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(54) Titre : COMPOSITION DURCISSABLE
(54) Title: HARDENABLE COMPOSITION

(57) **Abrégé/Abstract:**

A hardenable composition that despite a low viscosity, yields elastomers with a wide range of properties from hardness to softness and yields a transparent hardened matter excelling in weather resistance and thermal stability, which transparent hardened matter has a rubber elasticity realizing improvement to the hard and brittle properties of epoxy resin and exhibits a high adhesion strength. There is provided a hardenable composition comprising an epoxy resin and a vinyl polymer having at least one crosslinkable silyl group on the average. Use of this hardenable composition in bonding and sealing of a transparent material such as a polycarbonate or an acrylic resin, or a glass will realize working ensuring satisfactory exertion of transparency as an aesthetic characteristic thereof.



ABSTRACT

The present invention has its object to provide a curable composition, although having low viscosity itself, which gives
5 a cured product, when being cured, which has wide range of elasticity, from hard to soft, which is excellent in weather resistance and heat resistance, and the hardness and brittleness (characteristic to epoxy resins) of which have been improved to have rubber elasticity, and which has high adhesion
10 strength and is transparent. The curable composition of the present invention comprises a vinyl polymer containing at least one crosslinkable silyl group on average and an epoxy resin. When being used for adhering or sealing a transparent material such as glass, polycarbonates, and acrylic resins, the curable
15 composition of the invention is usable for treatment with sufficiently retaining the transparency, which is an aesthetic characteristic.

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DESCRIPTION

CURABLE COMPOSITION

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TECHNICAL FIELD

The present invention relates to a curable composition. More particularly, the invention relates to a curable composition which comprises a vinyl polymer (I) containing at least one crosslinkable silyl group on average, and an epoxy
10 resin (II).

BACKGROUND ART

An epoxy resin type adhesive has been use in a wide range of industrial fields covering automobiles, vehicles, aircrafts, ships, electronics, constructions, and civil engineering due
15 to the reliability of excellent adhesion strength and durability to various materials such as metals, plastics, wood, glass, ceramics, stone materials, and concrete.

However, a cured product of the adhesive generally has a high modulus of elasticity and low energy absorption
20 capability and thus has defective points, that is, hard and brittle. Therefore, it is supposed to be a problem to use the material for adhesion of a material having a considerably different linear expansion coefficient and a member that receives repetitive displacements by heat cycles just like
25 construction materials.

To solve this problem, so-called modified silicone type elastic adhesive obtained by blending a polyether polymer containing at least one crosslinkable silyl group with an epoxy resin has been widely used, however the elastic adhesive
30 obtained by blending an epoxy resin and a polyether polymer has various problems, e.g. inferior mutual compatibility, low option of blending ratio, insufficiency of weather resistance and heat resistance attributed to the polyether polymer.

To solve the above-mentioned problems, a curable
35 composition containing an epoxy resin and a crosslinkable silyl

group-containing (meth)acrylic polymer (see Japanese Kokai Publication Hei-02-214759 and Japanese Kokai Publication Hei-11-100433) are disclosed, however similarly to the above-mentioned curable composition containing an epoxy resin and a polyether polymer, the curable composition can give only opaque cured products when being cured.

If a transparent cured product can be obtained, in the case of adhering or sealing a transparent material such as glass, polycarbonates, and acrylic resins, the level of design may be maintained and therefore option of plans may be widened. Further, at the time of using the transparent cured product as a coating or lining, since an under-layer material can be seen, it becomes possible to obtain some advantages, that is, the design of the under-layer material can be utilized well, cracks etc. in a joint and/or the like parts can be easily found, and the like advantages.

SUMMARY OF THE INVENTION

The invention has its object to provide a curable composition that, although having low viscosity itself, gives a cured product, when being cured, which has wide range of elasticity, from hard to soft, which is excellent in weather resistance and/or heat resistance, and the hardness and brittleness (characteristic to epoxy resins) of which have been improved to have rubber elasticity, and which has high adhesion strength.

The invention provides a curable composition which comprises a mixture of a vinyl polymer and an epoxy resin as components, and gives a cured product excellent in transparency when the mixture is cured.

In view of the above state, the present inventors have made intensive investigations and have found that the above-mentioned problems can be solved by a curable composition which comprises a vinyl polymer (I) containing at least one crosslinkable silyl group on average, and an epoxy resin (II).

The finding has now led to completion of the invention.

That is, the curable composition of the invention is
a curable composition comprising a vinyl polymer (I)
containing at least one crosslinkable silyl group on average
5 and an epoxy resin (II),

which gives a transparent cured product when the mixture
of the vinyl polymer (I) and the epoxy resin (II) is cured.

Further, the curable composition of the invention is
a curable composition comprising a vinyl polymer (I)
10 containing at least one crosslinkable silyl group on average
and an epoxy resin (II),

which gives a cured product having a modulated structure
when being cured.

The preferred embodiment relates to
15 the curable composition

wherein a vinyl monomer constituting the main chain of
the vinyl polymer (I) is mainly selected from the group
consisting of (meth)acrylic monomers, acrylonitrile monomers,
aromatic vinyl monomers, fluorine-containing vinyl monomers
20 and silicon-containing vinyl monomers.

The preferred embodiment relates to
the curable composition
wherein the main chain of the vinyl polymer (I) is a
(meth)acrylic polymer.

25 The preferred embodiment relates to
the curable composition
wherein the main chain of the vinyl polymer (I) is an
acrylic polymer.

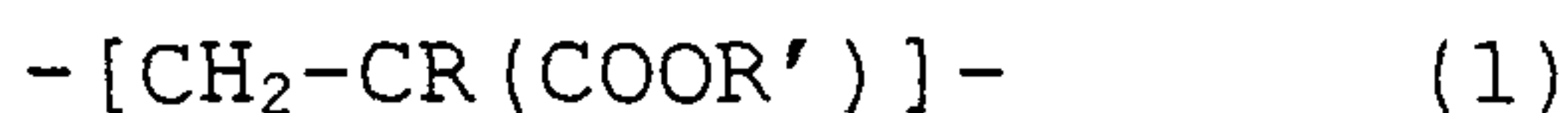
The preferred embodiment relates to
30 the curable composition
wherein the main chain of the vinyl polymer (I) is an
acrylic ester polymer.

The preferred embodiment relates to
the curable composition
35 wherein the main chain of the vinyl polymer (I) is a

polymer or a copolymer having higher polarity than that of a butyl acrylate homopolymer.

The preferred embodiment relates to the curable composition

5 wherein the main chain of the vinyl polymer (I) is a polymer or a copolymer having a repeating unit structure represented by the general formula 1:



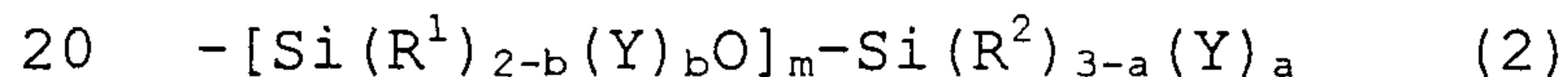
(wherein, R represents a hydrogen atom or a methyl group; R' 10 may be same or different and each represents an alkoxyalkyl group or an alkyl group having 1 to 3 carbon atoms.)

The preferred embodiment relates to the curable composition

15 wherein the vinyl polymer (I) has a molecular weight distribution of less than 1.8.

The preferred embodiment relates to the curable composition

wherein the crosslinkable silyl group is represented by the general formula 2:



{wherein, R¹ and R² may be same or different and each is an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms or a triorganosiloxy group represented by (R')₃SiO- (in 25 which R' is a univalent hydrocarbon group containing 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R¹ or R² groups, they may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, 30 they may be the same or different; a represents 0, 1, 2 or 3, b represents 0, 1 or 2, and m is an integer of 0 to 19, provided that the relation a + mb ≥ 1 should be satisfied.)

The preferred embodiment relates to the curable composition

35 wherein the main chain of the vinyl polymer (I) is produced

by living radical polymerization.

The preferred embodiment relates to
the curable composition

wherein the main chain of the vinyl polymer (I) is produced
5 by atom transfer radical polymerization.

The preferred embodiment relates to
the curable composition

wherein the crosslinkable silyl group of the vinyl
polymer (I) is at the molecular terminus.

10 The preferred embodiment relates to
the curable composition

wherein the epoxy resin (II) is an epoxy resin (II)
containing no aromatic rings.

The preferred embodiment relates to
15 the curable composition

wherein the epoxy resin (II) is an alicyclic epoxy resin.

The preferred embodiment relates to
the curable composition

wherein the alicyclic epoxy resin (II) is selected from
20 the group consisting of a hydrogenated bisphenol A epoxy resin
and a glycidyl ester epoxy resin.

The preferred embodiment relates to
the curable composition

which comprises a polyether polymer (III).

25 The preferred embodiment relates to
the curable composition

wherein the main chain of the polyether polymer (III) is
substantially polypropylene oxide.

The preferred embodiment relates to
30 the curable composition

wherein the polyether polymer (III) contains at least one
crosslinkable silyl group on average.

The preferred embodiment relates to
the curable composition

35 wherein the total luminous transmittance of the cured

product with a thickness of about 2 mm obtained by curing the above-mentioned mixture is 50% or higher.

The preferred embodiment relates to the curable composition

5 wherein the parallel luminous transmittance of the cured product with a thickness of about 2 mm obtained by curing the above-mentioned mixture is 10% or higher.

The curable composition of the invention, although having low viscosity itself, gives a cured product, when being cured,
10 which has wide range of elasticity, from hard to soft, which is excellent in weather resistance and/or heat resistance, and the hardness and brittleness (characteristic to epoxy resins) of which have been improved to have rubber elasticity, and which has high adhesion strength and is transparent.

15 When being used for adhering or sealing a transparent material such as glass, polycarbonates, and acrylic resins, the curable composition of the invention is usable for treatment with sufficiently retaining the transparency, which is an aesthetic characteristic. In the case of using the curable
20 composition of the invention for a coating agent or a lining agent, the design of an under-layer material can be utilized well and cracks etc. in a joint and/or the like parts can be easily found to make quick repairing possible.

25 DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, a curable composition of the invention will be described in detail.

The curable composition of the invention is a curable composition comprising a vinyl polymer (I) containing at least
30 one crosslinkable silyl group on average and an epoxy resin (II) which gives a transparent cured product when a mixture of the vinyl polymer (I) and the epoxy resin (II) is cured or gives a cured product having a modulated structure when being cured itself.

35 At first, the curable composition comprising a vinyl

polymer (I) containing at least one crosslinkable silyl group on average and an epoxy resin (II) which gives a transparent cured product when a mixture of the vinyl polymer (I) and the epoxy resin (II) is cured will be described below.

5 The term, transparency, in this invention not only means transparency sufficient to make an object seen without shape deformation of the object when the object is seen through a medium (that is, the cured product of the invention obtained when a mixture of the vinyl polymer (I) containing at least one
10 crosslinkable silyl group on average and the epoxy resin (II) is cured) but also includes semi-transparency sufficient to make the object seen with vague shape or fogged color. In particular, it is preferable that the total luminous transmittance of the cured product with a thickness of about
15 2 mm obtained when the above-mentioned mixture is cured is 50% or higher and/or the parallel luminous transmittance of the cured product is 10% or higher.

Here, the phrase, "thickness of about 2 mm" includes an allowance of ± 0.2 mm and therefore means a thickness in a range
20 from 1.8 to 2.2 mm since the thickness is changed during the production process or curing process in some cases although the cured product is produced so as to have a thickness of 2 mm on the basis of volume conversion.

<<Vinyl polymer (I)>>

25 <Main chain>

The present inventors have so far made a large number of inventions relating to various crosslinking functional group-terminated vinyl polymers, methods of producing the same, curable compositions comprising the same and uses thereof (see,
30 for example, Japanese Kokai Publication Hei-11-080249, Japanese Kokai Publication Hei-11-080250, Japanese Kokai Publication Hei-11-005815, Japanese Kokai Publication Hei-11-116617, Japanese Kokai Publication Hei-11-116606, Japanese Kokai Publication Hei-11-080571, Japanese Kokai
35 Publication Hei-11-080570, Japanese Kokai Publication

Hei-11-130931, Japanese Kokai Publication Hei-11-100433, Japanese Kokai Publication Hei-11-116763, Japanese Kokai Publication Hei-09-272714 and Japanese Kokai Publication Hei-09-272715). A vinyl polymer (I) according to the present invention is not particularly limited, and any of various polymers disclosed in the above-mentioned inventions can be suitably used.

A vinyl monomer which constitutes the main chain of the vinyl polymer of the present invention is not particularly limited, and any of various monomers can be used. Examples of the vinyl monomer include (meth)acrylic acid monomers, such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, tolyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, ethylene oxide adduct of (meth)acrylic acid, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, perfluoroethylmethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, perfluoroethyl-perfluorobutylmethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2,2-diperfluoromethylethyl (meth)acrylate, perfluoromethyl-perfluoroethylmethyl (meth)acrylate,

2-perfluoromethyl-2-perfluoroethylethyl (meth)acrylate,
2-perfluorohexylmethyl (meth)acrylate, 2-perfluorohexylethyl
(meth)acrylate, 2-perfluorodecylmethyl (meth)acrylate,
2-perfluorodecylethyl (meth)acrylate,
5 2-perfluorohexadecylmethyl (meth)acrylate, and
2-perfluorohexadecylethyl (meth)acrylate; aromatic vinyl
monomers, such as styrene, vinyltoluene, α -methylstyrene,
chlorostyrene, and styrenesulfonic acid and its salts;
fluorine-containing vinyl monomers, such as perfluoroethylene,
10 perfluoropropylene, and vinylidene fluoride;
silicon-containing vinyl monomers, such as
vinyltrimethoxysilane and vinyltriethoxysilane; maleic
anhydride, maleic acid, and monoalkyl esters and dialkyl esters
of maleic acid; fumaric acid and monoalkyl and dialkyl esters
15 of fumaric acid; maleimide monomers, such as, maleimide,
methylemaleimide, ethylemaleimide, propylemaleimide,
butylemaleimide, hexylemaleimide, octylemaleimide,
dodecylemaleimide, stearylemaleimide, phenylemaleimide, and
cyclohexylemaleimide; acrylonitrile monomers, such as
20 acrylonitrile and methacrylonitrile; amido-containing vinyl
monomers, such as acrylamide and methacrylamide; vinyl esters,
such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl
benzoate, and vinyl cinnamate; alkenes, such as ethylene and
propylene; conjugated dienes, such as butadiene and isoprene;
25 and vinyl chloride, vinylidene chloride, allyl chloride, and
allyl alcohol. These compounds may be used alone, or at least
two may be copolymerized. In the above expression, for example,
the term "(meth)acrylic acid" means acrylic acid and/or
methacrylic acid.

30 The main chain of the vinyl polymer is preferably one
produced by polymerizing predominantly at least one monomer
selected from the group consisting of (meth)acrylic monomers,
acrylonitrile monomers, aromatic vinyl monomers,
fluorine-containing vinyl monomers and silicon-containing
35 vinyl monomers. The term "predominantly" as used herein means

that the above-mentioned monomer accounts for not less than 30 mole percent, preferably not less than 50 mole percent, of the monomer units constituting the vinyl polymer.

In particular, from the viewpoint of physical properties of a product, styrene monomers and (meth)acrylic monomers are preferred. Acrylate monomers and methacrylate monomers are more preferred, acrylate monomers are further preferred. For general building and construction, and the like applications, butyl acrylate monomers are further more preferred from the viewpoint that low viscosity of formulations, low modulus, high elongation, good weather resistance, and good heat resistance of cured products obtained therefrom, and the like physical properties are required. On the other hand, for automobile and the like applications where the oil resistance and the like are required, copolymers predominantly composed of ethyl acrylate are further more preferred. The polymer predominantly composed of ethyl acrylate is somewhat inferior in characteristics at low temperature (cold resistance), although it is excellent in oil resistance. Therefore, it is possible to substitute a part of ethyl acrylate units into butyl acrylate units for improving the characteristics at low temperature. However, since the good oil resistance becomes deteriorated as a proportion of butyl acrylate increases, the proportion of butyl acrylate is preferably not more than 80 mol%, more preferably not more than 60 mol%, further preferably not more than 40 mol%, and particularly more preferably not more than 30 mol%, according to the applications where the oil resistance is required. Furthermore, to improve low-temperature characteristics or the like without deteriorating oil resistance, it is also preferable that 2-methoxyethyl acrylate or 2-ethoxyethyl acrylate having an oxygen-introduced alkyl group in its side chain. However, when heat resistance is required, the ratio thereof is preferably not more than 60 mol% and more preferably not more than 40 mol%, since heat resistance tends to be poor by introduction of an alkoxy group having ether

bond in a side chain. A polymer suitable for various uses or required purposes can be obtained by modifying the ratios of monomers in view of desired properties such as oil resistance, heat resistance or low-temperature characteristics. For example, as the polymer having well-balanced properties among oil resistance, heat resistance, low-temperature characteristics and the like, there may be mentioned, but is not limited to, a copolymer of ethyl acrylate / butyl acrylate / 2-methoxyethyl acrylate (40 to 50 / 20 to 30 / 20 to 30, by mole ratio), among others.

To make the cured product of the invention obtained when the mixture of the vinyl polymer and the epoxy resin is cured, the vinyl polymer is preferably compatible with the epoxy resin, and a polymer or a copolymer having higher polarity than that of a butyl acrylate homopolymer is suitable, and a polymer or a copolymer the main chain of which has a repeating unit structure represented by the general formula 1 is more preferred.



(wherein, R represents a hydrogen atom or a methyl group; R' may be same or different and each represents an alkoxyalkyl group or an alkyl group having 1 to 3 carbon atoms.)

The alkyl group is preferably a methyl, ethyl, n-propyl or isopropyl group, and the alkoxyalkyl group is preferably 2-methoxyethyl or 2-ethoxyethyl group, for example.

The polymer or copolymer having higher polarity than that of a butyl acrylate homopolymer is not particularly limited and examples are copolymers of butyl acrylate and a monomer with higher polarity than that of butyl acrylate. Examples of the monomer with higher polarity than that of butyl acrylate include, for example, ethyl acrylate and 2-methylethyl acrylate. For example, an ethyl acrylate / butyl acrylate / 2-methoxyethyl acrylate copolymer (40 to 50 / 20 to 30 / 20 to 30, by mole ratio) is sufficiently compatible with various kinds of epoxy resins and easy to give a transparent cured product and therefore it

is preferable.

To improve the compatibility with another polymer, for example, a modified silicone resin (an oxyalkylene polymer having a crosslinkable silyl group), a monomer having a long chain alkyl group such as stearyl and lauryl group may be copolymerized. Although not being limited particularly, copolymerization of 5 to 30% by mole of stearyl acrylate or lauryl acrylate remarkably improves the compatibility with the modified silicone resin. Since the compatibility differs depending on the molecular weight of each polymer, the ratio of the monomer to be copolymerized is preferable to be selected in accordance with the molecular weight. At that time, block copolymerization may be carried out. An effect can be caused with a small amount of the monomer.

The curable composition comprising the vinyl polymer having a functional silyl group may sometimes have a retarded curability because of storage, that is, the composition may be sometimes deteriorated in the storage stability. For example, copolymerization of methyl acrylate sometimes makes it possible to suppress the deterioration. The copolymerization may be also effective in the case of improving the strength of the cured product. In this case, similarly the ratio of the monomers to be copolymerized may be selected depending on the molecular weights and/or block copolymerization may be carried out.

In the present invention, these preferred monomers may be copolymerized, e.g., block-copolymerized, with another monomer. In this case, the content by weight of the preferred monomers is preferably 40% or more.

The molecular weight distribution [ratio (M_w/M_n) of the weight average molecular weight (M_w) to the number average molecular weight (M_n) determined by gel permeation chromatography] of the vinyl polymer of the present invention is not particularly limited, but the ratio is preferably less than 1.8, and further preferably 1.3 or less from the workability viewpoint. In GPC measurement in the present

invention, a number average molecular weight and the like may be generally determined in terms of polystyrene using chloroform as a mobile phase and a polystyrene gel column for measurement.

5 The number average molecular weight of the vinyl polymer of the present invention is not particularly restricted, and preferably in a range of 500 to 1,000,000 and more preferably 5,000 to 50,000 with gel permeation chromatography from the workability and physical properties viewpoints. Naturally, as
10 the molecular weight is lower, the compatibility with the epoxy resin becomes better and the cured products obtained tends to have higher modulus and low elongation and on the contrary, if the molecular weight is higher, inversed tendency would be observed.

15 <Method of main chain synthesis>

 In accordance with the invention, the method of synthesizing the vinyl polymer is not limited, and the free radical polymerization technique may be used. Further, the controlled radical polymerization technique is preferred, the
20 living radical polymerization technique is more preferred, and the atom transfer radical polymerization technique is particularly preferred. These techniques are described below.

Controlled radical polymerization

 Radical polymerization processes are classified into a
25 general radical polymerization process in which a monomer having a specified functional group and a vinyl monomer are simply copolymerized using an azo compound, a peroxide, or the like as a polymerization initiator, and a controlled radial polymerization process in which a specified functional group
30 can be introduced at a controlled position such as an end or the like.

 The general radical polymerization process is a simple process, and a monomer having a specified functional group can be introduced into a polymer only stochastically. When a
35 polymer with high functionality is desired, therefore, a

considerable amount of a monomer must be used. Conversely, use of a small amount of a monomer has the problem of increasing the ratio of a polymer in which the specified functional group is not introduced. There is also the problem of producing only
5 a polymer with a wide molecular weight distribution and high viscosity due to free radical polymerization.

The controlled radical polymerization process is further classified into a chain transfer agent process in which polymerization is performed using a chain transfer agent having
10 a specified functional group to produce a vinyl polymer having the functional group at an end, and a living radical polymerization process in which polymerization propagation termini propagate without causing termination reaction or the like to produce a polymer having a molecular weight
15 substantially equal to the design.

The chain transfer agent process is capable of producing a polymer with high functionality, but a considerable amount of a chain transfer agent having a specified functional group must be used relative to the initiator, thereby causing an
20 economical problem of the cost including the treatment cost. Like the general radical polymerization process, the chain transfer agent process also has the problem of producing only a polymer with a wide molecular weight distribution and high viscosity because it is free radical polymerization.

It is true that the living radical polymer process belongs to a radical polymerization process which has a high polymerization rate and is difficult to control because termination reaction easily occurs due to radical coupling or the like. However, unlike in the above-mentioned processes,
25 in the living radical polymerization process, termination reaction little occurs, a polymer having a narrow molecular weight distribution (M_w/M_n of about 1.1 to 1.5) can be produced, and the molecular weight can be freely controlled by changing the charge ratio of the monomer to the initiator.
30

35 Therefore, the living radical polymerization process is

capable of producing a polymer with a narrow molecular weight distribution and low viscosity and introducing a monomer having a specified functional group into a substantially desired position. Thus, this process is more preferred as a process
5 for producing the vinyl polymer having the specified functional group.

In a narrow sense, "living polymerization" means polymerization in which molecular chains propagate while maintaining activity at the termini. However, the living
10 polymerization generally includes pseudo-living polymerization in which molecular chains propagate in equilibrium between deactivated and activated termini. The definition in the present invention includes the latter.

In recent, the living radical polymerization has been
15 actively studied by various groups. Examples of studies include a process using a cobalt porphyrin complex, as shown in Journal of American Chemical Society (J. Am. Chem. Soc.), 1994, vol. 116, p. 7943, a process using a radical capping agent such as a nitroxide compound, as shown in Macromolecules, 1994,
20 vol. 27, p. 7228, and an atom transfer radical polymerization (ATRP) process using an organic halide or the like as an initiator and a transition metal complex as a catalyst.

Among these living radical polymerization processes, the atom transfer radical polymerization process in which a vinyl
25 monomer is polymerized using an organic halide or a halogenated sulfonyl compound as an initiator and a transition metal complex as a catalyst has the above-mentioned characteristics of the living radical polymerization and also has the characteristic that a terminus has a halogen or the like, which is relatively
30 useful for functional group conversion reaction, and the initiator and catalyst have high degrees of design freedom. Therefore, the atom transfer radical polymerization process is more preferred as a process for producing a vinyl polymer having a specified functional group. Examples of the atom transfer
35 radical polymerization process include the processes disclosed

in Matyjaszewski, et al., Journal of American Chemical Society (J. Am. Chem. Soc.), 1995, vol. 117, p. 5614, Macromolecules, 1995, vol. 28, p. 7901, Science, 1996, vol. 272, p. 866, WO96/30421, WO97/18247, WO98/01480 and WO98/40415, Sawamoto, 5 et al., Macromolecules, 1995, vol. 28, p. 1721, and Japanese Kokai Publication Hei-09-208616 and Japanese Kokai Publication Hei-08-41117.

In the present invention, any one of these living radical polymerization processes may be used without limitation, but 10 the atom transfer radical polymerization process is preferred.

Hereinafter, the living radical polymerization will be described in detail. First, the controlled radical polymerization process using a chain transfer agent, which may be used in the production of the vinyl polymers mentioned below, 15 will be described. The radical polymerization process using the chain transfer agent (telomer) is not particularly limited, but examples of a process for producing a vinyl polymer having a terminal structure suitable for the present invention include the following two processes:

20 A process for producing a halogen-terminated polymer using a halogenated hydrocarbon as the chain transfer agent as disclosed in Japanese Kokai Publication Hei-04-132706, and a method for producing a hydroxyl group-terminated polymer using a hydroxyl group-containing mercaptane or a hydroxyl 25 group-containing polysulfide or the like as the chain transfer agent as disclosed in Japanese Kokai Publication Sho-61-271306, Japanese Patent Publication No. 2594402, and Japanese Kokai Publication Sho-54-47782.

30 Next, the living radical polymerization will be described.

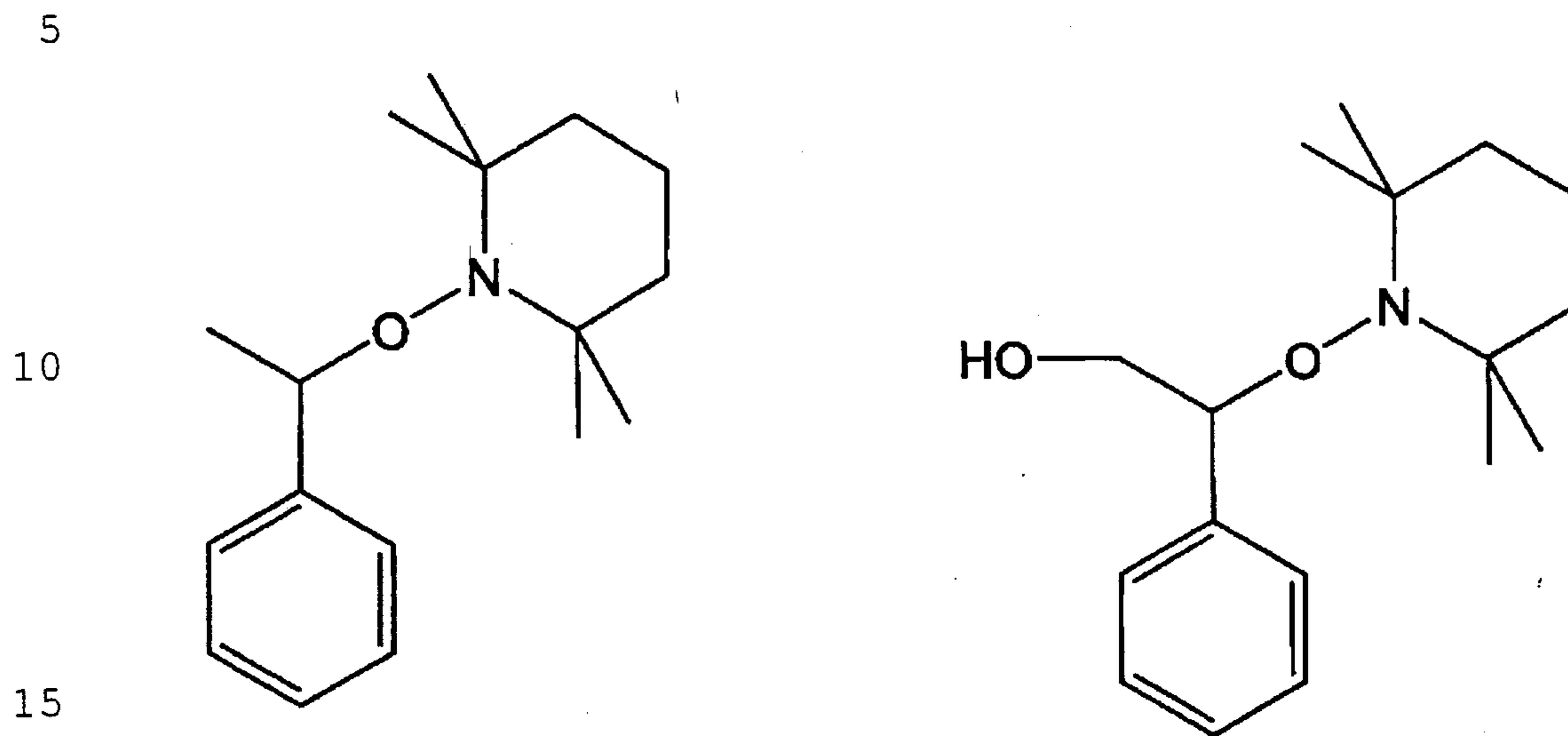
First, the process using a nitroxide compound and the like as a radical capping agent will be described. This polymerization process generally uses stable nitroxy free radical ($=N-O\cdot$) as a radical capping agent. Preferred examples 35 of such a compound include, but not limited to, nitroxy free

radicals produced from cyclic hydroxyamines, such as 2,2,6,6-substituted-1-piperidinyloxy radical and 2,2,5,5-substituted-1-pyrrolidinyloxy radical. As a substituent, an alkyl group having 4 or less carbon atoms, such as methyl or ethyl, is suitable. Specific examples of a nitroxyl free radical compound include, but not limited to, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), 2,2,6,6-tetraethyl-1-piperidinyloxy radical, 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxy radical, 2,2,5,5-tetramethyl-1-pyrrolidinyloxy radical, 1,1,3,3-tetramethyl-2-isoindolinyloxy radical, and N,N-di-tert-butylaminoxyl radical. Instead of the nitroxyl free radical, stable free radical such as galvinoxyl free radical may be used.

The radical capping agent is used in combination with the radical generator. The reaction product of the radical capping agent and the radical generator possibly serves as a polymerization initiator to promote polymerization of an addition-polymerizable monomer. The ratio between both agents used is not particularly limited, but the amount of the radical generator is preferably 0.1 to 10 moles per mole of the radical generator.

As a radical generator, any one of various compounds can be used, but a peroxide capable of generating radical under a polymerization temperature is preferred. Examples of the peroxide include, but not limited to, diacyl peroxides, such as benzoyl peroxide and lauroyl peroxide; dialkyl peroxides, such as dicumyl peroxide and di-tert-butyl peroxide; peroxy carbonates, such as diisopropyl peroxydicarbonate and bis(4-tert-butylcyclohexyl) peroxydicarbonate; and alkyl peresters, such as tert-butyl peroxyoctoate and tert-butyl peroxybenzoate. In particular, benzoyl peroxide is preferred. Instead of the peroxide, a radical generator such as a radical generating azo compound, e.g., azobisisobutyronitrile, may be used.

As reported in Macromolecules, 1995, 28, 2993, the alkoxyamine compound shown below may be used as the initiator instead of a combination of the radical capping agent and the radical generator.



When the alkoxyamine compound is used as the initiator, the use of a compound having a functional group such as a hydroxyl group as shown in the above figure produces a polymer having the functional group at an end. When this compound is used in the method of the present invention, a polymer having the functional group at an end is produced.

The conditions of polymerization using the nitroxide compound and/or the like as the radical capping agent, such as the monomer, the solvent, the polymerization temperature, and the like, are not limited. However, these conditions may be the same as those in atom transfer radical polymerization which will be described below.

Atom transfer radical polymerization

Next, the atom transfer radical polymerization suitable as the living radical polymerization of the present invention will be described.

The atom transfer radical polymerization uses, as the initiator, an organic halide, particularly an organic halide having a highly reactive carbon-halogen bond (e.g., a carbonyl

compound having a halogen at an α -position, or a compound having a halogen at a benzyl position), or a halogenated sulfonyl compound.

Specific examples of such a compound include the following:

$C_6H_5-CH_2X$, $C_6H_5-C(H)(X)CH_3$, and $C_6H_5-C(X)(CH_3)_2$

(wherein C_6H_5 is a phenyl group, X is chlorine, bromine, or iodine);

$R^3-C(H)(X)-CO_2R^4$, $R^3-C(CH_3)(X)-CO_2R^4$, $R^3-C(H)(X)-C(O)R^4$, and
 10 $R^3-C(CH_3)(X)-C(O)R^4$

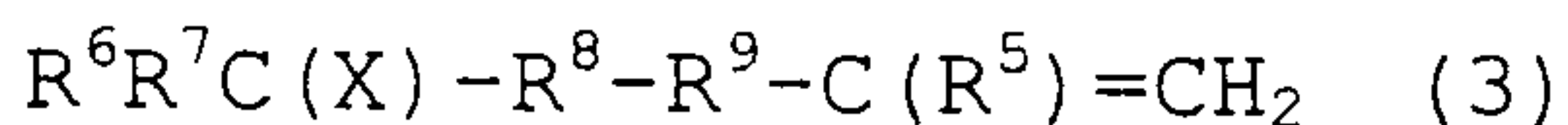
(wherein R^3 and R^4 each is a hydrogen atom or an alkyl group, an aryl group, or an aralkyl group having 1 to 20 carbon atoms; X is chlorine, bromine, or iodine); and

$R^3-C_6H_4-SO_2X$

15 (wherein R^3 is a hydrogen atom or an alkyl group, an aryl group, or an aralkyl group having 1 to 20 carbon atoms; X is chlorine, bromine, or iodine).

As the initiator of the atom transfer radical polymerization, an organic halide or halogenated sulfonyl
 20 compound having a functional group other than a functional group which initiates polymerization can be used. In this case, the resultant vinyl polymer has the functional group at one of the main chain ends and a polymerization propagation
 terminal-structure of atom transfer radical polymerization at
 25 the other end. Examples of such a functional group include alkenyl, crosslinkable silyl, hydroxyl, epoxy, amino, and amido group.

Examples of an organic halide having an alkenyl group include, but not limited to, compounds having the structure
 30 represented by the general formula 3:

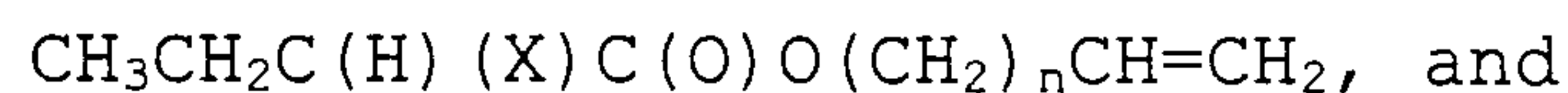
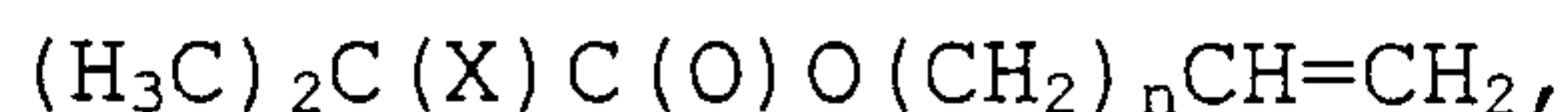
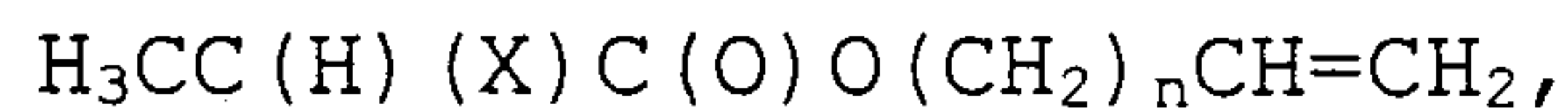


(wherein R^5 is a hydrogen atom or a methyl group; R^6 and R^7 each is a hydrogen atom, an alkyl group, an aryl group or an aralkyl group having 1 to 20 carbon atoms, or R^6 and R^7 are bonded together
 35 at the other ends; R^8 is $-C(O)O-$ (ester group), $-C(O)-$ (keto

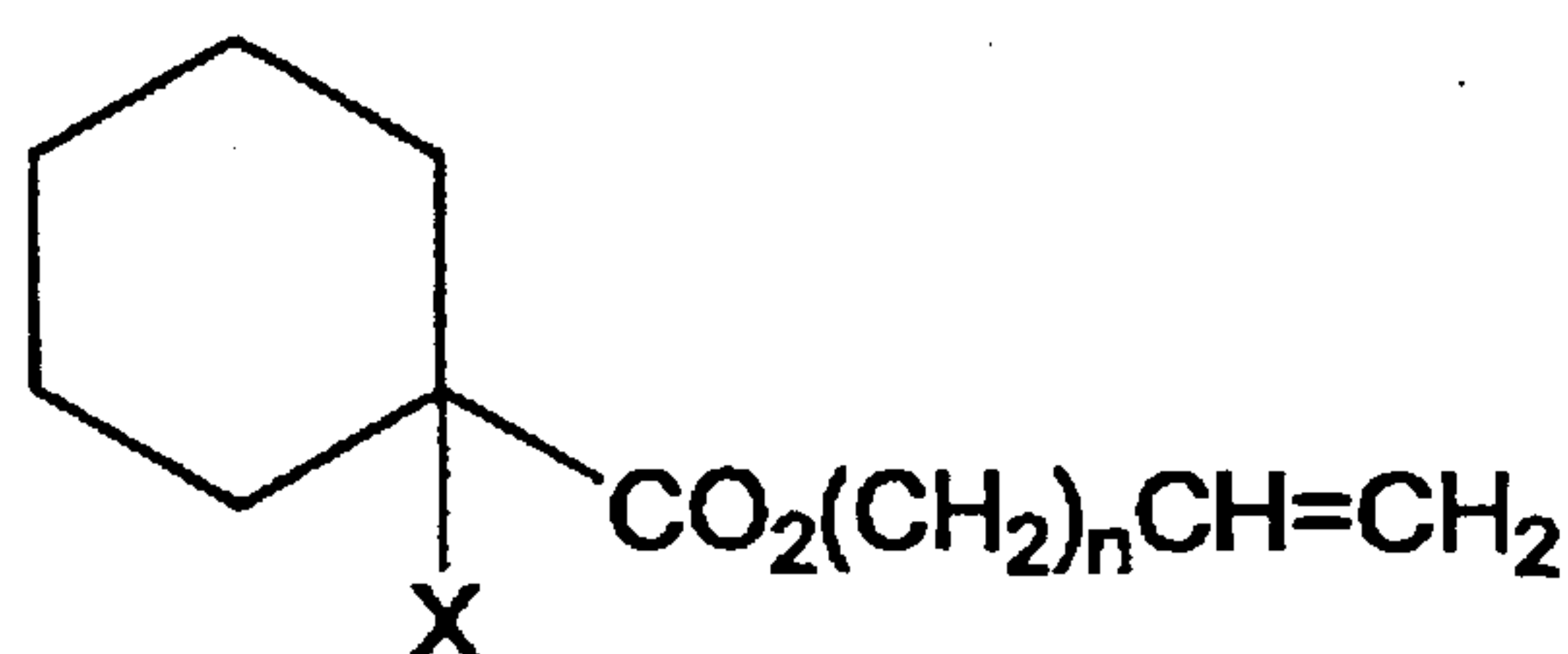
group), or an o-, m-, or p-phenylene group; R^9 is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may contain at least one ether bond; and X is chlorine, bromine, or iodine).

