

FIELD OF THE INVENTION

[0002] This invention relates to certain novel silicone polyethers, and both methods for
making and uses for them. More particularly, the invention relates to silicone polyethers
15 based on novel polyethers initiated by certain non-isomerizing alkenyl or alkynyl alcohols,
methods for making these silicone polyethers by hydrosilation, and their uses in personal care
and other products.

BACKGROUND OF THE INVENTION

20 [0003] Silicone polyethers are used in many applications, notably as surfactants and in the
preparation of personal care products, polyurethanes and paint, ink and coating formulations.
They may be produced by hydrosilation of a polyether initiated by an aliphatically
unsaturated alcohol with a silicone having a SiH functionality. The polyether used may be
produced from various initiators and epoxides under the influence of a variety of catalysts.
25 Selection of the exact starting materials and routes utilized is important in determining the
properties of the final polymer with even small changes producing very dramatic differences
at times. The synthesis chosen for the polyether may be the most critical choice.

[0004] Bennett in U.S. Patent Nos. 3,957,843 and 4,059,605 describes silicone based
polyethers made using polyethers initiated by alkenyl alcohols. The polyethers were formed
30 with a KOH catalyst. Japanese application, JP8-208426, appears to make a similar disclosure.
Polymers such as these, especially those prepared from tertiary alcohols, are known to exhibit
high polydispersity and at least those with polyethers based on ethylene oxide will tend to be
waxes as opposed to liquids.

[0005] Alkynyl alcohol initiated polyethers are difficult if not impossible to make using a
35 basic catalyst as there tends to be decomposition of the product, and there is also the issue of
migration of the triple bond. Use of Lewis acids solves these problems to some extent, but
results in formation of large amounts of difficult to remove byproducts and cyclization of the

polyethers. An example in the art showing use of a Lewis acid catalyst in this context is U.S. Patent 3,644,535 to Batty et al., while U.S. Patent 5,066,756 to Raleigh et al. mentions use of acid and basic catalysts.

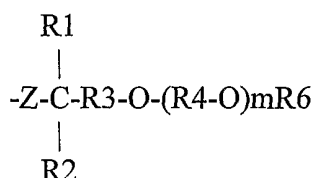
[0006] Use of metal cyanide type catalysts instead of conventional basic or Lewis acid catalysts may improve the situation. Use of cyanide and acid catalysts are described by Burkhart et al. in U.S. Patent No. 5,391,679 for certain specific situations; the silicone was attached to the alcohol first to form the initiator. A similar initiator is described by Watabe et al. in EP 0485637 along with a metal cyanide catalyst, as well as fluorinated polyethers. Jorgenson et al. in U.S. Patent Nos. 5,877,268 and 5,856,369 describe use of a metal cyanide catalyst focusing mostly on allyl and methallyl alcohol initiated polyethers; use of metal cyanide catalyst is criticized in some cases there, however.

[0007] Harper et al. in U.S. Patent No. 4,877,906 describes a method of removing metal cyanide catalysts from polyethers after their formation.

[0008] There is a need for new silicone based polyethers, perhaps especially those with multi-functionality and/or low polydispersity. This invention is directed to this need among others.

SUMMARY OF THE INVENTION

[0009] It is an object of the present invention to provide new silicone based polyethers. Thus, the invention relates to a silicone based polyether comprising a monovalent group, R, with R having an average formula:



wherein, Z is bonded to Si and -Z- is -CH₂CH₂- or -CH=CH-;

R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH₂CH₂-, or

R1 and R2 are independently H, halogen, NO₂, NH₂, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH=CH-, and regardless of choice of -Z-,

R1 and R2 may be independently aldehyde, keto or ester functional;

5 R3 is a divalent hydrocarbon group which may be substituted by one or more of halogen, NO₂, NH₂ or an amine group, or R3 is a nullity;

R4 is -CH(R5)-CH₂-, -CH₂-CH(R5)- or a combination of these;

10 R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when -Z- is -CH₂CH₂-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R4 groups per molecule;

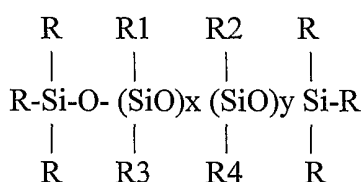
15 m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever -Z- is -CH₂CH₂- and the equivalent polydispersity of R is less than 1.4 or whenever R contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

R6 is H, an alkyl group or -C=O; and

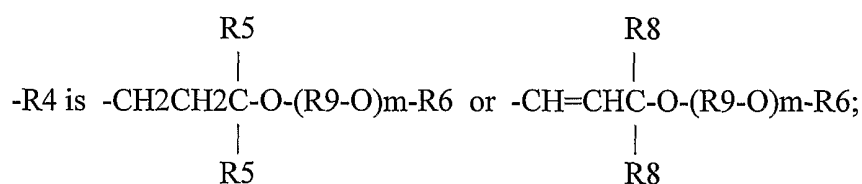


20 R7 is an alkyl group.

[0010] More specifically, the invention relates to a polymer of average formula:



wherein R, R1, R2 and R3 are independently alkyl groups having 30 carbons or less or phenyl;



x is 0 to 500;

y is 1 to 100;

m is 3 to 100;

