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(54) Title: POLYSILOXANE BLOCK COPOLYMER AND METHOD FOR PRODUCING THE SAME

(57) Abstract: A polysiloxane block copolymer is disclosed. The polysiloxane block copolymer comprising: (i) a polysiloxane block; and (ii) a sulfur atom-containing organo block; wherein the polysiloxane block copolymer has at least two thiol (HS-) groups per molecule. The polysiloxane block copolymer can be used for a crosslinking agent for an ene-thiol reaction type curable silicone composition.

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POLYSILOXANE BLOCK COPOLYMER AND METHOD FOR PRODUCING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application claims priority to and all advantages of U.S. Provisional Patent Application No. 62/980,358 filed on 23 February 2020, the content of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a polysiloxane block copolymer comprising a polysiloxane block and a sulfur atom-containing organo block, and a method for producing the same.

DESCRIPTION OF THE RELATED ART

[0003] Thiol (HS-) group-containing organo compounds such as pentaerythritol tetrakis(3-mercaptobutyrate) and trimethylolpropane tris(3-mercaptopropionate), are frequently used for crosslinking agents for ene-thiol reaction type curable silicone compositions.

[0004] For example, Patent Document 1 discloses a photocurable silicone composition comprising: an alkenyl group-containing organopolysiloxane; a thiol group-containing organo compound such as trimethylolpropane tris(3-thiopropionate), pentaerythritol tetrakis(3-thiopropionate), and trihydroxyethyl triisocyanuric acid tris(3-thiopropionate); and a photoinitiator.

[0005] However, such a photocurable silicone composition has a problem that the thiol group-containing organo compound has poor compatibility to the organopolysiloxane, so that the photocurable silicone composition exhibits poor transparency.

[0006] Therefore, it is desired to develop a crosslinking agent for the ene-thiol reaction type curable silicone composition, which exhibits good compatibility to the organopolysiloxane in the composition.

[Patent Literature]

[0007] Patent Document 1: United States Patent Application Publication No. 2019/0112430 A1

SUMMARY OF THE INVENTION

[Technical Problem]

[0008] An object of the present invention is to provide a novel polysiloxane block copolymer comprising a polysiloxane block and a sulfur atom-containing organo block, which can be used as a crosslinking agent for an ene-thiol reaction type curable silicone composition. Another object of the present invention is to provide a method for producing the polysiloxane block copolymer.

[Solution to Problem]

[0009] The polysiloxane block copolymer of the present invention comprises:

(i) a polysiloxane block represented by the general formula: $(R^1{}_2SiO)_n$, wherein each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond; and "n" is a positive number of at least about 5; and

(ii) an organo block containing at least three sulfur atoms and free of silicon atom in a chemical structure thereof;

wherein the polysiloxane block (i) is bonded to the organo block (ii) via a linkage represented by the general formula: (Si)-R^2-(S), wherein Si is an atom in a chemical structure of the polysiloxane block (i); S is an atom in a chemical structure of the organo block (ii); and R^2 is a C_{2-6} alkylene group; and

wherein the polysiloxane block copolymer has at least two thiol (HS-) groups per molecule.

[0010] In various embodiments, the polysiloxane block (i) is at least one selected from a group consisting of a polysiloxane block represented by the following formula:

$$[(CH_3)_2SiO]_n$$

a polysiloxane block represented by the following formula:

$[(C_6H_5)_2SiO]_n$

a polysiloxane block represented by the following formula:

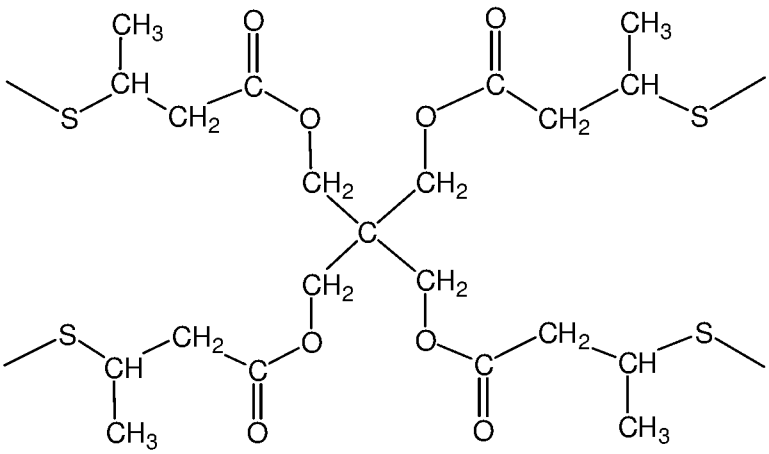
$[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}$

and a polysiloxane represented by the following formula:

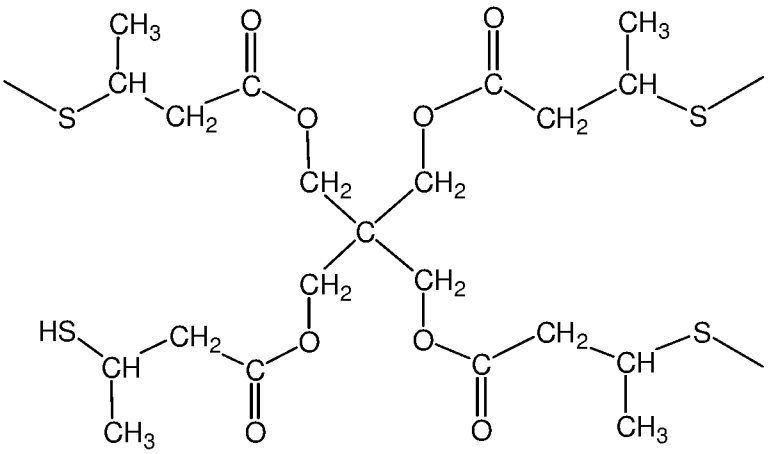
$[(CH_3)(C_6H_5)SiO]_n$

wherein each "n" is a positive number of at least about 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

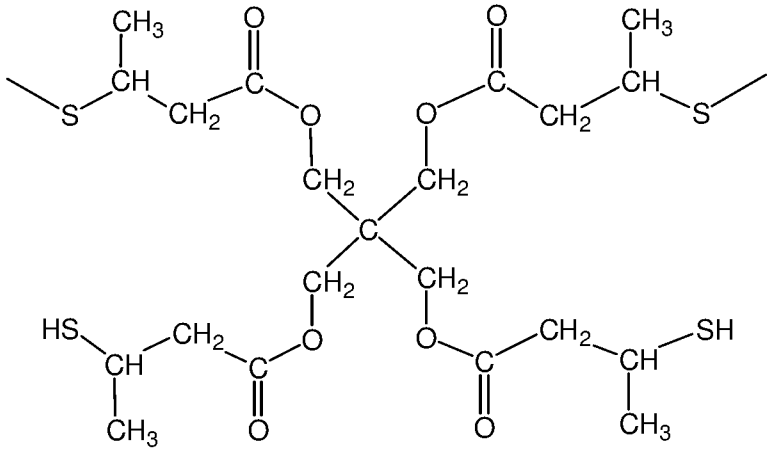
[0011] In various embodiments, the organo block (ii) is at least one selected form a group consisting of an organo block represented by the following formula:



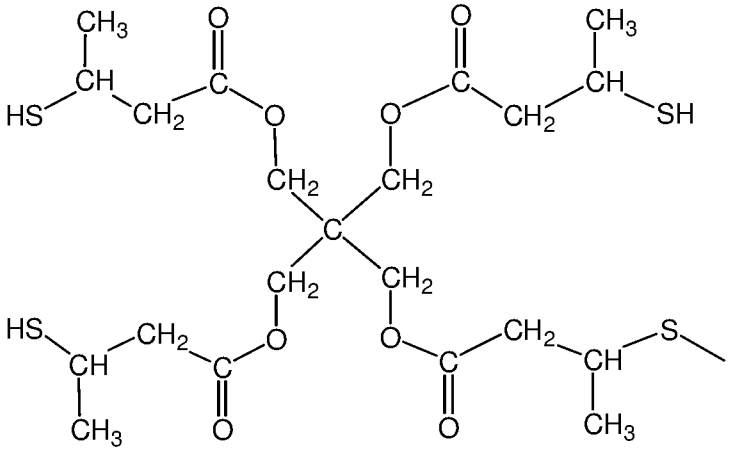
an organo block represented by the following formula:



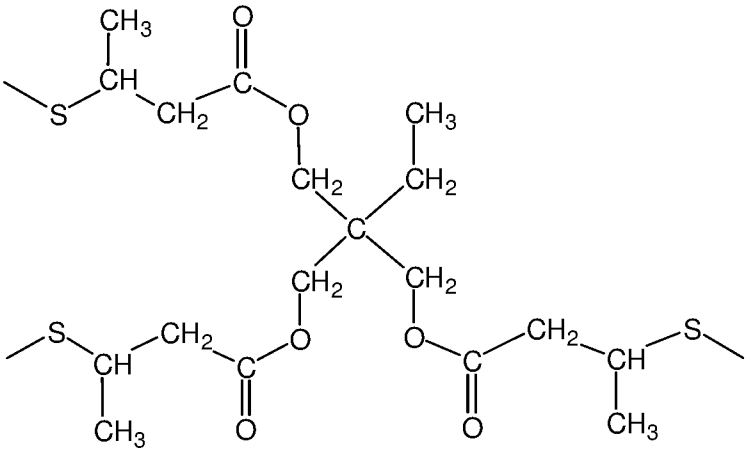
an organo block represented by the following formula:



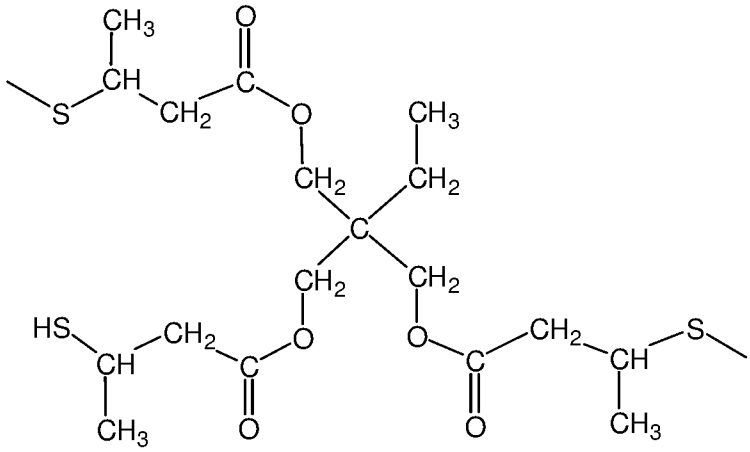
an organo block represented by the following formula:



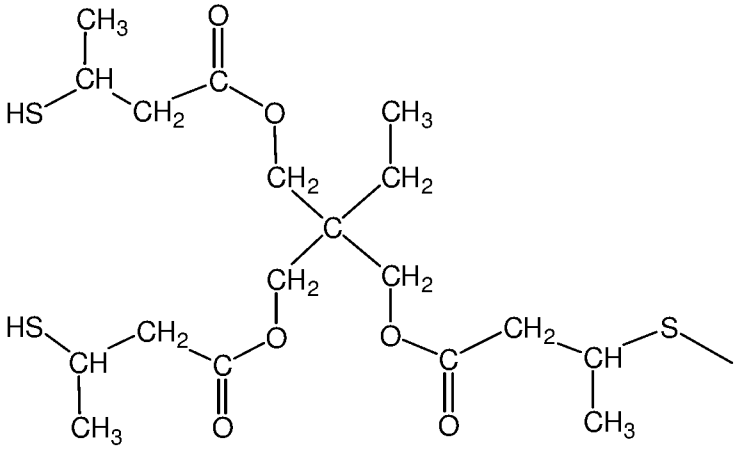
an organo block represented by the following formula:



an organo block represented by the following formula:



and an organo block represented by the following formula:



[0012] In various embodiments, the content of the polysiloxane block (i) is in a range of from about 60 to about 90 mass% of the sum of the polysiloxane block (i) and the organo block (ii).

[0013] The method for producing a polysiloxane block copolymer of the present invention, is characterized by reacting

(A) a polysiloxane represented by the general formula:

$$R^3(R^1{}_2SiO)_nSiR^1{}_2R^3$$

wherein each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond; each R^3 is independently a C_{2-6} alkenyl group; and "n" is a positive number of at least about 5; and

(B) an organo compound having at least three thiol groups per molecule;

in a presence of (C) a photoinitiator by irradiation with UV ray.

[0014] In various embodiments, the polysiloxane (A) is at least one selected from a group consisting of a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(C_6H_5)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(C_6H_5)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(C_6H_5)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}Si(CH_3)_2(CH=CH_2)$

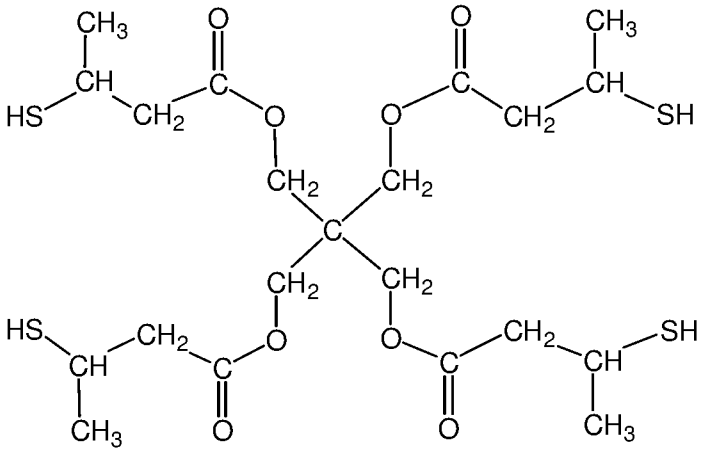
and a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)(C_6H_5)SiO]_nSi(CH_3)_2(CH=CH_2)$

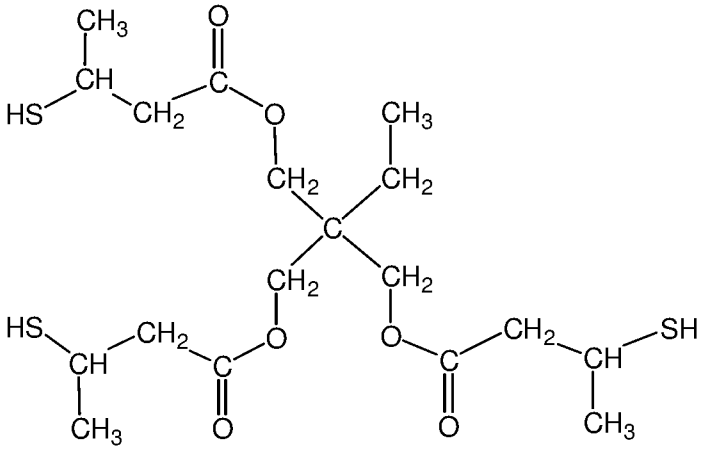
wherein each "n" is a positive number of at least about 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

[0015] In various embodiments, the polysiloxane (A) has a number average molecular weight of from about 500 to about 50,000 in accordance with a standard polystyrene basis by gel permeation chromatography.

[0016] In various embodiments, the organo compound (B) is at least one selected from a group consisting of an organo compound represented by the following formula:



and an organo compound represented by the following formula:



[0017] In various embodiments, the reaction amount of the organo compound (B) is in an amount such that the amount of the thiol groups provided by the present component is in a range of from about 2.0 to about 10.0 moles per 1 mole of the total alkenyl groups in the polysiloxane (A).

[Effects of Invention]

[0018] The polysiloxane block copolymer of the present invention is a novel copolymer and can be used as a crosslinking agent for an ene-thiol reaction type-curable silicone composition. The method of the present invention can produce the novel siloxane block copolymer efficiently.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The terms “comprising” or “comprise” are used herein in their broadest sense to mean and encompass the notions of “including,” “include,” “consist(ing) essentially of,” and “consist(ing)

of. The use of “for example,” “e.g.,” “such as,” and “including” to list illustrative examples does not limit to only the listed examples. Thus, “for example” or “such as” means “for example, but not limited to” or “such as, but not limited to” and encompasses other similar or equivalent examples. The term “about” as used herein serves to reasonably encompass or describe minor variations in numerical values measured by instrumental analysis or as a result of sample handling. Such minor variations may be in the order of ±0-25, ±0-10, ±0-5, or ±0-2.5, % of the numerical values. Further, the term “about” applies to both numerical values when associated with a range of values. Moreover, the term “about” may apply to numerical values even when not explicitly stated.

[0020] Generally, as used herein a hyphen “-” or dash “–” in a range of values is “to” or “through”; a “>” is “above” or “greater-than”; a “≥” is “at least” or “greater-than or equal to”; a “<” is “below” or “less-than”; and a “≤” is “at most” or “less-than or equal to.” On an individual basis, each of the aforementioned applications for patent, patents, and/or patent application publications, is expressly incorporated herein by reference in its entirety in one or more non-limiting embodiments.

[0021] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[0022] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range "of from 0.1 to 0.9" may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of "at least 10" inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range "of from 1 to 9" includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0023] The terms "polysiloxane block copolymer" used herein are designed to mean reaction products of a polysiloxane and an organo compound which does not have a siloxane unit, or

compositions essentially consisting of the reaction products. The polysiloxane block copolymer is generally formed having linear and/or three-dimensional units, typically formed via ene-thiol reactions.

<Polysiloxane block copolymer>

[0024] The polysiloxane block copolymer of the present invention comprises: (i) a polysiloxane block and (ii) an organo block. The polysiloxane block (i) is represented by the general formula: $(R^1{}_2SiO)_n$.

[0025] In the formula, each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond. Examples of the monovalent hydrocarbon groups for R^1 include C_{1-12} alkyl groups such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, and dodecyl groups; C_{6-12} aryl groups such as phenyl groups, tolyl groups, xylyl groups, and naphthyl groups; C_{7-12} aralkyl groups such as benzyl groups, and phenethyl groups; and groups in which some or all of the hydrogen atoms bonded in these groups are substituted with halogen atoms, such as a chlorine atom, a fluorine atom, and a bromine atom.

[0026] In the formula, "n" is a positive number of at least about 5, preferably at least about 10. This is because, when "n" is greater than or equal to the lower limit described above, compatibility of the polysiloxane block copolymer to organopolysiloxanes can increase.