5 Specific examples of substituents R^6 and R^7 include hydrogen, methyl, ethyl, n-propyl, isopropyl, butyl, pentyl, and hexyl group. Substituents R^6 and R^7 may be bonded together at the other ends to form a cyclic skeleton.

10 Specific examples of an alkenyl group-containing organic halide represented by the general formula 3 are the following:

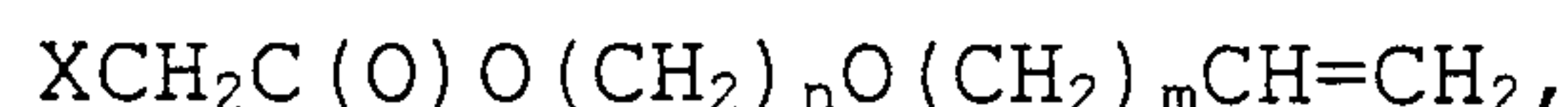


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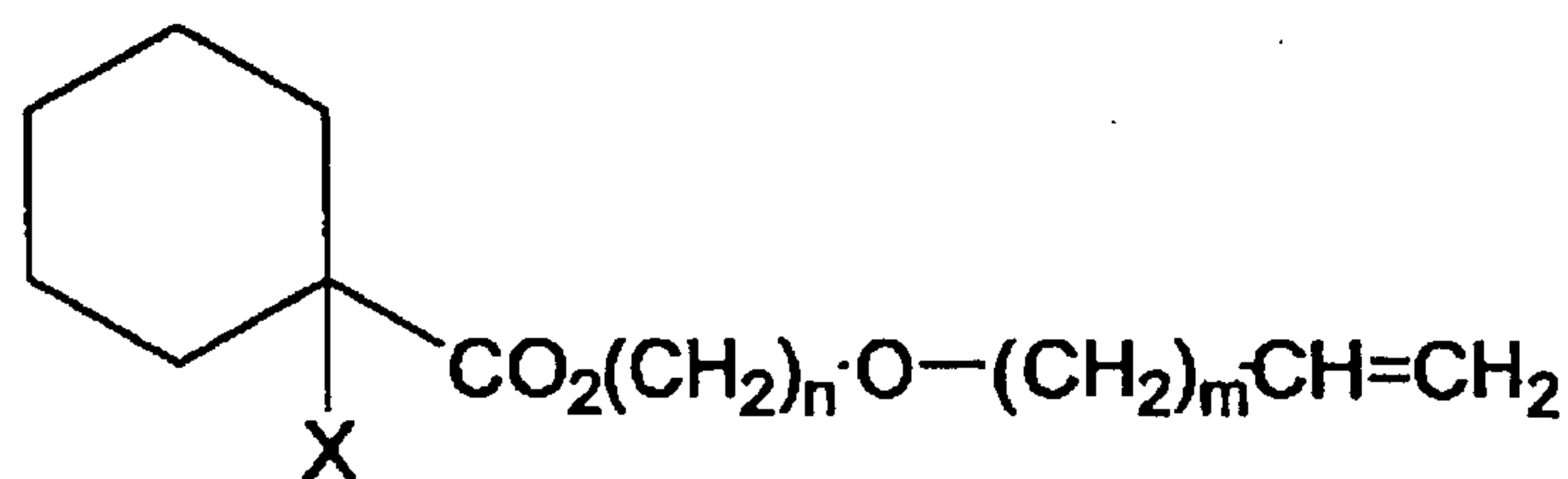
(wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20);



25 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2,$



30



(wherein X is chlorine, bromine, or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

35 o, m, p-XCH₂-C₆H₄-(CH₂)_n-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂, and

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂

(wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20);

5 o, m, p-XCH₂-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂, and

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_mCH=CH₂

(wherein X is chlorine, bromine, or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

10 o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂, and

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂

(wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20); and

15 o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂, and

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂

(wherein X is chlorine, bromine, or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20).

20 Other examples of an organic halide having an alkenyl group include compounds represented by the general formula 4:

$$\text{H}_2\text{C}=\text{C}(\text{R}^5)-\text{R}^9-\text{C}(\text{R}^6)(\text{X})-\text{R}^{10}-\text{R}^7 \quad (4)$$

(wherein R⁵, R⁶, R⁷, R⁹, and X represent the same as the above, and R¹⁰ represents a direct bond or -C(O)O- (ester group), -C(O)- (keto group), or an o-, m-, or p-phenylene group).

25 R⁹ is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain at least one ether bond). When R⁹ is a direct bond, the compound is a halogenated allyl compound in which a vinyl group is bonded to the carbon bonded
 30 to a halogen. In this case, the carbon-halogen bond is activated by the adjacent vinyl group, and thus a C(O)O or phenylene group is not necessarily required as R¹⁰, and a direct bond may be present. When R⁹ is not a direct bond, R¹⁰ is preferably a C(O)O, C(O), or phenylene group for activating the
 35 carbon-halogen bond.

Specific examples of the compounds represented by the general formula 4 include the following:

- $\text{CH}_2=\text{CHCH}_2\text{X}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{X}$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_3$,
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{H})(\text{X})\text{CH}_3$, $\text{CH}_2=\text{CHC}(\text{X})(\text{CH}_3)_2$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_2\text{H}_5$,
 5 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}(\text{CH}_3)_2$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_6\text{H}_5$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_2\text{C}_6\text{H}_5$,
 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, and
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$
 10 (wherein X is chlorine, bromine, or iodine, and R is an alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms).

Specific examples of a halogenated sulfonyl compound having an alkenyl group include the following:

- o-, m-, p- $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{C}_6\text{H}_4-\text{SO}_2\text{X}$, and
 15 o-, m-, p- $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2\text{X}$
 (wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20).

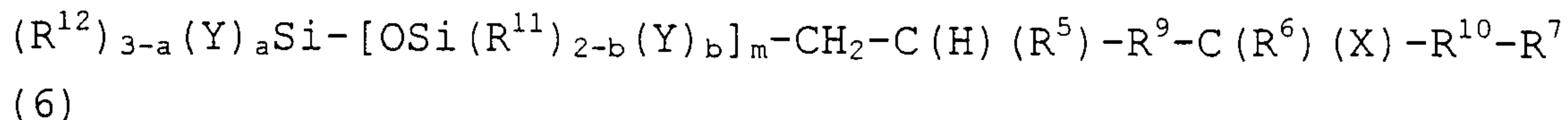
- Specific examples of an organic halide having a crosslinkable silyl group include, but not limited to, compounds with a structure represented by the general formula 5:

- $\text{R}^6\text{R}^7\text{C}(\text{X})-\text{R}^8-\text{R}^9-\text{C}(\text{H})(\text{R}^5)\text{CH}_2-[\text{Si}(\text{R}^{11})_{2-b}(\text{Y})_b\text{O}]_m-\text{Si}(\text{R}^{12})_{3-a}(\text{Y})_a$ (5)
 (wherein R^5 , R^6 , R^7 , R^8 , R^9 and X represent the same as the above, and R^{11} and R^{12} each represents an alkyl, aryl or aralkyl group
 25 having 1 to 20 carbon atoms, or a triorganosiloxy group represented by $(\text{R}')_3\text{SiO}-$ (the three R's each is a monovalent hydrocarbon group having 1 to 20 carbon atoms and may be the same or different); when two or more groups R^{11} or R^{12} are present, they may be the same or different; Y represents a hydroxyl group
 30 or a hydrolyzable group, and when two or more groups Y are present, they may be the same or different; a represents 0, 1, 2, or 3; b represents 0, 1, or 2; m is an integer of 0 to 19; and $a + mb \geq 1$ is satisfied).

- Specific examples of the compounds represented by the general formula 5 include the following:

- $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{OCH}_3)_3,$
 $\text{CH}_3\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{OCH}_3)_3,$
 $(\text{CH}_3)_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{OCH}_3)_3,$
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 5 $\text{CH}_3\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$ and
 $(\text{CH}_3)_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$
 (wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20);
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 10 $\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 $\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 15 $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$ and
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 (wherein X is chlorine, bromine, or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20); and
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 20 $\text{o, m, p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 25 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 30 $\text{o, m, p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o, m, p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$ and
 $\text{o, m, p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3$
 (wherein X is chlorine, bromine, or iodine).
 35 Other examples of the organic halide having a

crosslinkable silyl group include compounds with a structure represented by the general formula 6:



- 5 (wherein R^5 , R^6 , R^7 , R^9 , R^{10} , R^{11} , R^{12} , a , b , m , X and Y represent the same as the above).

Specific examples of such compounds include the following:

- (CH₃O)₃SiCH₂CH₂C(H)(X)C₆H₅,
 10 (CH₃O)₂(CH₃)SiCH₂CH₂C(H)(X)C₆H₅,
 (CH₃O)₃Si(CH₂)₂C(H)(X)-CO₂R,
 (CH₃O)₂(CH₃)Si(CH₂)₂C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-CO₂R,
 (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-CO₂R,
 15 (CH₃O)₃Si(CH₂)₄C(H)(X)-CO₂R,
 (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₉C(H)(X)-CO₂R,
 (CH₃O)₂(CH₃)Si(CH₂)₉C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-C₆H₅,
 20 (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-C₆H₅,
 (CH₃O)₃Si(CH₂)₄C(H)(X)-C₆H₅, and
 (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-C₆H₅

(wherein X is chlorine, bromine, or iodine, and R is alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms).

- 25 Examples of the hydroxyl group-containing organic halide or halogenated sulfonyl compound include, but not limited to, the following:



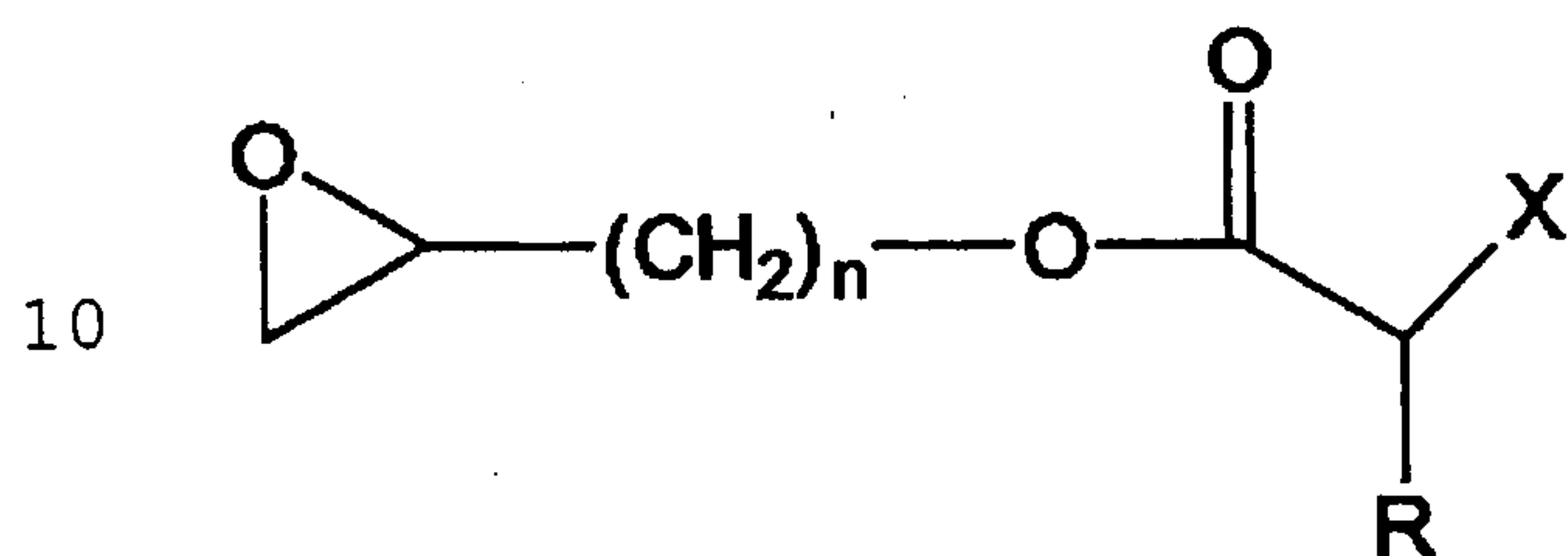
- (wherein X is chlorine, bromine, or iodine, R is a hydrogen atom
 30 or alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms, and n is an integer of 1 to 20).

Examples of the amino group-containing organic halide or halogenated sulfonyl compound include, but not limited to, the following:

- 35 H₂N-(CH₂)_n-OC(O)C(H)(R)(X)

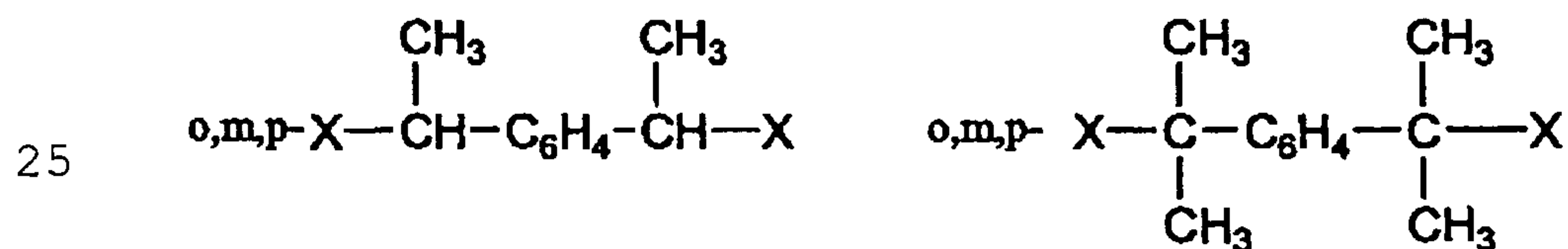
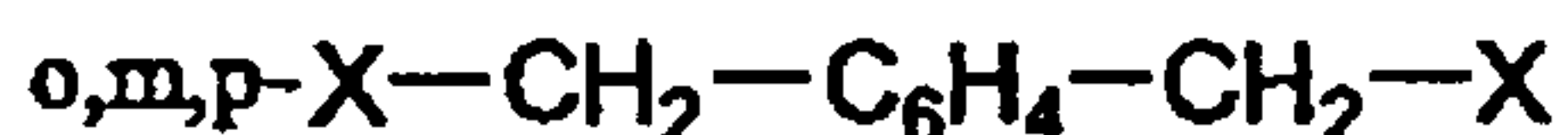
(wherein X is chlorine, bromine, or iodine, R is a hydrogen atom or alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms, and n is an integer of 1 to 20).

Examples of the epoxy group-containing organic halide or halogenated sulfonyl compound include, but not limited to, the following:

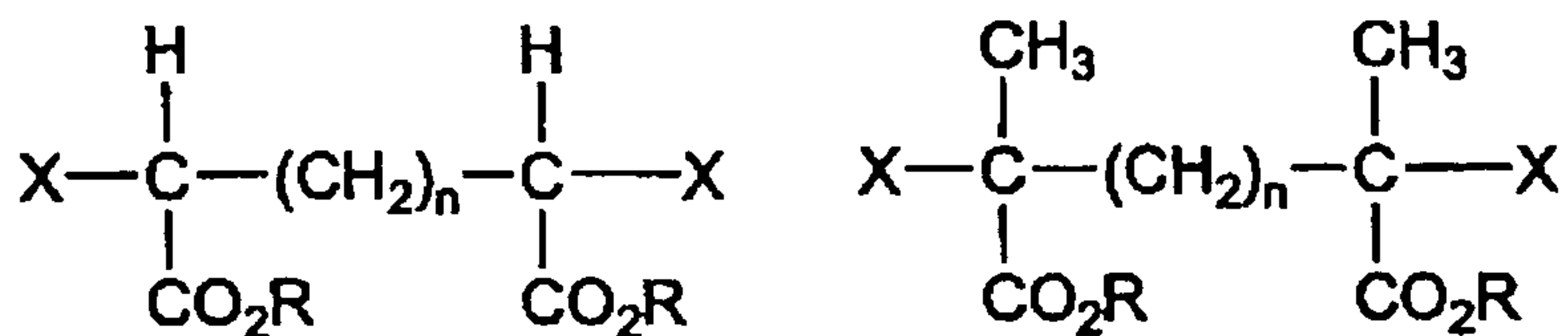


(wherein X is chlorine, bromine, or iodine, R is a hydrogen atom or alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms, and n is an integer of 1 to 20).

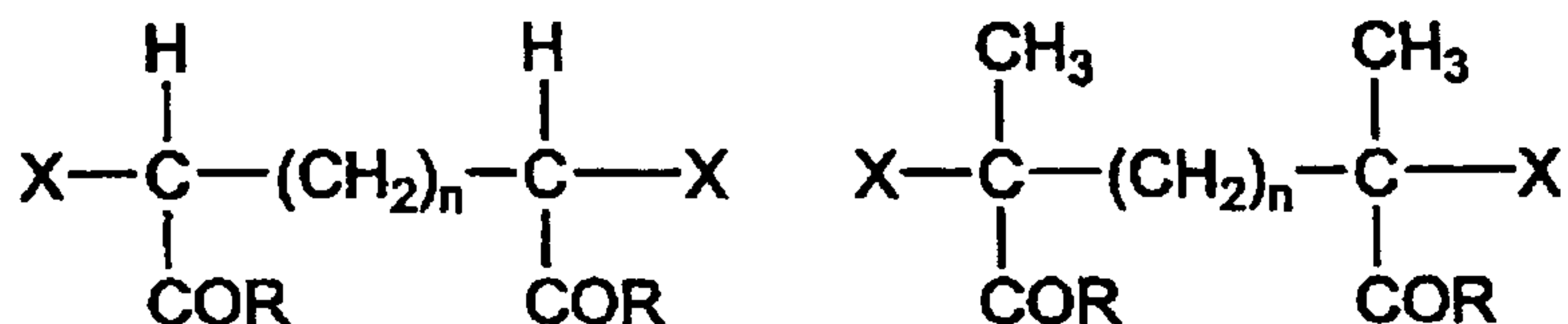
In order to obtain a polymer having at least two polymerization propagation terminal structures per molecule, an organic halide or halogenated sulfonyl compound having at least two initiation points is preferably used as the initiator. Examples of such a compound include the following:



(wherein C₆H₄ is a phenylene group, and X is chlorine, bromine, or iodine.)

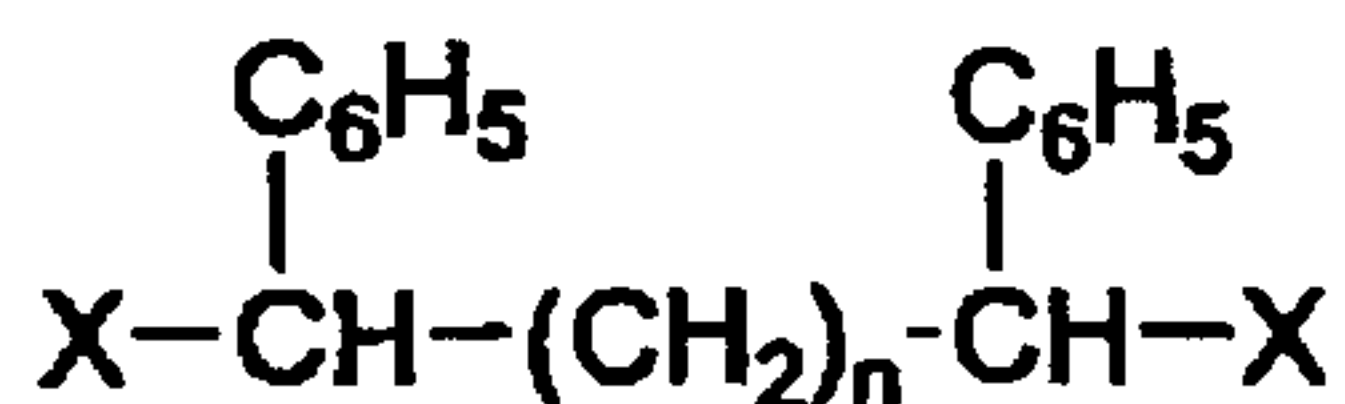
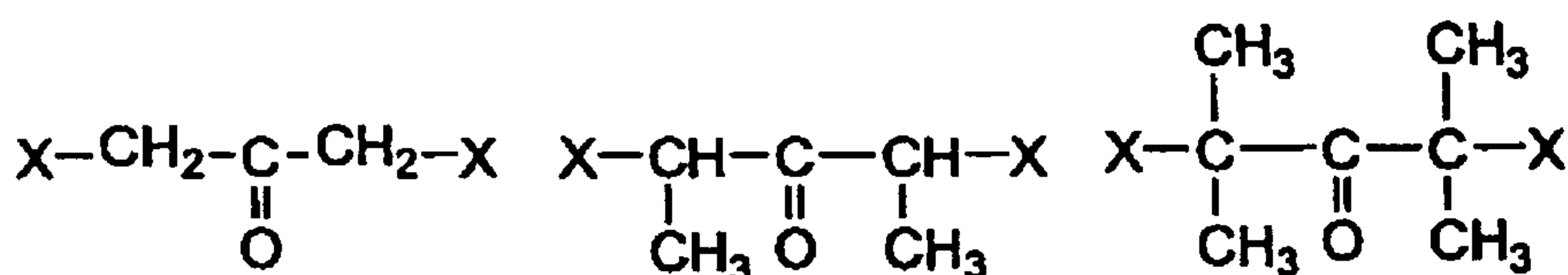


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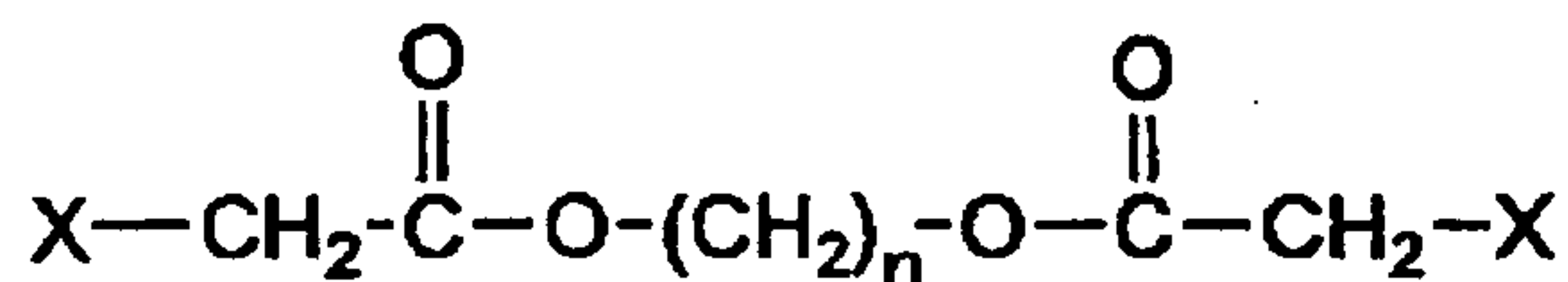
10 (wherein R is an alkyl, aryl, or aralkyl group having 1 to 20 carbon atoms, n is an integer of 0 to 20, and X is chlorine, bromine, or iodine.)

15

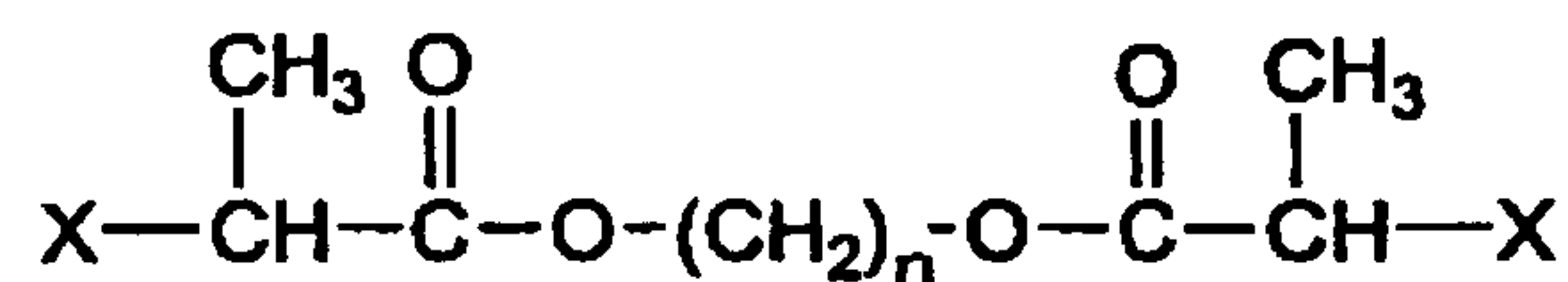


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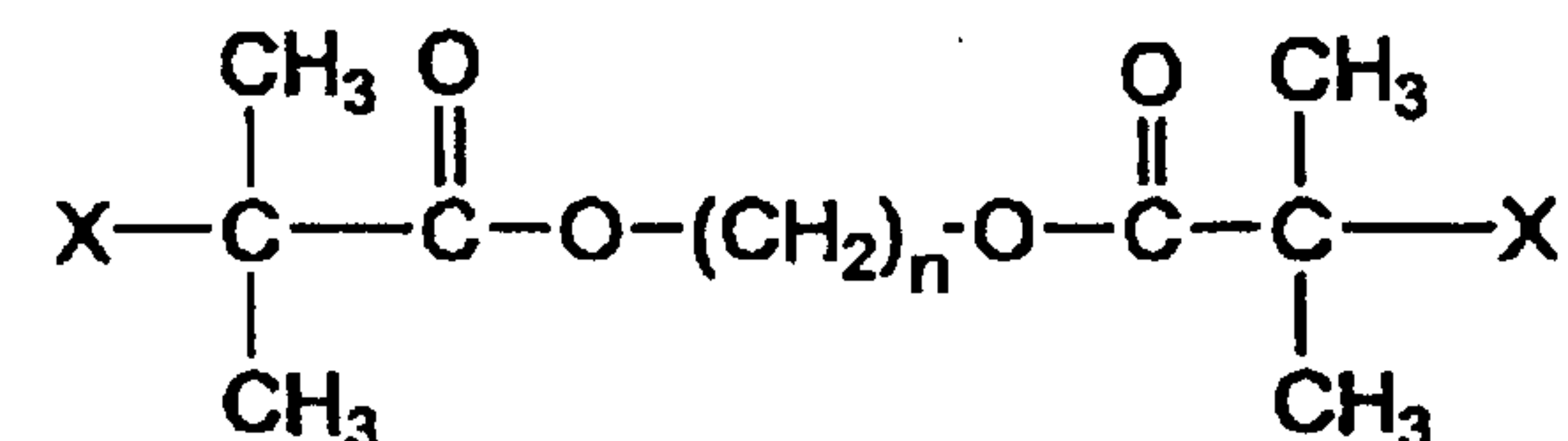
(wherein X is chlorine, bromine, or iodine, and n is an integer of 0 to 20.)



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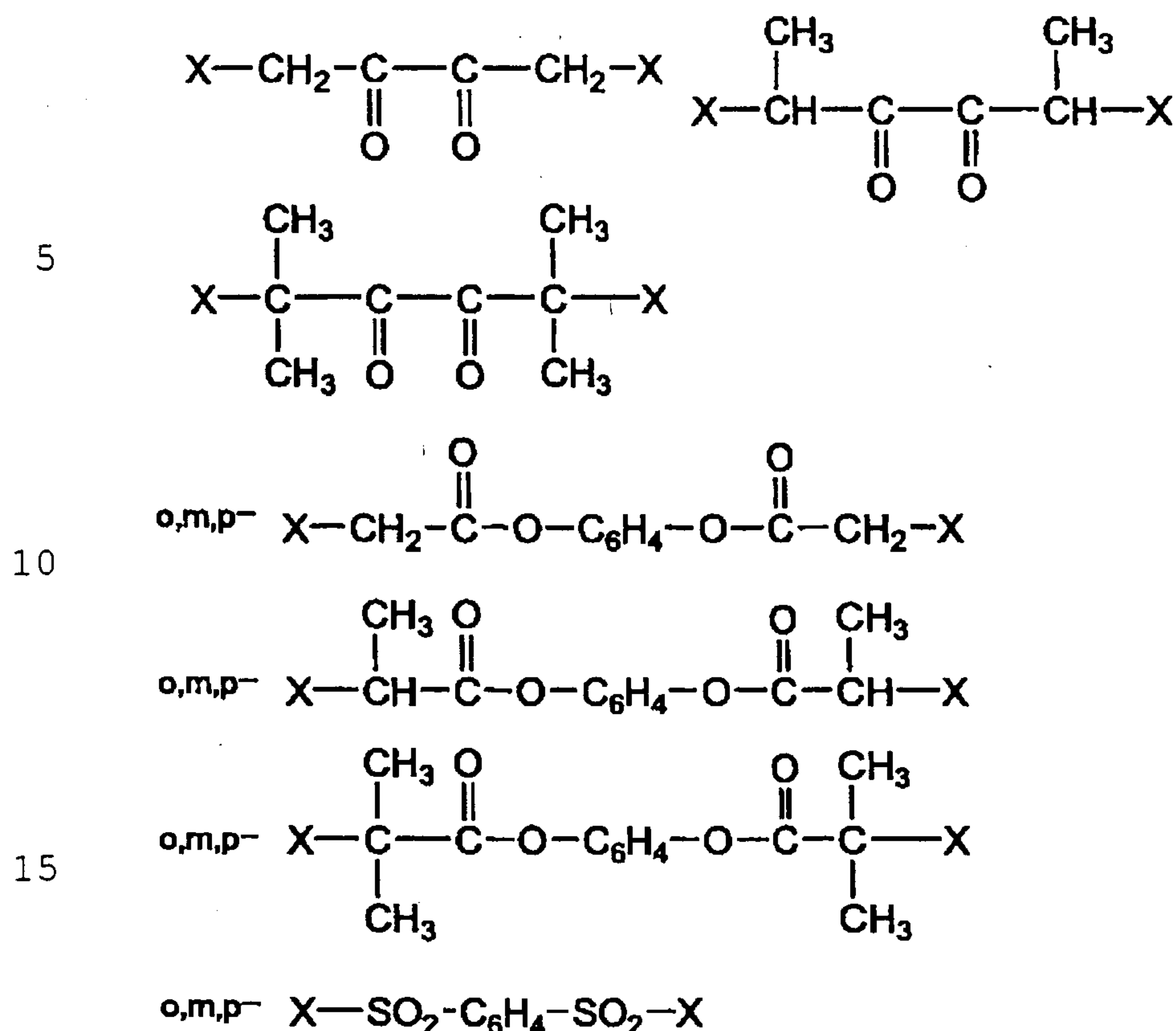


30



(wherein n is an integer of 1 to 20, and X is chlorine, bromine, or iodine.)

35



(wherein X is chlorine, bromine, or iodine.)

20 The vinyl monomer used in the polymerization is not particularly limited, and any of the compounds listed above can be preferably used.

The transition metal complex used as the polymerization catalyst is not particularly limited, but a metal complex composed of a VII, VIII, IX, X, or XI group element in the periodic table as a central metal is preferred. A complex of zero-valent copper, monovalent copper, divalent ruthenium, divalent iron, or divalent nickel is more preferred. Among these complexes, a copper complex is most preferred. Specific examples of a monovalent copper compound include cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, and cuprous perchlorate. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or its derivative, 1,10-phenanthroline or its derivative, or polyamine, e.g., tetramethylethylenediamine, pentamethyldiethylenetriamine,

35

or hexamethyl tris(2-aminoethyl)amine, is added for increasing catalyst activity. As a ligand, nitrogen-containing compounds are preferred, chelate nitrogen compounds are more preferred, N,N,N',N'',N''-pentamethyldiethylenetriamine is further
5 preferred. Also, a tris(triphenylphosphine) complex ($\text{RuCl}_2(\text{PPh}_3)_3$) of divalent ruthenium chloride is suitable as the catalyst. When a ruthenium compound is used as a catalyst, an aluminum alkoxide is added as an activator. Furthermore, a bistris(triphenylphosphine) complex ($\text{FeCl}_2(\text{PPh}_3)_2$) of divalent iron,
10 a bistris(triphenylphosphine) complex ($\text{NiCl}_2(\text{PPh}_3)_2$) of divalent nickel, or a bis(tributylphosphine) complex ($\text{NiBr}_2(\text{PBu}_3)_2$) of divalent nickel is preferred as the catalyst.

The polymerization can be performed without a solvent or in any of various solvents. Examples of the solvent include
15 hydrocarbon solvents, such as benzene and toluene; ether solvents, such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents, such as methylene chloride and chloroform; ketone solvents, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; alcohol solvents, such as
20 methanol, ethanol, propanol, isopropanol, n-butyl alcohol, and tert-butyl alcohol; nitrile solvents, such as acetonitrile, propionitrile, and benzonitrile; ester solvents, such as ethyl acetate and butyl acetate; and carbonate solvents, such as ethylene carbonate and propylene carbonate. These solvents
25 can be used alone or as a mixture of two or more.

The polymerization can be performed in a range of 0°C to 200°C, and preferably 50°C to 150°C without any purpose of restriction.

The atom transfer radical polymerization of the invention
30 includes so called reverse atom transfer radical polymerization. The reverse atom transfer radical polymerization is a method comprising reacting an ordinary atom transfer radical polymerization catalyst in its high oxidation state resulting from radical generation, for example Cu(II') when Cu(I) is used
35 as the catalyst, with an ordinary radical initiator, such as

a peroxide, to thereby bring about an equilibrium state like in atom transfer radical polymerization (cf. Macromolecules, 1999, 32, 2872).

<Functional groups>

5 Number of crosslinkable silyl groups

The number of crosslinkable silyl groups in the vinyl polymer is not particularly restricted and, from the viewpoint of the curability of the composition and the physical properties of the cured product, preferably not smaller than 1.1, more
10 preferably not smaller than 1.1 but not greater than 4.0, further preferably not smaller than 1.2 but not greater than 3.5, on average in one molecule.

Positions of crosslinkable silyl groups

In cases where the cured products resulting from curing
15 of the curable composition of the present invention are especially required to have rubber-like properties, it is preferred that at least one of crosslinkable functional groups be positioned at a terminus of the molecular chain so that the molecular weight between crosslinking sites, which has a great
20 influence on the rubber elasticity, can be increased. More preferably, all crosslinkable functional groups are located at molecular chain termini.

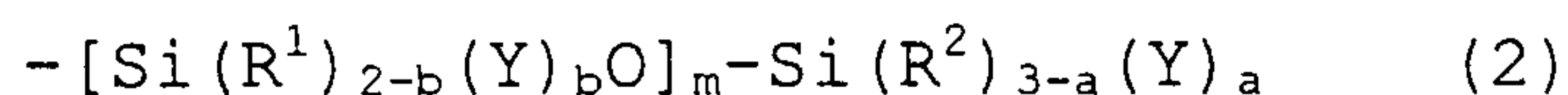
Methods of producing vinyl polymers, in particular (meth)acrylic polymers, having at least one crosslinkable silyl
25 group such as mentioned above at a molecular terminus thereof are disclosed in Japanese Kokoku Publication Hei-03-14068, Japanese Kokoku Publication Hei-04-55444 and Japanese Kokai Publication Hei-06-211922, among others. However, these methods are free radical polymerization methods in which the
30 above-mentioned "chain transfer agent methods" is used and, therefore, the polymers obtained generally have problems, namely they show a molecular weight distribution represented by M_w/M_n as wide as not less than 2 as well as a high viscosity, although they have crosslinkable silyl groups, in relatively
35 high proportions, at molecular chain termini. Therefore, for

obtaining vinyl polymers showing a narrow molecular weight distribution and a low viscosity and having crosslinkable silyl groups, in high proportions, at molecular chain termini, the above-described "living radical polymerization method" is preferably used. The present invention is not restricted to the polymers showing a narrow molecular weight distribution, however.

In the following, an explanation is made of these functional groups.