R5 is an alkyl group;

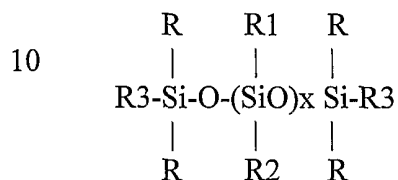
40 R6 is H, an alkyl group or C(O)R7;

R7 is an alkyl group;

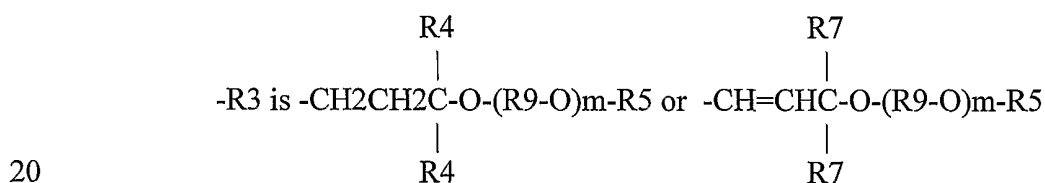
R8 is H or an alkyl group;

5 R9 is CH(R10)CH₂, CH₂CH(R10) or a combination of these;
 R10 is H, methyl, ethyl or phenyl; and
 the equivalent polydispersity of R4 is less than 1.4.

[0011] Similarly the invention relates to a polymer of average formula:



15 wherein R, R1 and R2 are independently alkyl groups having 30 carbons or less or phenyl;



x is 0 to 500;

m is 3 to 100;

R4 is an alkyl group;

25 R5 is H, alkyl or C(O)R6;

R6 is an alkyl group;

R7 is H or an alkyl group;

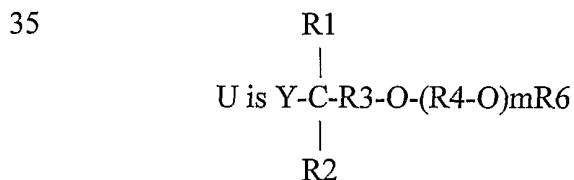
R9 is CH(R10)CH₂, CH₂CH(R10) or a combination of these;

R10 is H, methyl, ethyl or phenyl; and

30 the equivalent polydispersity of R3 is less than 1.4.

[0012] It is a further object of the present invention to provide a method for making these silicone based polyethers. Thus, the invention relates to a method for making a silicone based polyether, the method comprising:

hydrosilating U with a silicone containing an SiH group, where



wherein, Y- is CH₂=CH- or CH≡C-;

5 R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever Y- is CH₂=CH-, or

10 R1 and R2 are independently H, halogen, NO₂, NH₂, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever Y- is -CH≡C-, and regardless of choice of Y-,

R1 and R2 may be independently aldehyde, keto or ester functional;

R3 is a divalent hydrocarbon group which may be substituted by one or more of halogen, NO₂, NH₂ or an amine group, or R3 is a nullity;

15 R4 is -CH(R5)-CH₂-, -CH₂-CH(R5)- or a combination of these;

20 R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when Y- is CH₂=CH-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R4 groups per molecule;

m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever Y- is CH₂=CH- and the equivalent polydispersity of U is less than 1.4 or whenever U contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

25 R6 is H, an alkyl group or -C=O; and

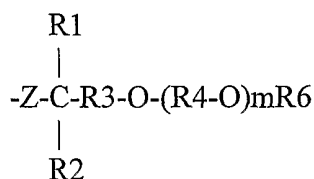


R7 is an alkyl group.

30 [0013] Another object of the present invention is to provide uses for subject silicone based polyethers. Thus, the invention further relates to methods for reducing surface tension. The present invention also relates to surfactants and paint, ink and coating formulations, personal care products for treating hair, skin and underarms, as well as polyurethane foams that contain the subject silicone based polyethers.

DETAILED DESCRIPTION OF THE INVENTION

35 [0014] The compositions according to the present invention include silicone based polyethers comprising a monovalent group, R, with R having an average formula:



wherein, Z is bonded to Si and -Z- is -CH₂CH₂- or -CH=CH-;

R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH₂CH₂-, or

R1 and R2 are independently H, halogen, NO₂, NH₂, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH=CH-, and regardless of choice of -Z-,

R1 and R2 may be independently aldehyde, keto or ester functional;

R3 is a divalent hydrocarbon group (such as aliphatic, including alkyl, alkenyl, alkynyl based whether linear or cyclic, aromatic or combinations thereof) which may be substituted by one or more of halogen, NO₂, NH₂ or an amine group, or R3 is a nullity;

R4 is -CH(R5)-CH₂-, -CH₂-CH(R5)- or a combination of these;

R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when -Z- is -CH₂CH₂-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R4 groups per molecule;

m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever -Z- is -CH₂CH₂- and the equivalent polydispersity of R is less than 1.4 or whenever R contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

R6 is H, an alkyl group or -C=O; and



R7 is an alkyl group.

[0015] In this specification and the claims that follow, no specific stereospecificity is intended in the depictions of any chemical structures, unless otherwise noted.

[0016] In this specification and the claims that follow "nullity" as in "R3 is a nullity" should be taken to mean that group referred to is absent. For example, if R3 is a nullity in -CH₂-R3-O-, then this structure is -CH₂-O-.