[0027] The polysiloxane block (i) is not limited, but is preferably at least one selected from a group consisting of a polysiloxane block represented by the following formula:

$$[(CH_3)_2SiO]_n$$

a polysiloxane block represented by the following formula:

$$[(C_6H_5)_2SiO]_n$$

a polysiloxane block represented by the following formula:

$$[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}$$

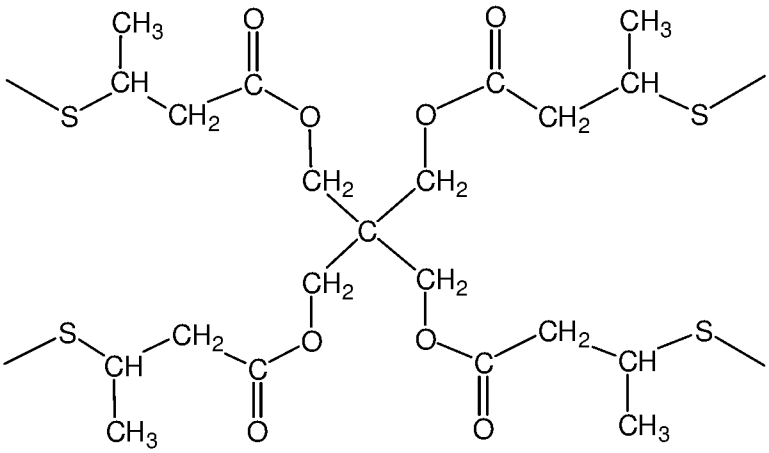
and a polysiloxane represented by the following formula:

$$[(CH_3)(C_6H_5)SiO]_n$$

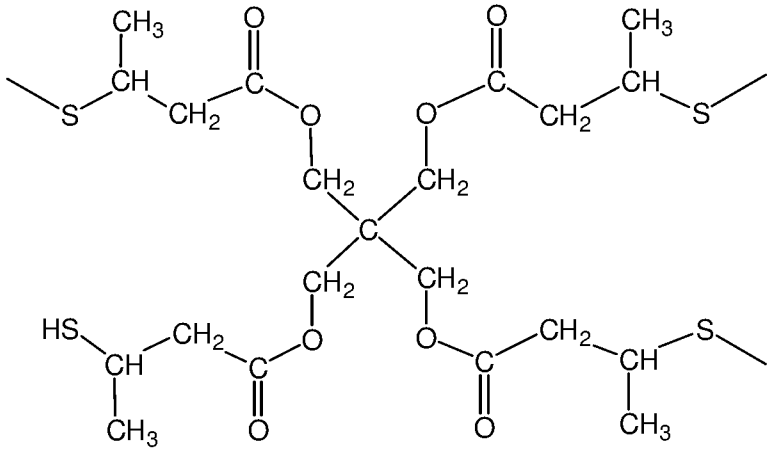
wherein each "n" is a positive number of at least 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

[0028] The polysiloxane block (i) essentially comprises the polysiloxane block represented by the general formula: $(R^1{}_2SiO)_n$, but it may comprise other siloxane units such as $R^1{}_3SiO_{1/2}$, $R^1SiO_{3/2}$, and $SiO_{4/2}$.

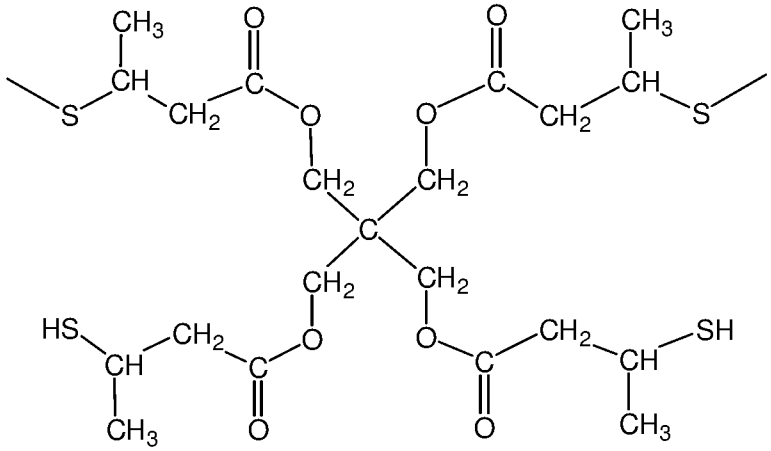
[0029] The organo block (ii) contains at least three sulfur atoms and is free of silicon (Si) atom in a chemical structure thereof. The organo block (ii) is not limited, but it is preferably at least one selected form a group consisting of an organo block represented by the following formula:



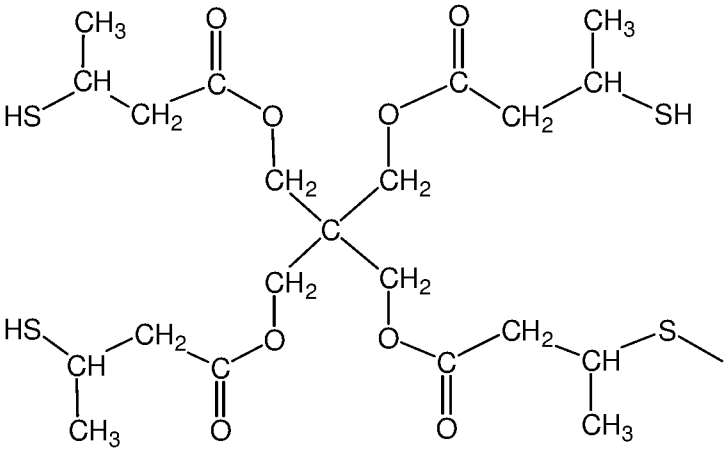
an organo block represented by the following formula:



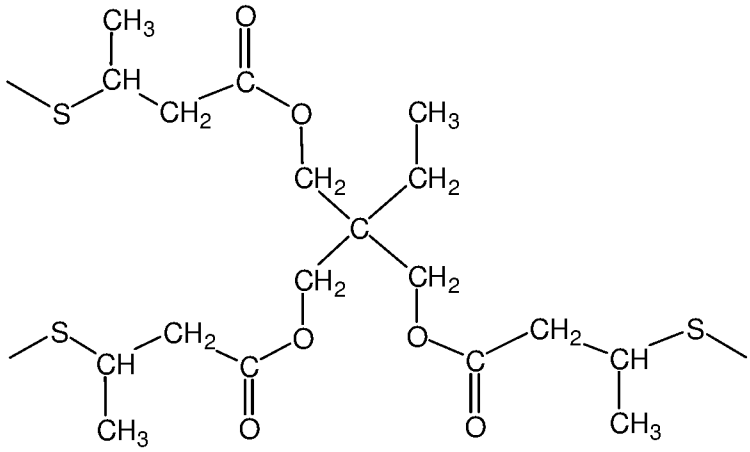
an organo block represented by the following formula:



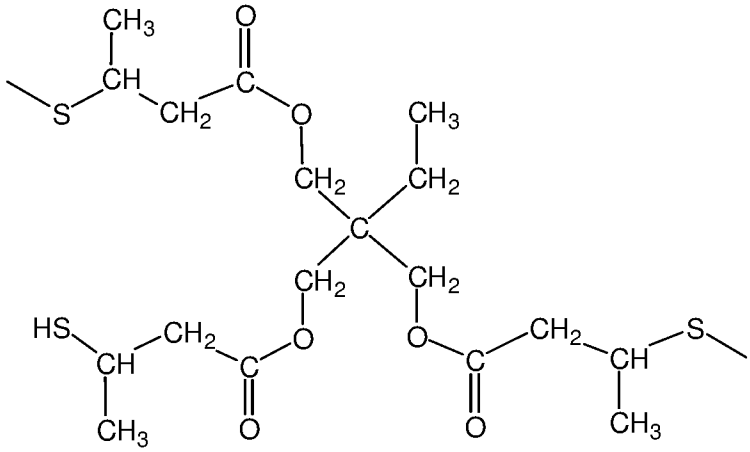
an organo block represented by the following formula:



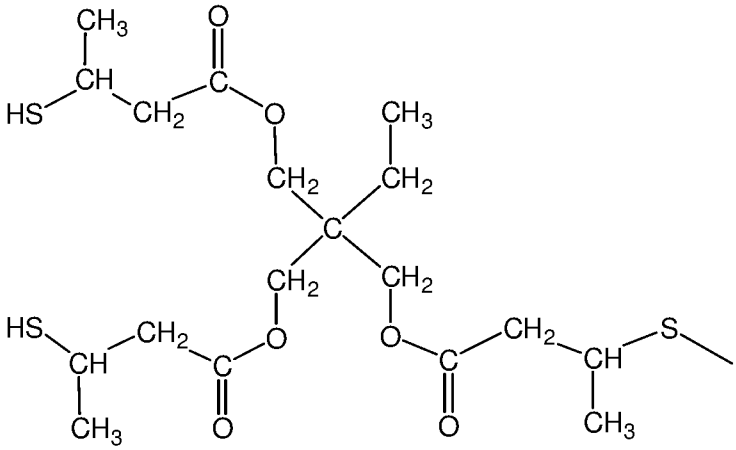
an organo block represented by the following formula:



an organo block represented by the following formula:



and an organo block represented by the following formula:



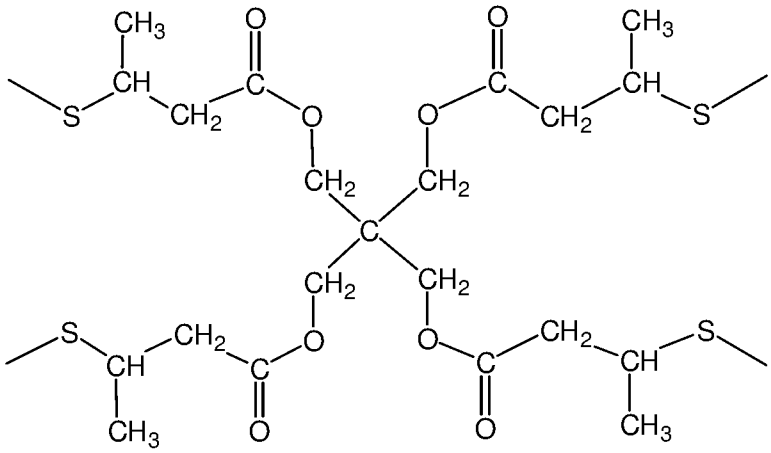
[0030] The polysiloxane block (i) is bonded to the organo block (ii) via a linkage represented by the general formula: (Si)-R^2-(S).

[0031] In the formula, Si is an atom in a chemical structure of the polysiloxane block (i) and S is an atom in a chemical structure of the organo block (ii).