10 Crosslinkable silyl groups

As the crosslinkable silyl groups to be used in the practice of the present invention, there may be mentioned those groups represented by the general formula 2:

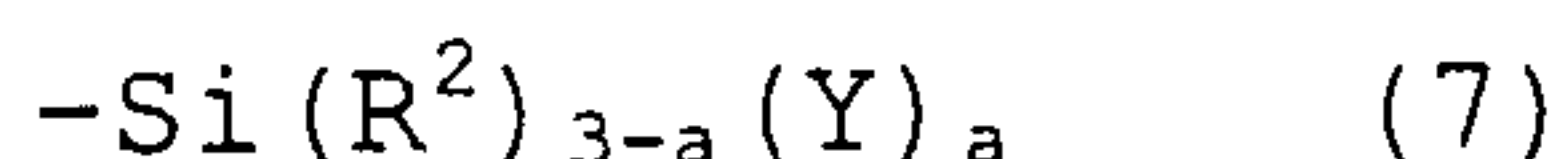


15 {wherein, R^1 and R^2 each is an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms or a triorganosiloxy group represented by $(\text{R}')_3\text{SiO}-$ (in which R' is a univalent hydrocarbon group containing 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R^1 or R^2 groups, they may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different; a represents 0, 1, 2 or 3, b represents 0, 1 or 2, and m is an integer of 0 to 19, provided that the relation $a + mb \geq 1$ should be satisfied.}

As the hydrolyzable group, there may be mentioned, among others, a hydrogen atom and those groups which are in general use, for example alkoxy, acyloxy, ketoximate, amino, amido, aminoxy, mercapto and alkenyloxy groups. Among them, alkoxy, amido and aminoxy groups are preferred. In view of mild hydrolyzability and ease of handling, alkoxy groups are particularly preferred. For alkoxy groups, the less carbon atoms an alkoxy group has, the more active said group is. Among alkoxy groups, methoxy group > ethoxy group > propoxy group >

... becomes less active in that order and, therefore, they can be selected according to the purpose and/or use.

One to three hydrolyzable groups and/or hydroxyl groups can be bound to each silicon atom and it is preferred that (a + Σb) be within the range of 1 to 5. When there are two or more hydrolyzable groups or hydroxyl groups in one crosslinkable silyl group, they may be the same or different. The number of silicon atoms forming the crosslinkable silyl group is not less than 1 and, in the case of silicon atoms connected by siloxane or like bonding, it is preferably not more than 20. Particularly preferred are crosslinkable silyl groups represented by the general formula 7:



(wherein R^2 and Y are as defined above; and a is an integer of 1 to 3) because of ready availability.

Considering the curability, the integer a is preferably 2 or more, though this is not critical.

In many cases, a polymer which has a hydrolysable silicon group consisted of two hydrolysable groups bound to one silicon atom is used as the vinyl polymer containing a crosslinkable silyl group. In the case where the polymer is used for an adhesive or at a low temperature, particularly where a very high curing rate is required, the curing rate of the polymer is insufficient. On the contrary, in the case where flexibility is required after curing, the crosslinking density has to be lowered and accordingly due to the insufficient crosslinking density, the stickiness (surface tack) is sometimes increased. In such a case, one in which a is 3 (e.g. trimethoxy functional group) is preferable.

One in which a is 3 (e.g. trimethoxy functional group) is faster in curability than one in which a is 2 (e.g. dimethoxy functional group) but, as for the storage stability and/or mechanical properties (e.g. elongation), one in which a is 2 is sometimes superior. For attaining a balance between curability and physical properties, one in which a is 2 (e.g.

dimethoxy functional group) and one in which a is 3 (e.g. trimethoxy functional group) may be used in combination.

For example, in the case where each of Ys is the same each other, the reactivity of the group represented by Y increases as the number represented by a increases, and therefore the curability and the mechanical properties of the cured product can be controlled by properly selecting Y and a and Y and a may be selected in accordance with the purposes and uses. Further, one in which a is 1 may be used as a chain expanding agent by being mixed with a polymer containing a crosslinkable silyl group, practically with at least one polymer selected from polysiloxane, polyoxypropylene, or polyisobutylene polymers. Accordingly, it becomes possible to obtain the composition with low viscosity before curing and high elongation at break, low bleeding property, less surface staining property, and excellent adhesiveness with a coating material after curing.

Crosslinkable silyl group introduction method

In the following, several methods of crosslinkable silyl group introduction into the vinyl polymer of the present invention are described without any purpose of restriction.

At first, a method of introducing the crosslinkable silyl group, alkenyl group, and hydroxyl group by conversion of the terminal functional groups will be described. Since these functional groups may be precursors for other groups, it is described in the backward order from the crosslinkable silyl group.

As methods of synthesizing a vinyl polymer containing at least one crosslinkable silyl group, there may be mentioned, among others,

(A) the method which comprises subjecting a crosslinkable silyl group-containing hydrosilane compound to addition to a vinyl polymer having at least one alkenyl group in the presence of a hydrosilylation catalyst,

(B) the method which comprises reacting a vinyl polymer having at least one hydroxyl group with a compound having, in

each molecule, a crosslinkable silyl group and a group capable of reacting with the hydroxyl group, such as an isocyanato group,

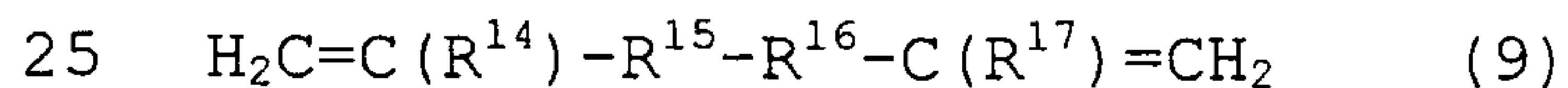
(C) the method which comprises subjecting a compound
5 having, in each molecule, a polymerizable alkenyl group and a crosslinkable silyl group to reaction in synthesizing a vinyl polymer by radical polymerization,

(D) the method which comprises subjecting a chain
transfer agent having a crosslinkable silyl group to reaction
10 in synthesizing a vinyl polymer by radical polymerization, and

(E) the method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a compound having, in each molecule, a crosslinkable silyl group and a stable carbanion.

15 The vinyl polymer having at least one alkenyl group, which is to be used in the above method (A), can be obtained by various methods. Several methods of synthesis are mentioned below, without any purpose of restriction, however.

(A-a) Method comprising subjecting to reaction a
20 compound having, in each molecule, a polymerizable alkenyl group together with a low polymerizability alkenyl group, such as one represented by the general formula 9 shown below as a second monomer in synthesizing a vinyl polymer by radical polymerization:



(wherein R^{14} represents a hydrogen atom or a methyl group, R^{15} represents $-\text{C}(\text{O})\text{O}-$ or an o-, m- or p-phenylene group, R^{16} represents a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds,
30 and R^{17} represents a hydrogen atom, an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms or an aralkyl group containing 7 to 20 carbon atoms).

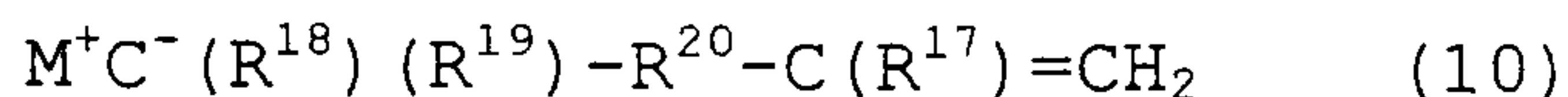
The time when the compound having, in each molecule, a polymerizable alkenyl group together with a low
35 polymerizability alkenyl group is subjected to reaction is not

particularly restricted but, in particular in living radical polymerization and when rubber-like properties are expected, the compound is preferably subjected to reaction as a second monomer at the final stage of the polymerization reaction or
 5 after completion of the reaction of the employed monomers.

(A-b) Method comprising subjecting to reaction a compound having at least two low polymerizability alkenyl groups, for example 1,5-hexadiene, 1,7-octadiene or 1,9-decadiene, at the final stage of the polymerization or after
 10 completion of the reaction of the monomers employed in vinyl polymer synthesis by living radical polymerization.

(A-c) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with one of various alkenyl-containing organometallic compounds, for
 15 example an organotin such as allyltributyltin or allyltrioctyltin, for substitution of the halogen.

(A-d) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a stabilized, alkenyl-containing carbanion such as one
 20 represented by the general formula 10, for substitution of the halogen:



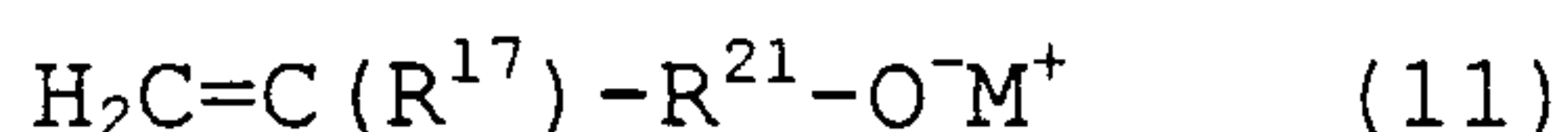
(wherein R^{17} is as defined above, R^{18} and R^{19} each is an electron-withdrawing group capable of stabilizing the
 25 carbanion C^- or one of them is such an electron-withdrawing group and the other represents a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms or a phenyl group, R^{20} represents a direct bond or a divalent organic group containing 1 to 10 carbon atoms, which may contain one or more ether bonds, and
 30 M^+ represents an alkali metal ion or a quaternary ammonium ion).

Particularly preferred as the electron-withdrawing group R^{18} and/or R^{19} are those which have a structure of $-CO_2R$, $-C(O)R$ or $-CN$.

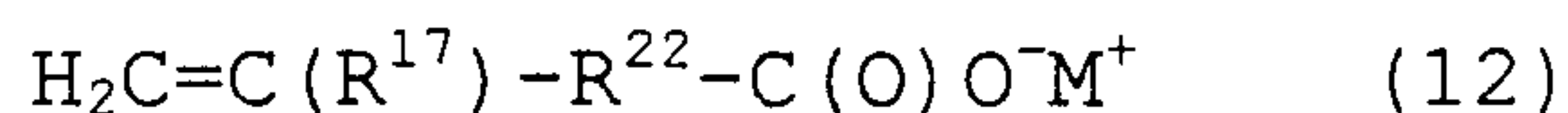
(A-e) Method comprising reacting a vinyl polymer having
 35 at least one highly reactive carbon-halogen bond with a simple

substance metal, such as zinc, or an organometallic compound and then reacting the thus-prepared enolate anion with an alkenyl-containing, electrophilic compound, such as an alkenyl-containing compound having a leaving group such as a halogen atom or an acetyl group, an alkenyl-containing carbonyl compound, an alkenyl-containing isocyanate compound or an alkenyl-containing acid halide.

(A-f) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with an alkenyl-containing oxy anion or carboxylate anion such as one represented by the general formula 11 or 12, for substitution of the halogen:



(wherein R^{17} and M^+ are as defined above and R^{21} is a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds);



(wherein R^{17} and M^+ are as defined above and R^{22} is a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds).

The method of synthesizing the above-mentioned vinyl polymer having at least one highly reactive carbon-halogen bond includes, but is not limited to, atom transfer radical polymerization methods using an organic halide or the like as initiator and a transition metal complex as catalyst, as mentioned above.

It is also possible to obtain the vinyl polymer having at least one alkenyl group from a vinyl polymer having at least one hydroxyl group. As utilizable methods, there may be mentioned, for example, the following, without any purpose of restriction.

(A-g) Method comprising reacting the hydroxyl group of a vinyl polymer having at least one hydroxyl group with a base, such as sodium methoxide, followed by reaction with an alkenyl-containing halide, such as allyl chloride.

(A-h) Method comprising reacting such hydroxyl group with an alkenyl-containing isocyanate compound, such as allyl isocyanate.

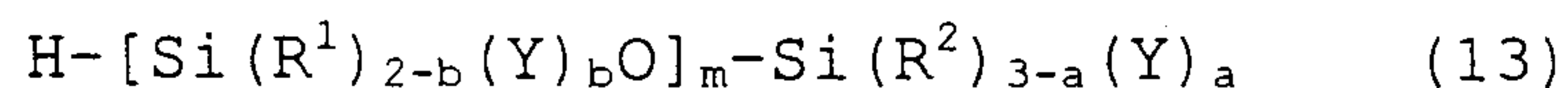
(A-i) Method comprising reacting such hydroxyl group with an alkenyl-containing acid halide, such as (meth)acrylic acid chloride, in the presence of a base, such as pyridine.

(A-j) Method comprising reacting such hydroxyl group with an alkenyl-containing carboxylic acid, such as acrylic acid, in the presence of an acid catalyst.

In the practice of the present invention, when no halogen is directly involved in the alkenyl group introduction, as in the method (A-a) or (A-b), the vinyl polymer is preferably synthesized by living radical polymerization. From the viewpoint of ready controllability, the method (A-b) is more preferred.

In cases where alkenyl group introduction is effected by conversion of the halogen atom of a vinyl polymer having at least one highly reactive carbon-halogen atom, use is preferably made of a vinyl polymer having at least one terminal carbon-halogen bond, which is highly reactive, as obtained by subjecting a vinyl monomer to radical polymerization (atom transfer radical polymerization) using, as an initiator, an organic halide or halogenated sulfonyl compound having at least one highly reactive carbon-halogen bond and, as a catalyst, a transition metal complex. In view of easier controllability, the method (A-f) is more preferred.

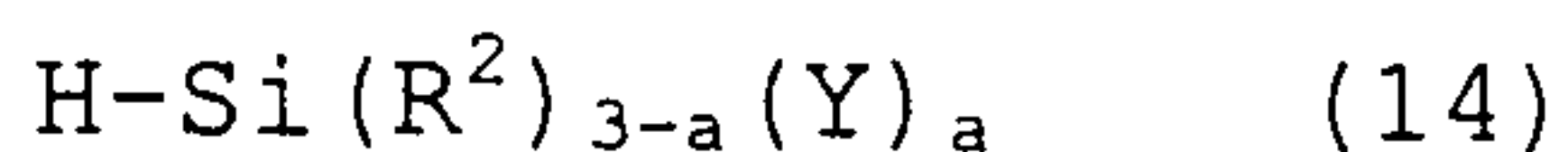
The crosslinkable silyl group-containing hydrosilane compound is not particularly restricted but includes, as typical examples, compounds represented by the general formula 13.



{wherein R^1 and R^2 each represents an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms or a triorganosiloxy group represented by $(\text{R}')_3\text{SiO}-$ (in which R' is

a univalent hydrocarbon group containing 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R¹ or R² groups, they may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different; a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation $a + mb \geq 1$ should be satisfied}.

Particularly preferred among those hydrosilane compounds in view of ready availability are crosslinkable group-containing compounds represented by the general formula 14:



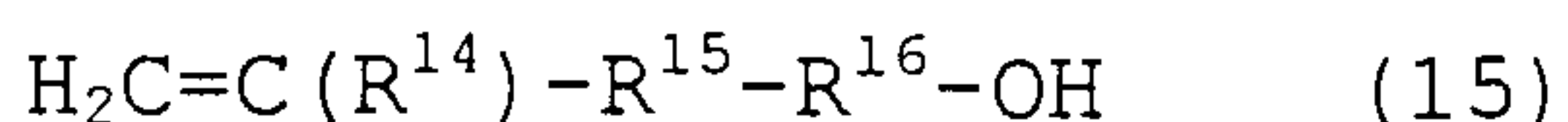
(wherein R² and Y are as defined above; and a is an integer of 1 to 3).

In subjecting the above crosslinkable silyl-containing hydrosilane compound to addition to the alkenyl group, a transition metal catalyst is generally used. The transition metal catalyst includes, among others, simple substance platinum; solid platinum dispersed on a support such as alumina, silica or carbon black; chloroplatinic acid; chloroplatinic acid complexes with alcohols, aldehydes, ketones or the like; platinum-olefin complexes; and platinum(0)-divinyltetramethyldisiloxane complex. As other catalysts than platinum compounds, there may be mentioned RhCl(PPh₃)₃, RhCl₃, RuCl₃, IrCl₃, FeCl₃, AlCl₃, PdCl₂·H₂O, NiCl₂ and TiCl₄, for instance.

The method of producing the vinyl polymer having at least one hydroxyl group, which polymer is to be used in the methods (B) and (A-g) to (A-j), includes, but is not limited to, the following, among others.

(B-a) Method comprising subjecting to reaction, as a second monomer, a compound having both a polymerizable alkenyl group and a hydroxyl group in each molecule, for example one represented by the general formula 15 given below, in

synthesizing the vinyl polymer by radical polymerization:



(wherein R^{14} , R^{15} and R^{16} are as defined above).

The time for subjecting to reaction the compound having both a polymerizable alkenyl group and a hydroxyl group in each molecule is not critical but, in particular in living radical polymerization, when rubber-like properties are demanded, the compound is preferably subjected to reaction as a second monomer at the final stage of the polymerization reaction or after completion of the reaction of the employed monomer.

(B-b) Method comprising subjecting an alkenyl alcohol, such as 10-undecenol, 5-hexenol or allyl alcohol, to reaction at the final stage of polymerization reaction or after completion of the reaction of the employed monomer in synthesizing the vinyl polymer by living radical polymerization.

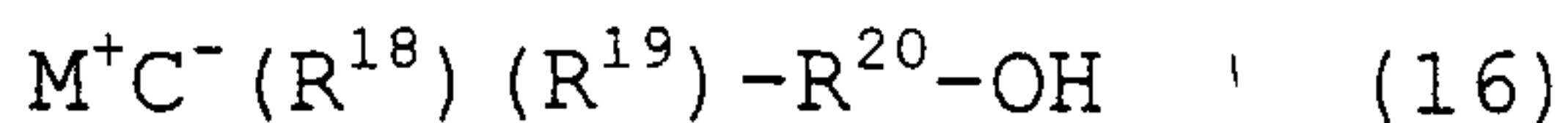
(B-c) Method comprising radical-polymerizing a vinyl monomer using a hydroxyl-containing chain transfer agent, such as a hydroxyl-containing polysulfide, in large amounts, as described in Japanese Kokai Publication Hei-05-262808, for instance.

(B-d) Method comprising subjecting a vinyl monomer to radical polymerization using hydrogen peroxide or a hydroxyl-containing initiator, as described in Japanese Kokai Publication Hei-06-239912 and Japanese Kokai Publication Hei-08-283310, for instance.

(B-e) Method comprising subjecting a vinyl monomer to radical polymerization using an alcohol in excess, as described in Japanese Kokai Publication Hei-06-116312, for instance.

(B-f) Method comprising introducing a terminal hydroxyl group by hydrolyzing the halogen atom of a vinyl polymer having at least one highly reactive carbon-halogen bond or reacting such halogen atom with a hydroxyl-containing compound, according to the method described in Japanese Kokai Publication Hei-04-132706, for instance.

(B-g) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a hydroxyl-containing stabilized carbanion, such as one represented by the general formula 16 for substitution of the
5 halogen atom:

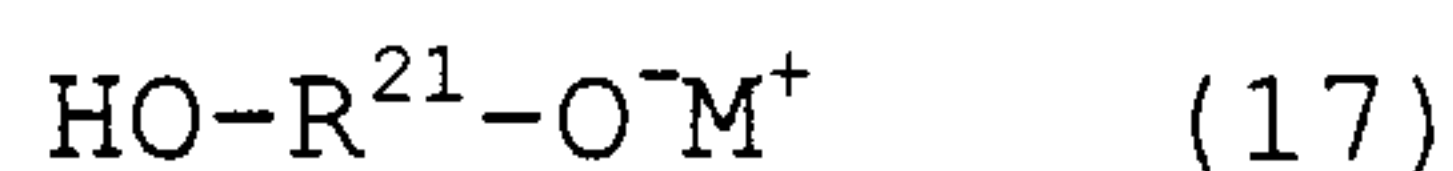


(wherein R^{18} , R^{19} and R^{20} are as defined above).

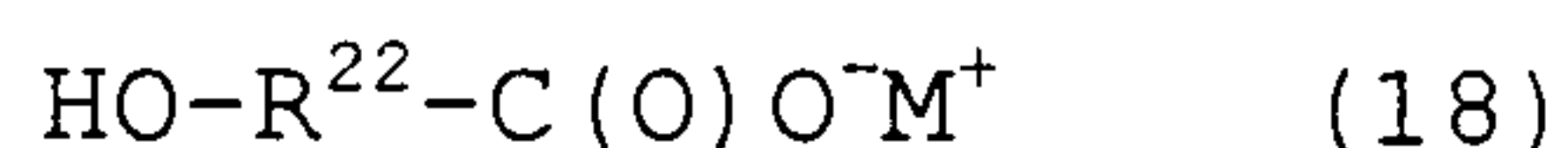
Particularly preferred as the electron-withdrawing groups R^{18} and R^{19} are those having a structure of $-CO_2R$, $-C(O)R$
10 or $-CN$.

(B-h) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a simple substance metal, such as zinc, or an organometallic compound and then reacting the thus-prepared enolate anion with an
15 aldehyde or ketone.

(B-i) Method comprising reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a hydroxyl-containing oxy anion or carboxylate anion, such as one represented by the general formula 17 or 18 given below, for
20 substitution of the halogen atom:



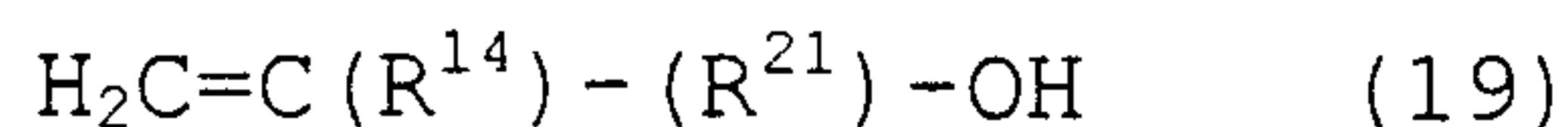
(wherein R^{21} and M^+ are as defined above);



(wherein R^{22} and M^+ are as defined above).

(B-j) Method comprising subjecting, as a second monomer, a compound having a low polymerizable alkenyl group and a hydroxyl group in each molecule to reaction at the final stage of the polymerization reaction or after completion of the reaction of the employed monomer in synthesizing the vinyl
30 polymer by living radical polymerization.

Such compound is not particularly restricted but may be a compound represented by the general formula 19, for instance:



(wherein R^{14} and R^{21} are as defined above).

35 The compound represented by the above general formula 19

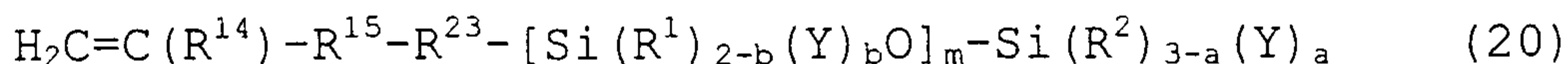
is not particularly restricted but, in view of ready availability, alkenyl alcohols such as 10-undecenol, 5-hexenol and allyl alcohol are preferred.

In the practice of the present invention, when no halogen is directly involved in hydroxyl group introduction, as in the methods (B-a) to (B-e) and (B-j), the vinyl polymer is preferably synthesized by living radical polymerization. The method (B-b) is more preferred from the viewpoint of ease of control.

In cases where hydroxyl group introduction is effected by conversion of the halogen atom of a vinyl polymer having at least one highly reactive carbon-halogen atom, use is preferably made of a vinyl polymer having at least one terminal carbon-halogen bond, which is highly reactive, as obtained by subjecting a vinyl monomer to radical polymerization (atom transfer radical polymerization) using an organic halide or halogenated sulfonyl compound as an initiator and, as a catalyst, a transition metal complex. From the viewpoint of ease of control, the method (B-i) is more preferred.

As the compound having a crosslinkable silyl group and a group capable of reacting with a hydroxyl group, such as an isocyanato group, in each molecule, there may be mentioned, for example, γ -isocyanatopropyltrimethoxysilane, γ -isocyanatopropylmethyldimethoxysilane, γ -isocyanatopropyltriethoxysilane and the like. If necessary, any of urethane formation reaction catalysts generally known in the art can be used.

The compound having both a polymerizable alkenyl group and a crosslinkable silyl group in each molecule, which is to be used in the method (C), includes, among others, trimethoxysilylpropyl (meth)acrylate, methyldimethoxysilylpropyl (meth)acrylate and like compounds represented by the general formula 20 given below:



(wherein R^1 , R^2 , R^{14} , R^{15} , Y , a , b and m are as defined above and

R^{23} is a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds).

The time for subjecting the compound having both a polymerizable alkenyl group and a crosslinkable silyl group in each molecule is not critical but, in particular in living radical polymerization and when rubber-like properties are demanded, the compound is preferably subjected to reaction as a second monomer at the final stage of the polymerization reaction or after completion of the reaction of the employed monomer.

The chain transfer agent having a crosslinkable silyl group, which is to be used in the chain transfer agent method (D), includes mercaptan having a crosslinkable silyl group, hydrosilane having a crosslinkable silyl group, and the like, described in Japanese Kokoku Publication Hei-03-14068, Japanese Kokoku Publication Hei-04-55444, for instance.

The method of synthesizing the vinyl polymer having at least one highly reactive carbon-halogen bond, which is to be used in the method (E), includes, but is not limited to, the atom transfer radical polymerization method which uses an organic halide or the like as an initiator and a transition metal complex as a catalyst.

As the compound having both a crosslinkable silyl group and a stabilized carbanion in each molecule, there may be mentioned compounds represented by the general formula 21:

$$M^+C^-(R^{18})(R^{19})-R^{24}-C(H)(R^{25})-CH_2-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a$$

(21)

(wherein R^1 , R^2 , R^{18} , R^{19} , Y , a , b and m are as defined above, R^{24} is a direct bond or a divalent organic group containing 1 to 10 carbon atoms, which may contain one or more ether bonds, and R^{25} represents a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms or an aralkyl group containing 7 to 10 carbon atoms).

Particularly preferred as the electron-withdrawing groups R^{18} and R^{19} are those having a structure of $-CO_2R$, $-C(O)R$

or -CN.

<Use of a plurality of vinyl polymers>

The above-mentioned vinyl polymers may be used alone and two or more vinyl polymers may be used in combination. In the case where only one kind vinyl polymer is used, it is preferable to use a vinyl polymer having a molecular weight of 5,000 to 50,000 and 1.2 to 3.5 crosslinkable silyl groups. In the case of combination use of two or more vinyl polymers, if a first polymer is a vinyl polymer having a molecular weight of 5,000 to 50,000 and 1.2 to 3.5 crosslinkable silyl groups and a second polymer is a polymer containing less crosslinkable silyl groups, it is possible to obtain the cured product with high elongation at break, low bleeding property, less surface staining property, and excellent adhesiveness with a coating material. Further, the viscosity of the composition can be lowered by setting the molecular weight of the second polymer to be lower. The molecular weight of the polymer to be the lower molecular weight component is preferably lower than 10,000, more preferably lower than 5,000 and the number of the crosslinkable silyl groups is preferably lower than 1.2 and more preferably lower than 1. Further, the molecular weight distribution is preferably lower than 1.8 since the viscosity is decreased more. If the vinyl polymer containing a crosslinkable functional group and a molecular weight distribution of 1.8 or higher and the vinyl polymer containing a crosslinkable silyl group at one terminus are added, the effect to lower the viscosity is significant.

It is preferred to use the vinyl polymer containing a crosslinkable silyl group at one terminus and obtained by the following production method as the polymer having a low molecular weight and less crosslinkable silyl groups, because the crosslinkable silyl group can be reliably introduced.

The vinyl polymer containing a crosslinkable silyl group at one terminus consists of approximately one terminal crosslinkable silyl group per one molecule. The

above-mentioned living radical polymerization method, particularly an atom transfer radical polymerization method is preferable to be employed, since the vinyl polymer containing a terminal crosslinkable silyl group at a high ratio, having
5 narrow molecular weight distribution of lower than 1.8, and low viscosity can be obtained.

As methods of introducing a crosslinkable silyl group at one terminus, the following method can be used, for example. Here, for a method of introducing a crosslinkable silyl group,
10 alkenyl group, and hydroxyl group by conversion of the terminal functional groups, it is described in the backward order from the method of introducing a crosslinkable silyl group because these functional groups may be precursors for other groups, .

As methods of synthesizing a vinyl polymer containing at
15 least one crosslinkable silyl group, there may be mentioned, among others.

There may be mentioned,

(1) the method which comprises subjecting a crosslinkable silyl group-containing hydrosilane compound to addition to a
20 polymer having one terminal alkenyl group in each molecule in the presence of a hydrosilylation catalyst,

(2) the method which comprises reacting a polymer having one terminal hydroxyl group in each molecule with a compound having, in each molecule, a crosslinkable silyl group and a
25 group capable of reacting with the hydroxyl group, such as an isocyanato group, and

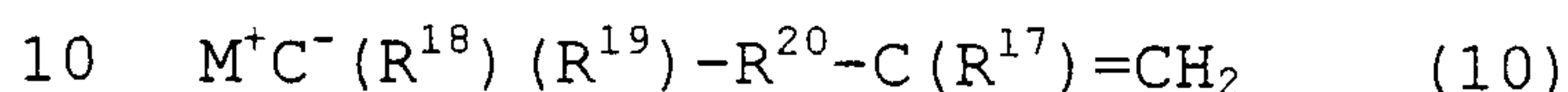
(3) the method which comprises reacting a polymer having one highly reactive terminal carbon-halogen bond in each molecule with a compound having, in each molecule, a
30 crosslinkable silyl group and a stable carbanion.

The polymer having one terminal alkenyl group in each molecule, which is to be used in the above method (1), can be obtained by various methods. Several methods of production are mentioned below, without any purpose of restriction, however.

35 (1-1) Method comprising reacting a polymer having one

highly reactive terminal carbon-halogen bond in each molecule with one of various alkenyl-containing organometallic compounds, for example an organotin such as allyltributyltin or allyltriocetyl tin, for substitution of the halogen.

5 (1-2) Method comprising reacting a polymer having one highly reactive terminal carbon-halogen bond in each molecule with a stabilized, alkenyl-containing carbanion such as one represented by the general formula 10, for substitution of the halogen:



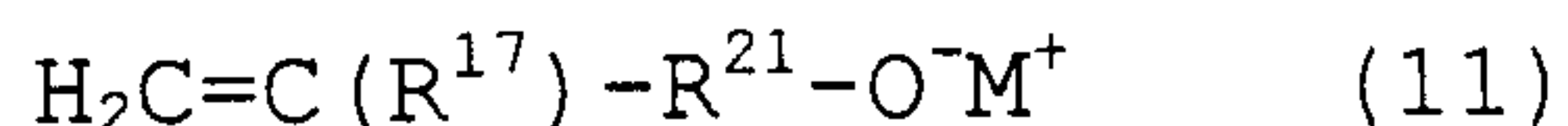
(wherein R^{18} and R^{19} each is an electron-withdrawing group capable of stabilizing the carbanion C^- or one of them is such an electron-withdrawing group and the other represents a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms or a phenyl group, R^{20} represents a direct bond or a divalent organic group containing 1 to 10 carbon atoms, which may contain one or more ether bonds, R^{17} represents a hydrogen atom, an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms or an aralkyl group containing 7 to 20 carbon atoms, and M^+ represents an alkali metal ion or a quaternary ammonium ion).

Particularly preferred as the electron-withdrawing group R^{18} and/or R^{19} are those which have a structure of $-CO_2R$, $-C(O)R$ or $-CN$.

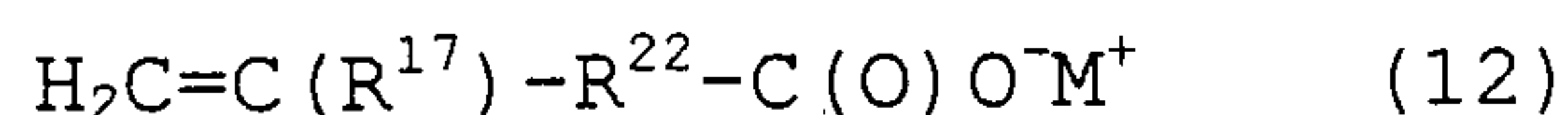
25 (1-3) Method comprising reacting a polymer having one highly reactive terminal carbon-halogen bond in each molecule with a simple substance metal, such as zinc, or an organometallic compound and then reacting the thus-prepared enolate anion with an alkenyl-containing, electrophilic compound, such as an alkenyl-containing compound having a leaving group such as a halogen atom or an acetyl group, an alkenyl-containing carbonyl compound, an alkenyl-containing isocyanate compound or an alkenyl-containing acid halide.

35 (1-4) Method comprising reacting a polymer having one highly reactive terminal carbon-halogen bond in each molecule

with an alkenyl-containing oxy anion or carboxylate anion such as one represented by the general formula 11 or 12, for substitution of the halogen:



- 5 (wherein R^{17} and M^+ are as defined above and R^{21} is a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds);



- 10 (wherein R^{17} and M^+ are as defined above and R^{22} is a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may contain one or more ether bonds).

The method of synthesizing the above-mentioned polymer having one highly reactive terminal carbon-halogen bond in each molecule includes, but is not limited to, atom transfer radical
15 polymerization methods using an organic halide or the like as initiator and a transition metal complex as catalyst, as mentioned above.

It is also possible to obtain the polymer having one terminal alkenyl group in each molecule from a polymer having
20 at least one terminal hydroxyl group. As utilizable methods, there may be mentioned, for example, the following, without any purpose of restriction.

(1-5) Method comprising reacting the hydroxyl group of a polymer having at least one terminal hydroxyl group with a
25 base, such as sodium methoxide, followed by reaction with an alkenyl-containing halide, such as allyl chloride.

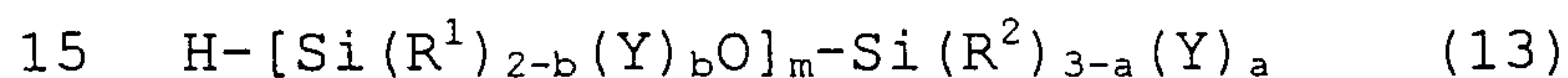
(1-6) Method comprising reacting such hydroxyl group with an alkenyl-containing isocyanate compound, such as allyl isocyanate.

30 (1-7) Method comprising reacting such hydroxyl group with an alkenyl-containing acid halide, such as (meth)acrylic acid chloride, in the presence of a base, such as pyridine.

(1-8) Method comprising reacting such hydroxyl group with an alkenyl-containing carboxylic acid, such as acrylic
35 acid, in the presence of an acid catalyst.

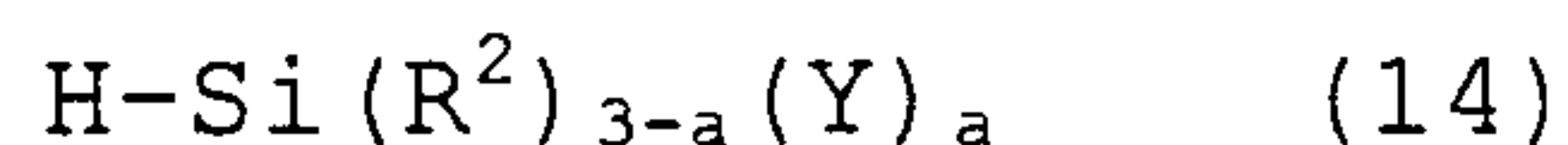
In cases where alkenyl group introduction is effected by conversion of the halogen atom of a polymer having one highly reactive terminal carbon-halogen bond in each molecule, use is preferably made of a polymer having, in each molecule, one terminal carbon-halogen bond, which is highly reactive, as obtained by subjecting a vinyl monomer to radical polymerization (atom transfer radical polymerization) using, as an initiator, an organic halide or halogenated sulfonyl compound having one highly reactive carbon-halogen bond in each molecule and, as a catalyst, a transition metal complex.

The crosslinkable silyl group-containing hydrosilane compound is not particularly restricted but includes, as typical examples, compounds represented by the general formula 13.



{wherein R^1 , R^2 , Y , a , b and m are as defined above and, when there are two or more R^1 or R^2 groups, they may be the same or different, provided that the relation $a + mb \geq 1$ should be satisfied}.

Particularly preferred among those hydrosilane compounds in view of ready availability are crosslinkable silyl group-containing compounds represented by the general formula 14:



(wherein R^2 and Y are as defined above; and a is an integer of 1 to 3).

In subjecting the above crosslinkable silyl-containing hydrosilane compound to addition to the alkenyl group, a transition metal catalyst is generally used. The transition metal catalyst includes, among others, simple substance platinum; solid platinum dispersed on a support such as alumina, silica or carbon black; chloroplatinic acid; chloroplatinic acid complexes with alcohols, aldehydes, ketones or the like; platinum-olefin complexes; and platinum(0)-divinyltetramethyldisiloxane complex. As other

catalysts than platinum compounds, there may be mentioned $\text{RhCl}(\text{PPh}_3)_3$, RhCl_3 , RuCl_3 , IrCl_3 , FeCl_3 , AlCl_3 , $\text{PdCl}_2 \cdot \text{H}_2\text{O}$, NiCl_2 and TiCl_4 , for instance.

5 The use amount of the vinyl polymer containing a crosslinkable silyl group at one terminus and preferably having a molecular weight distribution of less than 1.8 is preferably 5 to 400 parts by weight per 100 parts by weight of the vinyl polymers in terms of the modulus and elongation.

10 In the second aspect using two or more kinds of vinyl polymers in combination, the vinyl polymer having a molecular weight distribution of 1.8 or higher and the vinyl polymer having a molecular weight distribution of less than 1.8 may be used in combination. The vinyl polymer having a molecular weight distribution of 1.8 or higher may or may not comprise
15 the crosslinkable silyl group, however in the case of the vinyl polymer comprising the crosslinkable silyl group, the weather resistance, adhesion strength and strength at break are improved and therefore, the vinyl polymer is preferable. Further, the tensile strength of the cured product obtained from
20 the composition is expected to be high. The polymer derived from vinyl monomers as described above is usable as the main chain of the vinyl polymer having a molecular weight distribution of 1.8 or higher as the first polymer and the vinyl polymer having a molecular weight distribution of less than 1.8
25 as the second polymer, and both polymers are preferably acrylic ester polymers.