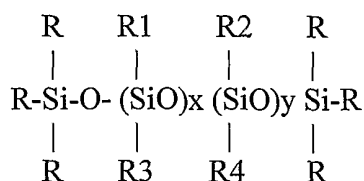
[0017] As used to describe chemical structures in this specification and claims that follow, "halogen" should be taken to mean a member of the group consisting of fluorine, chlorine, bromine, iodine and others of this series with chlorine and bromine being preferred. Similarly, "amine group" in this same context, should be taken to mean a monovalent group containing nitrogen bonded to at least one organic carbon such as -NHCH₃ or -CH₂-NH-CH₃.

[0018] Halogen and NO₂ containing polymers according to this invention may be desirable for themselves or because they may be converted to NH₂ containing polymers by methods such as simple exchange with ammonia or reduction, respectively. These functional groups along with aldehyde, keto and ester functionality can enhance the properties of the simpler polymers of this invention or provide reactive sites for various purposes. Even multifunctional polymers are possible and are often quite desirable in many applications.

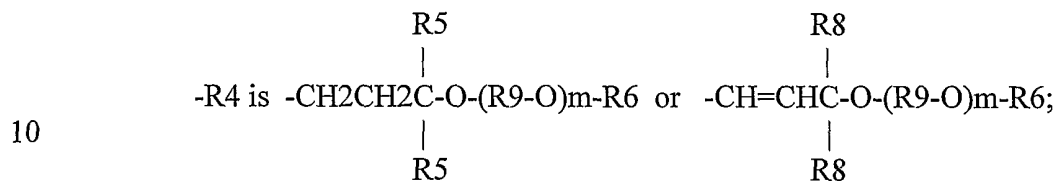
[0019] In applications such as personal care, it is often desirable that silicone based polyethers be fully liquid at "room temperature" (25 deg C and 760 mm Hg pressure) as even partial solidification can result in products that are unsightly messes. For this and other reasons, especially when the polyether portion of the polymer is derived to a large extent from ethylene oxide, lower molecular weight polymers are preferred. In most cases, this translates to an weight average molecular weight for the overall polymer to be less than 10,000 and the equivalent, weight average molecular weight for the polyether/initiator portion to be less than 700. By equivalent in this context is meant that this weight is based on the subject polymer side chains (polyether/initiator) as if they were separate molecules.

[0020] For similar quality control reasons, among others, it is desirable that the polydispersity of the overall polymers of the present invention not be very high. Practically speaking, this is usually determined by the polyether/initiator chains. Equivalent polydispersities of the these chains (determined as if these chains were separate molecules) should usually be less 1.6, preferably less than 1.4, more preferably less than 1.25 or less than 1.1 and most preferably less than 1.05 or lower (down to 1.0). These numerical ranges would apply to the polydispersity of the overall silicon based polyether as well.

[0021] Some embodiments of the compositions according to the present invention that are of great interest include polymers of average formula:



5 wherein R, R1, R2 and R3 are independently alkyl groups having 30 carbons or less or phenyl, preferably methyl;



x is 0 to 500;

y is 1 to 100;

15 m is 3 to 100;

R5 is an alkyl group, preferably methyl;

R6 is H, an alkyl group or C(O)R7;

R7 is an alkyl group;

R8 is H or an alkyl group, preferably methyl;

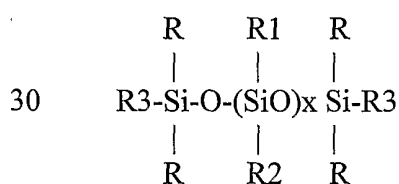
20 R9 is CH(R10)CH₂, CH₂CH(R10) or a combination of these;

R10 is H, methyl, ethyl or phenyl, preferably H; and

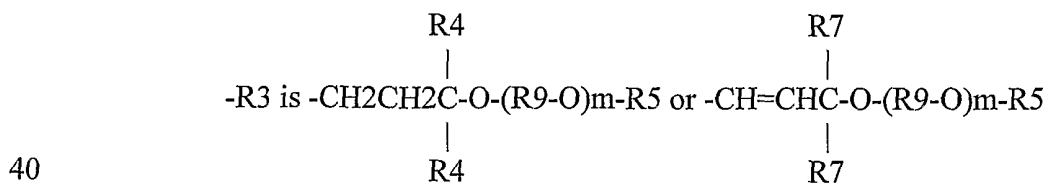
the equivalent polydispersity of R4 is less than 1.4.

[0022] In this embodiment, the structural units designated with x and y are not necessarily intended as being in blocks as might be implied. That is, these units may be in any order in the chain (except at the ends) as long as there are x and y of each, respectively, on average.

[0023] Other embodiments of the compositions according to the present invention that are of great interest include polymers of average formula:



35 wherein R, R1 and R2 are independently alkyl groups having 30 carbons or less or phenyl, preferably methyl;



x is 0 to 500;

m is 3 to 100;

R4 is an alkyl group, preferably methyl;

R5 is H, alkyl or C(O)R6;

R6 is an alkyl group;

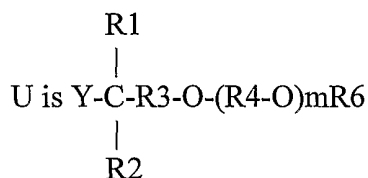
R7 is H or an alkyl group, preferably methyl;

R9 is CH(R10)CH2, CH2CH(R10) or a combination of these;

R10 is H, methyl, ethyl or phenyl, preferably H; and

the equivalent polydispersity of R3 is less than 1.4.