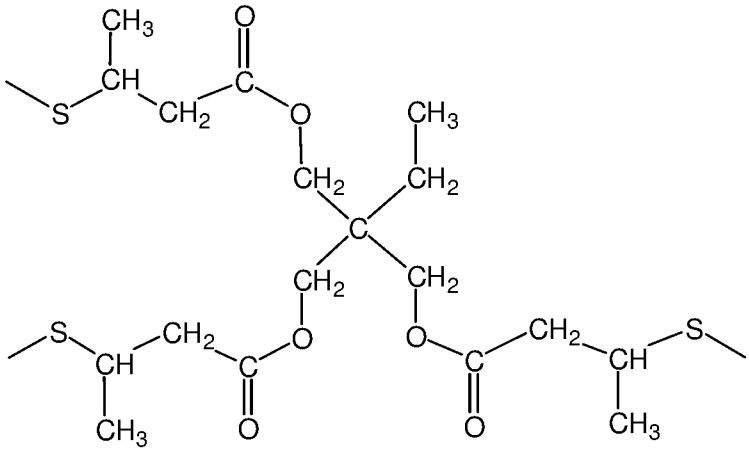
[0032] In the formula, R^2 is a C_{2-6} alkylene group. Examples of the alkenyl group include vinyl groups, allyl groups, butenyl groups, pentenyl groups, heptenyl groups, and hexenyl groups.

[0033] The content of the polysiloxane block (i) is not limited, but it is preferably in a range of from about 60 to about 90 mass% of the sum of the polysiloxane block (i) and the organo block (ii).

[0034] The polysiloxane block copolymer has at least two thiol (HS-) groups per molecule, so that it can be used as a crosslinking agent for an ene-thiol reaction type curable silicone composition. The bonding positions of the thiol groups in the polysiloxane block copolymer are not particularly limited, and examples thereof include a position in the organo block (ii) other than the organo block represented by the following formula:



and the organo block represented by the following formula:



[0035] The number average molecular weight (Mn) of the polysiloxane block copolymer on a standard polystyrene basis by gel permeation chromatography is not limited, but it is preferably in the range from about 3,000 to about 50,000, alternatively in the range from about 4,000 to about 10,000. This is because, when the molecular weight of the polysiloxane block copolymer is within the range described above, the resulting silicone block copolymer can promote to form a cured product having excellent tensile strength and low modulus.

<Method of producing a polysiloxane block copolymer>

[0036] The method of the present invention is characterized by reacting

(A) a polysiloxane represented by the general formula:

$$R^3(R^1{}_2SiO)_nSiR^1{}_2R^3$$

wherein each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond; each R^3 is independently a C_{2-6} alkenyl group; and "n" is a positive number of at least about 5; and

(B) an organo compound having at least three thiol groups per molecule;

in a presence of a photoinitiator by irradiation with UV ray.

[0037] The polysiloxane (A) is not limited, but is preferably at least one selected from a group consisting of a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a group consisting of a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(C_6H_5)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(C_6H_5)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(C_6H_5)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}Si(CH_3)_2(CH=CH_2)$

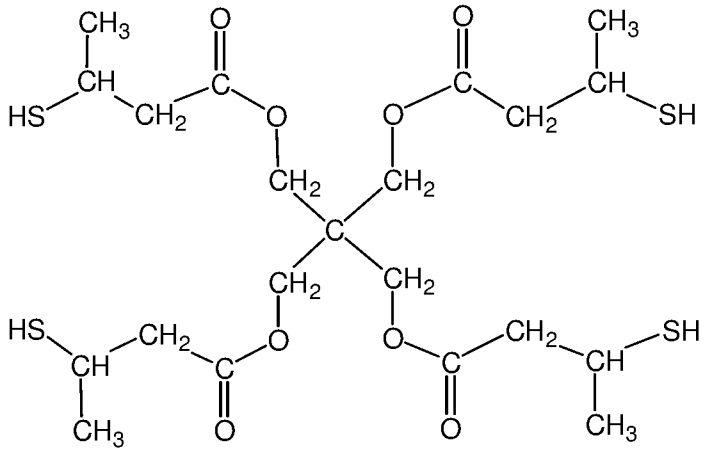
and a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)(C_6H_5)SiO]_nSi(CH_3)_2(CH=CH_2)$

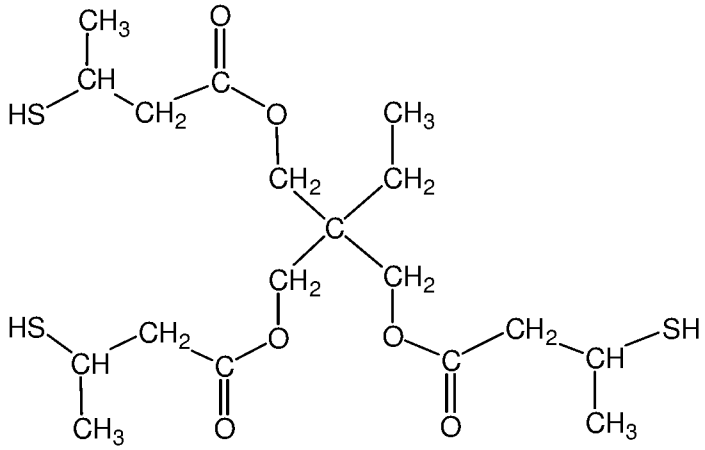
wherein each "n" is a positive number of at least about 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

[0038] The polysiloxane (A) preferably has a number average molecular weight of about 500 from about 50,000 in accordance with a standard polystyrene basis by gel permeation chromatography.

[0039] The organo compound (B) is not limited as long as an organo component has at least three thiol groups in a molecule, but it is preferably at least one selected from a group consisting of an organo compound represented by the following formula:



and an organo compound represented by the following formula:



[0040] The reaction amount of the organo compound (B) is not limited but it is preferably in an amount such that the amount of the thiol groups provided by the present component is in a range of from about 2.0 to about 10.0 moles, alternatively in a range of from about 2.5 to about 10.0 moles, or alternatively in a range of from about 2.5 to about 8.0 moles, per 1 mole of the total alkenyl groups in the polysiloxane (A). This is because, when the reaction amount of the organo compound (B) is within the range described above, transparency of the resulting polysiloxane block copolymer increases.

[0041] The reaction is initiated in a presence of (C) a photoinitiator by irradiation with UV ray. The photoinitiator is not limited. Examples of the photoinitiator (C) include phenone type photoinitiators such as 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651: manufactured by BASF), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (DAROCUR 1173: manufactured by

BASF), 1-hydroxy-cyclohexyl-phenyl-ketone (IRGACURE 184: manufactured by BASF), 1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-1-propan-1-one (IRGACURE 2959: manufactured by BASF), 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl) benzyl]-phenyl}-2-methyl-propan-1-one (IRGACURE 127: manufactured by BASF), 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one (IRGACURE 907: manufactured by BASF), 2-benzyl-2-dimethylamino-(4-morpholinophenyl)-butanone-1 (IRGACURE 369: manufactured by BASF), and 2-(dimethylamino)-2-[(4-methylphenyl) methyl]-1-[4-(4-morpholinyl) phenyl]-1-butanone (IRGACURE 379: manufactured by BASF); phosphine type photoinitiators such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, manufactured by BASF), ethyl(2,4,6-trimethylbenzoyl)phenyl phosphonate (TPO-L, manufactured by BASF), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (IRGACURE 819, manufactured by BASF); oxime ester type photoinitiators such as 1,2-octanedione, 1-[4-(phenylthio)-, 2-(O-benzoyl oxime)] (IRGACURE OXE 01: manufactured by BASF), and ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime) (IRGACURE OXE 02: manufactured by BASF AG); oxyphenylacetic acid type photoinitiators such as oxyphenylacetic acid, 2-[2-oxo-2-phenylacetoxyethoxy] ethyl ester and oxyphenylacetic acid, a mixture of 2-(2-hydroxyethoxy) ethyl ester (IRGACURE 754: manufactured by BASF); phenylglyoxylate type photoinitiators such as phenylglyoxylic acid methyl ester (DAROCUR MBF: manufactured by BASF); benzoate type photoinitiators such as ethyl-4-dimethylaminobenzoate (DAROCUR EDB: manufactured by BASF), and 2-ethylhexyl-4-dimethylaminobenzoate (DAROCUR EHA: manufactured by BASF); and organic peroxide type photoinitiators such as benzoyl peroxide and cumene hydroperoxide. Among them, 1-hydroxy-cyclohexyl-phenyl-ketone (IRGACURE 184: manufactured by BASF), 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651: manufactured by BASF), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (DAROCUR 1173: manufactured by BASF), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (IRGACURE 819, manufactured by BASF), and ethyl(2,4,6-

trimethylbenzoyl)phenyl phosphonate (TPO-L, manufactured by BASF) are preferred. The photoinitiator (C) may be used alone or in combination of two or more.

[0042] The content of the photoinitiator (C) is not limited, but it is preferably in a range of from about 0.001 to about 1 mass%, alternatively in a range of from about 0.005 to about 0.1 mass%, or alternatively in a range of from about 0.005 to about 0.1 mass%, of the total of the polysiloxane (A), the organo compound and the photoinitiator.

[0043] The reaction is conducted by ultraviolet irradiation. For example, low pressure, high pressure or ultrahigh pressure mercury lamp, metal halide lamp, (pulse) xenon lamp, or an electrodeless lamp is useful as an UV lamp. Irradiation dose is preferably in a range of from 2,000 to 10,000 mJ/cm^2, alternatively in a range of from 3,000 to 6,000 mJ/cm^2.

[Examples]

[0044] The polysiloxane block copolymer and the method for producing the same of the present invention will now be described using Practical Examples and Comparative Examples. The characteristics of the polysiloxane block copolymer were measured as follows.

<Refractive index>

[0045] Using an Abbe refractometer (wavelength of light source: 589 nm), the refractive index at 25°C was measured.

<Viscosity>

[0046] Viscosity at 23 ± 2 °C was measured by using a type B viscometer (Brookfield HA Type Rotational Viscometer with using Spindle #52 at 0.5 or 5 rpm) according to ASTM D 1084 “Standard Test Methods for Viscosity of Adhesive”.