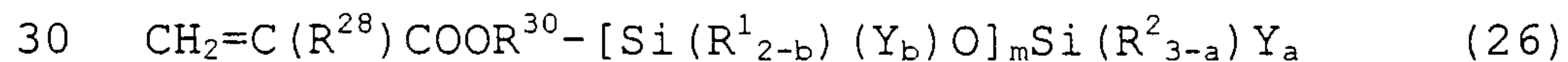
The above-mentioned vinyl polymer having a molecular weight distribution of 1.8 or higher may be obtained by a common vinyl polymerization method such as a solution polymerization
30 method by radical reaction. The polymerization may be carried out generally by a reaction of the above-mentioned monomers at 50 to 150°C in the presence of a radical initiator, a chain transfer agent and/or the like. In this case, polymers having a molecular weight distribution of 1.8 or higher are generally
35 obtained.

Examples of the above-mentioned initiator may include azo type initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutylnitrile), 4,4'-azobis(4-cyanovaleric) acid, 1,1'-azobis(1-cyclohexanecarbonitrile), azobisisobutyric acid amidine hydrochloride and 2,2'-azobis(2,4-dimethylvaleronitrile and organic peroxide type initiators such as benzoyl peroxide and di-tert-butyl peroxide, and from the viewpoint that they are not affected with the solvent to be used for the polymerization, that the risk of explosion or the like is low, and the like, azo type initiators are preferably used.

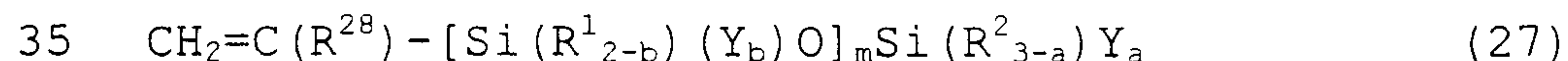
Examples of the chain transfer agent may include mercaptans such as n-dodecylmercaptan, tert-dodecylmercaptan, laurylmercaptan, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltriethoxysilane and γ -mercaptopropylmethyldiethoxysilane, halogen-containing compounds, and the like.

The polymerization may be carried out in a solvent. Preferable examples of the solvent are ethers, hydrocarbons, esters and other non-reactive solvents.

A method of introducing the crosslinkable silyl group may be a method of copolymerizing a compound having both of a polymerizable unsaturated bond and crosslinkable silyl group with a (meth)acrylic ester monomer unit. Examples of the compound having both of a polymerizable unsaturated bond and crosslinkable silyl group are monomers represented by the general formula 26:



(wherein, R^{28} represents the same as described above; R^{30} represents a divalent alkylene group having 1 to 6 carbon atoms; R^1 , R^2 , Y , a , b , and m independently represent the same as described above) or the general formula 27:



(wherein, R^{28} , R^1 , R^2 , Y, a, b, and m independently represent the same as described above) and practically may include γ -methacryloxypropylpolyalkoxysilanes such as γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, and γ -methacryloxypropyltriethoxysilane; γ -acryloxypropylpolyalkoxysilanes such as γ -acryloxypropyltrimethoxysilane, γ -acryloxypropylmethyldimethoxysilane, and γ -acryloxypropyltriethoxysilane; and vinylalkylpolyalkoxysilane such as vinyltrimethoxysilane, vinylmethyldimethoxysilane, and vinyltriethoxysilane; and the like. Further, if a compound having both of a mercapto group and crosslinkable silyl group is used as a chain transfer agent, the crosslinkable silyl group can be introduced into the polymer termini. Examples of the chain transfer agent may include mercaptans such as γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltriethoxysilane, and γ -mercaptopropylmethyldiethoxysilane.

The vinyl polymer containing a crosslinkable functional group and having a molecular weight distribution of 1.8 or higher is preferable to be a polymer having a number average molecular weight of 500 to 100,000 measured by GPC measurement on the basis of polystyrene conversion in terms of the handling easiness. Further, a polymer having a number average molecular weight of 1,500 to 30,000 is more preferable because of good weather resistance and workability of the cured product.

<<Epoxy resin (II)>>

Examples of the epoxy resin as the component (II) in the invention may include a bisphenol A epoxy resin, a bisphenol F epoxy resin, a bisphenol AD epoxy resin, a bisphenol S epoxy resin, a glycidyl ester epoxy resin, a glycidyl amine epoxy resin, a novolak epoxy resin, a glycidyl ether epoxy resin of a bisphenol A propylene oxide adduct, a hydrogen-added

bisphenol A (hydrogenated bisphenol A) epoxy resin, a fluoro epoxy resin, a rubber-modified epoxy resin containing polybutadiene or NBR, a flame-retardant epoxy resin such as tetrabromobisphenol A glycidyl ether, a p-oxybenzoic acid glycidyl ether ester epoxy resin, an m-aminophenol epoxy resin, a diaminodiphenylmethane epoxy resin, an urethane-modified epoxy resin having an urethane bond, various kinds of alcylic epoxy resins, N,N-diglycidylaniline, N,N-diglycidyl-o-toluidine, triglycidyl isocyanurate, polyalkylene glycol diglycidyl ether, glycidyl ether of polyhydric alcohol such as glycerin, a hydantoin epoxy resin, and an epoxide of an unsaturated polymer such as a petroleum resin, without any purpose of restriction, and commonly used epoxy resins may be used. These epoxy resins may be used alone or two or more of them may be used in combination.

Among these epoxy resins, those having at least 2 epoxy groups in one molecule are preferable since, for example, they have high reactivity and the cured product to be obtained tends to form three-dimensional mesh structure at the time of curing.

To make the cured product of the invention transparent which is obtained when the mixture of the vinyl polymer and the epoxy resin is cured, the epoxy resin is preferably compatible with the vinyl polymer.

In the case of using the vinyl polymer the main chain of which has higher polarity than that of a butyl acrylate homopolymer, the epoxy resin (II) may or may not contain an aromatic ring and the above-exemplified epoxy resins may be used without any limits and especially, the bisphenol A epoxy resin and the hydrogenated bisphenol A epoxy resin obtained by hydrogenating the aromatic ring of the bisphenol A epoxy resin are preferable, for example. Herein, as the vinyl polymer the main chain of which has higher polarity than that of a butyl acrylate homopolymer, the same vinyl polymer the main chain of which has higher polarity than that of a butyl acrylate homopolymer exemplified above can be used. In the case of using

a vinyl polymer other than the above-mentioned vinyl polymer the main chain of which has higher polarity than that of a butyl acrylate homopolymer, it is preferable to use epoxy resin having no aromatic rings as the epoxy resin (II), without any purpose of particular restriction.

The epoxy resin having no aromatic rings is not particularly limited and an alicyclic epoxy resin is preferable. Herein, "alicyclic epoxy resin" means an epoxy resin having no aromatic rings in the molecule and the glycidyl group may or may not be directly bonded to an alicyclic ring. Among them, a hydrogenated bisphenol A epoxy resin and a glycidyl ester epoxy resin in which a glycidyl group is not directly bonded to the alicyclic ring are more preferable.

As preferable embodiment of the invention, there may be mentioned, for example, a combination of an ethyl acrylate / butyl acrylate / 2-methoxyethyl acrylate copolymer (40 to 50 / 20 to 30 / 30 to 20, by mole ratio) with at least one selected from a bisphenol A epoxy resin, a bisphenol F epoxy resin, and a hydrogenated bisphenol A epoxy resin and a combination of the butyl acrylate homopolymer with the hydrogenated bisphenol A epoxy resin and/or hexahydrophthalic acid diglycidyl ester, without any purpose of restriction.

<<Mixing ratio of vinyl polymer (I) and epoxy resin (II)>>

In the curable composition of the invention, the mixing ratio of the vinyl polymer (I) containing at least one crosslinkable silyl group and the epoxy resin (II) is preferably (100/1) to (1/100) by weight, more preferably (100/5) to (5/100) by weight, and further preferably (100/10) to (10/100) by weight, however the mixing ratio is not particularly limited and may be set in accordance with the uses and purposes. Owing to the properties, the curable composition can be used, for example, as an elastic adhesive for adhesion of a material having a considerably different linear expansion coefficient or for a member that receives repetitive displacements by heat cycles and/or as a coating material for making an under-layer material

seen through due to its transparency. For example, in the case of using the composition for the elastic adhesive, if the mixing ratio of the epoxy resin is too high, the cured product becomes hard and peeling strength is lowered. On the other hand, if it is too low, the adhesion strength and water-proof property are lowered. Therefore, the epoxy resin is used generally in 10 to 150 parts by weight and preferably in 20 to 100 parts by weight per 100 parts by weight of the vinyl polymer (I).

<<Polyether polymer (III)>>

10 The curable composition of the invention may further contain a polyether polymer (III).

Main chain

15 The main chain of the polyether polymer is not particularly limited and polyethylene oxide, polypropylene oxide, polybutylene oxide, and polyphenylene oxide can be exemplified, for example. Among them, substantially polyoxyalkylene is preferable and polypropylene oxide is more preferable and other than propylene oxide, ethylene oxide, butylene oxide, phenylene oxide and/or the like may be contained. 20 Further, the polyether polymer may or may not contain an urethane bond in the main chain. Herein, the phrase, "the main chain is substantially polypropylene oxide" means that propylene oxide unit exists at a ratio of 50% or higher, preferably 70% or higher, and more preferably 90% or higher, 25 in the repeating units composing the main chain. If the viscosity is lower, the handling property becomes better, and therefore the polypropylene oxide polymer is more preferable to have a molecular weight distribution (Mw/Mn) of 1.5 or lower.

Crosslinkable functional group

30 The polyether polymer is preferable to have a crosslinkable functional group although it is not particularly limited, since the polymer is hardly eluted from the obtained cured product and the strength of the cured product is increased.

35 The crosslinkable functional group in the polyether

polymer is not particularly limited, and preferable examples are a crosslinkable silyl group, an alkenyl group, a hydroxyl group, an amino group, a polymerizable group having a carbon-carbon double bond, and an epoxy group. Particularly, the crosslinkable silyl group is preferable.

The number of the crosslinkable functional group of the polyether polymer is preferably at least 1, and it may be 1 or lower. In terms of curability of the composition, the polyether polymer preferably contains more than one functional groups, more preferably 1.1 to 4.0 and further preferably 1.5 to 2.5 functional groups on average. The crosslinkable functional group is preferable to exist at a terminus of the polyether polymer in terms of rubber elasticity of the cured product. The functional group is more preferable to exist at both termini of the polymer.

Molecular weight

The polyether polymer (III) preferably has a number average molecular weight of 7,500 or higher, and it may be 7,500 or lower. Particularly, it is preferable to use the polyether polymer having a number average molecular weight of 7,500 to 25,000. In the case where the number average molecular weight of the polyether polymer is lower than 7,500, the cured product tends to be hard and to have low elongation. On the other hand, in the case where the number average molecular weight exceeds 25,000, although the flexibility and elongation of the cured product are satisfactory, the adhesiveness of the polymer itself is considerably lowered and the practical applicability tends to become low. However, even if the molecular weight is low, in the case where the number of the crosslinkable functional group is low, the flexibility and elongation are sometimes improved and even if the molecular weight is high, in the case where the number of the crosslinkable functional group is high, the adhesiveness is sometimes increased. The number average molecular weight is particularly preferably 8,000 to 20,000, and it may be 8,000 or lower or 20,000 or higher.

Use amount of polyether polymer (III)

The use amount of the polyether polymer (III) may be optional, and it is preferably at a ratio of (100/1) to (1/100) by weight, more preferably (100/5) to (5/100) by weight, and
5 further preferably (100/10) to (10/100) by weight, per the total of the vinyl polymer (I) containing at least one crosslinkable silyl group on average and the epoxy resin (II). The addition amount may be set in accordance with the uses and purposes. In
10 this connection, if the addition amount is too much, one of the effects of the invention that the excellent heat resistance and weather resistance may be sometimes lowered.

The above-mentioned polyether polymer may be previously mixed with a (meth)acrylic polymer produced by general radical polymerization, or a high temperature- and
15 continuously-polymerized bulk polymer (e.g. SGO oligomer manufactured by Toagosei Co., Ltd.), or the silylated product thereof for mixing with the vinyl polymer.

<Polyether polymer containing at least one crosslinkable silyl group on average>

20 The polyether polymer (III) of the invention is preferably a polymer containing at least one crosslinkable silyl group on average.

Hereinafter, the polyether polymer containing at least one crosslinkable silyl group on average will be described.

25 Main chain

The main chain structure of the polyether polymer containing a crosslinkable silyl group is same as described above. The main chain may be linear or branched or mixture of both. Among them, particularly preferable examples of the main
30 chain are polyoxypropylene diol, polyoxypropylene triol, and their mixtures. Further, other monomer units etc. may be contained, and the monomer units represented by the above-mentioned formulae preferably exist at a ratio of 50% by weight or more, preferably 80% by weight or more, in the polymer.

35 The main chain may or may not contain an urethane bond

or an urea bond.

The molecular structure of the polyether polymer differs in accordance with the uses and the desired properties thereof and those described in Japanese Kokai Publication Sho-63-112642 can be used, for example. These polyoxyalkylenes may be obtained by common polymerization methods (anion polymerization using caustic alkali), methods using cesium metal catalysts, porphyrin/aluminum complex catalysts (such methods are exemplified in Japanese Kokai Publication Sho-61-197631, Sho-61-215622, Sho-61-215623, Sho-61-218632 and the like), composite metal cyanide complex catalysts (such methods are exemplified in Japanese Kokoku Publication Sho-46-27250, Sho-59-15336 and the like), and catalysts of polyphosphazene salts (such methods are exemplified in Japanese Kokai Publication Hei-10-273512), and the like methods.

The methods using porphyrin/aluminum complex catalysts, composite metal cyanide complex catalysts, or catalysts of polyphosphazene salts are suitable for obtaining oxyalkylene polymers with as narrow molecular weight distribution (M_w/M_n) as 1.6 or lower, preferably 1.5 or lower, and in the case where the molecular weight distribution is narrow, it is advantageous for keeping low modulus and high elongation of the cured product and keeping low viscosity for the composition.

Crosslinkable silyl group

Similarly to the vinyl polymer, groups represented by the general formula 2 may be used as the crosslinkable silyl group and groups represented by the general formula 7 are preferable. The description of the groups represented by the general formulae (2) and (7) is also applied to the polyether polymer containing the crosslinkable silyl group. The crosslinkable silyl group in the polyether polymer may have the same structure as or a different structure from that of the crosslinkable silyl group in the vinyl polymer containing the crosslinkable silyl group.

Since the bonding part of the crosslinkable silyl group

and the polyether part has resistance to hydrolysis, the bonding part is preferably an alkylene group such as trimethylene and tetramethylene so as to have at least 3 carbon atoms existing between the silicon atom of the silyl group and the ether oxygen atom of the polyether parts.

Number and position of crosslinkable silyl group

The number of the crosslinkable silyl group is preferably at least one on average and from the curability of the composition and/or the like viewpoints, the number is more preferably at least 1.2 or higher, further preferably 1.2 or higher and 4.0 or lower, and most preferably 1.5 to 2.5. In terms of the rubber elasticity of the cured product, the crosslinkable silyl group in the polyether polymer is preferably at a terminus of the molecular chain and more preferably at both termini of the polymer.

Even a polyether polymer containing 1.2 or less crosslinkable silyl groups on average may be used. In this case, the cured product with high elongation at break, low bleeding property, low surface staining property, and excellent adhesiveness to a coating material can be obtained. Further, if the molecular weight of the polymer is set to be low, the viscosity of the composition may be lowered. The lower limit of the number of the crosslinkable silyl group is preferably at least 0.1 or higher, more preferably 0.3 or higher, and further preferably 0.5 or higher. The crosslinkable silyl group is preferably at a terminus of a molecular chain. The crosslinkable silyl group of the polyether polymer preferably exists at only one terminus but not at the other terminus, however it is not particularly limited as long as the number of the crosslinkable silyl group is 1.2 or lower on average. In the case where the viscosity is lowered by using the polyether polymer containing less than 1.2 crosslinkable silyl groups on average, the molecular weight is preferably lower than 10,000 and more preferably lower than 5,000.

Crosslinkable silyl group introduction method

The crosslinkable silyl group may be introduced by a conventionally known method. That is, the following methods can be exemplified. For example, in the case of oxyalkylene polymers obtained by using a composite metal cyanide complex catalyst, a method is described in Japanese Kokai Publication Hei-3-72527 and in the case of oxyalkylene polymers obtained by using a polyphosphazene salt and active hydrogen as catalysts, a method is described in Japanese Kokai Publication Hei-11-60723.

(1) An unsaturated group-containing oxyalkylene polymer is obtained by reacting an oxyalkylene polymer having a functional group such as hydroxyl group at a terminus with an organic compound having an active group and an unsaturated group reactive on the functional group, or copolymerizing the oxyalkylene polymer with an unsaturated group-containing epoxy compound. Next, the obtained reaction product is reacted with a hydrosilane containing a crosslinkable silyl group to carry out hydrosilylation.

(2) The unsaturated group-containing oxyalkylene polymer obtained in the same manner as described in (1) is reacted with a compound having a mercapto group and the crosslinkable silyl group.

(3) An oxyalkylene polymer having a functional group (hereinafter, referred to as Y functional group) such as a hydroxyl group, an epoxy group, and an isocyanato group at a terminus is reacted with a compound having a functional group (hereinafter, referred to as Y' functional group) reactive on the Y functional group and the crosslinkable silyl group.

Examples of a silicon compound having the Y' functional group may be amino group-containing silanes such as γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -aminopropyltriethoxysilane, 3-amino-2-methylpropyltrimethoxysilane,

N-ethyl-3-amino-2-methylpropyltrimethoxysilane,
4-amino-3-methylpropyltrimethoxysilane,
4-amino-3-methylpropylmethyldimethoxysilane,
N-phenyl-3-aminopropyltrimethoxysilane, and partially
5 Michael addition reaction products of various kinds of amino
group-containing silane with maleic acid esters and acrylate
compounds; mercapto-containing silanes such as
 γ -mercaptopropyltrimethoxysilane and
 γ -mercaptopropylmethyldimethoxysilane; epoxy silanes such as
10 γ -glycidopropyltrimethoxysilane and
 β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane; vinyl
unsaturated group-containing silanes such as
vinyltriethoxysilane,
 γ -methacryloyloxypropyltrimethoxysilane, and
15 γ -acryloyloxypropylmethyldimethoxysilane; chlorine
atom-containing silanes such as
 γ -chloropropyltrimethoxysilane; isocyanato group-containing
silanes such as γ -isocyanatopropyltriethoxysilane,
 γ -isocyanatopropylmethyldimethoxysilane, and
20 γ -isocyanatopropyltrimethoxysilane; hydrosilanes such as
methyldimethoxysilane, trimethoxysilane,
methyldiethoxysilane and triethoxysilane; and the like,
without any purpose of particular restriction.

In the case of producing the polymer containing 1.2 or
25 less crosslinkable silyl groups on average, at the time of
introducing the crosslinkable silyl group, the following
methods may be used; a method of obtaining the polyether polymer
containing 1.2 or less crosslinkable silyl groups on average
by reacting a polyether polymer containing only one functional
30 group in the molecule and a compound containing crosslinkable
silyl group(s) in an equivalent or less amount to the functional
group; and a method of obtaining the polyether polymer
containing 1.2 or less crosslinkable silyl groups on average
by reacting a polyether polymer containing one or more
35 functional groups in the molecule on average and a compound

containing crosslinkable silyl group at a less ratio to the functional groups.

Use amount of polyether polymer containing a crosslinkable silyl group

5 The use amount of the polyether polymer (III) containing a crosslinkable silyl group may be optional, and it is preferably (100/1) to (1/100) by weight, more preferably (100/5) to (5/100) by weight, and further preferably (100/10) to (10/100) by weight, per the total of the vinyl polymer (I)
10 containing at least one crosslinkable silyl group on average and the epoxy resin (II). The addition amount may be set in accordance with the uses and purposes. However, if the addition amount is too much, excellent heat resistance or weather resistance, which is one of the excellent effects of the
15 invention, may be possibly lowered.

 In the case of using the polyether polymer containing 1.2 or less crosslinkable silyl groups on average, the use amount thereof is preferably at least 1 part by weight and at highest 200 parts by weight, more preferably at least 3 parts by weight
20 and at highest 100 parts by weight, and further preferably at least 5 parts by weight and at highest 80 parts by weight, per 100 parts by weight of the vinyl polymer (I). If it is lower than 1 part by weight, the addition effect is hardly caused and if it exceeds 200 parts by weight, the physical properties of
25 the cured product tend to be unstable.

 The mixing manner may be the following without any purpose of restriction: [1] adding the polyether polymer containing a crosslinkable silyl group and also the polyether polymer containing 1.2 or less crosslinkable silyl groups on average
30 to the vinyl polymer containing a crosslinkable silyl group represented by the general formula 2; [2] adding the polyether polymer containing a crosslinkable silyl group and the vinyl polymer containing a crosslinkable silyl group at one terminus; [3] in the case of adding the polyether polymer containing a
35 crosslinkable silyl group and the vinyl polymer having a

crosslinkable functional group and 1.8 or higher molecular weight distribution, adding the polyether polymer containing 1.2 or less crosslinkable silyl groups on average and also the vinyl polymer containing a crosslinkable silyl group at one terminus; and [4] adding the polyether polymer containing 1.2 or less crosslinkable silyl groups on average and also the vinyl polymer having a crosslinkable functional group and 1.8 or higher molecular weight distribution.

5 <<Various optional component of polymer having crosslinkable functional group>>

The curable composition of the invention may further comprise various polymers having a crosslinkable functional group as an optional component. Examples of the polymer having a crosslinkable functional group may be (i) a polyisobutylene polymer having a crosslinkable functional group, in particular a polyisobutylene polymer having a crosslinkable silyl group and (ii) a polysiloxane. One or more kinds of these polymers may be added.

At the time of adding these optional polymer components to the vinyl polymer containing a crosslinkable silyl group, according to the invention, a vinyl polymer having a hydrolysable silicon group containing two hydrolysable groups bonded to one silicon atom and an optional polymer component containing three hydrolysable groups bonded to one crosslinkable functional group may be combined. On the contrary, a vinyl polymer having a hydrolysable silicon group containing three hydrolysable groups bonded to one silicon atom and an optional polymer component containing two hydrolysable groups bonded to one crosslinkable functional group may be combined. Further, polymers each having a crosslinkable functional group containing three hydrolysable groups may be combined and polymers each having a crosslinkable functional group containing two hydrolysable groups may be combined. Further, mixtures of polymers having one to three crosslinkable functional groups are also acceptable.

<<Curable composition>>

The curable composition of the invention may often contain a curing catalyst and/or a curing agent. Further depending on the aimed physical properties, various kinds of additives may be added.

<Curing catalyst and curing agent>

Curing catalyst/curing agent for vinyl polymer (I) containing at least one crosslinkable silyl group on average

The vinyl polymer (I) containing crosslinkable silyl group is crosslinked and cured by forming a siloxane bond in the presence or absence of various kinds of conventionally known condensation catalyst. The physical property of the cured product may be controlled in a wide range from rubber-like to resin-like properties in accordance with the molecular weight and the main chain skeleton of the polymers.

As examples of the condensation catalyst, there may be mentioned, for example, dialkyltin diacarylates such as dibutyltin dilaurate, dibutyltin diacetate, dibutyltin diethylhexanoate, dibutyltin dioctate, dibutyltin dimethylmaleate, dibutyltin diethylmaleate, dibutyltin dibutylmaleate, dibutyltin diisooctylmaleate, dibutyltin ditridecylmaleate, dibutyltin dibenzylmaleate, dibutyltin maleate, dioctyltin diacetate, dioctyltin distearate, dioctyltin dilaurate, dioctyltin diethylmaleate, dioctyltin diisooctylate and the like, dialkyltin alkoxides such as dibutyltin dimethoxide, dibutyltin diphenoxide and the like, intermolecular coordination derivatives of dialkyltin such as dibutyltin diacetylacetonate, dibutyltin diethylacetoacetate and the like, reaction products of a dialkyltin oxide such as dibutyltin oxide and dioctyltin oxide with an ester compound such as dioctyl phthalate, diisodecyl phthalate and methyl maleate, reaction products of a dialkyltin oxide such as dibutyltin bistriethoxysilicate and dioctyltin bistriethoxysilicate with a silicate compound, oxy derivatives (stannoxane compounds) of these dialkyltin compounds, and the

like stannic compounds; stannous compounds such as stannous
ocylate, stannous naphthanate, stannous stearate, stannous
versatate and the like, and reaction products and mixtures of
these with an amine compound such as laurylamine, which will
5 be described later; monobutyltin compounds such as monobutyltin
trisoctoate and monobutyltin triisopropoxide, monooctyltin
compounds, and the like monoalkyl tins; titanate esters such
as tetrabutyl titanate, tetrapropyl titanate,
tetra(2-ethylhexyl)titanate and isopropoxytitanium
10 bis(ethylacetoacetate); organoaluminum compounds such as
aluminum trisacetylacetonate and aluminum
trisethylacetoacetate and diisopropoxyaluminum
ethylacetoacetate; carboxylic acid (e.g. 2-ethylhexanoic acid,
neodecanoic acid, versatic acid, oleic acid, and naphthenic
15 acid) metal salts such as bismuth carbonate, iron carbonate,
titanium carbonate, lead carbonate, vanadium carbonate,
zirconium carbonate, calcium carbonate, potassium carbonate,
barium carbonate, manganese carbonate, cerium carbonate,
nickel carbonate, cobalt carbonate, zinc carbonate and aluminum
20 carbonate, and reaction products and mixtures of these with an
amine compound such as laurylamine, which will be described
later; chelate compounds such as zirconium
tetraacetylacetonate, zirconium tributoxyacetylacetonate,
dibutoxyzirconium diacetylacetonate, zirconium
25 acetylacetonate-bis(ethylacetoacetate) and titanium
tetraacetylacetonate; aliphatic primary amines such as
methylamine, ethylamine, propylamine, isopropylamine,
butylamine, amylamine, hexylamine, octylamine,
2-ethylhexylamine, nonylamine, decylamine, laurylamine,
30 pentadecylamine, cetylamine, stearylamine and
cyclohexylamine; aliphatic secondary amines such as
dimethylamine, diethylamine, dipropylamine, diisopropylamine,
dibutylamine, diamylamine, dioctylamine,
di(2-ethylhexyl)amine, didecylamine, dilaurylamine,
35 dicetylamine, distearylamine, methylstearylamine,

ethylstearylamine and butylstearylamine; aliphatic tertiary amines such as tiramylamine, trihexylamine and trioctylamine; aliphatic unsaturated amines such as triallylamine and oleylamine; aromatic amines such as laurylaniline, stearylaniline, and triphenylamine; other amines, that is amine compounds such as monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, oleylamine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylenediamine, ethylenediamine, hexamethylenediamine, triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethylaminomethyl)phenol, morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole and 1,8-diazabicyclo(5,4,0)undecene-7 (DBU), and salts of these amine compounds and carboxylic acids etc.; reaction products and mixtures of an amine compound and an organic tin compound such as reaction products or mixtures of laurylamine and tin octylate; low molecular weight polyamide resins obtained from excess polyamines and polybasic acids; reaction products of excess polyamines and epoxy compounds; and γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -aminopropyltriisopropoxysilane, γ -aminopropylmethyldimethoxysilane, γ -aminopropylmethyldiethoxysilane, N-(β -aminoethyl)aminopropyltrimethoxysilane, N-(β -aminoethyl)aminopropylmethyldimethoxysilane, N-(β -aminoethyl)aminopropyltriethoxysilane, N-(β -aminoethyl)aminopropylmethyldiethoxysilane, N-(β -aminoethyl)aminopropyltriisopropoxysilane, γ -ureidopropyltrimethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, N-benzyl- γ -aminopropyltrimethoxysilane, and N-vinylbenzyl- γ -aminopropyltriethoxysilane. Further, examples of the catalysts may include modified derivatives of the above-mentioned compounds such as amino-modified silyl polymers, silylated aminopolymers, unsaturated aminosilane

complexes, amino group-containing silane coupling agents such as phenylamino-long chain alkylsilane and aminosilylated silicones, and the like silanol condensation catalysts; fatty acids such as versatic acid, organic acid-type phosphate ester compounds and the like acidic catalysts, basic catalysts, and the like conventionally known silanol condensation catalysts; and the like.

Examples of the organic acid-type phosphate ester compound, as an acidic catalyst, may include $(\text{CH}_3\text{O})_2\text{-P(=O)(-OH)}$,
 10 $(\text{CH}_3\text{O})\text{-P(=O)(-OH)}_2$, $(\text{C}_2\text{H}_5\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_2\text{H}_5\text{O})\text{-P(=O)(-OH)}_2$,
 $(\text{C}_3\text{H}_7\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_3\text{H}_7\text{O})\text{-P(=O)(-OH)}_2$, $(\text{C}_4\text{H}_9\text{O})_2\text{-P(=O)(-OH)}$,
 $(\text{C}_4\text{H}_9\text{O})\text{-P(=O)(-OH)}_2$, $(\text{C}_8\text{H}_{17}\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_8\text{H}_{17}\text{O})\text{-P(=O)(-OH)}_2$,
 $(\text{C}_{10}\text{H}_{21}\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_{10}\text{H}_{21}\text{O})\text{-P(=O)(-OH)}_2$,
 $(\text{C}_{13}\text{H}_{27}\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_{13}\text{H}_{27}\text{O})\text{-P(=O)(-OH)}_2$,
 15 $(\text{C}_{16}\text{H}_{33}\text{O})_2\text{-P(=O)(-OH)}$, $(\text{C}_{16}\text{H}_{33}\text{O})\text{-P(=O)(-OH)}_2$,
 $(\text{HO-C}_6\text{H}_{12}\text{O})_2\text{-P(=O)(-OH)}$, $(\text{HO-C}_6\text{H}_{12}\text{O})\text{-P(=O)(-OH)}_2$,
 $(\text{HO-C}_8\text{H}_{16}\text{O})\text{-P(=O)(-OH)}$, $(\text{HO-C}_8\text{H}_{16}\text{O})\text{-P(=O)(-OH)}_2$,
 $[(\text{CH}_2\text{OH})(\text{CHOH})\text{O}]_2\text{-P(=O)(-OH)}$, $[(\text{CH}_2\text{OH})(\text{CHOH})\text{O}]\text{-P(=O)(-OH)}_2$,
 $[(\text{CH}_2\text{OH})(\text{CHOH})\text{C}_2\text{H}_4\text{O}]_2\text{-P(=O)(-OH)}$, and
 20 $[(\text{CH}_2\text{OH})(\text{CHOH})\text{C}_2\text{H}_4\text{O}]\text{-P(=O)(-OH)}_2$, without any purpose of particular restriction.

The combination systems of these organic acids and amines are preferable since the catalytic activity becomes high and therefore the use amount can be saved. Among the combination
 25 systems of the organic acids and amines, a combination of an acidic phosphate ester with an amine and a combination of an organic carboxylic acid with an amine; particularly a combination of an organic acid-type phosphate ester with an amine and a combination of an aliphatic carboxylic acid with
 30 an amine are more preferable in terms of the higher catalytic activity and quick curability.

These catalysts may be used alone or two or more of them may be used in combination. The addition amount of the condensation catalyst is preferably in a range of 0.01 to 20
 35 parts (parts by weight, hereinafter the same) and more

preferably in a range of 0.5 to 5 parts per 100 parts of the polymer containing a crosslinkable silyl group. Herein, the phrase, the polymer containing a crosslinkable silyl group, means the vinyl polymer (I) containing at least one crosslinkable silyl group on average and also in the case of using the polyether polymer (III) containing at least one crosslinkable silyl group on average, it means both of the vinyl polymer (I) containing at least one crosslinkable silyl group on average and the polyether polymer (III) containing at least one crosslinkable silyl group on average. If the addition amount of the silanol condensation catalyst is lower than the above-mentioned range, the curing rate may be possibly retarded and it becomes hard to promote the curing reaction sufficiently sometimes. On the other hand, the addition amount of the silanol condensation catalyst exceeding the above-mentioned range is unfavorable, since heat generation and foaming occurs locally at the time of curing to make it difficult to obtain a good cured product, and the pot-life becomes too short to exhibit good workability. In addition, although it is not particularly limited, a tin curing catalyst may exhibit a preferable effect since it can make it easy to control the curability.

Although it is not particularly limited, in the case of obtaining the following one package composition, in terms of the curing rate and the storage stability of the composition, tin (IV) is preferable for the tin curing catalyst, however a combination of tin (II) with an organic amine or a tin-free compound is also usable.

Further, although it is not particularly limited, in the case of using the composition of the invention for a sealant for a siding board, or the like, regardless of being one-component or two-pack type, tin (IV) is preferable since, for example, use of tin (IV) makes it easy to moderate the stress of the cured product and thus causes no damage to the adherend and also suppresses peeling at the adhesion interface.

In recent years, environmental issue has been brought into focus and use of the tin catalyst tends to be avoided, in such a case, a tin-free catalyst, e.g. bismuth carboxylate and titanium carboxylate, may be selected.

5 In the curable composition of the invention, to further increase the activity of the condensation catalyst, similarly to the amine compound, it is also possible to use the above-mentioned amino group-containing silane coupling agent as a promoter. The amino group-containing silane coupling
10 agent is a compound having a group containing a silicon atom to which a hydrolysable group is bonded (hereinafter, referred to as hydrolysable silyl group) and an amino group. Examples of the hydrolysable group may be those exemplified above and methoxy, ethoxy and the like groups are preferable in terms of
15 the hydrolysis rate. The number of the hydrolysable group is preferably two or higher and particularly preferably three or higher.

The addition amount of the amine compound is preferably about 0.01 to 50 parts by weight and more preferably 0.1 to 20
20 parts by weight per 100 parts of the polymer containing a crosslinkable silyl group. If the addition amount of the amine compound is lower than 0.01 parts by weight, the curing rate may be possibly retarded and the curing reaction hardly proceed sufficiently in some cases. On the other hand, the addition
25 amount of the amine compound exceeding 30 parts by weight is unfavorable, since the pot-life is too shortened to exhibit good workability in some cases.

These amine compounds may be used alone or two or more of them may be used as a mixture.

30 Further, a silicon compound having no amino group or silanol group may be added as a promoter. Examples of the silane compound are not particularly limited and phenyltrimethoxysilane, phenylmethyldimethoxysilane, phenyldimethylmethoxysilane, diphenyldimethoxysilane,
35 diphenyldiethoxysilane, triphenylmethoxysilane and the like

are preferable. Particularly, diphenyldimethoxysilane and diphenyldiethoxysilane are most preferable since they are cheap and easily available.

The addition amount of the silicon compound is preferably about 0.01 to 20 parts by weight and more preferably 0.1 to 10 parts by weight per 100 parts of the polymer containing a crosslinkable silyl group. If the addition amount of the silicon compound is lower than the above-mentioned range, the effect of accelerating the curing reaction may be possibly lowered. On the other hand, if the addition amount of the silicon compound is higher than the above-mentioned range, the hardness and tensile strength of the cured product may be possibly lowered.

The type and the addition amount of the curing catalyst and curing agent make it possible to control the curability and mechanical property in the invention in accordance with the uses and purposes. Further, the type and the addition amount of the curing catalyst and curing agent may be changed in accordance with reactivity of the silyl group of the polymer containing a crosslinkable silyl group and in the case where the reactivity is high, curing can be carried out sufficiently with an amount as small as 0.01 to 1 part.

The type and the addition amount of the curing catalyst and curing agent may be selected in accordance with the crosslinkable silyl group of the vinyl polymer (I) of the invention and the type of Y and the number for a in the general formula 2 and thus the curability, mechanical property and the like in the invention may be controlled in accordance with the uses and purposes. In the case where Y is an alkoxy group, the reactivity is higher as the number of carbon atoms is low. On the other hand, the number for a is higher, the reactivity is higher and therefore curing can be carried out sufficiently with a small addition amount.

Curing catalyst and curing agent of epoxy resin (II)

The curable composition of the invention may contain a

curing agent for an epoxy resin. As the curing agent for an epoxy resin, conventionally known ones may be widely used. Examples are aliphatic amines such as ethylenediamine, diethylenetriamine, triethylenetetramine, 5 tetraethylenepentamine, diethylaminopropylamine, hexamethylenediamine, methylpentamethylenediamine, trimethylhexamethylenediamine, guanidine, tetramethylguanidine and oleylamine; alicyclic amines such as menthendiamine, isophoronediamine, norbornanediamine, 10 piperidine, N,N'-dimethylpiperazine, N-aminoethylpiperazine, Lamiron C-260 manufactured by BASF Corp., Araldite HY-964 manufactured by Ciba-Geigy, menthenediamine manufactured by Rohm & Haas Corporation, 1,2-diaminocyclohexane, diaminodicyclohexylmethane, 15 bis(4-amino-3-methylcyclohexyl)methane, bis(4-aminocyclohexyl)methane, polycyclohexylpolyamine and 1,8-diazabicyclo[5,4,0]undecane-7 (DBU); aromatic amines such as m-xylylenediamine, m-phenylenediamine, 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenylsulfone; 20 linear diamines represented by the formula, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{N}(\text{CH}_3)_2$ (wherein n represents an integer of 1 to 10), linear tertiary amines represented by the formula, $(\text{CH}_3)_2\text{-N}(\text{CH}_2)_n\text{-CH}_3$ (wherein n represents an integer of 0 to 10), alkyl tertiary monoamines represented by the formula, $\text{N}\{(\text{CH}_2)_n\text{CH}_3\}_3$ (wherein n represents 25 an integer of 1 to 10); aliphatic aromatic amines such as benzyldimethylamine, 2-(dimethylaminomethyl)phenol and 2,4,6-tris(dimethylaminomethyl)phenol; amines having ether bonds such as 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane 30 (ATU), morpholine, N-methylmorpholine, polyoxypropylenediamine, polyoxypropylenetriamine and polyoxyethylenediamine; hydroxyl-containing amines such as diethanolamine and triethanolamine; triethylenediamine, pyridine, picoline, diazacycloundecene, acid anhydrides such 35 as phthalic anhydride, trimellitic anhydride, pyromellitic

anhydride, benzophenonetetracarboxylic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylnadic anhydride, hexahydrophthalic anhydride, and dodecylsuccinic anhydride; polyamides and various kinds of polyamide resins obtained by reaction of a polyamine such as diethylenetriamine and triethylenetetramine with a dimer acid; polyamidoamines such as polyamides using a polycarboxylic acid other than dimer acids; various kinds of imidazoles such as 2-ethyl-4-methylimidazole; dicyanodiamides and derivatives thereof; polyoxypropylene amines such as polyoxypropylene diamines and polyoxypropylene triamines; phenols; epoxy-modified amines obtained by reaction of an epoxy compound with the above-exemplified amines, Mannich-modified amines obtained by reaction of formalin and/or a phenol with the above-exemplified amines, Michael addition-modified amines, ketimines obtained by condensation reaction of an amine compound and a carbonyl compound, and the like modified amines; amine salts such as 2,4,6-tris(dimethylaminomethyl)phenol 2-ethylhexanoic acid salt; compounds having an amino group and a hydrolysable silyl in one molecule such as N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane; and the like. Specific examples of ketimine compounds are described in Japanese Kokai Publication Hei-7-242737 and the like.