[0024] The methods according to the present invention include those for making silicone based polyethers, such methods including those comprising: hydrosilating U with a silicone containing an SiH group, where



wherein, Y- is CH2=CH- or CH≡C-;

R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO2, NH2 or an amine group whenever Y- is CH2=CH-, or

R1 and R2 are independently H, halogen, NO2, NH2, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO2, NH2 or an amine group whenever Y- is -CH≡C-, and regardless of choice of Y-,

R1 and R2 may be independently aldehyde, keto or ester functional;

R3 is a divalent hydrocarbon group (which may be particularly groups as defined for the corresponding invented compositions above) which may be substituted by one or more of halogen, NO2, NH2 or an amine group, or R3 is a nullity;

R4 is -CH(R5)-CH2-, -CH2-CH(R5)- or a combination of these;

R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when Y- is CH2=CH-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and

5 methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R₄ groups per molecule;

m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever Y- is CH₂=CH- and the equivalent polydispersity of U is less than 1.4 or whenever U contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

10 R₆ is H, an alkyl group or -C=O; and



R₇ is an alkyl group.

[0025] The hydrosilation reaction is well known in the art. It is usually carried out in the presence of a catalyst such as one based on platinum which are also well known in the art, some examples of which are described below.

[0026] As was explained for the equivalent polydispersity of the polyether/initiator side chains in the overall polymer according to the present invention, that for its (possible) precursor (referred to above as "U") correspondingly should usually be less than 1.6, preferably less than 1.4, more preferably less than 1.25 or less than 1.1 and most preferably less than 1.05 or lower (down to 1.0). This polydispersity should be understood to include impurities that are added along with U to the hydrosilation reaction mixture, but these ranges may apply to U alone.

[0027] It is preferred that U be of high purity for hydrosilation. U should be greater than 85 weight percent, preferably U should be greater than 92 weight percent and most preferably U should be greater than 96 weight percent of the material containing U added to the hydrosilation reaction mixture.

[0028] It is of note that the initiators for the polyethers used in making the polymers according to the present invention are, at least for the most part, alcohols that contain unsaturated groups that do not (at least usually do not) isomerize. This results in lower odor polymers as it is less likely that smelly products like propionaldehyde will form from them. It is also very efficient to use 1:1 stoichiometric ratios for polyether:silicone in the present hydrosilations in many cases, particularly when using polyethers at lower polydispersities.

[0029] These factors promote production of high purity silicone based polyethers (even directly without further or much further purification) which is very important in many applications such as personal care. It is possible to get products of much higher clarity which is of special concern especially in the case where polyethers with longer chains formed

5 mostly from ethylene oxide are concerned. Here, especially at higher polydispersity, higher molecular weight molecules can solidify, ruining clarity.

[0030] The polyether precursors of the silicone based polyethers of the present invention are believed to be novel and methods for their synthesis (including catalysts used) may be as well. Both are described, at least in part, in co-pending applications assigned or to be assigned to the Dow Chemical Company (and at least in some cases having some common inventors with the present application) and these and those derived from them are incorporated by reference to the extent possible and such that they do not contradict the disclosures herein and may be referred to as necessary to make the present disclosure enabling and the present claims enabled. These applications are:

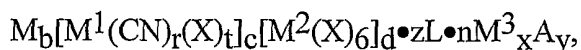
15 [0031] PCT/US00/18619, "Method for Fractionating Poly(ethylene oxide) Formed Using Metallic Cyanide Catalyst", filed July 7, 2000 and due to publish on or after January 9, 2001.

[0032] PCT/US00/18620, "Polymerization of Alkylene Oxides Using Metal Cyanide Catalysts and Unsaturated Initiator Compounds", filed July 7, 2000 and due to publish on or after January 9, 2001;

20 [0033] PCT/US00/18621, "Polymerization of Alkylene Oxides Onto Functionalized Initiators", filed July 7, 2000 and due to publish on or after January 9, 2001;

[0034] PCT/US00/18664, "Polymerization of Ethylene Oxide Using Metal Cyanide Catalysts", filed July 7, 2000 and due to publish on or after January 9, 2001.

[0035] Metal cyanide catalysts are suited for making the polyethers used to produce the silicone polyethers of the present invention as has been noted previously. This may be especially true when it is desired to have base sensitive groups in the polyether. One form of these catalysts (referred to in this specification and the claims that follow as "DMC catalyst") is:



30 wherein M is a metal ion that forms an insoluble precipitate with the $M^1(CN)_r(X)_t$ group and which has at least one water or organic solvent soluble salt;

M^1 and M^2 are transition metal ions that may be the same or different;

each X independently represents a group other than cyanide that coordinates with an M^1 or M^2 ion;

35 L represents an organic complexing agent;

5 $M^3_xA_y$ represents a water or organic solvent soluble salt of metal ion M^3 and anion A, wherein M^3 is the same as or different than M;
 b and c are positive numbers that together with d, reflect an electrostatically neutral complex;
 d is zero or a positive number;
 x and y are numbers that reflect an electrostatically neutral salt;
 10 r is from 4 to 6, t is from 0 to 2 and it is preferred that $r+t = 6$;
 z is zero or a positive number and n is a positive number indicating the relative quantities of the complexing agent L and of the metal salt, $M^3_xA_y$, respectively.