<Number average molecular weight (Mn)>

[0047] A number average molecular weight (Mn) of the polysiloxane block copolymer was measured by using a gel permeation chromatography and it was converted into a number

average molecular weight of a standard polystyrene.

<Appearance>

[0048] Appearance of the polysiloxane block copolymer at 25°C was observed by visual inspection.

<Practical Examples 1-11 and Comparative Examples 1-5>

[0049] A round bottom flask fitted with a polytetrafluoroethylene (PTFE) stirrer was loaded with a polysiloxane (A), an organo compound (B) and a photoinitiator (C) in a mass% described in Table 1. The mixture was subjected to irradiation with Ultraviolet light at a UV illuminance of 5,000 mJ/cm^2. After irradiation, a reaction mixture was analyzed by an infrared spectrophotometer, and ^{13}C-nuclear magnetic resonance spectrum analysis. Absence of the vinyl groups in the reaction mixture was confirmed using the infrared spectrophotometer. And formation of C-S-C in the reaction mixture was confirmed using the ^{13}C-nuclear magnetic resonance spectrum analysis. As a result of NMR analysis, it was found that the reaction mixture was a polysiloxane block copolymer comprising the polysiloxane block and the organo compound block, and having at least two thiol groups per molecule. The results are given in Table 1. The SH/Vi ratio in Table 1 indicates the ratio of the number of moles of thiol (HS-) groups in the organo compound (B) per 1 mole of the vinyl group in the polysiloxane (A).

[0050] The following polysiloxanes were used as polysiloxane (A).

(a1): a dimethylpolysiloxane having a number average molecular weight of 3600 and refractive index of 1.41, and represented by the following formula:

$$(CH_3)_2(CH_2{=}CH)SiO[(CH_3)_2SiO]_{46}Si(CH_3)_2(CH{=}CH_2)$$

(a2): a dimethylpolysiloxane having a number average molecular weight of 1330 and refractive index of 1.46, and represented by the following formula:

$$(C_6H_5)_2(CH_2{=}CH)SiO[(CH_3)_2SiO]_{12}Si(C_6H_5)_2(CH{=}CH_2)$$

(a3): a copolymer of dimethylsiloxane and diphenylsiloxane having a number average molecular weight of 15040 and refractive index of 1.48, and represented by the following formula:

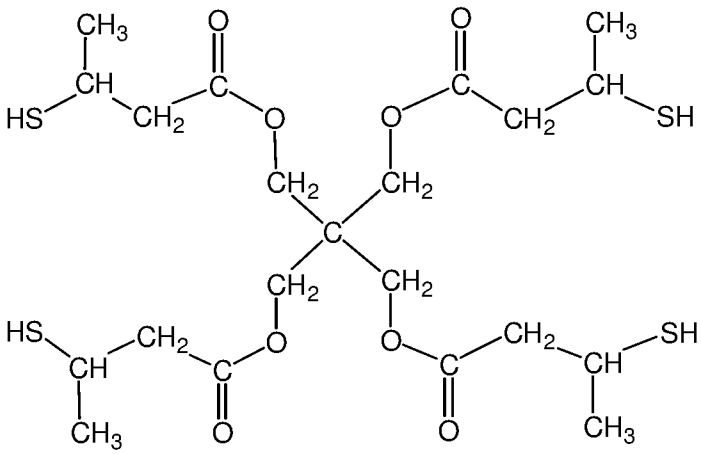
$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_{120}[(C_6H_5)_2SiO]_{30}Si(CH_3)_2(CH=CH_2)$

(a4): a methylphenylpolysiloxane having a number average molecular weight of 3590 and refractive index of 1.53, and represented by the following formula:

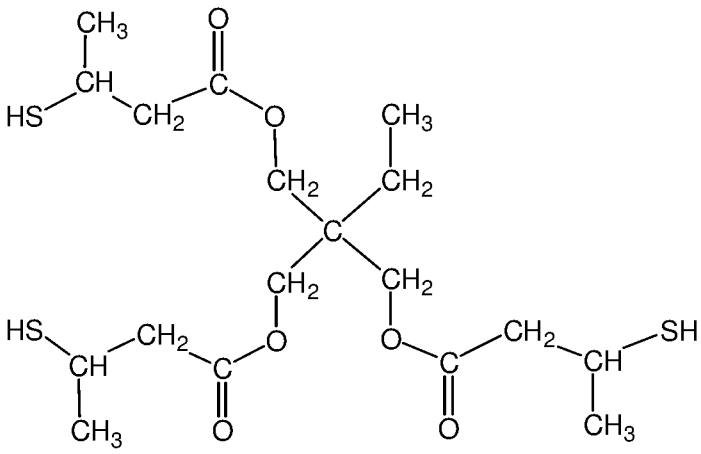
$(CH_3)_2(CH_2=CH)SiO[(CH_3)(C_6H_5)SiO]_{25}Si(CH_3)_2(CH=CH_2)$

[0051] The following organo compounds were used as organo compound (B).

(b1): pentaerythritol tetrakis(3-mercaptobutyrate) having a molecular weight of 545, refractive index of 1.52, and represented by the following formula:



(b2): trimethylolpropane tris(3-mercaptopropionate) having a molecular weight of 399, refractive index of 1.52, and represented by the following formula:



[0052] The following photoinitiators were used as photoinitiator (C).

(c1): 1-hydroxy-cyclohexyl-phenyl-ketone

(c2): 2,2-dimethoxy-1,2-diphenylethan-1-one

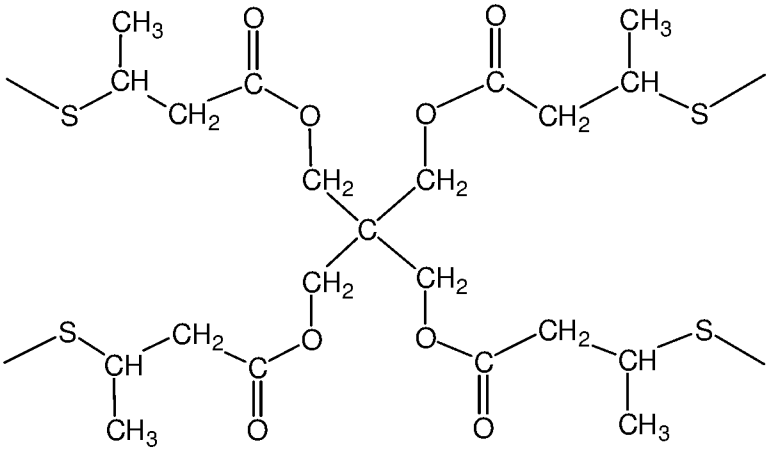
(c3): 2-hydroxy-2-methyl-1-phenyl-propan-1-one

(c4): phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

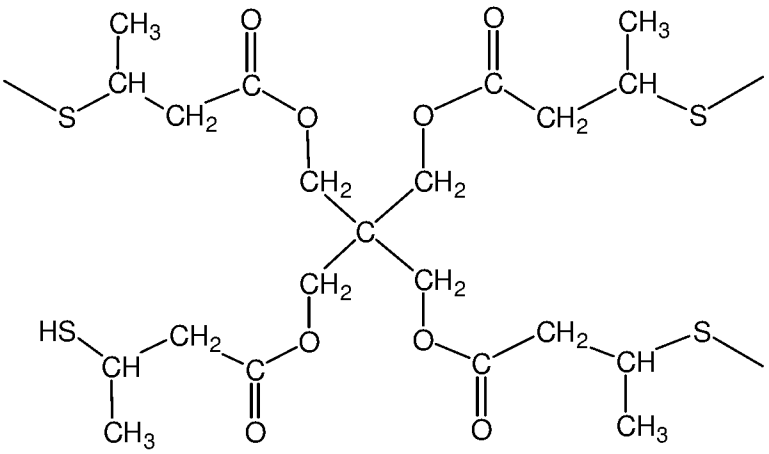
(c5): ethyl(2,4,6-trimethylbenzoyl)phenyl phosphonate

[0053] In Table 1, D, D^{Ph}, and D^{Ph2} stands for $(CH_3)_2SiO$ unit, $(CH_3)(C_6H_5)SiO$ unit, and $(C_6H_5)_2SiO$ unit, respectively.

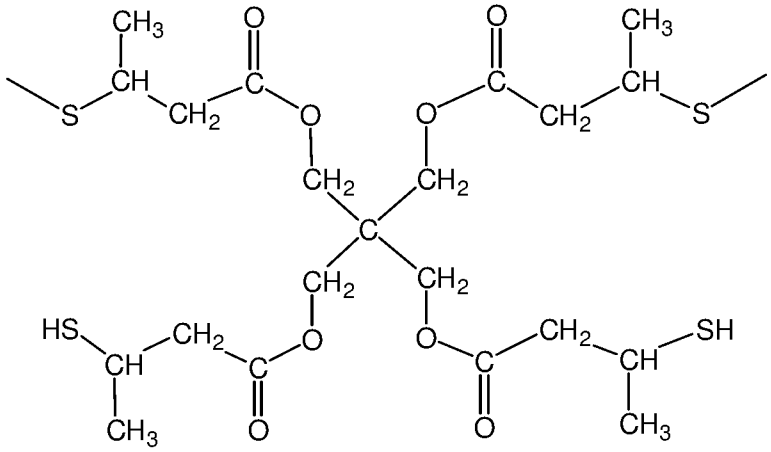
[0054] In Table 1, PE stands for a mixture of an organo block represented by the following formula:



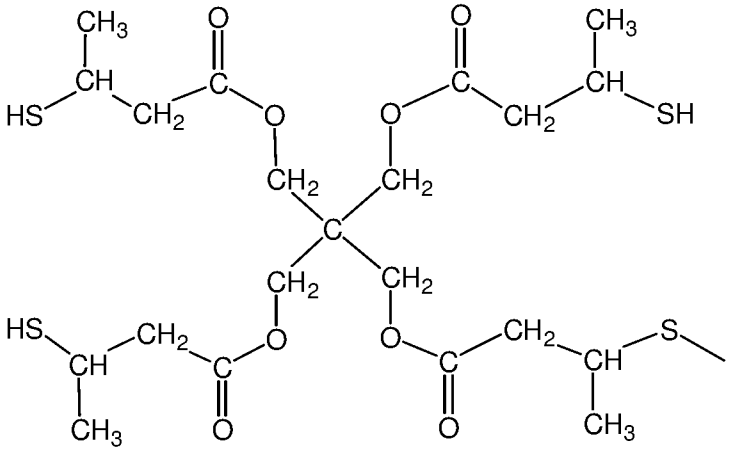
an organo block represented by the following formula:



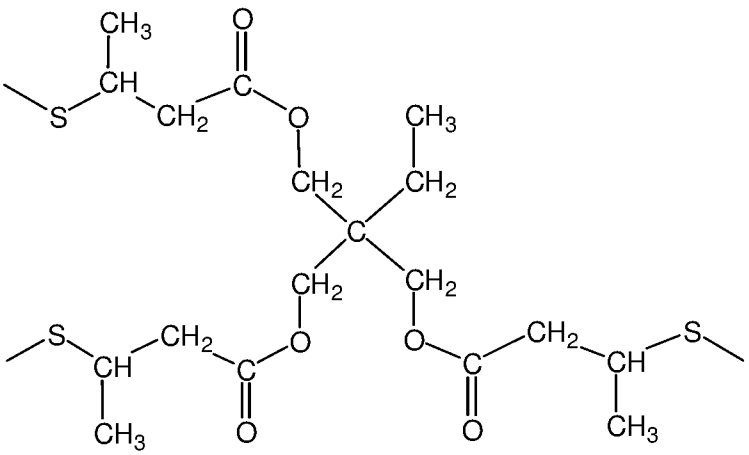
an organo block represented by the following formula:



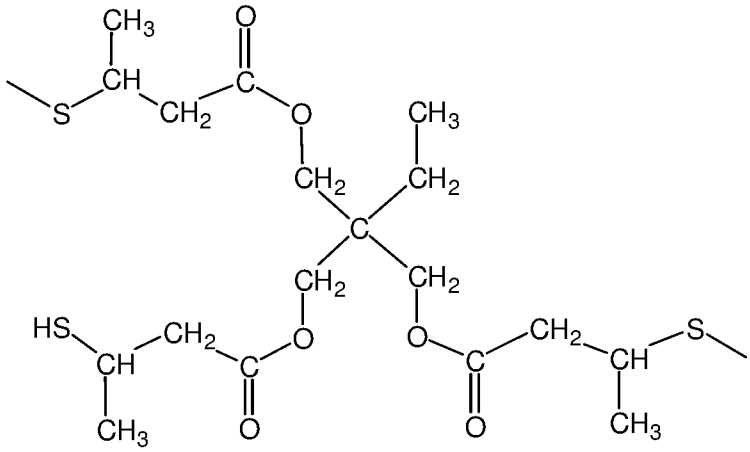
and an organo block represented by the following formula:



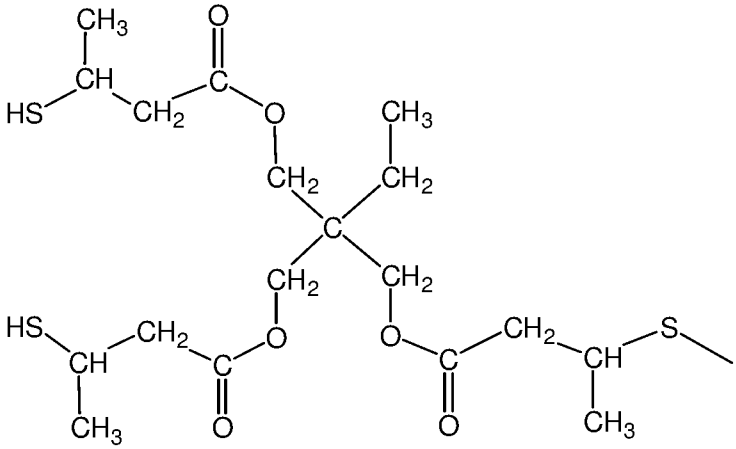
[0055] In Table 1, TMMP stands for a mixture of an organo block represented by the following formula:



an organo block represented by the following formula:



and an organo block represented by the following formula:



[0056] [Table 1]

		Practical Examples							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
(A)	**(a1)**	-	5.00	11.00	15.00	60.00	11.00	11.00	11.00
	(a2)	63.34	59.47	54.84	51.76	17.06	54.84	54.84	54.84
	(a3)	-	-	-	-	-	-	-	-
	(a4)	-	-	-	-	-	-	-	-
(B)	**(b1)**	36.61	35.48	34.11	33.19	22.89	34.11	34.11	34.11
	(b2)	-	-	-	-	-	-	-	-
(C)	**(c1)**	0.05	0.05	0.05	0.05	0.05	-	-	-
	(c2)	-	-	-	-	-	0.05	-	-
	(c3)	-	-	-	-	-	-	0.05	-

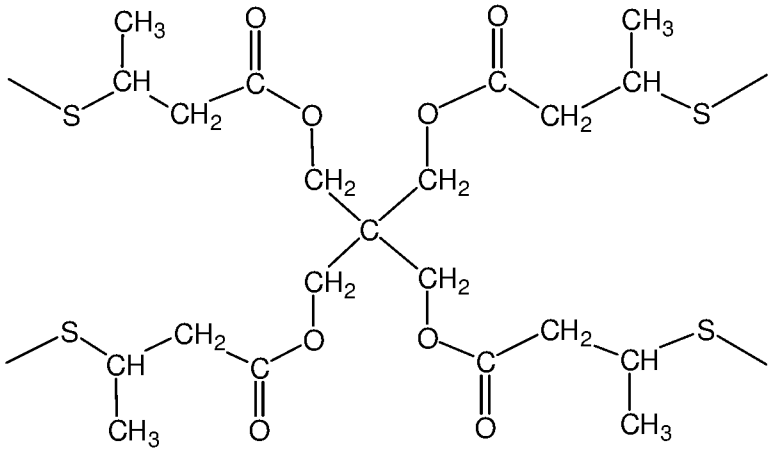
	(c4)	-	-	-	-	-	-	-	0.05
	(c5)	-	-	-	-	-	-	-	-
SH/Vi ratio		2.81	2.81	2.81	2.81	2.84	2.81	2.81	2.81
Polysiloxane Block		D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}	D_{46}+ D_{12}
Organo Block		PE	PE	PE	PE	PE	PE	PE	PE
Refractive Index		1.50	1.49	1.48	1.47	1.45	1.48	1.48	1.48
Mn		ND	ND	9,800	ND	ND	ND	ND	ND
Appearance		Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear

[0057] [Table 1] (Continued)

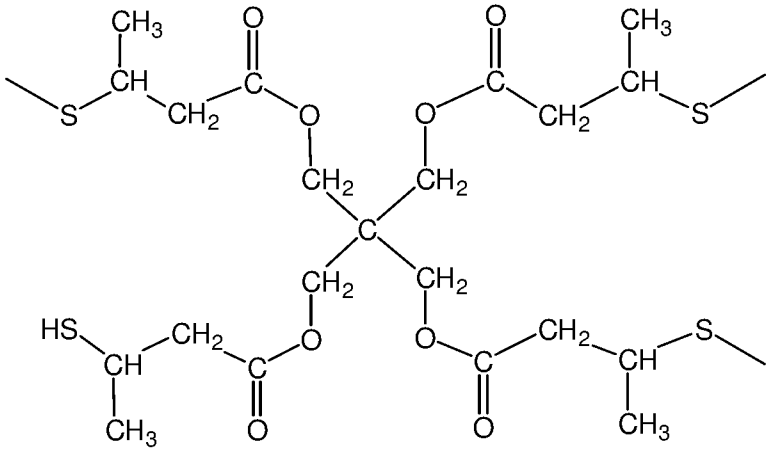
		Practical Examples			**Comparative Examples**				
		9	**10**	**11**	**1**	**2**	**3**	**4**	**5**
(A)	**(a1)**	11.00	11.00	-	-	70.00	70.00	63.34	-
	(a2)	54.84	54.84	-	-	9.35	9.35	-	-
	(a3)	-	-	-	-	-	-	-	63.34
	(a4)	-	-	63.34	63.34	-	-	-	-
(B)	**(b1)**	34.11	-	36.61	-	20.60	-	36.61	36.61
	(b2)	-	34.11	-	36.61	-	20.60	-	-
(C)	**(c1)**	-	0.05	0.05	0.05	0.05	0.05	0.05	0.05
	(c2)	-	-	-	-	-		-	-
	(c3)	-	-	-	-	-	-	-	-
	(c4)	-	-	-	-	-	-	-	-
	(c5)	0.05	-	-	-	-	-	-	-
SH/Vi ratio		2.81	2.89	7.59	7.79	2.85	2.93	7.64	31.82
Polysiloxane Block		D_{46}+ D_{12}	D_{46}+ D_{12}	D^{Ph}_{25}	-	-	-	-	-
Organo Block		PE	TMMP	PE	-	-	-	-	-
Refractive Index		1.48	1.48	1.53	-	-	-	-	-
Mn		9,800	ND	ND	ND	ND	ND	ND	ND
Appearance		Clear	Clear	Clear	Opaque	Opaque	Opaque	Opaque	Opaque