These curing agents may be used alone or two or more of them may be used in combination. Although it is not particularly limited, among these curing agents for epoxy resin, 2,4,6-tris(dimethylaminomethyl)phenol and polyoxypropylene diamines are preferable in terms of curability and physical property balance.

Although depending on the addition amount of the epoxy resin (II), these curing agent for epoxy resin is added in a range generally of about 1 to 60 parts by weight and preferably of about 2 to 50 parts by weight per 100 parts by weight of the epoxy resin (II). If it is lower than 1 part by weight, the curing of the epoxy resin becomes insufficient and the adhesion

strength tends to be lowered. On the other hand, if it exceeds 60 parts by weight, bleeding occurs at the interface and adhesiveness tends to be undesirably lowered.

The curable resin composition is preferable to contain
5 a compound containing a group reactive on both of the
crosslinkable silyl group of the vinyl polymer (I) and the epoxy
group of the epoxy resin (II) since the strength is further
improved. Specific examples are
N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane,
10 N-(β -aminoethyl)- γ -aminopropyltriethoxysilane,
 γ -glycidoxypropyltrimethoxysilane and the like.
<Dehydration agent>

During storage, the curable composition sometimes
becomes sticky and gelled due to the moisture etc. entrained
15 at the time of production to result in deterioration of the
workability at the time of use. Further, due to the increased
viscosity and gelation of the curable composition, the physical
properties of the cured product obtained using the curable
composition are deteriorated after curing and thus there occurs
20 a problem of deterioration of the sealing property etc., which
is the aim of the invention. That is, the curable composition
sometimes has a problem in the storage stability.

To improve the storage stability of the curable
composition, there is a method for decreasing the moisture
25 content of the curable composition by azeotropic dehydration.
For example, there is a method that about 0.1 to 10 parts by
weight of a volatile organic compound having a very low
azeotropic boiling point to water is added to and evenly mixed
with water in order to take out an azeotropic composition of
30 water-organic compound with sucking by a vacuum pump under a
condition of heating at about 50 to 90°C. Examples of the
volatile organic compound having a very low azeotropic boiling
point to water are halides such as methylene chloride,
chloroform, carbon tetrachloride and trichloroethylene;
35 alcohols such as ethanol, allyl alcohol, 1-propanol and

butanol; esters such as ethyl acetate and methyl propionate; ketones such as methyl ethyl ketone and 3-methyl-2-butanone; ethers such as ethyl ether and isopropyl ether; hydrocarbons such as benzene, toluene, xylene and hexane; and the like.

5 However, since this method involves an evaporation step, it is required to add other volatile addition agents or carry out a treatment and/or recovery etc. of the volatile organic compound used for azeotropic boiling. Therefore, it is sometimes more preferable to add the following dehydration agent in some cases.

10 As described above, the curable composition of the invention may contain the dehydration agent for removing moisture from the composition in order to improve the storage stability. Examples of the dehydration agent are, for example, inorganic solids such as phosphorus pentoxide, sodium hydrogen
15 carbonate, sodium sulfate (anhydrous sodium sulfate) and molecular sieves. These solid dehydration agents may be used, however after addition of the agent, the pH of the composition sometimes tends to be acidic or basic to cause condensation, resulting in adverse deterioration of the storage stability in
20 some cases or deterioration of the workability because of requirement for solid removal thereafter. Therefore, the following liquid-state hydrolysable ester compound is preferable. Examples of the hydrolysable ester compound are selected from the group consisting of trialkyl orthoformate
25 such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate and tributyl orthoformate; trialkyl orthoacetate such as trimethyl orthoacetate, triethyl orthoacetate, tripropyl orthoacetate and tributyl orthoacetate; and the like.

30 Further, as another hydrolysable ester compound, there may be mentioned a hydrolysable organic silicon compound represented by the formula $R_{4-n}SiY_n$ (wherein Y represents a hydrolysable group; R represents an organic group which may or may not have a functional group; and n is an integer of 1 to
35 4 and preferably 3 or 4). Specific examples of the compound

are vinyltrimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, phenyltriethoxysilane, methyltriacetoxysilane, tetramethyl orthosilicate (tetramethoxysilane or methyl silicate),
5 tetraethyl orthosilicate (tetraethoxysilane or ethyl silicate), tetrapropyl orthosilicate, tetrabutyl orthosilicate and the like silane compounds and partially hydrolyzed condensates thereof; γ -aminopropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane,
10 N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane,
15 N-(β -aminoethyl)- γ -aminopropylmethyldimethoxysilane and the like silane coupling agents and partially hydrolyzed condensates thereof; and the like. These compounds may be used alone or two or more of them may be used in combination.

The use amount of the storage stability-improving agent
20 is preferably 0.1 to 30 parts by weight, more preferably 0.3 to 20 parts by weight, and further preferably 0.5 to 10 parts by weight, per 100 parts by weight of the vinyl polymer (I).

At the time of adding the storage stability-improving agent, it is preferable to add the agent after the curable
25 composition is dehydrated, however it may be added in the state the composition contains moisture as it does.

<Adhesion promoter>

The curable composition of the invention may contain a silane coupling agent and an adhesion promoter other than the
30 silane coupling agent. If adhesion promoter is added, the risk of peeling off of a sealant from an adherend such as a siding board may be decreased due to alteration of jointing width or the like by external power. In some cases, a primer for improving the adhesiveness is not required so as to simplify
35 the processing work. Examples of the silane coupling agent are

silane coupling agents having a functional group such as an amino group, mercapto group, epoxy group, carboxyl group, vinyl group, isocyanato group, isocyanurate group, and a halogen and specific examples of them are isocyanato group-containing
5 silanes such as γ -isocyanateopropyltrimethoxysilane, γ -isocyanateopropyltriethoxysilane, γ -isocyanateopropylmethyldiethoxysilane, and γ -isocyanateopropylmethyldimethoxysilane; amino-containing silanes such as γ -aminopropyltrimethoxysilane,
10 γ -aminopropyltriethoxysilane, γ -aminopropyltripropoxysilane, γ -aminopropylmethyldimethoxysilane, γ -aminopropylmethyldiethoxysilane, γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane,
15 γ -(2-aminoethyl)aminopropyltriethoxysilane, γ -(2-aminoethyl)aminopropylmethyldiethoxysilane, γ -(2-aminoethyl)aminopropyltriisopropoxysilane, γ -ureidopropyltrimethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane,
20 N-benzyl- γ -aminopropyltrimethoxysilane and N-vinylbenzyl- γ -aminopropyltriethoxysilane; mercapto group-containing silanes such as γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane,
25 γ -mercaptopropylmethyldimethoxysilane and γ -mercaptopropylmethyldiethoxysilane; epoxy group-containing silanes such as γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldimethoxysilane,
30 β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane and β -(3,4-epoxycyclohexyl)ethyltriethoxysilane; carboxysilanes such as β -carboxyethyltriethoxysilane, β -carboxyethylphenylbis(2-methoxyethoxy)silane and N- β -(carboxymethyl)aminoethyl- γ -aminopropyltrimethoxysilane
35 ; vinyl unsaturated group-containing silanes such as

vinyltrimethoxysilane, vinyltriethoxysilane,
γ-methacryloyloxypropylmethyldimethoxysilane and
γ-acryloyloxypropylmethyltriethoxysilane;
halogen-containing silanes such as

5 γ-chloropropyltrimethoxysilane; isocyanurate silanes such as
tris(trimethoxysilyl)isocyanurate; polysulfanes such as
bis(3-triethoxysilylpropyl)tetrasulfane; and the like.
Further, reaction products of the above-mentioned amino
group-containing silane and epoxy group-containing silane,
10 reaction products of an amino group-containing silane and an
acryloyloxy group-containing silane, and reaction products of
an amino group-containing silane and an isocyanato
group-containing silane are also usable. Further, derivatives
obtained by modifying the above-mentioned silane, for example,
15 amino-modified silyl polymers, silylated aminopolymers,
unsaturated aminosilane complexes, phenylamino long-chain
alkylsilanes, amino-silylated silicones, block isocyanato
silanes, silylated polyesters and the like may be usable as the
silane coupling agent. Further, ketimine compounds obtained
20 by reaction of the above-mentioned amino group-containing
silane and a ketone compound such as methyl isobutyl ketone,
and the like may be usable as the silane coupling agent.

In general, the silane coupling agent is preferably used
in 0.1 to 20 parts per 100 parts of the polymer containing a
25 crosslinkable silyl group. Particularly, it is more
preferable to be used in 0.5 to 10 parts. The effect of the
addition of the silane coupling agent to the curable composition
of the invention is a remarkable adhesiveness improvement in
the case of using the curable composition for various kinds of
30 adherends, that is inorganic substrates such as glass, aluminum,
stainless steel, zinc, copper and mortar and organic substrates
such as vinyl chloride, acrylic compounds, polyesters,
polyethylene, polypropylene and polycarbonate under
non-primer condition or primer treatment condition. In the
35 case of use under non-primer condition, the effect of improving

the adhesiveness to various kinds of adherends is particularly substantial. Further, if the use amount is about 1 part per 100 parts of the polymer containing a crosslinkable silyl group, the use scarcely affects the transparency of the cured product.

5 Specific examples of the adhesion promoter other than the silane coupling agents are not particularly limited and may include epoxy resin, phenol resin, linear or branched block copolymers such as polystyrene-polybutadiene-polystyrene, polystyrene-polyisoprene-polystyrene,
10 polystyrene-polyisoprene/butadiene copolymer-polystyrene, polystyrene-polyethylene/propylene copolymer-polystyrene, polystyrene-polyethylene/butylene copolymer-polystyrene and polystyrene-polyisobutene-polystyrene, alkyl sulfonate esters, sulfur, alkyl titanates, aromatic polyisocyanates, and
15 the like. The epoxy resin may be used being reacted with the amino group-containing silane.

The above-mentioned adhesion promoters may be used alone or two or more of them may be used as a mixture. The adhesiveness to the adherend may be improved by addition of the adhesion
20 promoters. Although it is not particularly limited, to improve the adhesiveness, particularly the adhesiveness to a metal face such as an oil pan, it is preferable to use 0.1 to 20 parts by weight of the silane coupling agent among the above-mentioned adhesion promoters in combination.

25 The type and the addition amount of the adhesion promoter can be selected in accordance with the crosslinkable silyl group of the vinyl polymer (I) of the invention and the type of Y and the number a in the general formula 2, and the curability and the mechanical property etc. of the invention may be controlled
30 in accordance with the purposes and uses. The above-mentioned selection requires attention since it affects the curability and elongation in particular.

<Plasticizer>

Various kinds of plasticizers may be used for the curable
35 composition of the invention according to need. If a

plasticizer is used in combination with a filler, which will be described later, the elongation of the cured product can be increased and a large amount of filler can be advantageously added, however it is not necessarily indispensable agent. The plasticizers are not particularly limited and may be selected from the following in accordance with the purpose such as adjustment of the physical property, adjustment of the material state and the like: phthalic acid esters such as dibutyl phthalate, diheptyl phthalate, di(2-ethylhexyl)phthalate, diisodecyl phthalate, butyl benzyl phthalate; non-aromatic dibasic acid esters such as dioctyl adipate, dioctyl sebacate, dibutyl sebacate and isodecyl succinate; aliphatic esters such as butyl oleate and methyl acetyl ricinoleate; polyalkylene glycol esters such as diethylene glycol dibenzoate, triethylene glycol dibenzoate and pentaerythritol ester; phosphoric acid esters such as tricresyl phosphate and tributyl phosphate; trimellitic acid esters; polystyrenes such as polystyrene and poly- α -methylstyrene; polybutadiene, polybutene, polyisobutylene, butadiene-acrylonitrile, polychloroprene; chloro paraffins; hydrocarbon oils such as alkyl diphenyl and partially-hydrogenated tarphenyl; process oils; polyether polyols such as polyethylene glycol, polypropylene glycol, ethylene oxide-propylene oxide copolymer and polytetramethylene glycol, polyether alkyl-derivatives obtained by converting the hydroxyl groups at one terminus, both termini or all termini of the above-mentioned polyether polyols to alkyl ester group or alkyl ether group etc., and the like polyethers; epoxy group-containing plasticizers such as epoxylated soybean oil, benzyl epoxystearate and E-PS; polyester plasticizers obtained from a dibasic acid such as sebacic acid, adipic acid, azelaic acid and phthalic acid and a dihydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and dipropylene glycol; vinyl polymers obtained by polymerizing vinyl monomers by various methods, e.g. acrylic plasticizers; and the like.

Among them, a polymer plasticizer with a number average molecular weight of 500 to 15,000 is capable of adjusting the viscosity and slump property of the curable composition and the mechanical properties such as tensile strength and elongation of the cured product obtained by curing the composition while being added to the composition, and as compared with the case a low molecular plasticizer, that is, a plasticizer containing no polymer component in the molecule, is used, the polymer plasticizer keeps the initial physical properties for a long duration and improves the quick drying property (also called as coatability) in the case where an alkyd paint is applied to the cured product. Additionally, although it is not limited, the polymer plasticizer may or may not have functional groups.

The number average molecular weight of the above-mentioned polymer plasticizer is 500 to 15,000, and it is preferably 800 to 10,000 and more preferably 1,000 to 8,000. If the molecular weight is too low, the plasticizer is eluted by heat or rain fall with the lapse of time or the initial physical properties cannot be maintained for a long duration and the alkyd coatability improvement tends to become impossible. On the other hand, if the molecular weight is too high, the viscosity becomes high and the workability tends to be worsened.

Among the exemplified polymer plasticizers, the polyether plasticizers and (meth)acrylic polymer plasticizers are preferable in terms of the high elongation and high weather resistance. A synthetic method of the acrylic polymers may be, for example, conventional methods for carrying out solution polymerization and non-solvent acrylic polymer production methods. The latter acrylic plasticizer is produced by high temperature continuous polymerization manner using no solvent or chain transfer agent (reference to U.S. Patent No. 4414370, Japanese Kokai Publication Sho-59-6207, Japanese Kokoku Publication Hei-5-58005, Japanese Kokai Publication Hei-1-313522, U.S. Patent No. 5010166) and these plasticizers

are more preferable for the purposes of the invention. Examples of them are not particularly limited and may include, for example, ARUFON UP series (UP-1000, UP-1110, UP-2000, and UP-2130 (called as SGO) manufactured by Toagosei Co., Ltd. (reference to Bosui Journal (Water-proof property Journal), June 2002). Living radical polymerization method can be exemplified as another synthesis method. According to this method, a preferable polymer with a narrow molecular weight distribution and a low viscosity can be produced and therefore this method is preferable and an atom transfer radical polymerization method is more preferable. However, the methods are not limited to these exemplified methods.

The molecular weight distribution of the polymer plasticizer is not particularly limited, and in terms of the viscosity, it is preferable to be narrow and it is preferably lower than 1.8. It is more preferably 1.7 or lower, further preferably 1.6 or lower, furthermore preferably 1.5 or lower, even more preferably 1.4 or lower, and most preferably 1.3 or lower.

In terms of the viscosity, the plasticizer preferably has a branched structure in the main chain for the same molecular weight since the viscosity is lowered more. The above-mentioned high temperature continuous polymerization method is an example of methods which give such a plasticizer.

The plasticizers including the above-mentioned polymer plasticizers may be used alone or two or more of them may be used in combination, however addition is not necessarily indispensable. Further, if necessary, the polymer plasticizer may be used in combination with a low molecular weight plasticizer to an extent that the physical property is not adversely affected. Further, for example, in the case where the composition contains the vinyl polymer of the invention and a polyether polymer as one optional polymer component having a crosslinkable functional group, phthalic acid esters and acrylic polymers are particularly preferable in terms of the

compatibility of the mixture.

The plasticizer may be added at the time of polymer production.

When the plasticizer is used, the use amount of the plasticizer is not particularly limited and preferably 5 to 150 parts by weight, more preferably 10 to 120 parts by weight, and further preferably 20 to 100 parts by weight, per 100 parts of the polymer containing a crosslinkable silyl group. If it is lower than 5 parts by weight, the effect as a plasticizer is not efficiently caused and if it exceeds 150 parts by weight, the mechanical strength of the cured product tends to become insufficient.

<Filler>

The curable composition of the invention may contain various kinds of fillers, according to need, to an extent that the transparency of the invention is not affected. The fillers are not particularly limited and may include reinforcing fillers such as wood flour, pulp, cotton chips, asbestos, glass fiber, carbon fiber, mica, walnut shell flour, rice hull flour, graphite, china clay, kaolin, silica (e.g. fumed silica, precipitated silica, crystalline silica, fused silica, dolomite, silicic anhydride, hydrous silicic acid and amorphous spherical silica), and carbon black; fillers such as ground calcium carbonate, precipitated calcium carbonate, magnesium carbonate, china clay, calcined clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, aluminum fine powder, flint powder, zinc oxide, activated zinc white, zinc powder, zinc carbonate, shirasu balloon, glass microballoon, organic microballoon of a phenol resin and/or a vinylidene chloride resin, resin powder such as PVC powder and PMMA powder, and the like fillers; fibrous fillers such as asbestos, glass fibers and glass filaments, carbon fibers, Kevlar fibers and polyethylene fibers; and the like.

Preferable fillers among them are precipitated silica, fumed silica, crystalline silica, fused silica, dolomite,

carbon black, calcium carbonate, titanium oxide, talc and the like.

In the case where it is aimed to obtain the cured product with high transparency or strength by adding the fillers, the filler to be added may be selected from mainly fumed silica, precipitated silica, silicic anhydride, hydrous silicic acid, carbon black, surface treated fine calcium carbonate, crystalline silica, fused silica, calcined clay, clay and activated zinc white. These fillers are suitable for a sealant for transparent construction and adhesive for transparent DIY. Above all, ultrafine powder silica with a specific surface area of $10 \text{ m}^2/\text{g}$ or higher, generally 50 to $400 \text{ m}^2/\text{g}$ and preferably about 100 to $300 \text{ m}^2/\text{g}$ (measured by BET absorption method) is preferable. Further, silica previously surface-treated for hydrophobic treatment with an organosilicon compound such as an organosilane, an organosilazane, and a diorganocyclopolyloxane is more preferable.

Specific examples of the silica filler with high reinforcing property are not particularly limited and may include Aerosil (fumed silica) manufactured by Nippon Aerosil Co., Ltd., Nipsil (precipitated silica) manufactured by Nippon Silica Industrial, and the like. Silica with an average particle diameter of 1 nm to $30 \mu\text{m}$ can be used. With respect to fumed silica, if fumed silica with an average particle diameter of primary particles in a range from 1 nm to 50 nm is used, the reinforcing effect is particularly efficient and therefore it is more preferable. In this connection, the average particle diameter in the invention is measured by sieving method. In particular, the average particle diameter is measured by classifying a powder by sieves (micro sieves or the like) with various mesh sizes and measuring the value (weight average particle diameter) corresponding to the mesh size of the sieve through which 50% by weight of the total amount of the powder subjected to the measurement is passed. The composition reinforced by the filler is excellent in the prompt

fixation and suitable for automotive glass grading adhesion.

The transparency can also be obtained by using a resin powder such as PMMA powder as the filler.

In particular when low-strength, high-elongation cured products are to be obtained using such fillers, one or more fillers selected from among titanium oxide, calcium carbonate, talc, ferric oxide, zinc oxide, shirasu balloons and the like may be added. Generally, calcium carbonate, when small in specific surface area, may be insufficiently effective at improving the strength at break, elongation at break, adhesion and weather-resistant adhesion of cured products. As the specific surface area value increases, the effects of improving the strength at break, elongation at break, adhesion and weather-resistant adhesion become better. As the calcium carbonate, cubic, noncubic, amorphous, and the like shape ones may be used.

Furthermore, calcium carbonate is more preferably surface-treated with a surface treating agent. When surface-treated calcium carbonate is used, it is expected that the workability of the composition of the invention be improved and the effects of improving the adhesion and weather-resistant adhesion of the curable composition be more improved as compared with the use of non-surface-treated calcium carbonate. Useful as the surface treating agent are organic substances such as fatty acids, fatty acid soaps and fatty acid esters, various surfactants, and various coupling agents such as silane coupling agents and titanate coupling agents. Specific examples include, but are not limited to, fatty acids such as caproic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid and oleic acid, sodium, potassium and other salts of such fatty acids, and alkyl esters of such fatty acids. As specific examples of the surfactants, there may be mentioned sulfate ester type anionic surfactants such as polyoxyethylene alkyl ether sulfate esters and long-chain

alcohol sulfate esters, and sodium, potassium and other salts thereof, sulfonic acid type anionic surfactants such as alkylbenzenesulfonic acids, alkyl naphthalenesulfonic acids, paraffinsulfonic acids, α -olefinsulfonic acids and
5 alkylsulfosuccinic acid, and sodium, potassium and other salts thereof, and the like. In the surface treatment, the surface treating agent is used in an amount preferably within the range of 0.1 to 20% by weight, more preferably within the range of 1 to 5% by weight, relative to calcium carbonate. When the
10 amount for treatment is smaller than 0.1% by weight, the effects of improving the workability, adhesion and weather-resistant adhesion may be insufficient and, when it exceeds 20% by weight, the storage stability of the curable composition may decrease.

When calcium carbonate is used in expectation of
15 producing the effects of improving the thixotropic properties of the formulations and the strength at break, elongation at break, adhesion, weather-resistant adhesion and the like of the cured product, in particular, precipitated calcium carbonate is preferably used, although this does not mean any particular
20 restriction.

On the other hand, ground calcium carbonate is sometimes added for the purpose of reducing the viscosity of the formulations, increasing the weight thereof and reducing the cost, for example. When ground calcium carbonate is used, such
25 species as mentioned below can be used.

Ground calcium carbonate is prepared from natural chalk, marble, limestone or the like by mechanical grinding/processing. The method of grinding includes the dry method and wet method. Wet ground products are unfavorable in many cases since they
30 often deteriorate the storage stability of the curable composition of the invention. Upon classification, ground calcium carbonate gives various products differing in average particle size. In cases where the effects of improving the strength at break, elongation at break, adhesion and
35 weather-resistant adhesion are expected, the specific surface

area value is preferably not less than $1.5 \text{ m}^2/\text{g}$ and not more than $50 \text{ m}^2/\text{g}$, more preferably not less than $2 \text{ m}^2/\text{g}$ and not more than $50 \text{ m}^2/\text{g}$, still more preferably not less than $2.4 \text{ m}^2/\text{g}$ and not more than $50 \text{ m}^2/\text{g}$, most preferably not less than $3 \text{ m}^2/\text{g}$ and not more than $50 \text{ m}^2/\text{g}$, although this does not mean any particular restriction. When the specific surface area is smaller than $1.5 \text{ m}^2/\text{g}$, those improving effects may be insufficient. Of course, the above does not apply to the cases where it is only intended to reduce the viscosity and/or increase the weight.

10 The specific surface area value is the measured value obtained by using, as the measurement method, the air permeation method (method for specific surface area determination based on the permeability of a powder-packed layer to air) carried out according to JIS K 5101. Preferred for use as the measuring
15 instrument is a Shimadzu model SS-100 specific surface area measuring apparatus.

Those fillers may be used singly or two or more of them may be used in combination according to the intended purpose or necessity. For example, the combined use, according to need,
20 of ground calcium carbonate having a specific surface area value of not smaller than $1.5 \text{ m}^2/\text{g}$ and precipitated calcium carbonate is fully expected to suppress the viscosity increase in the formulations to a moderate level and produce the effects of improving the strength at break, elongation at break, adhesion
25 and weather-resistant adhesion of cured products, although this does not mean any particular restriction.

When a filler is used, the filler is preferably used in an amount within the range of 5 to 1,000 parts by weight, more preferably within the range of 20 to 500 parts by weight,
30 particularly preferably within the range of 40 to 300 parts by weight, per 100 parts by weight of the crosslinkable silyl group-containing polymer. When the addition level is lower than 5 parts by weight, the effects of improving the strength at break, elongation at break, adhesion and weather-resistant
35 adhesion may be insufficient and, when the amount exceeds 1,000

parts by weight, the workability of the curable composition may deteriorate. Those fillers may be used singly or two or more of them may be used in combination.

Here, addition of large amount of dolomite, carbon black, calcium carbonate, titanium oxide, talc and the like sometimes deteriorates the transparency of the present invention and results in producing an opaque cured product of the invention, and attentions are therefore required.

<Hollow microsphere>

Furthermore, for the purpose of reducing the weight and cost without causing significant deteriorations in physical properties, hollow microspheres may be used in combination with such a reinforcing filler as mentioned above as long as the transparency of the present invention does not deteriorate.

Such hollow microspheres (hereinafter referred to as "balloons") are not particularly restricted but include, for example, hollow spheres constituted of an inorganic or organic material and having a diameter of preferably not greater than 1 mm, more preferably not greater than 500 μm , and even more preferably not greater than 200 μm , as described in "Kinosei Fira no Saishin Gijutsu (Latest Technology of Functional Fillers)" (CMC Publishing CO., LTD). In particular, hollow microspheres having a true specific gravity of not higher than 1.0 g/cm^3 are preferably used and, more preferably, hollow microspheres having a true specific gravity of not higher than 0.5 g/cm^3 are used.

The inorganic balloons include silicic balloons and non-silicic balloons. Examples of the silicic balloons are shirasu balloons, perlite, glass (silica) balloons, fly ash balloons and the like, and examples of the non-silicic balloons are alumina balloons, zirconia balloons, carbon balloons and the like. Commercially available as specific examples of such inorganic balloons are Idichi Kasei's Winlite and Sanki Kogyo Co., Ltd.'s Sankilite (shirasu balloons), FUJI SILYSIA CHEMICAL LTD.'s Fuji Balloon, Nippon Sheet Glass Co., Ltd.'s Calloon,

Sumitomo 3M Limited's Cel-Star Z-28, Emerson & Cuming Company's Micro Balloon, Pittsburgh Corning Corporation's Celamic Glassmodules and Sumitomo 3M Limited's Glass Bubbles, Asahi Glass Co., Ltd.' Q-Cel and Taiheiyo Cement Corporation's
5 E-Spheres (glass (silica) balloons), Pfamarketing's Cerospheres and Fillite U.S.A.'s Fillite (fly ash balloons), Showa Denko K.K.'s BW (alumina balloons), Zircoa Inc.'s Hollow Zirconium Spheres (zirconia balloons), and Kureha Chemical Industry's Kurekasphere and General Technologies Inc.'
10 Carbosphere (carbon balloons).

The organic balloons include thermosetting resin balloons and thermoplastic resin balloons. Examples of the thermosetting resin balloons are phenol balloons, epoxy balloons and urea balloons, and examples of the thermoplastic
15 balloons are Saran balloons, polystyrene balloons, polymethacrylate balloons, polyvinyl alcohol balloons and styrene-acrylic type balloons. Crosslinked thermoplastic resin balloons can also be used. The balloons so referred to herein may be balloons after expansion or balloons produced by
20 expansion following incorporation of a blowing agent-containing resin.

As specific examples of such organic balloons which are commercially available, there may be mentioned Union Carbide Corporation's Ucar and Phenolic Microballoons (phenol
25 balloons), Emerson & Cuming Company's Eccospheres (epoxy balloons), Emerson & Cuming Company's Eccospheres VF-0 (urea balloons), Dow Chemical Company's Saran Microspheres, Janan Fillite Co., Ltd.'s Expancel and Matsumoto Yushi Seiyaku Co., Ltd.'s Matsumoto Microspheres (Saran balloons), Arco Polymers
30 Inc.'s Dylite Expandable Polystyrene and BASF-Wyandotte's Expandable Polystyrene Beads (polystyrene balloons), and JSR Corporation's SX863(P) (crosslinked styrene-acrylic balloons).

The above-mentioned balloon species may be used singly
35 or two or more of them may be used in admixture. Furthermore,

those balloons surface-treated with a fatty acid, a fatty acid ester, rosin, rosin acid lignin, a silane coupling agent, a titan coupling agent, an aluminum coupling agent, polypropylene glycol or the like for improving the dispersibility and the workability of the formulations may also be used. These balloons are used for making the curable composition containing them lightweight for cost down, delustering the surface, optional designing by sputtering etc., or the like without deteriorating the improvement in the workability such as
10 antisagging property before curing and flexibility, expansion and strength after curing.

The balloon content is not particularly restricted but the balloons can be used preferably in an amount within the range of 0.1 to 50 parts by weight, more preferably 0.1 to 30 parts
15 by weight, per 100 parts by weight of the crosslinkable silyl group-containing polymer. When this amount is smaller than 0.1 part by weight, the weight-reducing effect is slight and, when it exceeds 50 parts by weight, decreases in tensile strength, among the mechanical properties after curing of the
20 balloon-containing formulations, are observed in some instances. When the balloons have a specific gravity of not lower than 0.1, the amount is preferably 3 to 50 parts by weight, more preferably 5 to 30 parts by weight.

<Physical property modifier>

25 In the curable composition of the invention, there may be incorporated a physical property modifier capable of adjusting the tensile properties of the resulting cured products, according to need.

The physical property modifiers are not particularly
30 restricted but include, for example, alkylalkoxysilanes such as methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane and n-propyltrimethoxysilane; alkylisopropenoxysilanes such as dimethyldiisopropenoxysilane, methyltriisopropenoxysilane,
35 γ-glycidoxypropylmethyldiisopropenoxysilane, functional

group-containing alkoxysilanes such as
γ-glycidoxypropylmethyldimethoxysilane,
γ-glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane,
vinyl dimethylmethoxysilane, γ-aminopropyltrimethoxysilane,
5 N-(β-aminoethyl)aminopropylmethyldimethoxysilane,
γ-mercaptopropyltrimethoxysilane and
γ-mercaptopropylmethyldimethoxysilane; silicone varnishes;
polysiloxanes; and the like. By using such as a physical
property modifier, it is possible to increase the hardness of
10 the cured products after curing of the curable composition of
the invention or decrease such hardness and attain
extensibility. Such physical property modifiers as mentioned
above may be used singly or two or more of them may be used in
combination.

15 <Silanol-containing compound>

A silanol-containing compound may optionally be added
into the curable composition of the present invention for
modifying the physical property of the cured product to be
obtained, and the like purpose. The term "silanol-containing
20 compound" as used herein means a compound having one silanol
group in a molecule and/or a compound capable of forming a
compound having one silanol group in a molecule by a reaction
with moisture. When these compounds are used, only one of the
above two compounds may be used, or both of them may be used
25 simultaneously.

The compounds having one silanol group in a molecule,
which is one of the silanol-containing compounds, is not
particularly restricted. Among others, there may be mentioned
compounds which can be represented by the formula $(R''')_3\text{SiOH}$
30 (wherein R''' 's are the same or different kind of substituted
or non-substituted alkyl or aryl group), for example, the
following compounds:

$(\text{CH}_3)_3\text{SiOH}$, $(\text{CH}_3\text{CH}_2)_3\text{SiOH}$, $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{SiOH}$, $(n\text{-Bu})_3\text{SiOH}$,
 $(\text{sec-Bu})_3\text{SiOH}$, $(t\text{-Bu})_3\text{SiOH}$, $(t\text{-Bu})\text{Si}(\text{CH}_3)_2\text{OH}$, $(\text{C}_5\text{H}_{11})_3\text{SiOH}$,
35 $(\text{C}_6\text{H}_{13})_3\text{SiOH}$, $(\text{C}_6\text{H}_5)_3\text{SiOH}$, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_3)\text{OH}$, $(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_2\text{OH}$,

$(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_2\text{H}_5)\text{OH}$, $\text{C}_6\text{H}_5\text{Si}(\text{C}_2\text{H}_5)_2\text{OH}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{OH}$,
 $\text{C}_{10}\text{H}_7\text{Si}(\text{CH}_3)_2\text{OH}$,

(wherein C_6H_5 represents a phenyl group and C_{10}H_7 represents a naphthyl group);

- 5 silanol group-containing cyclic polysiloxanes compounds, for example, the following compounds;