[0036] Some particular DMC catalysts of interest include:

zinc hexacyanocobaltate•zL•n $ZnCl_2$,

15 zinc hexacyanocobaltate•zL•n $LaCl_3$,

zinc hexacyanocobaltate•zL•n $CrCl_3$,

magnesium hexacyanocobaltate•zL•n $ZnCl_2$,

magnesium hexacyanocobaltate•zL•n $LaCl_3$, and

magnesium hexacyanocobaltate•zL•n $CrCl_3$,

20 where L is tertiary butanol, a polyether polyol, 1,2-dimethoxyethane or combinations thereof.

[0037] General methods to prepare these catalysts are well known in the art with specifics given in the PCT applications noted above.

[0038] These catalysts may be insoluble in nonpolar solvents like n-hexane, while the polyethers may be soluble, thus this can be useful in removing the catalyst from the polyether product. Other methods for catalyst removal have been previously described or noted.

[0039] Another method according to the present invention is a method to reduce the surface tension of a system comprising adding a silicone based polyether of the present invention to the system or a component or components used to produce the system.

[0040] Other compositions according to the present invention include those that are also manufactures that contain silicone based polyethers of the present invention. Examples of these manufactures include surfactants (which could be made solely of a silicone based polyether), personal care products such as treatments for hair, skin or underarms and paint, ink or coating formulations that contain these silicone polyethers, as well as polyurethane foams containing such polyethers as a stabilizer or otherwise.

5 [0041] Note that polydispersities given in the examples to follow were, and those referred to elsewhere may be, determined (while equivalents may be found based on corresponding polyethers or the like) by gel permeation chromatography ("GPC") using the following procedure.

10 [0042] Polydispersity was determined using GPC with a differential refractometer. Samples were prepared by dissolving them in tetrahydrofuran with analysis under the following conditions:

Column: PL-gel Mixed E

Eluent: tetrahydrofuran

Flow: 1 ml/min

15 Temperature: 40 deg C

Concentration: 0.25%

Injection volume: 150 microliters

Calibration: Polymer Laboratories Polyethylene Glycol Calibrants.

20 [0043] Note that in this disclosure and the claims that follow that "Me" in a chemical formula means "methyl" or "-CH₃", unless otherwise indicated.

EXAMPLES

[0044] Titles for the examples should not be taken as limiting in any way, but merely illustrative.

25 **Example 1** *An Alkynyl Alcohol Initiated Polyether*

30 [0045] A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (3.40 g) and 216.40 g of 2-methyl-3-butyne-2-ol are charged to a 2 gallon (7.57 liter) reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (100 g) is added. After one hour, feed of ethylene oxide is started and is fed for 2.5 hours. A total of 845 g ethylene oxide is added. The yield is 1000 g of a light yellow liquid which became opaque (white) upon standing overnight but remained fluid. GPC (gel permeation chromatography) analysis shows the product to have a number average molecular weight, " M_n ", of 445, and a polydispersity of 1.25. ¹³C NMR analysis showed that some starting material remains in the product.

5

Example 2 *Alkenyl Alcohol Initiated Polyethers*

[0046] (a) A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (6.0 g) and 271.87 g of 2-methyl-3-buten-2-ol are charged to a 2 gallon (7.57 liter) reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (135 g) is added. After thirty minutes, an additional 50 g of ethylene oxide is added. After another 90 minutes, another 50 g of ethylene oxide is added. About two hours after that, an ethylene oxide feed to the reactor is begun, starting at 1g/min and gradually increasing to 4 g/min and then decreasing to 3.5 g/min, until a total of 1105 g ethylene oxide has been added. The yield is 1260 g of a very light colored liquid which became opaque (white) upon standing overnight but remained fluid. GPC (gel permeation chromatography) analysis shows the product to have a number average molecular weight, " M_n ", of 380, with a main fraction at M_n 360 (polydispersity of 1.31) and a small fraction at M_n 1560 (polydispersity of 1.03). Overall polydispersity for the crude polyether is 1.37. C^{13} NMR analysis showed that some starting material remains in the product.

[0047] (b) A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (0.53 g) and 235.05 g of 2-methyl-3-buten-2-ol are homogenized and charged under nitrogen to a 2 gallon (7.57 liter) reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (about 50-150 g) is added. When the pressure in the reactor drops, indicating the start of polymerization, a feed of ethylene oxide is begun. The feed rate is varied until a constant reactor pressure is obtained. A total of 2165 g of ethylene oxide is added. As the reaction progresses, a vigorous exotherm develops. The product has a M_n of 940 via GPC and a polydispersity of approximately 1.1.