<Practical Example 12>

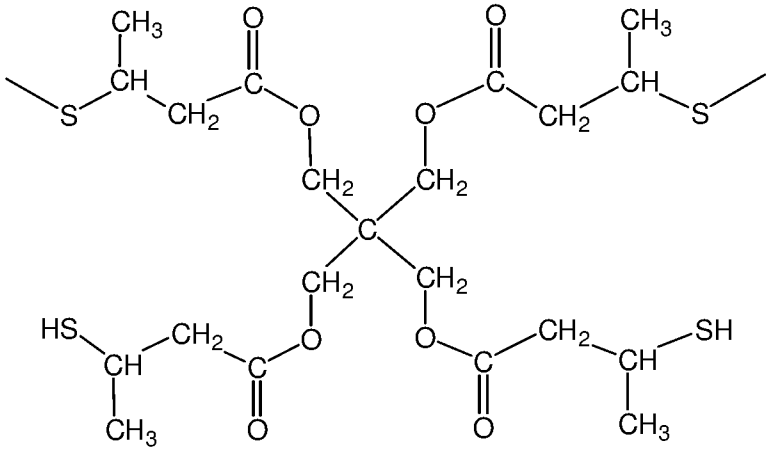
[0058] A round bottom flask fitted with a polytetrafluoroethylene (PTFE) stirrer was loaded with 11.00 mass% of component (a1), 54.84 mass% of component (a2), 34.11 mass% of component (b1) and 0.05 mass% of component (c1). The ratio of the number of moles of thiol (HS-) groups in component (b1) per 1 mole of the vinyl group in components (a1) and (a2) is 2.81. The mixture was subjected to irradiation with Ultraviolet light. After irradiation, a reaction mixture was analyzed by an infrared spectrophotometer, and ^{13}C-nuclear magnetic resonance spectrum analysis. Absence of the vinyl groups in the reaction mixture was confirmed using the infrared spectrophotometer. And formation of C-S-C in the reaction mixture was confirmed using the ^{13}C-nuclear magnetic resonance spectrum analysis. As a result of NMR analysis, it was found that the reaction mixture was a polysiloxane block copolymer comprising: a polysiloxane block represented by the formula: $[(CH_3)_2SiO]_{46}$, a polysiloxane block represented by the formula: $[(CH_3)_2SiO]_{12}Si(C_6H_5)_2(CH{=}CH_2)$, and an organo block represented by the following formula:



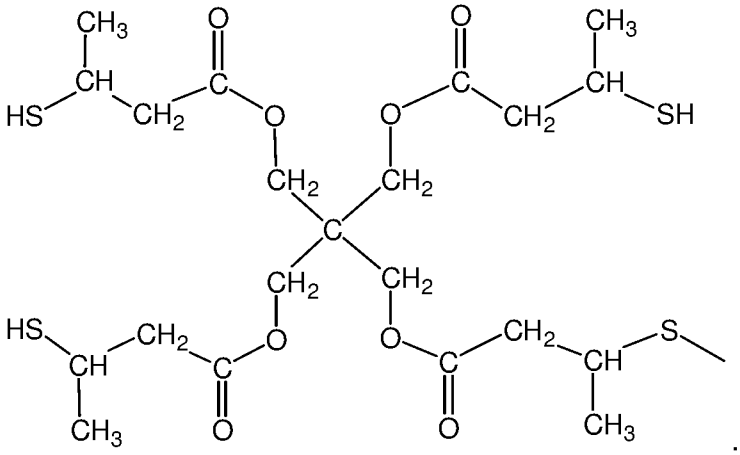
an organo block represented by the following formula:



an organo block represented by the following formula:



and an organo block represented by the following formula:



The results are given in Table 2.

[0059] [Table 2]

	Practical Example 12					
Exposed UV energy (mJ/cm^2)	2,000	3,000	5,000	7,000	9,000	10,000
Viscosity (mPa·s)	23,000	35,000	98,000	98,000	98,000	98,000
Mn	6,800	9,000	9,800	9,800	9,800	9,800
Appearance	Clear	Clear	Clear	Clear	Clear	Clear

[0060] According to the results in Table 2 above, it was found that the exposed UV energy of about 5,000 mJ/cm^2 was sufficient for producing the polysiloxane block copolymer.

[Industrial Applicability]

[0061] Since the polysiloxane block copolymer of the present invention has at least two thiol groups per molecule, it can be used as a crosslinking agent for an ene-thiol reaction type curable silicone composition.

CLAIMS

1. A polysiloxane block copolymer comprising:

(i) a polysiloxane block represented by the general formula: $(R^1{}_2SiO)_n$, wherein each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond; and "n" is a positive number of at least about 5; and

(ii) an organo block containing at least three sulfur atoms and free of silicon atom in a chemical structure thereof;

wherein the polysiloxane block (i) is bonded to the organo block (ii) via a linkage represented by the general formula: (Si)-R^2-(S), wherein Si is an atom in a chemical structure of the polysiloxane block (i); S is an atom in a chemical structure of the organo block (ii); and R^2 is a C_{2-6} alkylene group; and

wherein the polysiloxane block copolymer has at least two thiol (HS-) groups per molecule.

2. The polysiloxane block copolymer according to claim 1, wherein the polysiloxane block (i) is at least one selected from a group consisting of a polysiloxane block represented by the following formula:

$[(CH_3)_2SiO]_n$

a polysiloxane block represented by the following formula:

$[(C_6H_5)_2SiO]_n$

a polysiloxane block represented by the following formula:

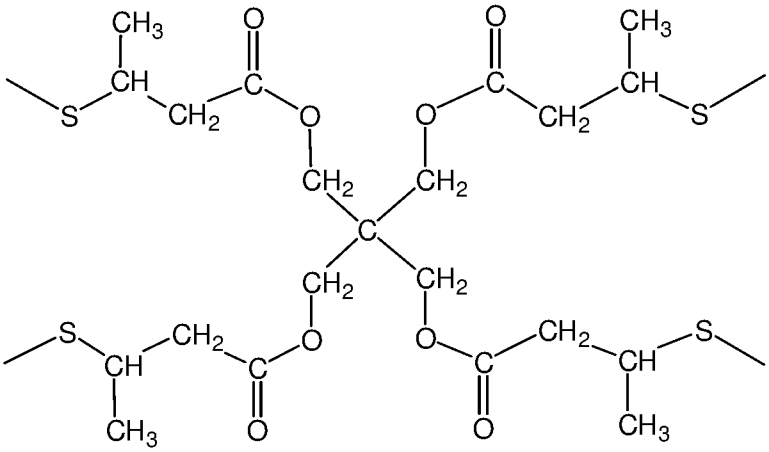
$[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}$

and a polysiloxane represented by the following formula:

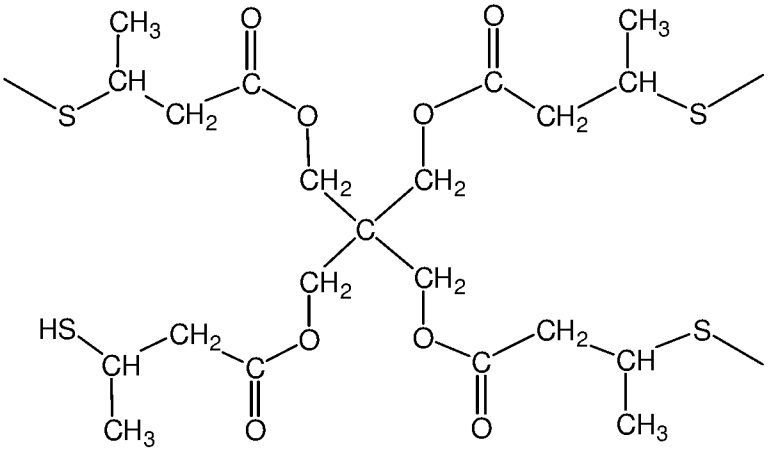
$[(CH_3)(C_6H_5)SiO]_n$

wherein each "n" is a positive number of at least about 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

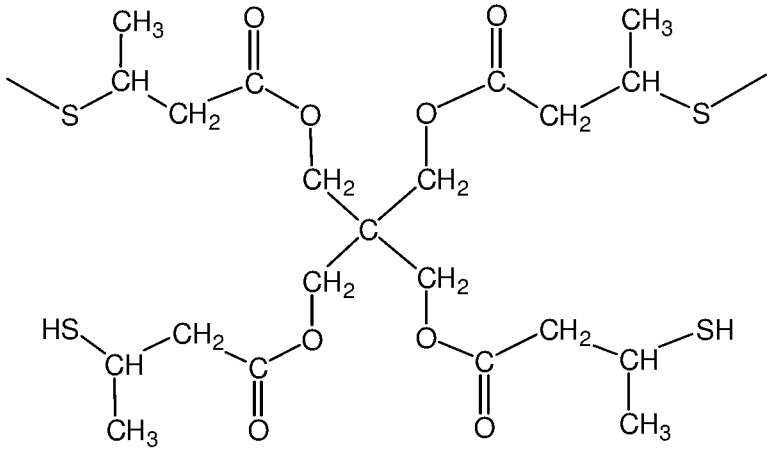
3. The polysiloxane block copolymer according to claim 1, wherein the organo block (ii) is at least one selected form a group consisting of an organo block represented by the following formula:



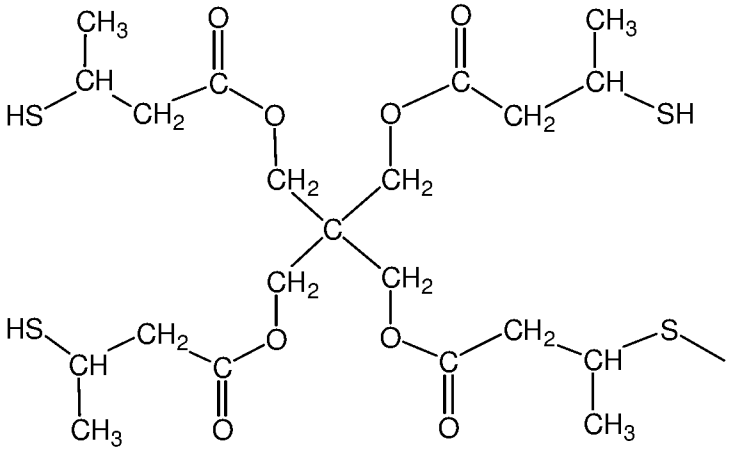
an organo block represented by the following formula:



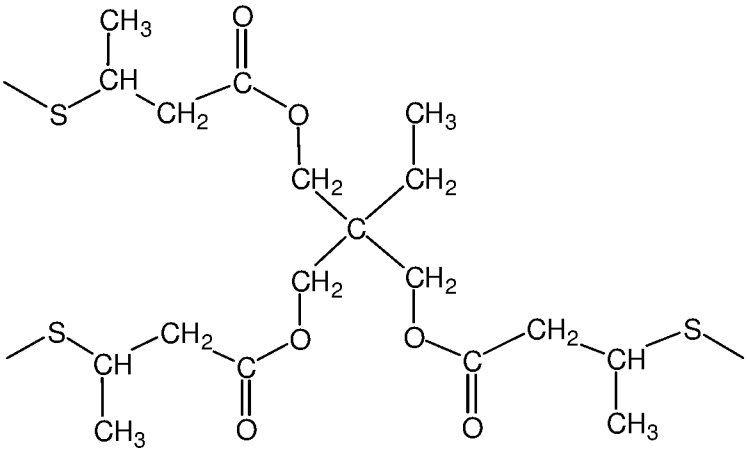
an organo block represented by the following formula:



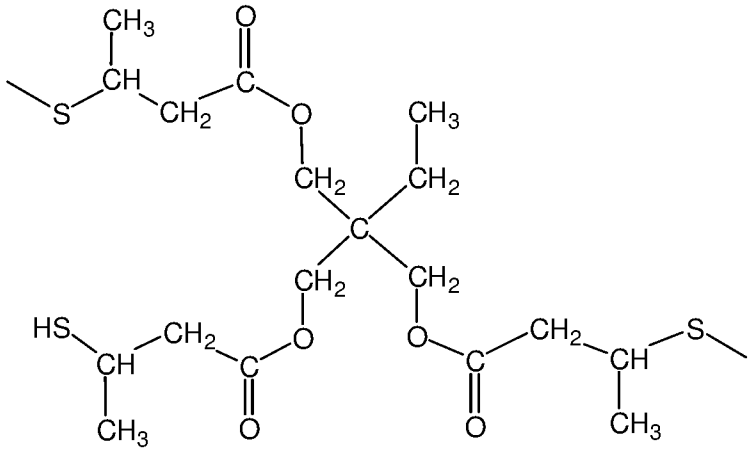
an organo block represented by the following formula:



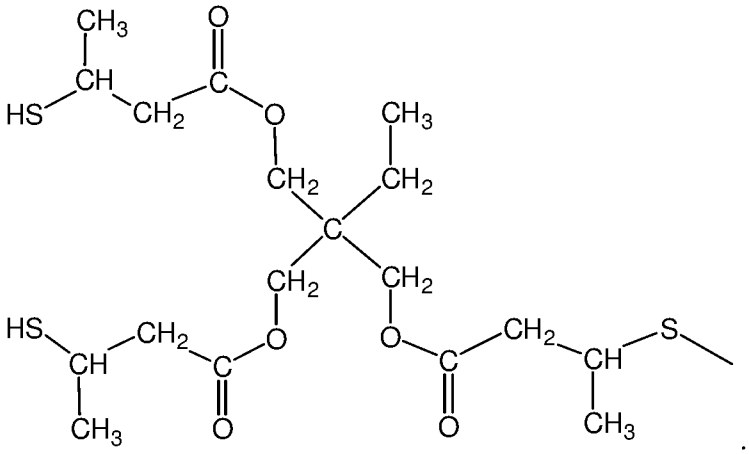
an organo block represented by the following formula:



an organo block represented by the following formula:



and an organo block represented by the following formula:



4. The polysiloxane block copolymer according to claim 1, wherein the content of the polysiloxane block (i) is in a range of from about 60 to about 90 mass% of the sum of the polysiloxane block (i) and the organo block (ii).

5. A method for producing a polysiloxane block copolymer, the method comprising reacting

(A) a polysiloxane represented by the general formula:

$$R^3(R^1{}_2SiO)_nSiR^1{}_2R^3$$

wherein each R^1 is independently a C_{1-12} monovalent hydrocarbon group free of an aliphatic unsaturated bond, each R^3 is independently a C_{2-6} alkenyl group, and "n" is a positive number of at least about 5; and

(B) an organo compound having at least three thiol groups per molecule;

in a presence of

(C) a photoinitiator by irradiation with UV ray.

6. The method according to claim 5, wherein the polysiloxane (A) is at least one selected from a group consisting of a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(C_6H_5)_2SiO]_nSi(CH_3)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(C_6H_5)_2(CH_2=CH)SiO[(CH_3)_2SiO]_nSi(C_6H_5)_2(CH=CH_2)$

a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)_2SiO]_{n1}[(C_6H_5)_2SiO]_{n2}Si(CH_3)_2(CH=CH_2)$

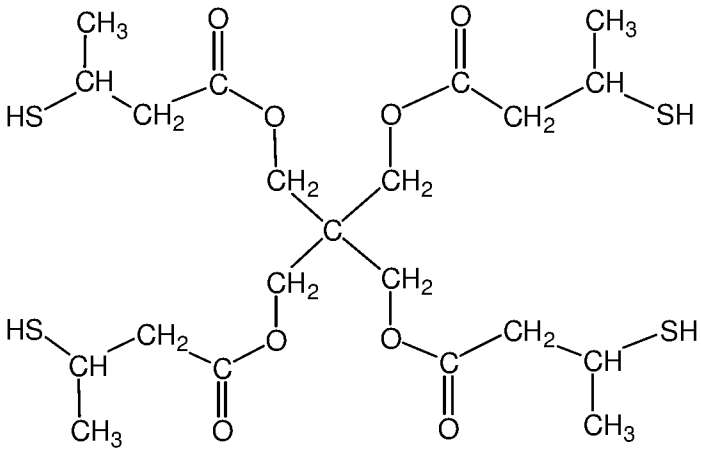
and a polysiloxane represented by the following formula:

$(CH_3)_2(CH_2=CH)SiO[(CH_3)(C_6H_5)SiO]_nSi(CH_3)_2(CH=CH_2)$

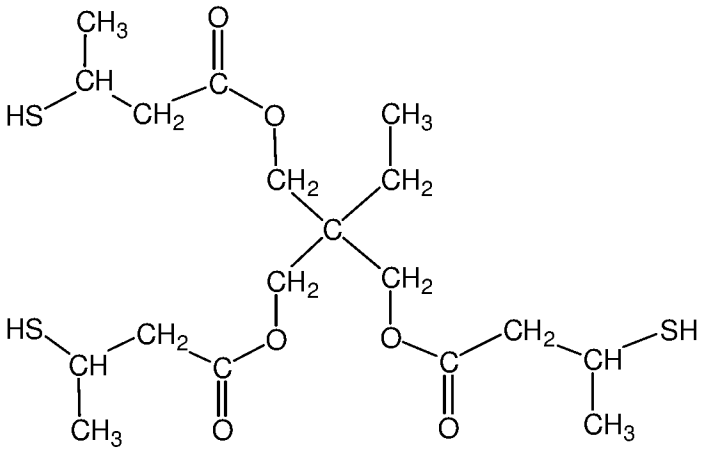
wherein each "n" is a positive number of at least about 5; and each "n1" and "n2" is a positive number, provided that "n1+n2" is a positive number of at least about 5.

7. The method according to claim 5, wherein the polysiloxane (A) has a number average molecular weight of from about 500 to about 50,000 in accordance with a standard polystyrene basis by gel permeation chromatography.

8. The method according to claim 5, wherein the organo compound (B) is at least one selected from a group consisting of an organo compound represented by the following formula:



and an organo compound represented by the following formula:



9. The method according to claim 5, wherein the reaction amount of the organo compound (B) is in an amount such that the amount of the thiol groups provided by the present component is in a range of from about 2.0 to about 10.0 moles per 1 mole of the total alkenyl groups in the polysiloxane (A).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2021/018525

A. CLASSIFICATION OF SUBJECT MATTER

C08G 77/42(2006.01)i; **C08G 77/392**(2006.01)i; **C08G 77/28**(2006.01)i

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)

C08G 77/42(2006.01); B05D 3/06(2006.01); C08G 77/20(2006.01); C08G 77/28(2006.01); C08G 77/442(2006.01); C08K 5/10(2006.01); C08K 5/101(2006.01); C08L 83/04(2006.01); C08L 83/07(2006.01); C09D 133/14(2006.01); C09D 183/08(2006.01)

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal), STN(Registry, Caplus), Google & keywords: polysiloxane, block, thiol, crosslinker, alkenyl

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2537878 A1 (HANSE CHEMIE AG) 26 December 2012 (2012-12-26) paragraphs [0036]-[0039], [0055], [0056], [0058]; claims 1-9	1-9
X	WO 2015-036414 A1 (BASF SE) 19 March 2015 (2015-03-19) claims 1, 4-9, 11	1-9
DA	US 2019-0112430 A1 (DOW SILICONES CORPORATION et al.) 18 April 2019 (2019-04-18) paragraph [0020]; claims 1-9	1-9
A	WO 2017-082180 A1 (DOW CORNING TORAY CO., LTD.) 18 May 2017 (2017-05-18) paragraphs [0017], [0023], [0024]; claims 1-10	1-9
A	WO 2019-099347 A1 (CARBON, INC.) 23 May 2019 (2019-05-23) pages 17-19	1-9

☑ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"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
"T" 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
"X" 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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 June 2021	**10 June 2021**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2021/018525

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2018-117974 A1 (AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH) 28 June 2018 (2018-06-28) claims 1-18	1-9

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2021/018525

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WO 2018-117974 A1	28 June 2018	None	