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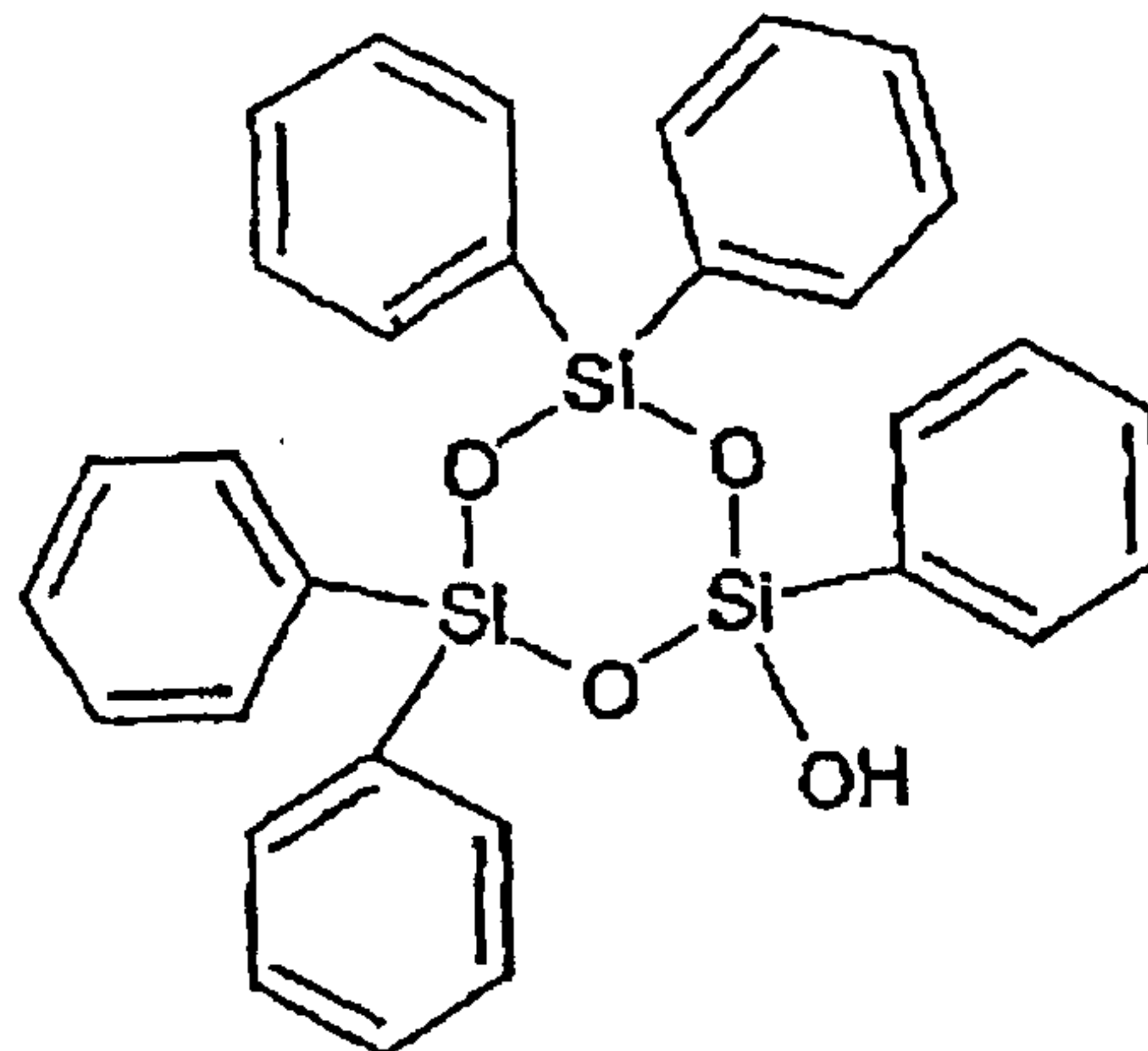
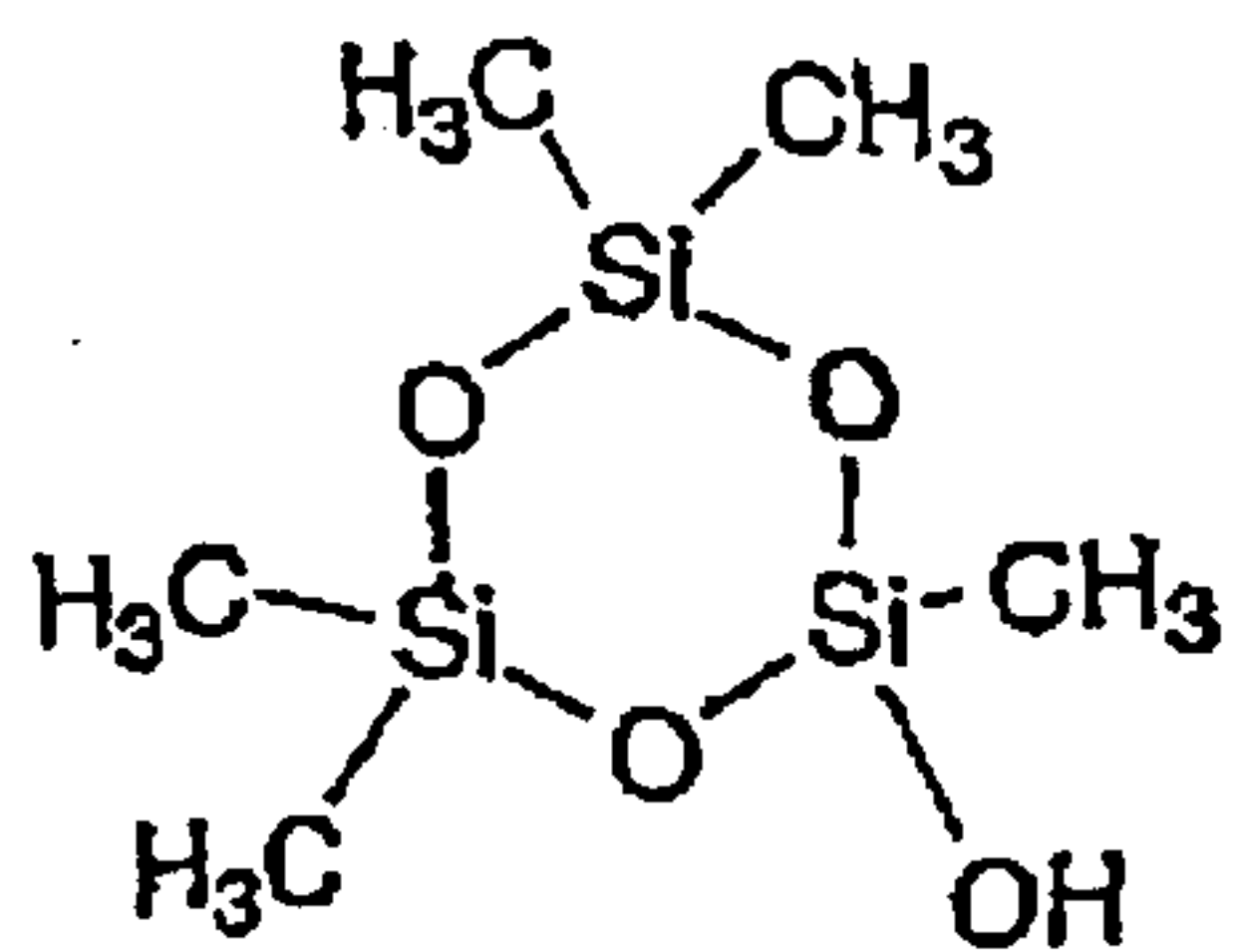
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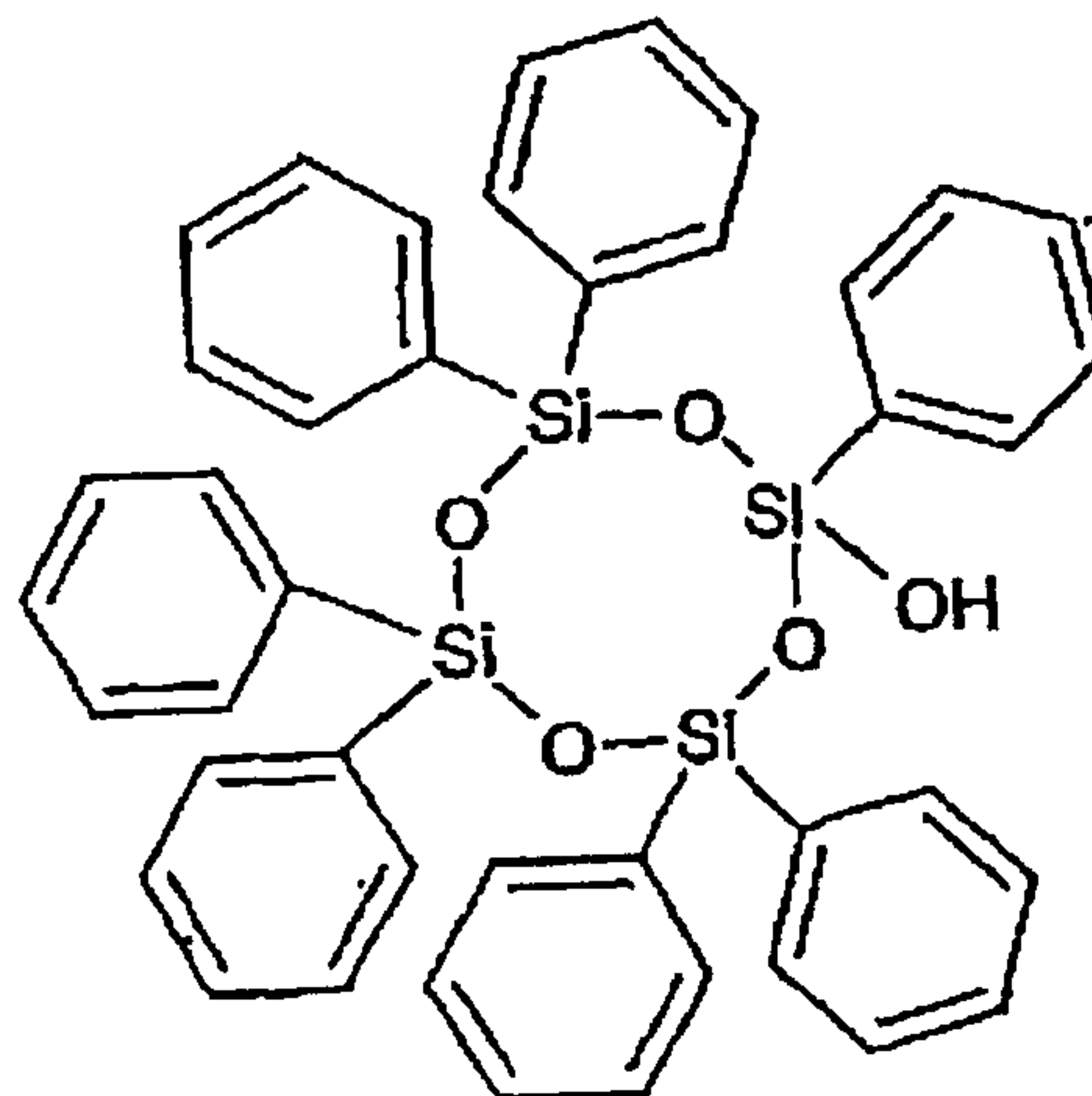
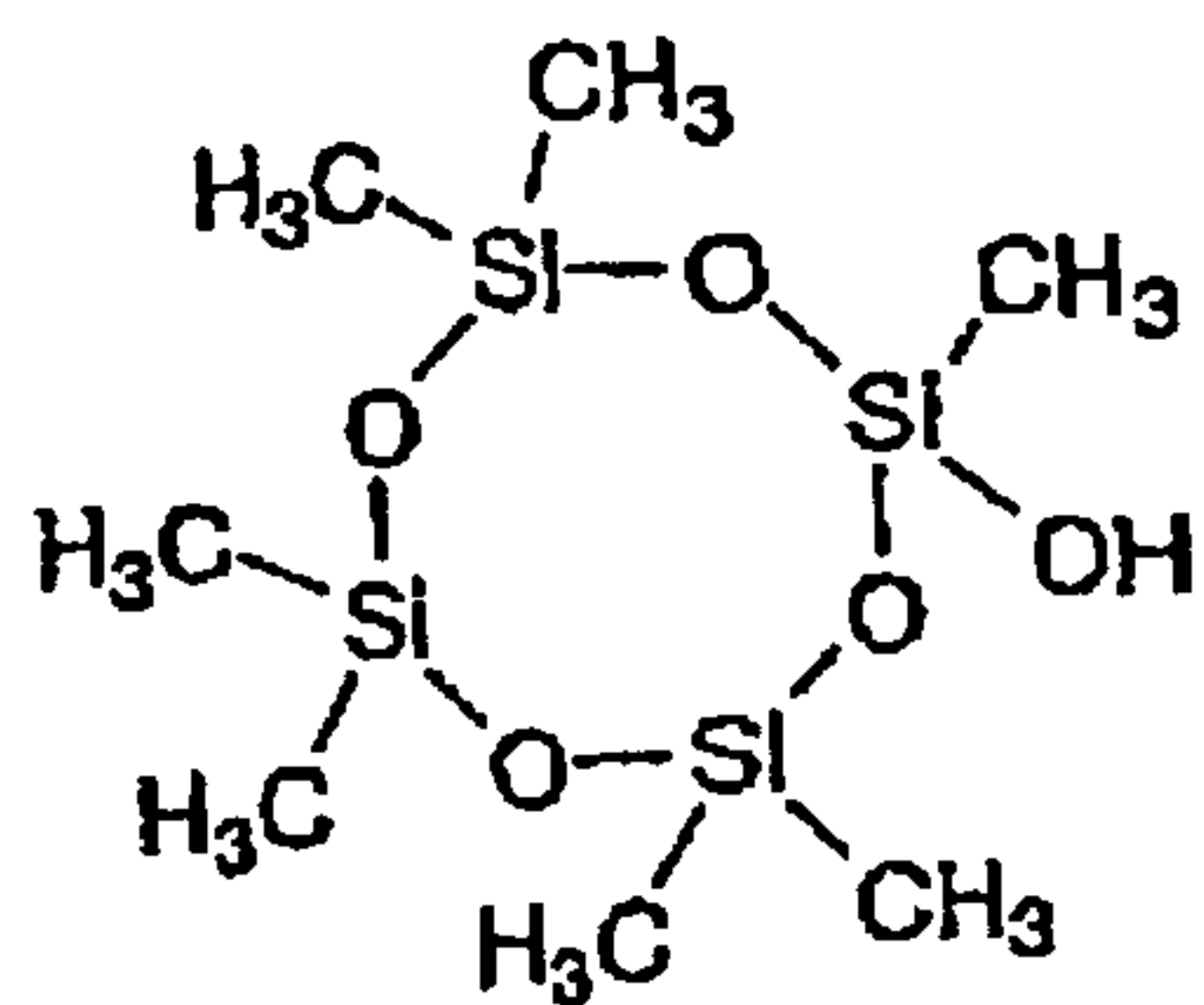
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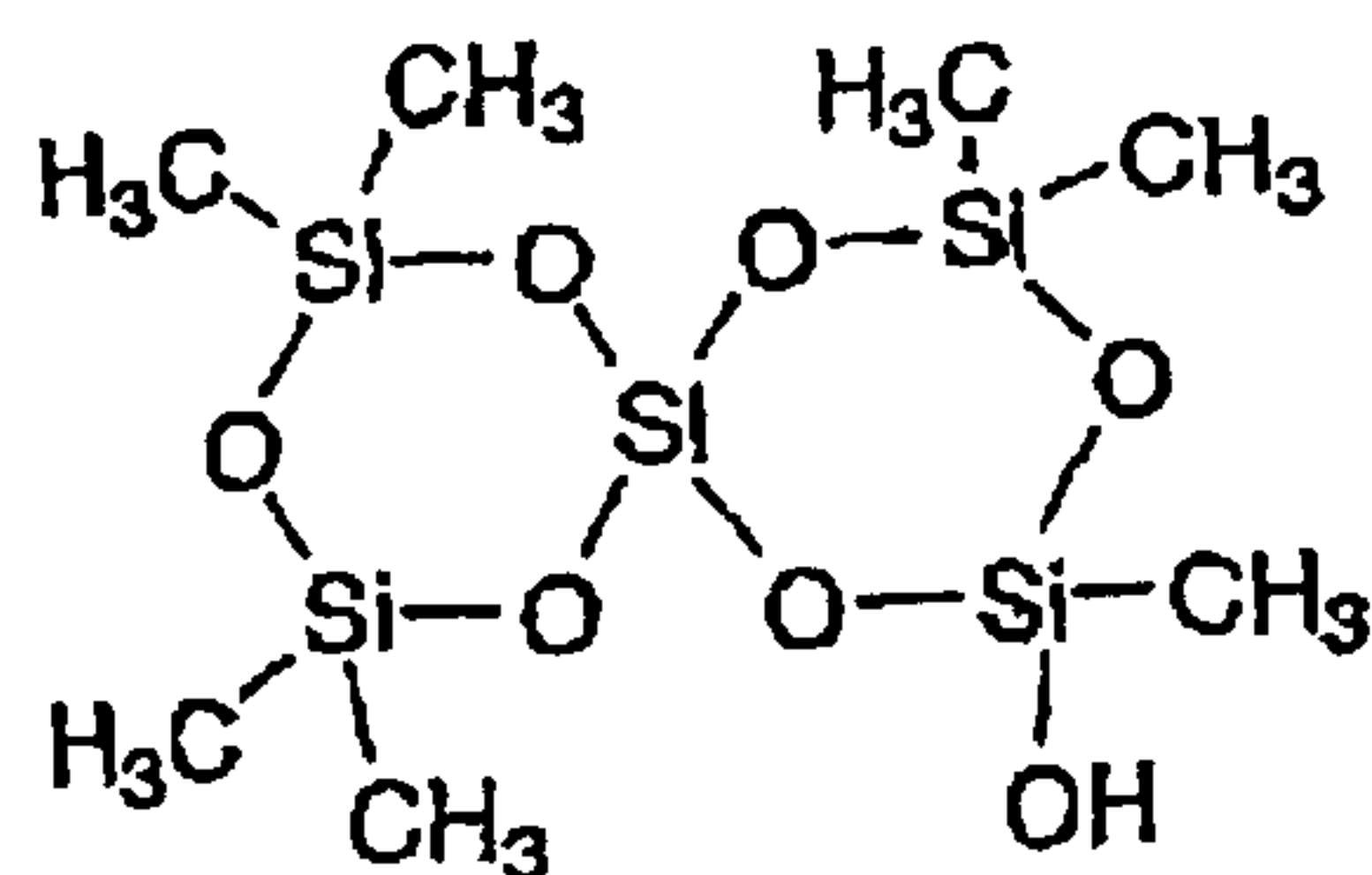
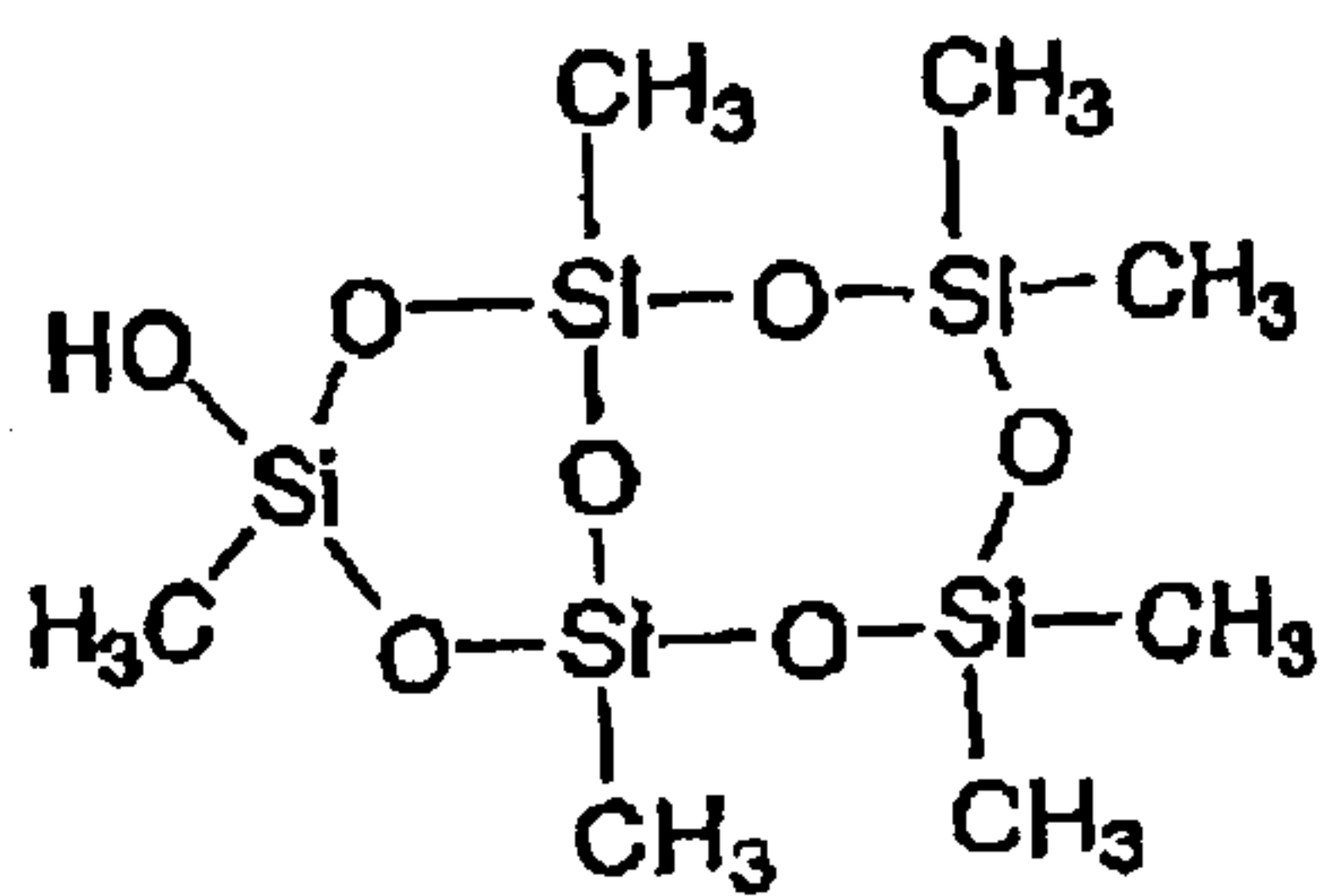


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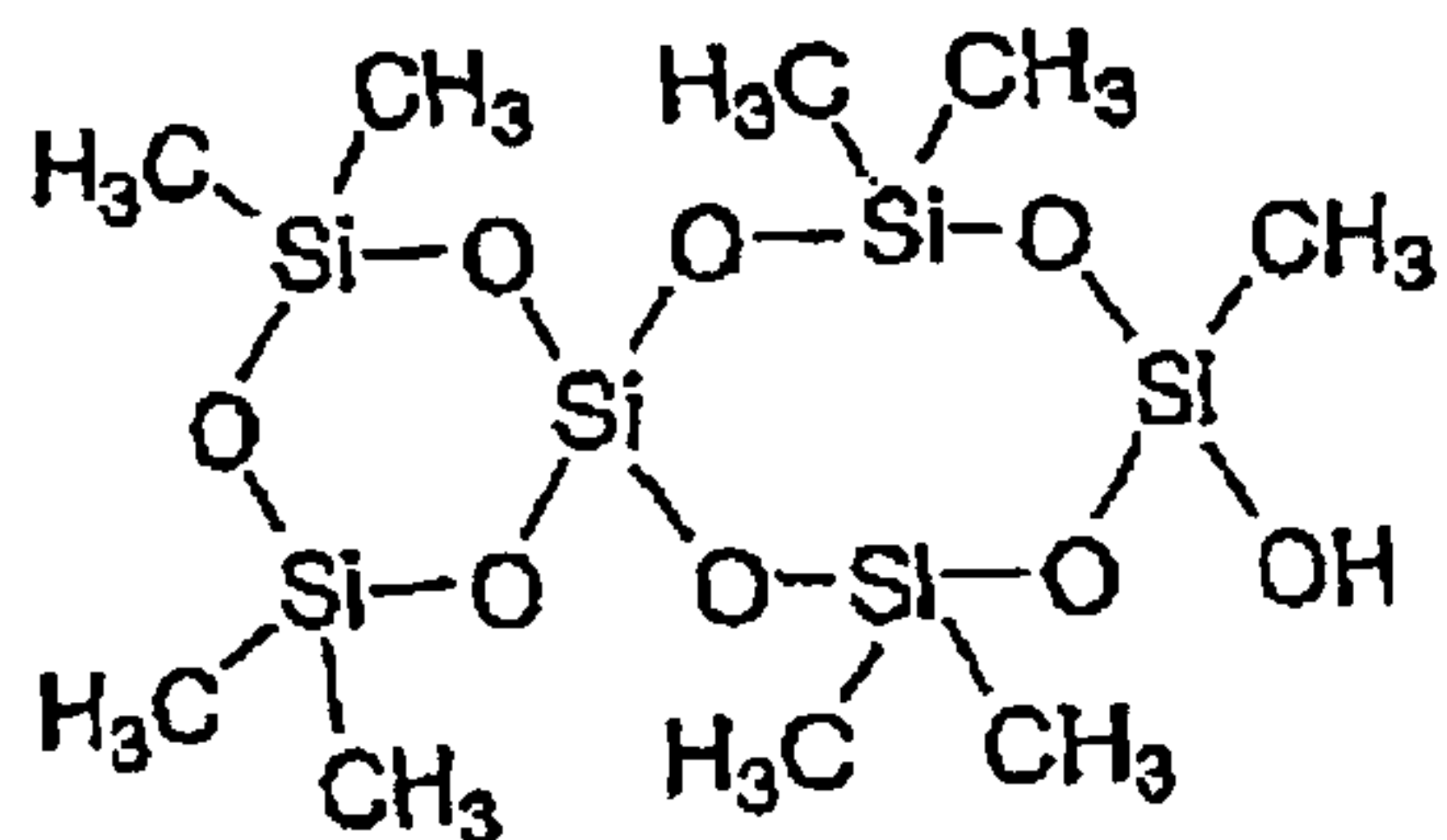
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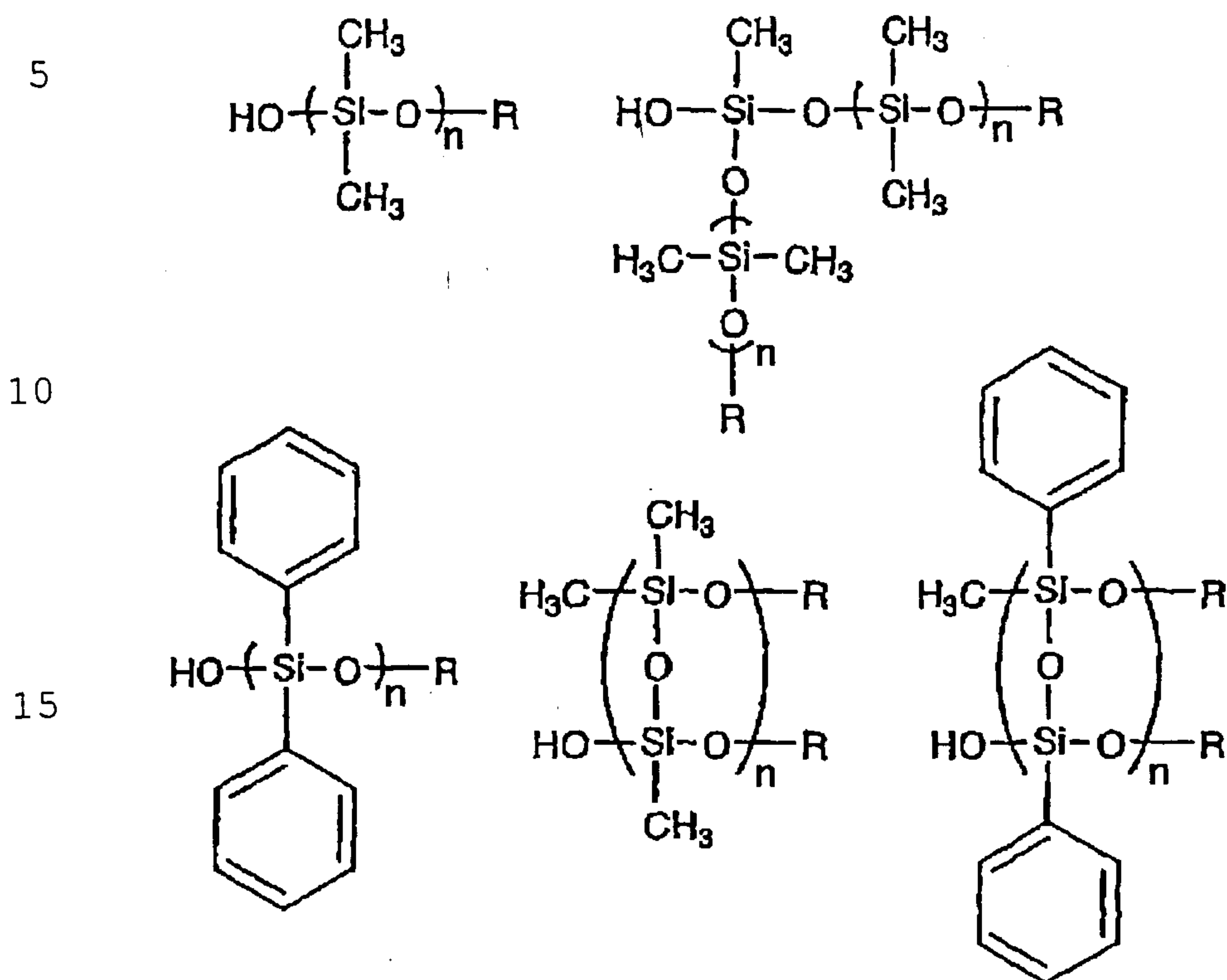
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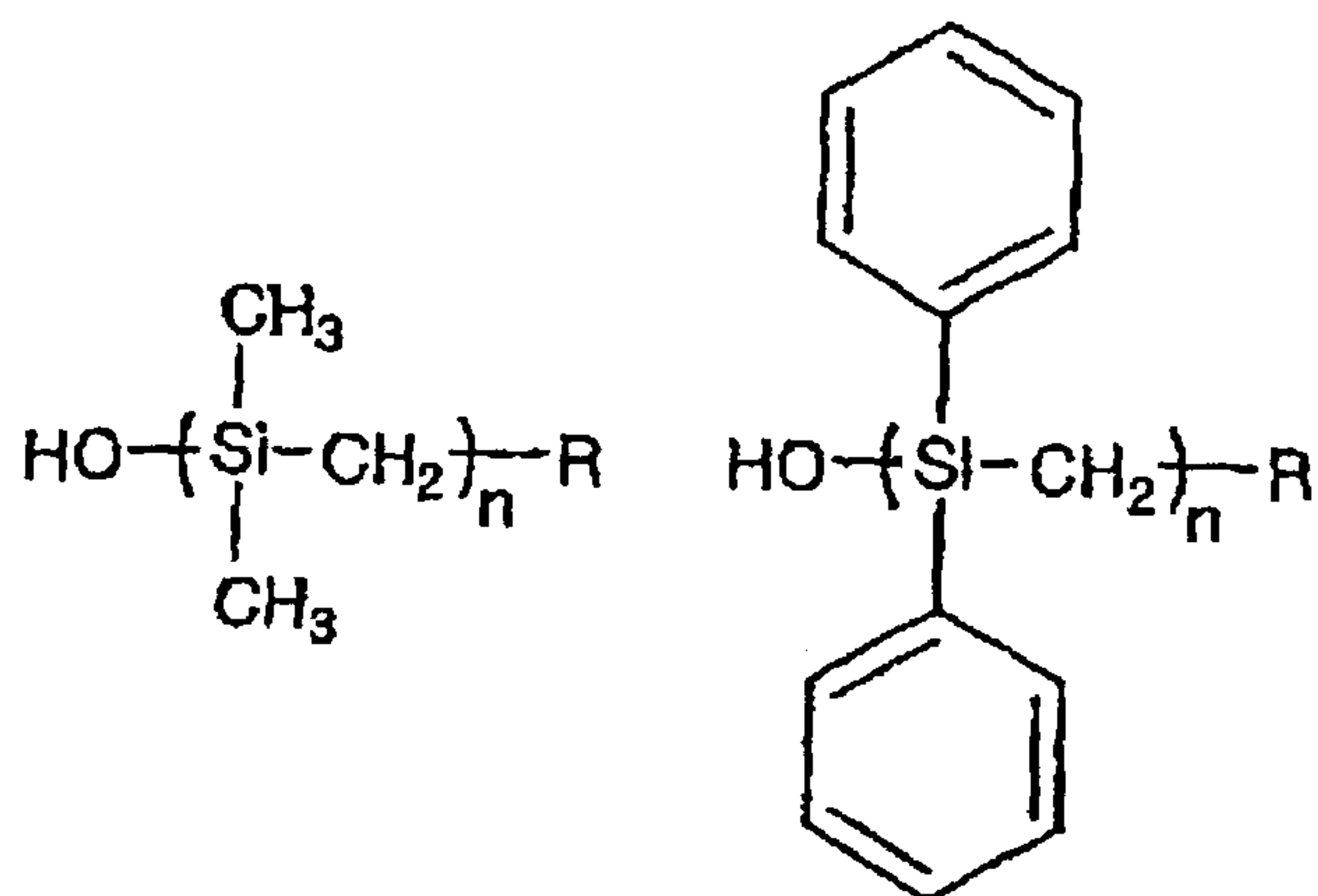
silanol group-containing chain polysiloxanes compounds, for example, the following compounds:



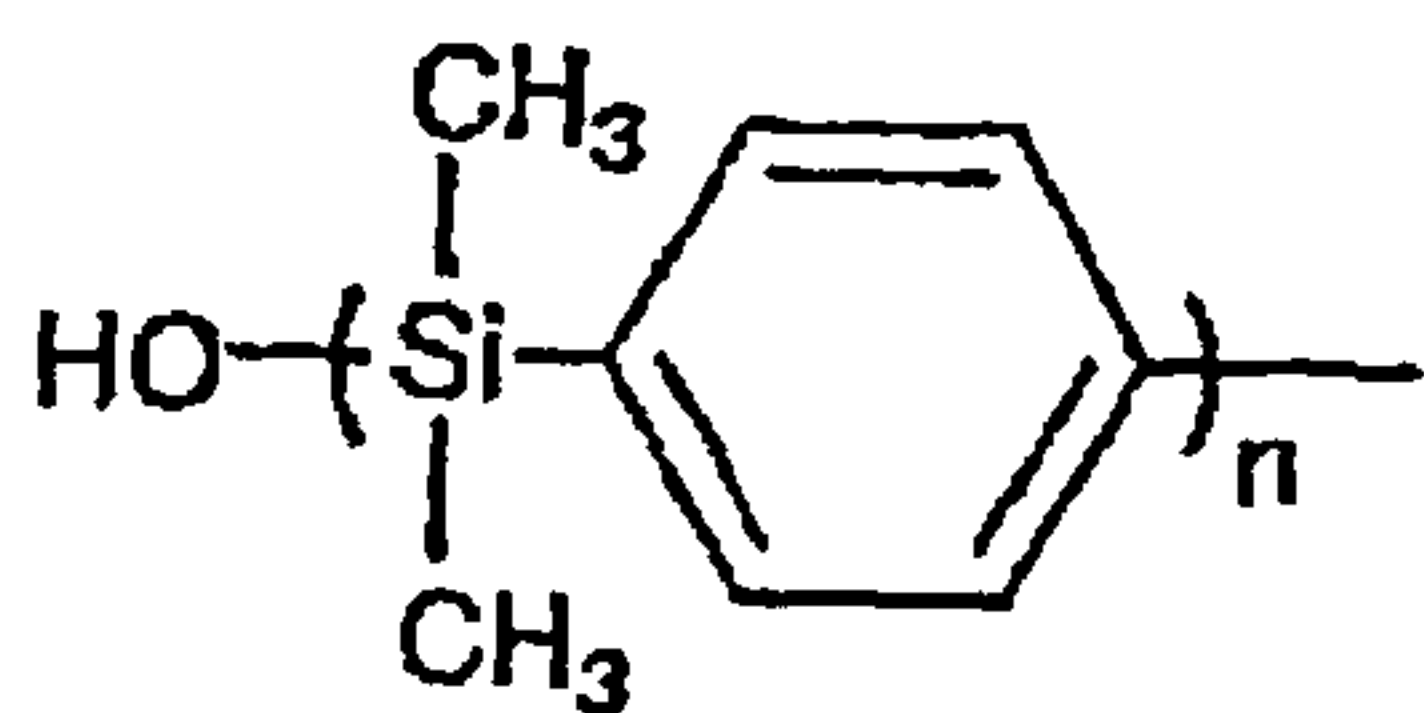
(wherein R represents a hydrocarbon group containing 1 to 10 carbon atom; and n represents an integer of 1 to 20):

compounds the polymer main chain of which is composed of silicon and carbon atoms and in which a silanol group is bonded at the molecular terminus, for example, the following compounds:

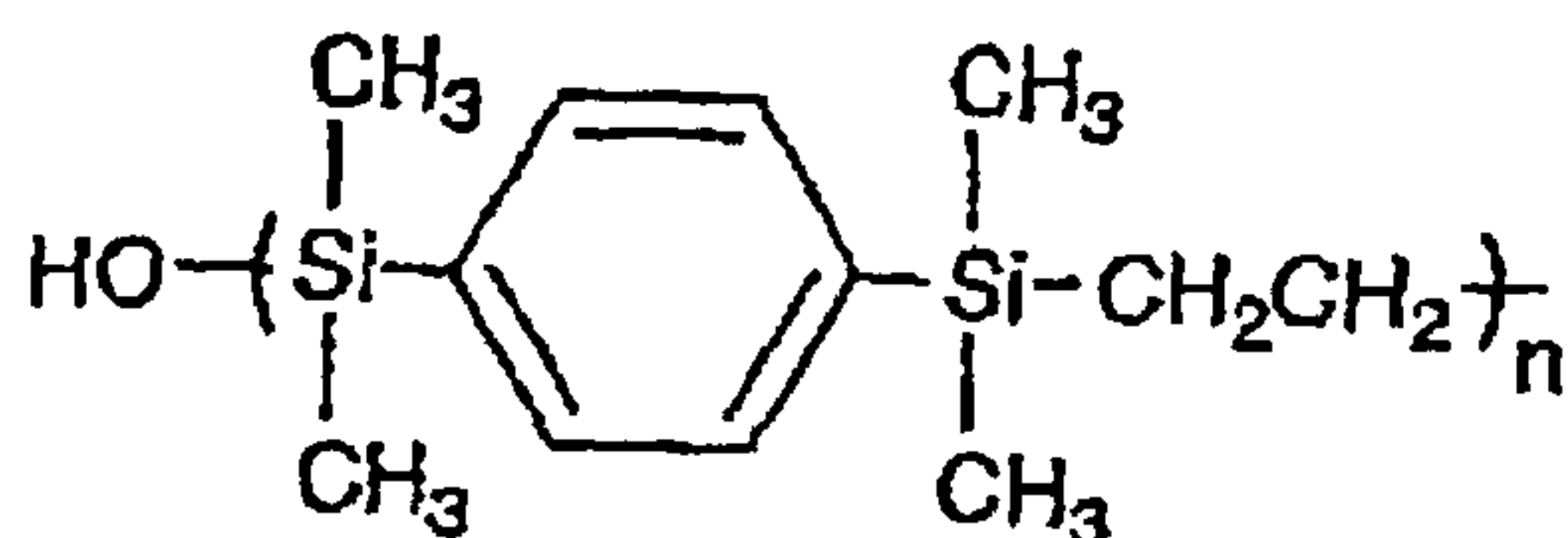
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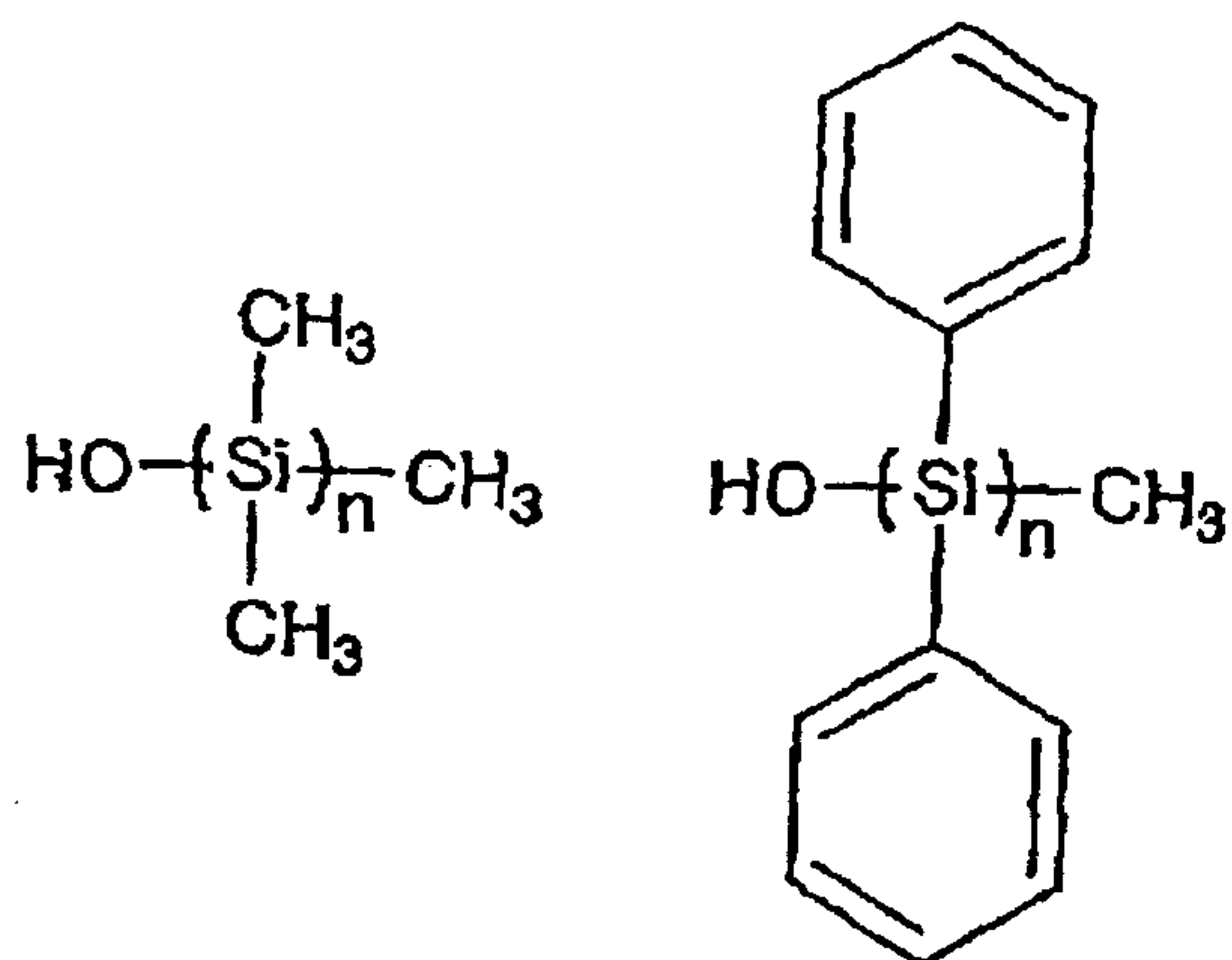