Example 3 *A Polyether with Halogenated Initiator*

[0048] A polyether may be prepared using the same general procedure as described in Example 1 with 1-chloro-2-methyl-3-butyne-2-ol as the initiator. (Corresponding substituted

5 or functionalized polyethers such as NO₂ and NH₂ containing or keto functionalized can be made similarly from corresponding initiators and a similar procedure.)

Example 4 A Silicone Based Polyether

10 [0049] 47.7 g of a polysiloxane hydride having the average structure Me₃Si(OSiMe₂)_{8.7}(OSiMeH)_{3.7}OSiMe₃ was combined with 104.6g of a polyethyleneoxide having the average structure H₂C=CHC(Me)₂(OCH₂CH₂)_{9.75}OH (having a polydispersity of about 1.2 as determined by GPC), 15g of isopropyl alcohol and 0.05g of potassium acetate. This mixture was heated to 89 deg C and enough chloroplatinic acid was added to give 8.9 ppm of platinum. Thereafter the mixture was heated between 89 and 103 deg C for 6 hours
15 during which time the system became clear. Analysis by FTIR (Fourier transform infrared spectroscopy) indicated that all of the SiH had reacted. The product was stripped to 150 deg C at a reduced pressure of 10 mm of Hg to give 147.1g of clear copolymer; refractive index was 1.4519.

20 **Example 5 A Silicone Based Polyether**

[0050] 29.9 g of (Me₃SiO)₂SiMeH was combined with 50.0 g of a polyethyleneoxide having the average structure HC≡CC(Me)₂(OCH₂CH₂)_{6.60}OH (having a polydispersity of about 1.2 as determined by GPC), 15 g of isopropyl alcohol and 0.05 g of sodium acetate. This mixture was warmed to 90 deg C and catalyzed with two drops of 4 weight percent
25 chloroplatinic acid. These conditions were maintained for about 9 hours during which SiH levels fell to about 12 ppm. The product was devolatilized to a condition of 105 deg C at a pressure of 5 mm Hg to give 74.1 g of copolymer; refractive index was 1.4480. Generation of a Gibb's Plot indicated a CMC (critical micelle concentration) of 4.64E-03 weight percent and a surface tension at CMC of 21.58 dynes/cm.

30 **Example 6 A Silicone Based Polyether**

[0051] 85 g of a polysiloxane hydride having the average structure HMe₂Si(OSiMe₂)₁₃OSiMe₂H was combined with 50 g of a polyethyleneoxide having the average structure
35 HC≡CC(Me)₂(OCH₂CH₂)_{6.60}OH (having a polydispersity of about 1.2 as determined by GPC), 0.05 g of sodium acetate and 34 g of isopropyl alcohol.

5 This mixture was heated to 83 deg C with enough chloroplatinic acid in isopropyl alcohol to give a level of 12 ppm of platinum metal. After 5 hours the level of SiH had been reduced to 7 ppm whereafter the product was devolatilized to a condition of 105 deg C and a pressure of 5 mm Hg giving 132 g of copolymer; refractive index was 1.4318.

10 **Example 7 A Silicone Based Polyether**

[0052] 23.3 g of $(\text{Me}_3\text{SiO})_2\text{SiMeH}$ was combined with 50.0 g of a polyethyleneoxide having the average structure $\text{H}_2\text{C}=\text{CHC}(\text{Me})_2(\text{OCH}_2\text{CH}_2)_{10.1}\text{OH}$ (having a polydispersity of about 1.2 as determined by GPC), 0.05 g of potassium acetate and 20 g of toluene. This mixture was heated to 85 deg C and catalyzed with enough 4 weight percent chloroplatinic acid to give a platinum level of 16 ppm. Temperatures of 85 deg C to 105 deg C were maintained for four hours. The copolymer was devolatilized at 100 deg C at a pressure of 5 mm Hg to give 70.1 g of product; refractive index was 1.4474. Generation of a Gibb's Plot indicated a CMC of $5.08\text{E}-03$ weight percent and a surface tension at CMC of 21.89 dynes/cm.

20 **Example 8 A Silicone Based Polyether**

[0053] 34.1 g of a polysiloxane hydride having the average structure $\text{Me}_3\text{Si}(\text{OSiMe}_2)_{8.7}(\text{OSiMeH})_{3.7}\text{OSiMe}_3$ was combined with 50.0 g of a polyethyleneoxide having the average structure $\text{HC}\equiv\text{CC}(\text{Me})_2(\text{OCH}_2\text{CH}_2)_{6.60}\text{OH}$ (having a polydispersity of about 1.2 as determined by GPC), 15 cm³ of toluene, 20 cm³ of isopropyl alcohol and 0.05g of potassium acetate. These were heated to 95 deg C with sufficient chloroplatinic acid to give 19 ppm platinum. After 6 hours of heating the product was devolatilized at 105 deg C at a pressure of 5 mm Hg to give 81.2 g of copolymer; index of refraction was 1.4520. Gibb's Plot data included a CMC of $1.36\text{E}-03$ weight percent and a surface tension at CMC of 24.24 dynes/cm.