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20 (wherein R represents a hydrocarbon group containing 1 to 10 carbon atom; and n represents an integer of 1 to 20): compounds in which silanol group is bonded to the main chain of polysilane at a molecular terminus, for example, the following compounds:

25

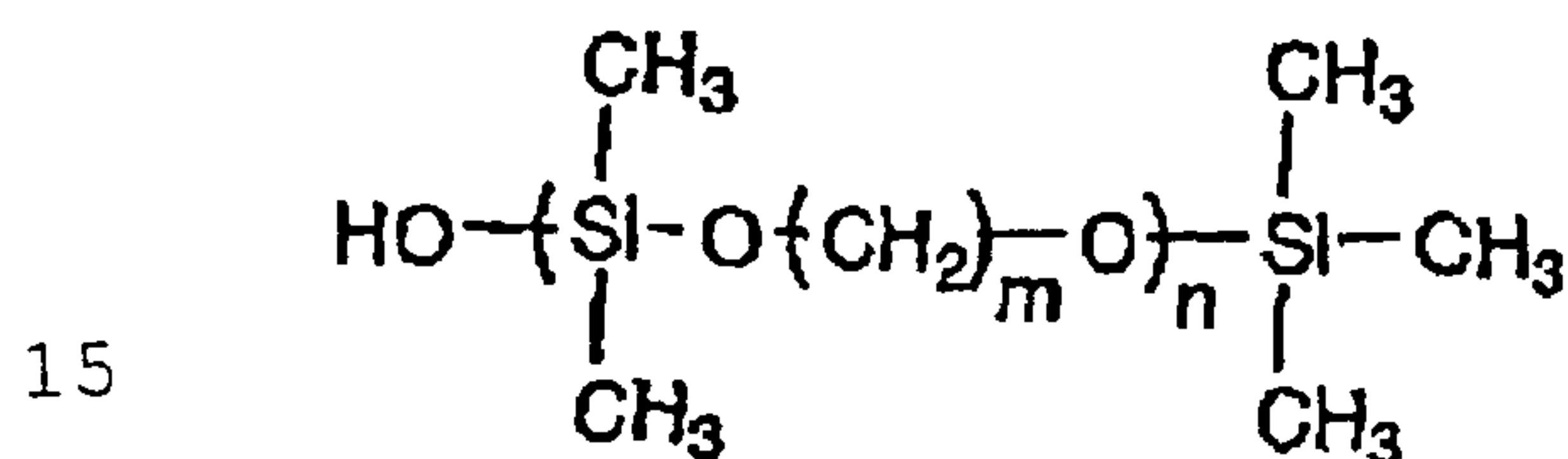
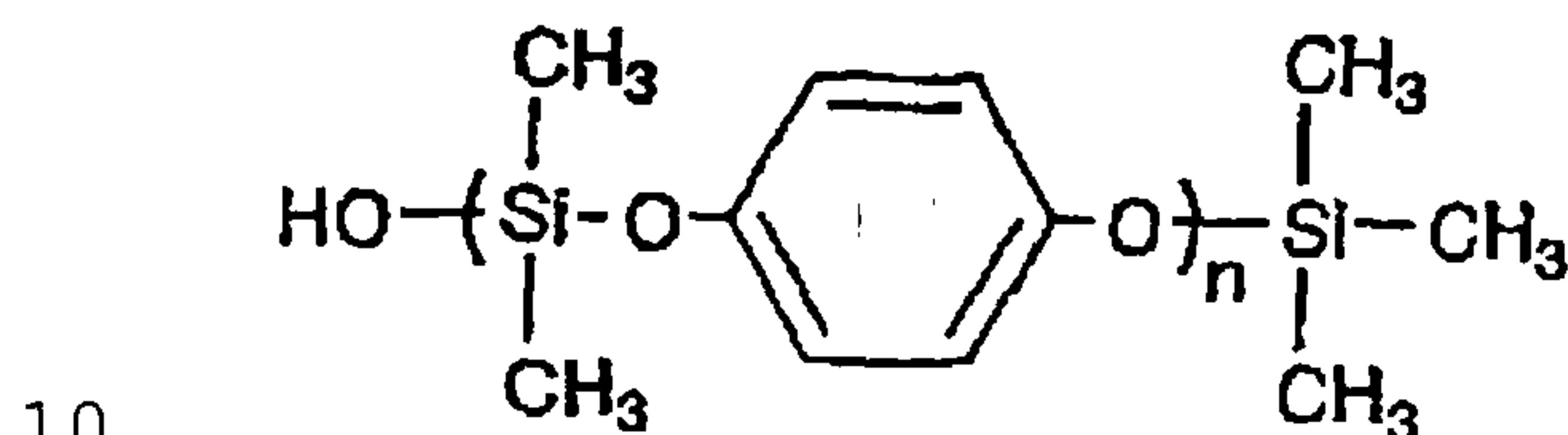


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(wherein n represents an integer of 1 to 20):

and compounds the polymer main chain of which is composed of silicon, carbon and oxygen atoms and in which a silanol group is bonded at the molecular terminus, for example, the following compounds:



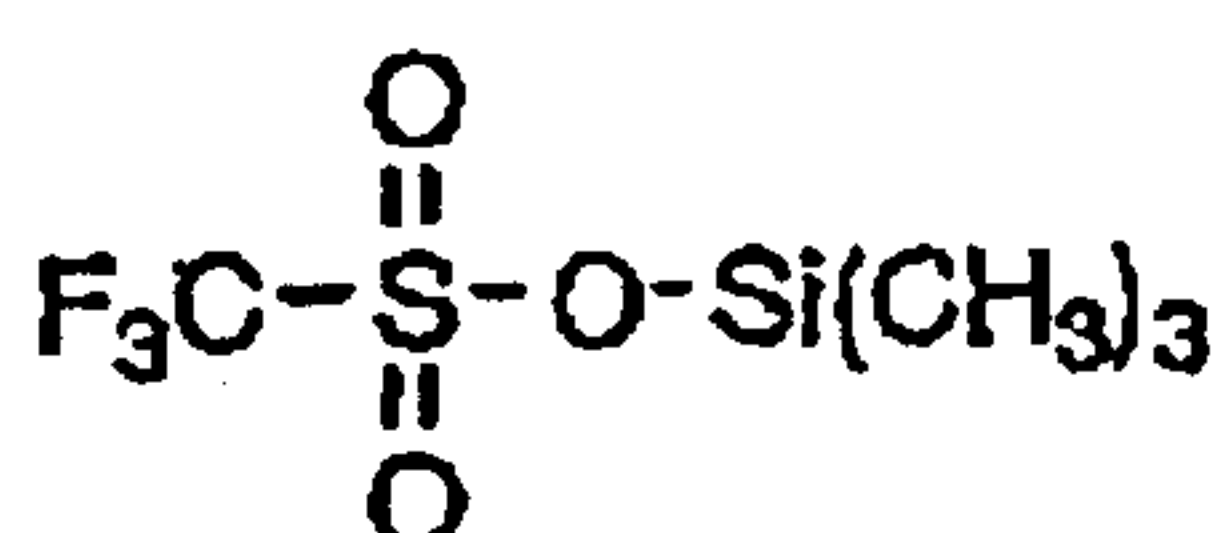
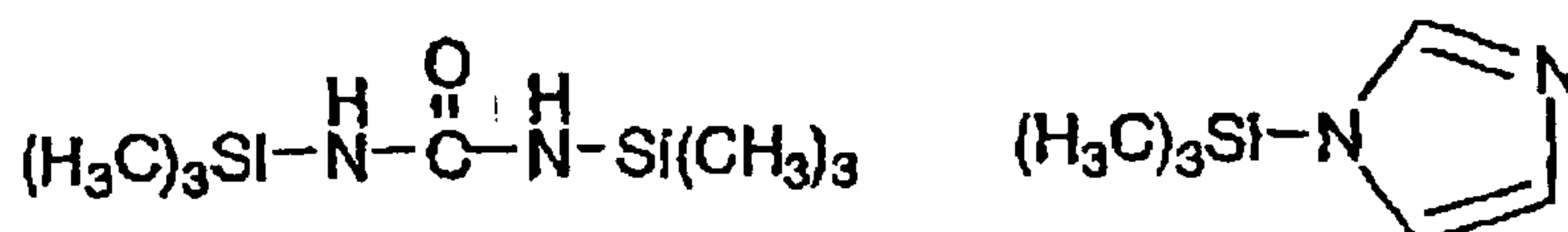
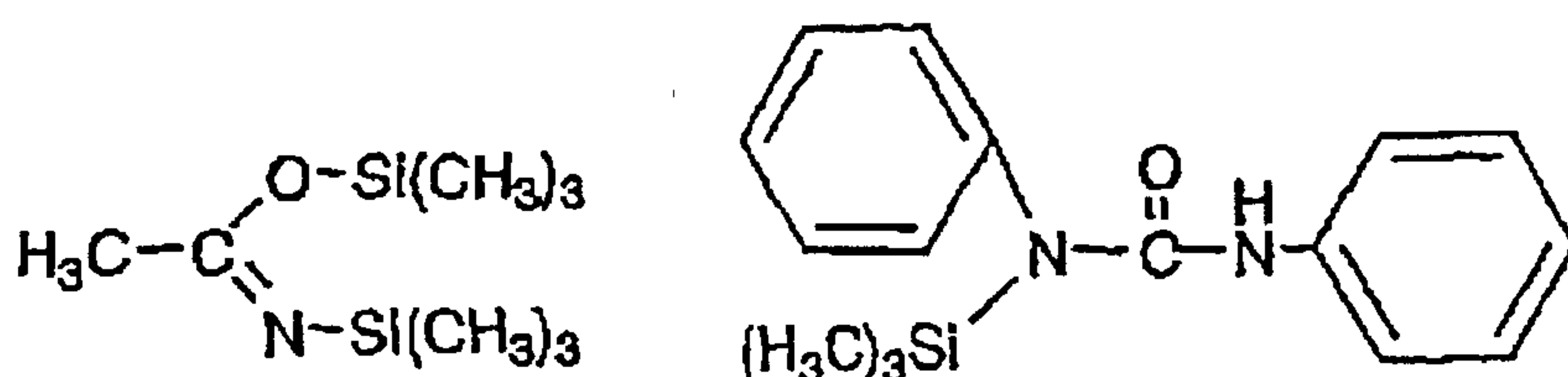
(wherein n represents an integer of 1 to 20; and m represents an integer of 1 to 20): and the like. Among them, from the ready availability and effect viewpoint, $(\text{CH}_3)_3\text{SiOH}$ and the like are preferred because they are low-molecular-weight compounds.

Flexibility of a cured product is given by a reaction of a compound having one silanol group in one molecule with a crosslinkable silyl group of the crosslinkable silyl group-containing polymer or a siloxane bond formed by crosslinking, to thereby reduce crosslinking points. Further, compositions low in surface tack and excellent in dust adhesion preventing effect are thus obtained.

The compounds capable of forming a compound having one silanol group in a molecule by a reaction with moisture are not particularly restricted. Such compounds which may be suitably used are

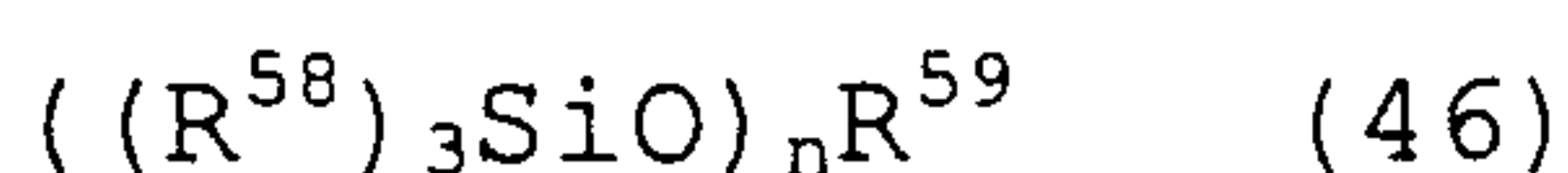
N,O-bis(trimethylsilyl)acetamide,
 N-(trimethylsilyl)acetamide,
 bis(trimethylsilyl)trifluoroacetamide,
 N-methyl-N-trimethylsilyltrifluoroacetamide,

bis(trimethylsilyl)urea,
N-(t-butyldimethylsilyl)N-methyltrifluoroacetamide,
(N,N-dimethylamino)trimethylsilane,
(N,N-diethylamino)trimethylsilane, hexamethyldisilazane,
5 1,1,3,3-tetramethyldisilazane, N-(trimethylsilyl)imidazole,
trimethylsilyltrifluoromethanesulfonate,
trimethylsilylphenoxide, trimethylsilylated product of
n-octanol, trimethylsilylated product of 2-ethylhexanol,
tris(trimethylsilyl)ated product of glycerin,
10 tris(trimethylsilyl)ated product of trimethylolpropane,
tris(trimethylsilyl)ated product of pentaerythritol,
tetra(trimethylsilyl)ated product of pentaerythritol,
(CH₃)₃SiNHSi(CH₃)₃, (CH₃)₃SiNSi(CH₃)₂, allyloxytrimethylsilane,
N,O-bis(trimethylsilyl)acetamide,
15 N-(trimethylsilyl)acetamide,
bis(trimethylsilyl)trifluoroacetamide,
N-methyl-N-trimethylsilyltrifluoroacetamide,
bis(trimethylsilyl)urea,
N-(t-butyldimethylsilyl)N-methyltrifluoroacetamide,
20 (N,N-dimethylamino)trimethylsilane,
(N,N-diethylamino)trimethylsilane, hexamethyldisilazane,
1,1,3,3-tetramethyldisilazane, N-(trimethylsilyl)imidazole,
trimethylsilyltrifluoromethanesulfonate,
trimethylsilylphenoxide, trimethylsilylated product of
25 n-octanol, trimethylsilylated product of 2-ethylhexanol,
tris(trimethylsilyl)ated product of glycerin,
tris(trimethylsilyl)ated product of trimethylolpropane,
tris(trimethylsilyl)ated product of pentaerythritol,
tetra(trimethylsilyl)ated product of pentaerythritol,
30 (CH₃)₃SiNHSi(CH₃)₃, (CH₃)₃SiNSi(CH₃)₂,
and the following compounds:



Among them, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ is particularly preferred in view of an amount of contained silanol group in a hydrolysis product.

Furthermore, compounds capable of forming a compound having one silanol group in a molecule by a reaction with moisture are not particularly restricted, but the compounds represented by the following general formula 46 are preferred in addition to the above compounds:



(wherein R^{58} is as defined above; n represents a positive number; and R^{59} represents a group exclusive of a part of or all of the active hydrogen from an active hydrogen-containing compound).

R^{58} is preferably methyl, ethyl, vinyl, t-butyl, or phenyl group, and more preferably methyl group.

$(\text{R}^{58})_3\text{SiO}$ group is preferably trimethylsilyl group in which all three R^{58} s are methyl group, and n is preferably 1 to 5.

Active hydrogen-containing compounds, which are origins of the above R^{59} , are not particularly restricted, but includes, among others, alcohols such as methanol, ethanol, n-butanol,

i-butanol, t-butanol, n-octanol, 2-ethylhexanol, benzyl alcohol, ethylene glycol, diethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, propanediol, tetramethylene glycol, polytetramethylene glycol, glycerin, trimethylolpropane and pentaerythritol; phenols such as phenol, cresol, bisphenol A and hydroquinone; carboxylic acids such as formic acid, acetic acid, propionic acid, lauric acid, palmitic acid, stearic acid, behenic acid, acrylic acid, methacrylic acid, oleic acid, linolic acid, linolenic acid, sorbic acid, oxalic acid, malonic acid, succinic acid, adipic acid, maleic acid, benzoic acid, phthalic acid, terephthalic acid and trimellitic acid; ammonia; amines such as methylamine, dimethylamine, ethylamine, diethylamine, n-butylamine and imidazole; acid amides such as acetamide and benzamide; ureas such as urea and N,N'-diphenylurea; and ketones such as acetone, acetylketone and 2,4-heptadione.

Although it is not particularly limited, a compound capable of forming a compound having one silanol group in a molecule by a reaction with moisture, represented by the above general formula 46, is obtainable by, for example, subjecting the above-mentioned active hydrogen-containing compound or the like to the reaction with the compound having a group capable of reacting with the active hydrogen, such as halogen group, together with a $(R^{58})_3Si$ group, which is sometimes referred to as "silylating agent", such as trimethylsilyl chloride or dimethyl(t-butyl)chloride. In the above description, R^{58} is the same one as defined above.

The compounds represented by the general formula 46 includes allyloxytrimethylsilane, N,O-bis(trimethylsilyl)acetamide, N-(trimethylsilyl)acetamide, bis(trimethylsilyl)trifluoroacetamide, N-methyl-N-trimethylsilyltrifluoroacetamide, bis(trimethylsilyl)urea,

N-(t-butyldimethylsilyl)N-methyltrifluoroacetamide,
 (N,N-dimethylamino)trimethylsilane,
 (N,N-diethylamino)trimethylsilane, hexamethyldisilazane,
 1,1,3,3,-tetramethyldisilazane, N-(trimethylsilyl)imidazole,
 5 trimethylsilyltrifluoromethanesulfonate,
 trimethylsilylphenoxide, trimethylsilylated product of
 n-octanol, trimethylsilylated product of 2-ethylhexanol,
 tris(trimethylsilyl)ated product of glycerin,
 tris(trimethylsilyl)ated product of trimethylolpropane,
 10 tris(trimethylsilyl)ated product of pentaerythritol,
 tetra(trimethylsilyl)ated product of pentaerythritol,
 trimethylsilylated product of polypropyleneglycol,
 trimethylsilylated product of polypropylenetriol and the like
 trimethylsilylated product of polyether polyol,
 15 trimethylsilylated product of polypropylenetetraol,
 trimethylsilylated product of acrylpolyol, and the like.
 These may be used singly or in combination of two or more.

Additionally, the compounds which may be represented by
 the general formula $((R^{60})_3SiO)(R^{61}O)_s)_tZ$,
 20 $CH_3O(CH_2CH(CH_3)O)_5Si(CH_3)_3$, $CH_2=CHCH_2(CH_2CH(CH_3)O)_5Si(CH_3)_3$,
 $(CH_3)_3SiO(CH_2CH(CH_3)O)_5Si(CH_3)_3$, and
 $(CH_3)_3SiO(CH_2CH(CH_3)O)_7Si(CH_3)_3$
 (wherein R^{60} represents the same or different kind of
 substituted or unsubstituted univalent hydrocarbon group; R^{61}
 25 is an bivalent hydrocarbon group containing 1 to 8 carbon atoms;
 s and t are positive numbers, s is 1 to 6 and s times t is not
 less than 5; and Z is an mono- to hexa-valent organic group),
 are also suitably used. These may be used singly or in
 combination of two or more.

30 Among the compounds capable of forming a compound having
 one silanol group in a molecule by a reaction with moisture,
 the active hydrogen compounds which is formed after hydrolysis
 are preferably phenols, acid amides and alcohols since there
 are no adverse affects on storage stability, weatherability or
 35 the like. More preferred are phenols and alcohols, in which

the active hydrogen compound is a hydroxyl group.

Among the above compounds, preferred are

N,O-bis(trimethylsilyl)acetamide,

N-(trimethylsilyl)acetamide, trimethylsilylphenoxide,

5 trimethylsilylated product of n-octanol, trimethylsilylated product of 2-ethylhexanol, tris(trimethylsilyl)ated product of trimethylolpropane, tris(trimethylsilyl)ated product of pentaerythritol, tetra(trimethylsilyl)ated product of pentaerythritol, and the like.

10 The compounds capable of forming a compound having one silanol group in a molecule by a reaction with moisture produces the compound having one silanol group in a molecule by reacting with moisture during storage, at the time of curing, or after curing. It is presumed that flexibility of a cured product is
15 given by a reaction of the thus-formed compound having one silanol group in a molecule with a crosslinkable silyl group of the vinyl polymer (I) or a siloxane bond formed by crosslinking, to thereby reduce crosslinking points.

The structure of the silanol-containing compound can be
20 selected in accordance with the crosslinkable silyl group of the vinyl polymer (I) of the invention and the type of Y and the number of a in the general formula 2 and the curability and the mechanical strength etc. of the invention can be controlled in accordance with the purposes and uses.

25 The silanol-containing compound may be used in combination with an air oxidation-curable substance, which will be described later, and combination use is preferable to keep the modulus of the cured product low and to improve the curability of the alkyd paint applied to the surface and dust
30 adhesion preventing property.

The addition level of the silanol-containing compound can be properly adjusted depending on the expected physical properties. The addition level of the silanol-containing compound is preferably 0.1 to 50 parts by weight, more
35 preferably 0.3 to 20 parts by weight and still more preferably

0.5 to 10 parts by weight, per 100 parts by weight of the crosslinkable silyl group-containing polymer. When the level is below 0.1 parts by weight, the effects caused by addition may not appear, and on the contrary, when it exceeds 50 parts by weight, crosslinking may be insufficient and strength or gel fraction ratio of the cured product are excessively deteriorated.

The time to add the silanol compound is not particularly restricted, but it may be added in the production process of the polymer, or may be added in the preparation process of a curable composition.

<Thixotropic agent (antisagging agent)>

If necessary, a thixotropic agent (antisagging agent) may be added to the curable composition of the invention to prevent sagging and improve the workability, as long as the transparency of the present invention does not deteriorate.

The thixotropic agent (antisagging agent) may also be called as a thixotropy-providing agent. The term "providing thixotropy" means supplying something with fluidity when a strong power is applied at the time being extruded in bead-like state from a cartridge, being applied by a spatula etc., or being sprayed by a spray etc. and supplying something with the property of not dripping during the curing after coating or application.

The thixotropic agent (antisagging agent) is not particularly limited but includes, for example, amide waxes such as DISPARON (manufactured by Kusumoto Chemicals, Ltd.), hydrogenated castor oil, hydrogenated castor oil derivatives, fatty acid derivatives, metal soaps such as calcium stearate, aluminum stearate and barium stearate, organic compounds such as 1,3,5-tris(trialkoxysilylalkyl)isocyanurate, and inorganic compounds such as calcium carbonate, micronized silica and carbon black which are surface-treated with fatty acids or resin acids.

The micronized silica means a natural or artificial

inorganic filler containing silicon dioxide as a main component. In particular, examples include kaolin, clay, activated kaolin, silica sand, silicic stone, china clay, aluminum silicate anhydride, hydrous magnesium silicate, talc, pearlite, white carbon, mica fine flour, bentonite, organic bentonite and the like.

Especially, ultrafine granular silica anhydride and organic bentonite obtained by vapor phase reaction of a silicon-containing volatile compound are preferable. They preferably have a specific surface area of at least 50 m²/g, more preferably 50 to 400 m²/g. Both of a hydrophilic silica and a hydrophobic silica may be used. The surface treatment may or may not be carried out, however preferred is a hydrophobic silica obtained by a hydrophobic surface treatment with silazanes, chlorosilanes, alkoxysilanes or polysiloxanes which contain, as an organic substituent bonded to a silicon atom, only a methyl group.

Specific examples of the above-mentioned surface treatment agents are silazanes such as hexamethyldisilazane; halo silanes such as trimethylchlorosilane, dimethyldichlorosilane and methyltrichlorosilane; alkoxysilanes such as trimethylalkoxysilane, dimethyldialkoxysilane and methyltrialkoxysilane (herein, an alkoxy group may include a methoxy, ethoxy, propoxy, butoxy and the like groups); siloxanes such as cyclic and linear polydimethylsiloxane; and the like, and they may be used alone or two or more of them may be used in combination. Among them, a micronized hydrophobic silica surface-treated with siloxanes (dimethylsilicone oil) is preferable in terms of the thixotropy-providing effect.

Further, in the case where the micronized silica is used in combination with polyether compounds such as diethylene glycol, triethylene glycol and polyethylene glycol, reaction products of a polyether compound with a functional silane, and nonionic surfactants having an ethylene oxide chain, the

thixotropy is increased. One or more kinds of nonionic surfactants may be used.

Specific examples of the micronized silica may be commercialized products such as Aerosil R974, R972, R972V, R972CF, R805, R812, R812S, RY200, RX200, RY200S, #130, #200, #300, and R202 manufactured by Nippon Aerosil Co., Ltd.; Nipsil SS series manufactured by Nippon Silica Industrial; Rheorosil MT-10, MT-30, QS-102, and QS-108 manufactured by Tokuyama Soda Co., Ltd., Cabosil TS-720, MS-5, and MS-7 manufactured by Cabot Corporation, and S-BEN and ORGANITE manufactured by HOJUN Co., Ltd.

Organic bentonite means powder-like substances mainly obtained from montmorillonite mineral finely milled and then surface-treated with various organic substances. Examples of the organic substances are aliphatic primary amines and aliphatic quaternary amines (each of them is preferred to have 20 or less carbon atoms). Specific examples of the organic bentonite are Orben D and New D Orben manufactured by Shiraishi Kogyo Kaisha, Ltd., Hardsil manufactured Tsuchiya Kaolin Co., Clay #30 manufactured by Burgess Pigment Company, #33 manufactured by Southern Clay Products, Inc., Bentone 34 (dimethyloctadecylammonium bentonite) manufactured by National Lead Company, and the like.

The thixotropy index means the ratio of the apparent viscosity at a low rotation rate (e.g. 0.5 to 12 rpm) and a high rotation rate (e.g. 2.5 to 60 rpm) in viscosity measurement by a rotation viscometer (herein, the ratio of the high rotation rate and low rotation rate is preferably at least 5 and more preferably 5 to 10).

These thixotropic agents (antisagging agents) may be used alone or two or more of them may be used in combination.
<Photocurable substance>

To the curable composition of the invention, there may be added a photocurable substance, according to need. The photocurable substance is a substance whose molecular structure

undergoes a chemical change in a short time under the action of light and which thus causes changes of physical properties such as curing. By adding such photocurable substance, it becomes possible to reduce the tackiness (residual tack) of the cured product surface after curing of the curable composition. This photocurable substance is a substance capable of curing upon irradiation with light. A typical photocurable substance is a substance capable of curing when allowed to stand at an indoor place in the sun (near a window) at room temperature for 1 day, for example. A large number of compounds of this type are known, including organic monomers, oligomers, resins, and compositions containing them, and they are not particularly restricted in kind but include, for example, unsaturated acrylic compounds, vinyl cinnamate polymers, azidated resins, epoxy compounds, vinylether compounds and the like.

As the unsaturated acrylic compounds, there may be specifically mentioned, for example, (meth)acrylate esters of low-molecular-weight alcohols (oligoester acrylate) such as ethylene glycol, glycerol, trimethylolpropane, pentaerythritol and neopentyl alcohol; (meth)acrylate esters of alcohols derived from acids such as bisphenol A, acids such as isocyanuric acid or such low-molecular-weight alcohols as mentioned above by modification with ethylene oxide and/or propylene oxide; (meth)acrylate esters of hydroxyl-terminated polyether polyols whose main chain is a polyether, polymer polyols obtained by radical polymerization of a vinyl monomer(s) in a polyol whose main chain is a polyether, hydroxyl-terminated polyester polyols whose main chain is a polyester, polyols whose main chain is a vinyl or (meth)acrylic polymer and which have hydroxyl groups in the main chain, and like polyols; (meth)acrylate esters whose main chain is a vinyl or (meth)acrylic polymer and which is obtained by copolymerization of a polyfunctional acrylate(s) into the main chain thereof; epoxy acrylate oligomers obtained by reacting a bisphenol A-based, novolak type or other epoxy resin with

(meth)acrylic acid; urethane acrylate type oligomers containing urethane bonds and (meth)acryl groups within the molecular chain as obtained by reacting a polyol, a polyisocyanate and a hydroxyl group-containing

5 (meth)acrylate; and the like.

The vinyl cinnamate polymers are photosensitive resins whose cinnamoyl groups function as photosensitive groups and include cinnamic acid-esterified polyvinyl alcohol species and various other polyvinyl cinnamate derivatives.

10 The azidated resins are known as photosensitive resins with the azido group serving as a photosensitive group and generally include photosensitive rubber solutions with an azide compound added as a photosensitive substance and, further, detailed examples are found in "Kankosei Jushi (Photosensitive
15 Resins)" (published March 17, 1972 by Insatsu Gakkai Shuppanbu, pages 93 ff, 106 ff, 117 ff). These can be used either singly or in admixture, with a sensitizer added, if necessary.

The epoxy compounds and vinyl ether compounds may be, for example, polyisobutyrenes terminated with epoxy group and vinyl
20 ether group, respectively.

Among the photocurable substances mentioned above, unsaturated acrylic compounds are preferred in view of their easy handleability.

The photocurable substance is preferably added in an
25 amount of 0.01 to 20 parts by weight per 100 parts by weight of the crosslinkable silyl group-containing polymer. At addition levels below 0.01 part by weight, the effects will be insignificant and, at levels exceeding 20 parts by weight, the physical properties may be adversely affected. The addition
30 of a sensitizer such as a ketone or nitro compound or a promoter such as an amine can enhance the effects in some instances.
<Air oxidation-curable substance>

In the curable composition of the invention, there may be incorporated an air oxidation-curable substance, if
35 necessary. The air oxidation-curable substance is a compound

containing an unsaturated group capable of being crosslinked for curing by oxygen in the air. By adding such air oxidation-curable substance, it becomes possible to reduce the tack (also referred as residual tack) of the cured product surface on the occasion of curing of the curable composition. The air oxidation-curable substance according to the present invention is a substance capable of curing upon contacting with air and, more specifically, has a property such that it cures as a result of reaction with oxygen in the air. A typical air oxidation-curable substance can be cured upon allowing it to stand in the air in a room for 1 day, for example.

As specific examples of the air oxidation-curable substance, there may be mentioned, for example, drying oils such as tung oil and linseed oil; various alkyd resins obtained by modification of such drying oils; drying oil-modified acrylic polymers, epoxy resins, silicone resins, urethane resins; 1,2-polybutadiene, 1,4-polybutadiene, C5-C8 diene polymers and copolymers and, further, various modifications of such polymers and copolymers (e.g. maleinated modifications, boiled oil modifications); and the like. Among these, tung oil, liquid ones among the diene polymers (liquid diene polymers) and modifications thereof are particularly preferred.

As specific examples of the liquid diene polymers, there may be mentioned, for example, liquid polymers obtained by polymerization or copolymerization of diene compounds such as butadiene, chloroprene, isoprene and 1,3-pentadiene, NBR, SBR and like polymers obtained by copolymerization of such diene compounds (as main components) with a monomer copolymerizable therewith, such as acrylonitrile or styrene, and, further, various modification thereof (e.g. maleinated modifications, boiled oil modifications). These may be used singly or two or more of them may be used in combination. Among these liquid diene compounds, liquid polybutadiene species are preferred.

The air oxidation-curable substances may be used singly or two or more of them may be used in combination. The use of

a catalyst capable of promoting the oxidation curing or a metal drier in combination with the air oxidation-curable substance can enhance the effects in certain instances. As such catalysts or metal driers, there may be mentioned, for example, metal salts such as cobalt naphthenate, lead naphthenate, zirconium naphthenate, cobalt octylate and zirconium octylate, amine compounds, and the like.

The air oxidation-curable substance may be used in combination with the above-mentioned photocurable substances and further with the above-mentioned silanol-containing compound. The combination use of these two components or three components provides further effect and it is particularly preferable since the combination use remarkably causes, in some cases, the stain-preventing effect in the case of exposure for a long duration and even in the area where pollution with dust and micropowder-like sand is severe.

The air oxidation-curable substance is preferably added in an amount of 0.01 to 20 parts by weight per 100 parts by weight of the crosslinkable silyl group-containing polymer. At levels below 0.01 part by weight, the effects will be insignificant and, at levels exceeding 20 parts by weight, the physical properties may be adversely affected.

<Antioxidant>

In the curable composition of the invention, there may be incorporated an antioxidant, if necessary. Various antioxidants are known and mention may be made of various species described, for example, in "Sankaboshizai Handbook (Handbook of Antioxidants)" published by Taiseisha LTD. and "Kobunshi Zairyo no Rekka to Anteika (Degradation and Stabilization of Polymer Materials)" (pp. 235-242) published by CMC Chemical Publishing CO., LTD. The antioxidants which can be used are not limited to these, however. There may be mentioned, for example, thioethers such as MARK PEP-36 and MARK AO-23 (both being products of Asahi Denka Co., Ltd.), phosphorus-containing antioxidants such as IRGAFOS 38, IRGAFOS

168 and IRGAFOS P-EPQ (the three being products of Ciba Specialty Chemicals). For example, such hindered phenol compounds as enumerated below are preferred.

5 As specific examples of the hindered phenol compounds, the following can be mentioned.

2,6-Di-tert-butyl-4-methylphenol,
 2,6-di-tert-butyl-4-ethylphenol, mono(or di or
 tri) (α -methylbenzyl)phenol,
 2,2'-methylenebis(4-ethyl-6-tert-butylphenol),
 10 2,2'-methylenebis(4-methyl-6-tert-butylphenol),
 4,4'-butylidenebis(3-methyl-6-tert-butylphenol),
 4,4'-thiobis(3-methyl-6-tert-butylphenol),
 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone,
 triethylene glycol
 15 bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate],
 1,6-hexanediol
 bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate],
 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)
 -1,3,5-triazine, pentaerythrityl
 20 tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate],
 2,2-thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)
 propionate],
 octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
 N,N'-hexamethylenebis
 25 (3,5-di-tert-butyl-4-hydroxyhydrocinnamide), diethyl
 3,5-di-tert-butyl-4-hydroxybenzylphosphonate,
 1,3,5-trimethyl-2,4,6-tris
 (3,5-di-tert-butyl-4-hydroxybenzyl)benzene, bis(ethyl
 3,5-di-tert-butyl-4-hydroxybenzylphosphonato)calcium,
 30 tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate,
 2,4-2,4-bis[(octylthio)methyl]-o-cresol,
 N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]
 hydrazine, tris(2,4-di-tert-butylphenyl)phosphite,
 2-(5-methyl-2-hydroxyphenyl)benzotriazole,
 35 2-[2-hydroxy-3,5-bis(α , α -dimethylbenzyl)phenyl]

-2H-benzotriazole,
 2-(3,5-di-tert-butyl-2-hydroxyphenyl)benzotriazole,
 2-(3-tert-butyl-5-methyl-2-hydroxyphenyl)
 -5-chlorobenzotriazole,
 5 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole,
 2-(3,5-di-tert-amyl-2-hydroxyphenyl)benzotriazole,
 2-(2'-hydroxy-5'-tert-octylphenyl)benzotriazole, methyl
 3-[3-tert-butyl-5-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]
 propionate-polyethylene glycol (molecular weight about 300)
 10 condensate, hydroxyphenylbenzotriazole derivatives,
 bis(1,2,2,6,6-pentamethyl-4-piperidyl)
 2-(3,5-di-tert-butyl-4-hydroxybenzyl)-2-n-butylmalonate,
 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate,
 and the like.

15 Examples of the relevant product names include, but are
 not limited to, Nocrac 200, Nocrac M-17, Nocrac SP, Nocrac SP-N,
 Nocrac NS-5, Nocrac NS-6, Nocrac NS-30, Nocrac 300, Nocrac NS-7
 and Nocrac DAH (all being products of Ouchi Shinko Chemical
 Industrial Co., Ltd.), MARK AO-30, MARK AO-40, MARK AO-50, MARK
 20 AO-60, MARK AO-616, MARK AO-635, MARK AO-658, MARK AO-80, MARK
 AO-15, MARK AO-18, MARK 328 and MARK AO-37 (all being products
 of Asahi Denka Co., Ltd.), IRGANOX 245, IRGANOX 259, IRGANOX
 565, IRGANOX 1010, IRGANOX 1024, IRGANOX 1035, IRGANOX 1076,
 IRGANOX 1081, IRGANOX 1098, IRGANOX 1222, IRGANOX 1330 and
 25 IRGANOX 1425WL (all being products of Ciba Specialty Chemicals),
 and Sumilizer GM and Sumilizer GA-80 (both being products of
 Sumitomo Chemical Co., Ltd.).

30 The antioxidant may be used in combination with the light
 stabilizer mentioned below, and such combined use enhances the
 effects thereof and may improve the heat resistance in
 particular, hence is particularly preferred. Such ready-made
 mixtures of an antioxidant and a light stabilizer as TINUVIN
 C353 and TINUVIN B75 (both being products of Ciba Specialty
 Chemicals) and the like may also be used.

35 The addition level of the antioxidant is preferably

within the range of 0.1 to 10 parts by weight per 100 parts by weight of the crosslinkable silyl group-containing polymer. At levels below 0.1 part by weight, the weather resistance-improving effect is insignificant, while levels exceeding 5 parts by weight make no great difference in effect any longer, hence are economically disadvantageous.

<Light stabilizer>

In the curable composition of the invention, there may be incorporated a light stabilizer, if necessary. Various light stabilizers are known and mention may be made of various species described, for example, in "Sankaboshizai Handbook (Handbook of Antioxidants)" published by Taiseisha LTD. and "Kobunshi Zairyo no Rekka to Anteika (Degradation and Stabilization of Polymer Materials)" (pp. 235-242) published by CMC Chemical Publishing CO., LTD. The light stabilizers which can be used are not limited to these, however, and ultraviolet absorbers and hindered amine-type light stabilizing compounds are preferred among these light stabilizers. As specific examples, there may be mentioned, for example, benzotriazole compounds such as TINUVIN P, TINUVIN 234, TINUVIN 320, TINUVIN 326, TINUVIN 327, TINUVIN 329 and TINUVIN 213 (all being products of Ciba Specialty Chemicals), triazines such as TINUVIN 1577, benzophenones such as CHIMASSORB 81, benzoate compounds such as TINUVIN 120 (all being products of Ciba Specialty Chemicals), and the like.