30 **Example 9 A Silicone Based Polyether**

[0054] 64.0 g of a polysiloxane hydride having the average structure $\text{HMe}_2\text{Si}(\text{OSiMe}_2)_{13}\text{OSiMe}_2\text{H}$ was combined with 57.6 g of a polyethyleneoxide having the average structure $\text{H}_2\text{C}=\text{CHC}(\text{Me})_2(\text{OCH}_2\text{CH}_2)_{9.93}\text{OH}$ (having a polydispersity of about 1.2 as measured using GPC), 0.05 g of potassium acetate and 15 g of isopropyl alcohol. This

5 mixture was heated to 90 deg C and enough chloroplatinic acid was added to give a platinum level of 15 ppm. These conditions were maintained for 3 hours giving a clear copolymer which was devolatilized at 105 deg C at a pressure of 10 mm Hg to give 118.1g of product; index of refraction was 1.4355.

10 **Example 10** *A Silicone Based Polyether With Halogenated Initiator*

[0055] A silicone based polyether may be prepared using the general procedure of Example 4 with $\text{H}_2\text{C}=\text{CHC}(\text{CH}_2\text{Br})_2(\text{OCH}_2\text{CH}_2)_9.75\text{OH}$ as the starting polyether. (Corresponding substituted or functionalized silicone based polyethers such as NO_2 and NH_2 containing or keto functionalized can be made similarly from corresponding polyethers and a similar procedure.)

15 [0056] The terms “average structure” and “average formula” when used in this specification and the claims that follow should be understood to be number or equivalently molar averages, unless otherwise stated.

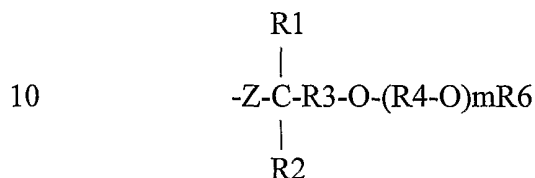
20 [0057] Ranges given in this specification and the claims that follow, whether numerical or otherwise, should be understood, unless otherwise stated, to specifically specify and disclose all elements subsumed in addition to the endpoints. For example, a disclosure of 1-3 should be understood to specifically disclose 1.4, 2, 2.6, and other numbers subsumed within the range, as well as 1 and 3; a disclosure of C1 to C3 alkyl should be understood to specifically disclose ethyl, as well as methyl and propyl. A disclosure of alkyl correspondingly discloses methyl, ethyl, propyl and the like specifically. “Up to” and “less than” should be taken to function as ranges for purposes of this definition, even though only one endpoint is explicitly given with the other (if any) taken from the context.

25 [0058] The specific embodiments of the present invention given previously are intended as illustrative and should not be interpreted as limiting the claims unless stated otherwise.

THAT WHICH IS CLAIMED IS:

5

1. A silicone based polyether comprising a monovalent group, R, with R having an average formula:



wherein, Z is bonded to Si and -Z- is -CH₂CH₂- or -CH=CH-;

15

R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH₂CH₂-, or

20

R1 and R2 are independently H, halogen, NO₂, NH₂, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever -Z- is -CH=CH-, and regardless of choice of -Z-,

R1 and R2 may be independently aldehyde, keto or ester functional;

R3 is a divalent hydrocarbon group which may be substituted by one or more of halogen, NO₂, NH₂ or an amine group, or R3 is a nullity;

25

R4 is -CH(R₅)-CH₂-, -CH₂-CH(R₅)- or a combination of these;

R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when -Z- is -CH₂CH₂-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R4 groups per molecule;

30

m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever -Z- is -CH₂CH₂- and the equivalent polydispersity of R is less than 1.4 or whenever R contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

35

5 R6 is H, an alkyl group or $-C=O$; and



R7 is an alkyl group.

10 2. The silicone based polyether according to claim 1, wherein -Z- is -
CH₂CH₂-.

3. The silicone based polyether according to claim 1, wherein -Z- is -CH=CH-.

15 4. The silicone based polyether according to claim 1, wherein at least one of
R1, R2 and R3 is chlorine or bromine, or chlorine or bromine substituted.

20 5. The silicone based polyether according to claim 1, wherein at least one of
R1, R2 and R3 is NO₂, NH₂, or an amine group or substituted with NO₂, NH₂ or an amine
group.

6. The silicone based polyether according to claim 1, wherein R5 is all H.

25 7. The silicone based polyether according to claim 1, wherein R5 is all ethyl or
all phenyl or solely a combination of ethyl and phenyl.

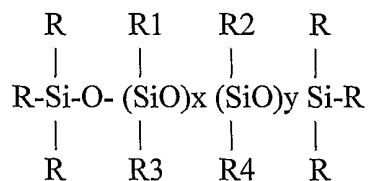
8. The silicone based polyether according to claim 1, wherein the weight
average molecular weight of the silicone based polyether is less than 10,000 and the weight
average equivalent weight of R is less than 700.

30 9. The silicone based polyether according to claim 1 that exists as a liquid at
25 deg C and 760 mm Hg pressure.

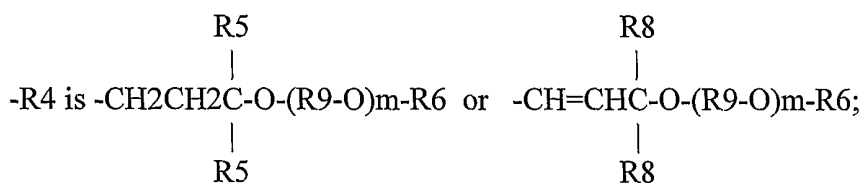
35 10. The silicone based polyether according to claim 1, wherein the equivalent
polydispersity of R is less than 1.4.

11. The silicone based polyether according to claim 1, wherein the equivalent
polydispersity of R is 1.25 or less.

12. A polymer of average formula:



wherein R, R1, R2 and R3 are independently alkyl groups having 30 carbons or less or phenyl;



x is 0 to 500;

y is 1 to 100;

m is 3 to 100;

R5 is an alkyl group;

R6 is H, an alkyl group or C(O)R7;

R7 is an alkyl group;

R8 is H or an alkyl group;

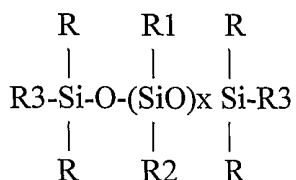
R9 is CH(R10)CH₂, CH₂CH(R10) or a combination of these;

R10 is H, methyl, ethyl or phenyl; and

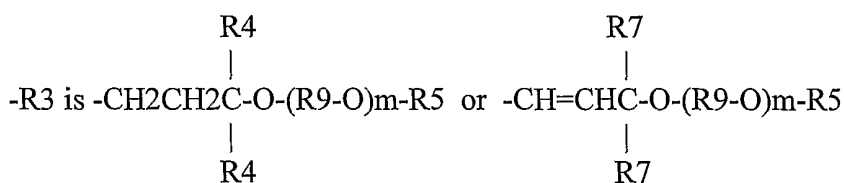
the equivalent polydispersity of R4 is less than 1.4.

13. The polymer composition according to claim 12, wherein R10 is H.

14. A polymer of average formula:



wherein R, R1 and R2 are independently alkyl groups having 30 carbons or less or phenyl;



x is 0 to 500;

m is 3 to 100;

R4 is an alkyl group;

R5 is H, alkyl or C(O)R6;

R6 is an alkyl group;

R7 is H or an alkyl group;

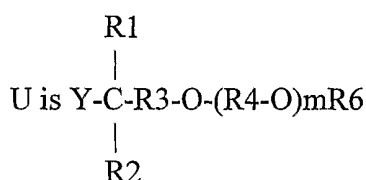
R9 is CH(R10)CH₂, CH₂CH(R10) or a combination of these;

R10 is H, methyl, ethyl or phenyl; and

the equivalent polydispersity of R3 is less than 1.4.

15. The polymer composition of claim 14, wherein R10 is H.

16. A method for making a silicone based polyether, the method comprising:
hydrosilating U with a silicone containing an SiH group, where



wherein, Y- is CH₂=CH- or CH≡C-;

R1 and R2 are independently alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever Y- is CH₂=CH-, or

R1 and R2 are independently H, halogen, NO₂, NH₂, an amine group, alkyl, phenyl, an alkyl substituted phenyl, a phenyl substituted alkyl, one of the four latter mentioned groups substituted or further substituted by one or more of halogen, NO₂, NH₂ or an amine group whenever Y- is CH≡C-, and regardless of choice of Y-,

R1 and R2 may be independently aldehyde, keto or ester functional;

5 R3 is a divalent hydrocarbon group which may be substituted by one or more of halogen, NO₂, NH₂ or an amine group, or R3 is a nullity;

R4 is -CH(R5)-CH₂-, -CH₂-CH(R5)- or a combination of these;

10 R5 is H, methyl, ethyl, phenyl or may vary among these within the same molecule in any proportion or order, with the proviso that when Y- is CH₂=CH-, R1 and R2 are free of halogen and nitrogen, and all R5 groups are solely some combination of H and methyl, then -CH₂CH₂- groups must make up on average at least 60 percent by weight of the total R4 groups per molecule;

15 m = 3 to 100 with the proviso that the range for m is expanded to 1 to 100 whenever Y- is CH₂=CH- and the equivalent polydispersity of U is less than 1.4 or whenever U contains halogen, NO₂, NH₂, an amine group, or is aldehyde, keto or ester functional;

R6 is H, an alkyl group or -C=O; and



R7 is an alkyl group.

20 17. The method of claim 16, wherein Y- is CH₂=CH-.

18. The method of claim 16, wherein Y- is CH≡C-.

25 19. The method of claim 16, wherein U contains chlorine, bromine, NO₂, NH₂ or an amine group.

20. The method of claim 16, wherein the polydispersity of U is less than 1.4.

30 21. The method of claim 16, wherein the polydispersity of U is less than 1.25.

22. The method of claim 16, wherein at least a portion of U employed was produced using a DMC catalyst.

35 23. A silicone based polyether produced by the method of claim 22.

5

24. A method to reduce the surface tension of a system comprising:
adding the silicone polyether of claim 10 to the system or a component or components, to be
used to produce the system.

10 25. A treatment for hair, skin or underarms comprising the silicone polyether
of claim 10.

26. A polyurethane foam comprising the silicone polyether of claim 10.

15 27. A surfactant or paint, ink or coating formulation comprising the silicone
polyether of claim 10.