Additionally, hindered amine compounds are preferred, and such compounds are the following; dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensate, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl} {(2,2,6,6-tetramethyl-4-piperidyl)imino}], N,N'-bis(3-aminopropyl)ethylenediamine-2,4-bis [N-butyl-N-(1,2,2,6,6-pentamethyl-4-piperidyl)amino]-6-chloro-1,3,5-triazine condensate, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate,

bis(2,2,6,6-tetramethyl-4-piperidiny) succinate and the like.

Examples of the relevant product names include, but are not limited to, TINUVIN 622LD, TINUVIN 144 and CHIMASSORB 944LD, CHIMASSORB 119FL, Irganofos 168 (all being products of Ciba Specialty Chemicals), MARK LA-52, MARK LA-57, MARK LA-62, MARK LA-67, MARK LA-63, MARK LA-68, MARK LA-82 and MARK LA-87 (all being products of Asahi Denka Co., Ltd.), and Sanol LS-770, Sanol LS-765, Sanol LS-292, Sanol LS-2626, Sanol LS-1114, Sanol LS-744 and Sanol LS-440 (all being products of Sankyo Organic Chemicals Co., Ltd.), and the like.

The light stabilizer may be used in combination with the antioxidant mentioned above, and such combined use enhances the effects thereof and may improve the weather resistance in particular, hence is particularly preferred. The combination is not particularly limited and preferably a combination of the above-mentioned hindered phenol-type antioxidant with a benzotriazole-type ultraviolet absorber etc. and a combination of the above-mentioned hindered phenol-type antioxidant with a hindered amine-type light stabilizer compound. Further, a combination of the above-mentioned hindered phenol-type antioxidant with the benzotriazole-type ultraviolet absorber and the hindered amine-type light stabilizer compound is also preferable. Such ready-made mixtures of a light stabilizer and an antioxidant as TINUVIN C353 and TINUVIN B75 (both being products of Ciba Specialty Chemicals) and the like may also be used.

The hindered amine-type light stabilizer may be used in combination with the photocurable substance mentioned above, and such combined use enhances the effects thereof and may improve the weather resistance in particular, hence is particularly preferred. Although the combination is not particularly limited, however a quaternary amine-containing hindered amine-type light stabilizer is preferable since the viscosity increase during storage is slight and the storage

stability is excellent.

The addition level of the light stabilizer is preferably within the range of 0.1 to 10 parts by weight per 100 parts by weight of the crosslinkable silyl group-containing polymer.

- 5 At levels below 0.1 part by weight, the weather resistance-improving effect is insignificant, while levels exceeding 5 parts by weight make no great difference in effect any longer, hence are economically disadvantageous.

<Compatibility-improving agent>

- 10 The curable composition of the invention may contain a compatibility-improving agent. Specific examples of the agent are copolymers of a plurality of vinyl monomers described in Japanese Kokai Publication 2001-329025, and the like.

15 <Compound having α,β -diol structure or α,γ -diol structure in molecule>

- The curable composition of the invention may contain a compound having α,β -diol structure or α,γ -diol structure in molecule. Compounds conventionally known well may be used as the compound having the α,β -diol structure or α,γ -diol structure in molecule. In this specification, the above-mentioned α,β -diol structure means the structure in which mutually neighboring carbon atoms have two hydroxyl groups and the above-mentioned α,γ -diol structure means the structure in which neighboring every another carbon atom have two hydroxyl groups.
- 20 As represented by glycerin etc., polyols such as triols and tetraols having both or either one of the α,β -diol structure and the α,γ -diol structure are also included.

- Examples of the compound having the α,β -diol structure or the α,γ -diol structure in the molecule are not particularly limited and may include diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, pinacol, 2,2-dimethyl-1,3-propanediol, and 2-methyl-2-hydroxymethyl-1,3-propanediol; triols such as glycerin, 1,2,6-hexanetriol,
- 30 1,1,1-tris(hydroxymethyl)propane,
- 35

2,2-bis(hydroxymethyl)butanol; tetra or higher hydric polyols such as pentaerythritol, D-sorbitol, D-mannitol, diglycerin, and polyglycerin; glycerin monocarboxylic acid esters such as glycerin monostearate, glycerin monoisostearate, glycerin
5 monooleate, glycerin monolaurate, glycerin monopalmitate, glycerin monocaprylate, glycerin monoacetate, and glycerin monobehenate; polyglycerin carboxylic acid esters such as diglycerin monostearate, diglycerin monooleate, diglycerin monolaurate, tetraglycerin monostearate, tetraglycerin
10 monooleate, tetraglycerin monolaurate, tetraglycerin distearate, tetraglycerin dioleate, tetraglycerin dilaurate, decaglycerin monostearate, decaglycerin monooleate, decaglycerin monolaurate, decaglycerin distearate, decaglycerin dioleate, and decaglycerin dilaurate;
15 pentaerythritol monocarboxylic acid esters such as pentaerythritol monostearate, pentaerythritol monoisostearate, pentaerythritol monooleate, and pentaerythritol monolaurate; pentaerythritol dicarboxylic acid esters such as pentaerythritol distearate,
20 pentaerythritol dioleate, and pentaerythritol dilaurate; sorbitan monocarboxylic acid esters such as sorbitan monostearate, sorbitan monooleate, sorbitan monolaurate, sorbitan monopalmitate, and sorbitan monobehenate; sorbitan dicarboxylic acid esters such as sorbitan distearate, sorbitan
25 dioleate, sorbitan dilaurate, sorbitan dipalmitate, and sorbitan dibehenate; glycerin monoalkyl ethers such as glycerin monostearyl ether, glycerin monooleyl ether, glycerin monolauryl ether, and glycerin mono-2-ethylhexyl ether; polyglycerin alkyl ethers such as diglycerin monostearyl ether,
30 diglycerin monooleyl ether, diglycerin monolauryl ether, tetraglycerin monostearyl ether, tetraglycerin monooleyl ether, tetraglycerin monolauryl ether, tetraglycerin distearyl ether, tetraglycerin dioleyl ether, tetraglycerin dilauryl ether, decaglycerin monostearyl ether, decaglycerin
35 monooleyl ether, decaglycerin monolauryl ether, decaglycerin

distearyl ether, decaglycerin dioleylether, and decaglycerin dilauryl ether; pentaerythritol monoalkyl ethers such as pentaerythritol monostearyl ether, pentaerythritol monooleyl ether, and pentaerythritol monolauryl ether; pentaerythritol
5 dialkyl ethers such as pentaerythritol distearyl ether, pentaerythritol dioleylether, and pentaerythritol dilauryl ether; sorbitan monoalkyl ethers such as sorbitan monostearyl ether, sorbitan monooleyl ether, and sorbitan monolauryl ether; sorbitan dialkyl ethers such as sorbitan distearyl ether,
10 sorbitan dioleylether, and sorbitan dilauryl ether; and the like.

Many of the above-mentioned compounds are widely used as emulsifiers, surfactants, dispersants, defoaming agents, anti-clouding agents, solubilizers, thickening agents, and
15 lubricants and easily available.

The above-mentioned compounds may be used alone or two or more of them may be used in combination. The use amount of the compounds is preferably 0.01 to 100 parts by weight per 100 parts by weight of the vinyl polymer (I). If it is lower than
20 0.01 parts by weight, the aimed effect cannot be caused and if it exceeds 100 parts by weight, it results in occurrence of a problem that the mechanical strength of the cured product becomes insufficient and therefore it is not preferable. The amount is more preferably 0.1 to 20 parts by weight.

25 <Other additives>

If necessary, one or more of various additives may be added to the curable composition of the invention for the purpose of adjusting various physical properties of the curable composition or cured products. Such additives include, for
30 example, flame retardants, curability modifiers, metal deactivators, antiozonants, phosphorus-containing peroxide decomposers, lubricants, pigments, blowing agents and the like. These various additives may be used singly or two or more of them may be used in combination.

35 Specific examples of such additives are described, for

example in Japanese Kokoku Publication Hei-04-69659, Japanese Kokoku Publication Hei-07-108928, Japanese Kokai Publication Sho-63-254149 and Japanese Kokai Publication Sho-64-22904.

5 The curable composition of the invention may be used practically without a solvent. In terms of the workability etc., a solvent may be used, however it is desirable to use no solvent from a viewpoint of the adverse effect on the environments.

10 The curable composition of the invention may be produced as a one package formulation, which is to be cured by the moisture in the air after application, by compounding all the components/ingredients and tightly sealing in a container for storage, or as a two-pack type formulation by separately preparing the vinyl polymer (I), the epoxy resin (II), and
15 respective curing agents and curing catalysts, each of which being previously mixed with a filler, a plasticizer, water and the like components, respectively, so that such formulations containing each polymer composition may be mixed together prior to use.

For example, although it is not limited, an amine as a
20 curing agent for the vinyl polymer (I) and the epoxy resin (II), an aminosilane as an adhesion promoter, and the like may be mixed together as A agent, and a tin compound as a curing catalyst for the vinyl polymer (I) and the epoxy resin (II), water, and the like may be mixed together as B agent, so that these A agent
25 and B agent may be mixed together immediately prior to use.

In the case of such two-pack type, a colorant or colorants can be added on the occasion of mixing of the two compositions to an extent that the transparency of the invention is not affected. Thus, in providing sealants matching in color to the
30 given siding boards, for example, a wide assortment of colors become available with limited stocks and thus it becomes easy to cope with the market demand for many colors; this is more favorable for low buildings and the like. At the time where such one-pack type composition is used and applied, water may
35 be added to and, for example, mixed with the composition for

curing after the composition is taken out of the container.

By mixing the colorant or colorants, for example a pigment or pigments, with a plasticizer and/or a filler, as the case may be, and using the thus-prepared paste, it becomes possible
5 to facilitate the working process. Furthermore, it is possible to finely adjust the curing rate at the working field by adding a retarder on the occasion of mixing up the two compositions.

The curable composition of the invention is a curable composition comprising the vinyl polymer (I) containing at
10 least one crosslinkable silyl group on average and the epoxy resin (II) which gives a cured product having a modulated structure when being cured. Accordingly, an effect to easily make the cured product to be transparent can be caused.

Herein, "modulated structure" means the state that the
15 microphase separation occurs and thus in the modulated structure, phase separation limited to microscopic scale is caused. It may also mean the state that Spinodal decomposition is caused. It differs from the island structure in which domains with about 0.1 to 0.5 μm are observed in either one phase.

20 As the vinyl polymer (I) containing at least one crosslinkable silyl group on average and the epoxy resin (II) of the invention, the above-mentioned vinyl polymer (I) and the epoxy resin (II) can be used. Preferable examples of the vinyl polymer (I) are those which are compatible with the epoxy resin
25 (II). Specific examples are butyl acrylate homopolymers and ethyl acrylate / butyl acrylate / 2-methoxyethyl acrylate copolymers (40 to 50 / 20 to 30 / 30 to 20, by mole ratio). Preferable examples of the epoxy resin (II) are those which are compatible with the vinyl polymer (I). Specific examples are
30 bisphenol A epoxy resins, bisphenol F epoxy resins, hydrogenated bisphenol A epoxy resins, and hexahydrophthalic acid diglycidyl esters.

A preferable aspect of the curable composition of the invention may be a combination of the above-mentioned
35 preferable vinyl polymer (I) and epoxy resin (II). The curable

composition comprising the above preferable combination tends to have the modulated structure at the time of curing the curable composition and as a result it becomes easy to obtain the transparent cured product. Further, the mechanical property is remarkably improved in some cases.

The mixing ratio of the vinyl polymer (I) and the epoxy resin (II) in the curable composition of the invention may be the mixing ratio described above.

The curable composition of the invention may further contain a polyether polymer (III). As the polyether polymer (III), the same polyether polymers (III) described above can be used. Among them, modified silicones having a crosslinkable silyl group are preferable since, for example, the rigid cured product can be obtained and gel ratio thereof is increased. The addition amount of the polyether polymer (III) may be the same as the addition amount described above.

The curable composition of the invention may be mixed with various kinds of polymers having a crosslinkable functional group as an optional component. As the polymer containing a crosslinkable functional group, the same polymers as described above can be used.

The curable composition of the invention may contain a curing catalyst and/or a curing agent. Further, based on the desired purposes, various kinds of ingredients/additives may be added to an extent that the modulated structure of the cured product obtained from the curable composition of the invention is not affect, and examples of the ingredients/additives are a dehydration agent, an adhesion promoter, a plasticizer, a filler, a hollow microsphere, a physical property modifier, a silanol-containing compound, a thixotropic agent, a photocurable substance, an air oxidation substance, an antioxidant, a light stabilizer, a compatibility-improving agent, a flame retardant, a curability adjustment agent, a metal inactivation agent, an ozone deterioration-preventing agent, a phosphorus type peroxide-decomposing agent, a lubricant, a

pigment, a foaming agent and the like. As the curing catalyst, curing agent, ingredient and additive, those described above may be used.

Although the curable composition of the invention substantially maintains the modulated structure of the cured product to be obtained even if a filler such as calcium carbonate or carbon black is added, the cured product becomes opaque because of the coloration characteristic to the filler such as calcium carbonate or carbon black in some cases.

10 <<Uses>>

Although not being particularly limited, the curable composition of the invention is usable for various uses, for example sealants for construction and industries such as elastic sealants for building and construction, sealants for siding boards, sealants for pair glass, and sealants for vehicles; electric and electronic parts such as sealants for rear faces of solar cells; insulating materials such as insulating coating materials for electric wires and cables; pressure sensitive adhesives, adhesives, elastic adhesives, contact adhesives, adhesives for tiles, reactive hot melt adhesives, painting materials, powdery coating materials, coating materials, foams, seal materials for can covers etc., electric and electronic potting agents, films, gaskets, casting materials, various kinds of molding materials, artificial marble, rustproof and waterproof sealants for end faces (cut sections) of net glass or laminated glass, materials for vibration absorption/vibration suppression/noise reduction/seismic isolation used in an automobile, a vessel, a household electrical appliance and the like, liquid sealants used in automobile parts, electric parts, various kinds of machine parts and the like, and the like.

The molded article showing rubber elasticity and obtained from the curable composition of the invention can be used widely and mainly for gaskets and packing. For example, in an automobile filed, it can be used for seal materials for keeping

air-tightness, vibration-absorption materials for glass, vibration-absorption materials for vehicle body parts, and especially for window seal gaskets and gaskets for door glass. For chassis parts, it can be used as engine and suspension rubber
5 for vibration absorption/noise reduction, particularly for engine mounting rubber. For engine parts, it can be used for hoses for cooling, fuel supply, exhaust control or the like, sealing materials for engine oil, and the like. Further, it can be used for parts of exhaust gas-cleaning apparatus and
10 brake parts. In a household electrical appliance field, it can be used for packing, O-rings, belts and the like. More particularly, it can be used ornaments, water-proof packing, vibration-absorption rubber and anti-insect packing for lighting and illuminating appliances, vibration
15 absorption/noise reduction/air seal materials for cleaners, dripping covers, water-proof packing, heater packing, electrode part packing and safety valve diaphragms for electric water heating apparatus, hoses, water-proof packing and electromagnetic valves for sake-heating apparatus,
20 water-proof packing, water supply tank-packing, water-absorbing valves, water-receiving packing, connection hose, belts, heat-insulating heater-packing, steam outlet-sealants and the like for steam oven microwave and jar-type rice cookers, oil packing, O-rings, drain packing,
25 pressure tubes, air blow-tubes, air suction-/blow-packing, vibration-absorption rubber, oil supply port-packing, oil meter-packing, oil sending-pipes, diaphragm valves, gas tubes and the like for combustion apparatuses, speaker gaskets, speaker edge, turn table sheets, belts, pulleys and the like
30 for acoustic appliances, and the like. In a building and construction field, it can be used for gaskets for structures (zipper gaskets), pneumatic-structure roofings, water-proof materials, shaped sealants, vibration-absorption materials, noise-reduction materials, setting blocks, slide member and the
35 like. In a sporting field, it can be used for all-weather paving

materials, gymnasium floor materials and the like sport floor applications, shoe bottom materials, bottom inserts and the like sport shoes applications, golf balls and the like balls for ball games applications, and the like. In a field of
5 vibration-absorption rubber, it can be used for vibration-absorption rubber for automobiles, vibration-absorption rubber for railway cars, vibration-absorption rubber for aircrafts, fenders and the like. In a marine and civil engineering field, it can be used for
10 construction materials such as rubber expansive joints, journals, water-stopping plates, water-proof sheets, rubber dams, elastic paving materials, vibration-absorption pads, and protectors; for sub-materials for working such as rubber frames, rubber packers, rubber skirts, sponge mats, mortar hoses, and
15 mortar strainers; for auxiliary materials for working such as rubber sheets and air hoses; for safety products such as rubber buoyant and wave-absorbing materials; for environment preservation products such as oil fences, silt fences, anti-pollution materials, marine hoses, dredging hoses, and oil
20 skimmers; and the like. Further, it may be used as rubber plates, mats, foam plates and the like.

Especially, the curable composition of the invention is particularly useful for sealing materials and adhesives and particularly useful for uses for which weather resistance
25 and/or heat resistance are required and uses for which transparency is required. Since the curable composition of the invention is excellent in weather resistance and adhesiveness, it can be used for adhesion work for outer wall tiles without work of embedding in jointing. Further, it is useful as an
30 elastic adhesive for adhesion of a material having a considerably different linear expansion coefficient or for a member that receives repetitive displacements by heat cycles, and/or as a coating material for making an under-layer material seen through due to its transparency, and/or as an adhesive for
35 adhering transparent materials such as glass, polycarbonates

and polyacrylic resins, and/or the like applications.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the invention will be described more in
5 detail with reference to practical Examples and Comparative
Examples, however the invention should not be limited to the
following Examples.

"Part" and "%" in the following Synthesis Examples,
Examples, and Comparative Examples respectively mean "part by
10 weight" and "% by weight".

Synthesis Examples of polymers of the invention are shown
below.

In Synthesis Examples below, phrases "number average
molecular weight" and "molecular weight distribution (ratio of
15 the weight average molecular weight and number average
molecular weight)" were calculated by conversion into
standardized polystyrene method using gel permeation
chromatography (GPC). As GPC columns were used
polystyrene-crosslinked gel-packed columns (Shodex GPC K-804,
20 manufactured by Showa Denko K.K.) and as GPC solvent was used
chloroform.

Synthesis Example of crosslinkable silyl group-containing poly(n-butyl acrylate) polymer

25 (Synthesis Example 1)

Under nitrogen atmosphere, CuBr (1.09 kg), acetonitrile
(11.4 kg), butyl acrylate (26.0 kg) and diethyl
2,5-dibromoadipate (2.28 kg) were added to a 250 L-reactor and
stirred at 70 to 80°C for about 30 minutes.
30 Pentamethyldiethylenetriamine was added in order to start the
reaction. Butyl acrylate (104 kg) was continuously
supplemented for 2 hours after 30 minutes from the start of the
reaction. During the reaction, pentamethyldiethylenetriamine
was properly added and the inner temperature was kept at 70 to
35 90°C. The total amount of the pentamethyldiethylenetriamine

consumed by that time was 220 g. After 4 hours from the start of the reaction, the reaction system was stirred under heating condition and reduced pressure at 80°C for removing volatile components. Acetonitrile (45.7 kg), 1,7-octadiene (14.0 kg),
5 and pentamethyldiethylenetriamine (439 g) were added to the resulting reaction system and continuously stirred for 8 hours. The mixture was stirred under heating condition and reduced pressure at 80°C for removing volatile components.

Toluene was added to the resulting condensed product for
10 dissolving the polymer, followed by addition of china clay as a filtration aid and aluminum silicate and hydrotalcite as adsorbents, and then the resulting system was stirred under heating condition at an inner temperature of 100°C under oxygen-nitrogen mixed gas atmosphere (oxygen concentration 6%).
15 Solid matter in the mixed solution was removed by filtration and the filtrate was stirred under heating condition and reduced pressure at an inner temperature of 100°C for removing volatile components.

Aluminum silicate and hydrotalcite as adsorbents, and a
20 heat deterioration-preventing agent were further added to the condensed product, and the product was successively stirred under heating condition and reduced pressure (average temperature; about 175°C, and degree of reduced pressure; 10 Torr or lower).

25 Aluminum silicate and hydrotalcite as adsorbents were further added and an antioxidant was also added, and the product was successively stirred under heating condition at an inner temperature of 150°C under oxygen-nitrogen mixed gas atmosphere (oxygen concentration 6%).

30 Toluene was added to the resulting condensed product for dissolving the polymer, followed by removing of the solid matter in the mixed solution by filtration, and the filtrate was stirred under heating condition and reduced pressure for removing volatile components so as to give an alkenyl
35 group-containing polymer.

The alkenyl group-containing polymer, dimethoxymethylsilane (2.0 mole equivalents per one alkenyl group), methyl orthoformate (1.0 mole equivalent per one alkenyl group), and a platinum catalyst [xylene solution of bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)-platinum complex catalyst; hereinafter, referred to as platinum catalyst] (10 mg on the basis of platinum per 1 kg of the polymer) were mixed and stirred under heating condition and nitrogen atmosphere at 100°C. After confirmation of disappearance of alkenyl group, the reaction mixture was concentrated to give dimethoxysilyl group-terminated poly(n-butyl acrylate) polymer [P1]. The number average molecular weight and the molecular weight distribution of the obtained polymer were about 26,000 and 1.3, respectively. The average number of silyl groups introduced into one molecule of the polymer was measured by ¹H-NMR analysis to find it was about 1.8.

Synthesis Example of crosslinkable silyl group-containing poly(n-butyl acrylate / ethyl acrylate / 2-methoxyethyl acrylate) copolymer
(Synthesis Example 2)

Under nitrogen atmosphere, CuBr (1.21 kg), acetonitrile (10.8 kg), butyl acrylate (7.19 kg), ethyl acrylate (10.3 kg), 2-methoxyethyl acrylate (8.47 kg) and diethyl 2,5-dibromoadipate (3.37 kg) were added to a 250 L-reactor and stirred at 70 to 80°C for about 30 minutes. Pentamethyldiethylenetriamine was added in order to start the reaction. A mixture of butyl acrylate (28.8 kg), ethyl acrylate (41.3 kg) and 2-methoxyethyl acrylate (33.9 kg) was continuously supplemented for 2 hours after 30 minutes from the start of the reaction. During the reaction, pentamethyldiethylenetriamine was properly added and the inner temperature was kept at 70 to 90°C. The total amount of the pentamethyldiethylenetriamine consumed by that time was 243 g. After 4 hours from the start of the reaction, the reaction system

was stirred under heating condition and reduced pressure at 80°C for removing volatile components. Acetonitrile (32.5 kg), 1,7-octadiene (30.9 kg), and pentamethyldiethylenetriamine (486 g) were added to the resulting reaction system and
5 continuously stirred for 4 hours. The mixture was stirred under heating condition and reduced pressure at 80°C for removing volatile components.

Toluene was added to the resulting condensed product for dissolving the polymer, followed by addition of china clay as
10 a filtration aid and aluminum silicate and hydrotalcite as adsorbents, and then the resulting system was stirred under heating condition and oxygen-nitrogen mixed gas atmosphere (oxygen concentration 6%). Solid matter in the mixed solution was removed by filtration and the filtrate was stirred under
15 heating condition and reduced pressure at an inner temperature of 100°C for removing volatile components.

Aluminum silicate and hydrotalcite as adsorbents, and a heat deterioration-preventing agent were further added to the condensed product, and the product was successively stirred
20 under heating condition and reduced pressure (average temperature; about 175°C, and degree of reduced pressure; 10 Torr or lower).

Aluminum silicate and hydrotalcite as adsorbents were further added and an antioxidant was also added, and the product
25 was successively stirred under heating condition and oxygen-nitrogen mixed gas atmosphere (oxygen concentration 6%).

Toluene was added to the resulting condensed product for dissolving the polymer, followed by removing of the solid matter
30 in the mixed solution by filtration, and the filtrate was stirred under heating condition and reduced pressure for removing volatile components so as to give an alkenyl group-containing polymer.

The alkenyl group-containing polymer,
35 dimethoxymethylsilane (2.0 mole equivalents per one alkenyl

group), methyl orthoformate (1.0 mole equivalent per one alkenyl group), and a platinum catalyst [xylene solution of bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)-platinum complex catalyst; hereinafter, referred to as platinum catalyst] (10 mg on the basis of platinum per 1 kg of the polymer) were mixed and stirred under heating condition and nitrogen atmosphere at 100°C. After confirmation of disappearance of alkenyl group, the reaction mixture was concentrated to give dimethoxysilyl group-terminated poly(n-butyl acrylate / ethyl acrylate / 2-methoxyethyl acrylate) copolymer [P2]. The number average molecular weight and the molecular weight distribution of the obtained copolymer were about 18,000 and 1.2, respectively. The average number of silyl groups introduced into one molecule of the copolymer was measured by ¹H-NMR analysis to find it was about 1.9.

Synthesis Example of crosslinkable silyl group-containing poly(n-butyl acrylate / ethyl acrylate / 2-methoxyethyl acrylate) copolymer

(Synthesis Example 3)

Under nitrogen atmosphere, CuBr (0.78 kg), acetonitrile (8.7 kg), butyl acrylate (16.3 kg), ethyl acrylate (3.3 kg), 2-methoxyethyl acrylate (0.4 kg) and diethyl 2,5-dibromoadipate (1.22 kg) were added to a 250 L-reactor and stirred at 60 to 70°C for about 15 minutes. Pentamethyldiethylenetriamine was added in order to start the reaction. A mixture of butyl acrylate (65.2 kg), ethyl acrylate (13.1 kg) and 2-methoxyethyl acrylate (1.7 kg) was continuously supplemented for 2 hours after 30 minutes from the start of the reaction. During the reaction, pentamethyldiethylenetriamine was properly added and the inner temperature was kept at 70 to 90°C. The total amount of the pentamethyldiethylenetriamine consumed by that time was 177 g. After 4 hours from the start of the reaction, the reaction system was stirred under heating condition and reduced pressure at 80°C for removing volatile

components. Acetonitrile (34.9 kg), 1,7-octadiene (22.5 kg), and pentamethyldiethylenetriamine (353 g) were added to the resulting reaction system and continuously stirred for 4 hours. The mixture was stirred under heating condition and reduced
5 pressure at 80°C for removing volatile components.

Toluene was added to the resulting condensed product for dissolving the polymer, followed by addition of china clay as a filtration aid and aluminum silicate and hydrotalcite as adsorbents, and then the resulting system was stirred under
10 heating condition and oxygen-nitrogen mixed gas atmosphere (oxygen concentration 6%). Solid matter in the mixed solution was removed by filtration and the filtrate was stirred under heating condition and reduced pressure at an inner temperature of 100°C for removing volatile components.

15 Aluminum silicate and hydrotalcite as adsorbents, and a heat deterioration-preventing agent were further added to the condensed product, and the product was successively stirred under heating condition and reduced pressure (average temperature; about 175°C, and degree of reduced pressure; 10
20 Torr or lower).

Aluminum silicate and hydrotalcite as adsorbents were further added and an antioxidant and toluene were also added, and the product was successively stirred under heating condition and oxygen-nitrogen mixed gas atmosphere (oxygen
25 concentration 6%, inner temperature 165 to 170°C).

Toluene was further added to the resulting condensed product for diluting the polymer, followed by removing of the solid matter in the mixed solution by filtration, and the filtrate was stirred under heating condition and reduced
30 pressure for removing volatile components so as to give an alkenyl group-containing polymer.

The alkenyl group-containing polymer, dimethoxymethylsilane (3.5 mole equivalents per one alkenyl group), methyl orthoformate (1.0 mole equivalent per one
35 alkenyl group), and a platinum catalyst [xylene solution of

bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)-platinum complex catalyst; hereinafter, referred to as platinum catalyst] (10 mg on the basis of platinum per 1 kg of the polymer) were mixed and stirred under heating condition and nitrogen atmosphere at 100°C. After confirmation of disappearance of alkenyl group, the reaction mixture was concentrated to give dimethoxysilyl group-terminated poly(n-butyl acrylate / ethyl acrylate / 2-methoxyethyl acrylate) copolymer [P3]. The number average molecular weight and the molecular weight distribution of the obtained copolymer were about 36,000 and 1.3, respectively. The average number of silyl groups introduced into one molecule of the copolymer was measured by ¹H-NMR analysis to find it was about 1.7.

15 (Examples 1 to 17)

Mixtures of the polymers [polymers P1 and P2] obtained in the above-mentioned Synthesis Examples and the respective kinds of components containing the respective epoxy resins were mixed and stirred sufficiently by hands to give curable compositions. The obtained curable compositions were subjected to evaluations of the strength at break, elongation at break, T-shape peeling strength, tensile shear strength, transparency, total luminous transmittance, and parallel luminous transmittance. The results are shown in Tables 1 and 2.

Herein, the strength at break, elongation at break, T-shape peeling strength, tensile shear strength, transparency, total luminous transmittance, and parallel luminous transmittance were evaluated by the following evaluation methods.

(Strength at break and elongation at break)

Under heating condition and reduced pressure, the obtained curable compositions were applied to form about 2 mm-thick sheet-like coatings and the sheet-like coatings were kept still for 3 days at a room temperature and further for 4

days at 50°C for curing and aging. All of the cured products obtained showed sufficient rubber elasticity. After curing and aging, 2(1/3) type dumbbell form specimens defined in JIS K 7113 were punched out from the cured products and subjected to a tensile test (using Autograph manufactured by Shimadzu Corporation, measurement temperature: 23°C; pulling speed: 200 mm/sec.).

(Evaluation of transparency)

In the same manner as described in the evaluation method of the strength at break, 2 mm-thick sheet-like cured products were produced and put onto a newspaper and the newspaper was observed through the sheet-like cured products from above to evaluate the transparency based on the visibility of letters. In the case where letters were clearly distinguished, the products were regarded to be transparent and in the case where letters were not at all distinguished, the products were determined to be opaque.

(Total luminous transmittance and parallel luminous transmittance)

The total luminous transmittance and parallel luminous transmittance were measured for some of the cured products after the above-mentioned curing and aging by using a turbidimeter (NDH-300A: manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.).

(T-shape peeling strength)

According to JIS K 6854, specimens for T-shape peeling strength measurement were produced by applying obtained curable compositions in about 100 µm-thickness to a 0.1 mm-thick degreased aluminum adherend. The specimens were cured and aged at a room temperature for 3 days and further for 4 days at 50°C and subjected to a tensile test (using Autograph manufactured by Shimadzu Corporation, measurement temperature: 23°C; pulling speed: 200 mm/sec.).

(Tensile shear strength)

According to JIS K 6850, specimens for tensile shear

strength measurement were produced by applying obtained curable compositions in about 100 μm -thickness to a 2 mm-thick degreased aluminum adherend. The specimens were cured and aged at a room temperature for 3 days and further for 4 days at 50°C and
5 subjected to a tensile test (using Autograph manufactured by Shimadzu Corporation, measurement temperature: 23°C; pulling speed: 50 mm/sec.).

The respectively added components, the number of their addition parts, and the respective results are shown in Tables
10 1 and 2.

With respect to the curable compositions of Examples 2 and 7, the morphology of the cured products obtained from the curable compositions was observed by transmittance electron microscopic photographs (JEM-1200EX, manufactured by JEOL Ltd.,
15 acceleration voltage 80 kV, RuO₄ dyeing, freeze ultra-thin cutting method). As shown in Fig. 1 and Fig. 2, the modulated structure was observed.

(Comparative Examples 1 and 2)

20 Various test specimens were produced in the same manner as in Examples 1 to 15 except that the epoxy resin was not added, and these specimens were also subjected to various tests for tensile property and the like. The respectively added components, the number of their addition parts, and the
25 respective results are shown in Table 3.

(Comparative Example 3)

Various test specimens were produced in the same manner as in Examples 1 to 15 except that the vinyl polymer containing
30 a crosslinkable silyl group was not added, and these specimens were also subjected to various tests for tensile property and the like. The respectively added components, the number of their addition parts, and the respective results are shown in Table 3.

35

(Comparative Examples 4 and 5)

Various test specimens were produced in the same manner as in Examples 1 to 15 except that a commercialized product, that is, modified silicone polymer (SAT 350, manufactured by KANEKA CORPORATION) was used as the polyether polymer containing a crosslinkable silyl group in lieu of the vinyl polymer containing a crosslinkable silyl group, and these specimens were also subjected to various tests for tensile property and the like. The respectively added components, the number of their addition parts, and the respective results are shown in Table 3.

The following epoxy resins and addition components were used for Examples and Comparative Examples.

15 EPOLIGHT 4000: hydrogenated bisphenol A epoxy resin (manufactured by Kyoeisha Chemical Co., Ltd.)

 EPIKOTE 191P: glycidyl ester epoxy resin (manufactured by Asahi Denka Co., Ltd.)

20 EPIKOTE 828: bisphenol A epoxy resin (manufactured by Japan Epoxy Resin Co., Ltd.)

 EPIKOTE 806: bisphenol F epoxy resin (manufactured by Japan Epoxy Resin Co., Ltd.)

25 #918: No. 918 (dibutyl tin compound, a catalyst for a crosslinkable silyl group-containing polymer: manufactured by Sankyo Organic Chemicals Co., Ltd.)

 ANCAMINE K54: 2,4,6-tris-dimethylaminomethyl-phenol (curing agent for epoxy resins; manufactured by Air Products and Chemicals, Inc.)

30 A-1122: N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane (manufactured by Nippon Unicar Company Limited)

 IRGANOX 1010: antioxidant (Ciba Specialty Chemicals)

Table 1

Tensile property	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Polymer P1	40	50	60	80				
Polymer P2					40	50	60	80
SAT350								
EPOLIGHT-4000	60	50	40	20				
EPIKOTE-191P					60	50	40	20
EPIKOTE-828								
EPIKOTE-806								
# 918	0.4	0.5	0.6	0.8	0.4	0.5	0.6	0.8
ANGAMINE K54	6	5	4	2	6	5	4	2
A-1122	1	1	1	1	1	1	1	1
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Strength at break (MPa)	11.1	9.1	7.1	3.0	20.8	17.0	11.6	2.4
Elongation at break(%)	50	120	210	260	40	100	180	200
T-shape peeling strength(N/25mm)	12	30	34	28	32	21	23	19
Tensile shear strength(N/cm ²)	900	850	700	590	1180	1200	1400	870
Appearance of cured product	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent
Total luminous transmittance(%)			89				73	
Parallel luminous transmittance(%)			63				50	

Table 2

Tensile property	Example9	Example10	Example11	Example12	Example13	Example14	Example15	Example16	Example17
Polymer P1									
Polymer P2	40	50	60	80	50	60	80	50	70
SAT350									
EPOLIGHT-4000	60	50	40	20					
EPIKOTE-191P									
EPIKOTE-828					50	40	20		
EPIKOTE-806								50	30
#918	0.4	0.5	0.6	0.8	0.5	0.6	0.8	0.5	0.7
ANCAMINE K54	6	5	4	2	5	4	2	5	3
A-1122	1	1	1	1	1	1	1	1	1
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Strength at break (MPa)	14.4	9.9	9.0	2.8	26.9	5.5	3.8	15.5	6.0
Elongation at break(%)	70	100	130	170	30	10	80	10	50
T-shape peeling strength(N/25mm)	17	35	31	22	13	13	18	16	17
Tensile shear strength(N/cm ²)	1000	950	820	710	630	700	580	850	510
Appearance of cured product	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent
Total luminous transmittance(%)			71			75		65	75
Parallel luminous transmittance(%)			29			46		34	32

Table 3

	Tensile property	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
	Polymer P1	100				
5	Polymer P2		100			
	SAT350				50	67
	EPOLIGHT-4000					
	EPIKOTE-191P					
	EPIKOTE-828			100	50	33
	EPIKOTE-806					
10	#918	1.0	1.0		0.5	0.7
	ANCAMINE K54	—	—	10	5	3
	A-1122	1	1	1	1	1
	Water	0.5	0.5	0.5	0.5	0.5
	Strength at break (MPa)	0.3	0.5	12.0	10.9	11.8
15	Elongation at break(%)	150	130	0	830	700
	T-shape peeling strength(N/25mm)	15	11	3	95	90
	Tensile shear strength(N/cm ²)	170	230	960	1010	600
	Appearance of cured product	Transparent	Transparent	Transparent	Opaque	Opaque
	Total luminous transmittance(%)				19	21
20	Parallel luminous transmittance(%)				2	2

The curable compositions of Examples and the cured products obtained from the curable compositions were all found transparent and having rubber elasticity by improvement of the hard and brittle properties of the epoxy resins. They also had high adhesion strength.

(Examples 18 to 25 and Comparative Examples 6 and 7)

Mixtures of the polymers [polymers P1 and P2] obtained in the above-mentioned Synthesis Examples and the respective kinds of components containing the respective epoxy resins were mixed and stirred sufficiently by hands to give curable compositions. Under heating condition and reduced pressure, the obtained curable compositions were applied to form about 2 mm-thick sheet-like coatings and the sheet-like coatings were

kept still for 3 days at a room temperature and further for 4 days at 50°C for curing and aging. After curing and aging, 2(1/3) type dumbbell form specimens defined in JIS K 7113 were punched out from the cured products and heated for a prescribed period in a thermostat at 150°C. The mechanical and physical properties before and after the heating were compared by a tensile test (using Autograph manufactured by Shimadzu Corporation, measurement temperature: 23°C; pulling speed: 200 mm/sec.). The respectively added components, the number of their addition parts, and the respective results are shown in Table 4.

Table 4

Tensile property	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Comparative Example 6	Comparative Example 7
Polymer P1							50	70		
Polymer P2	50	70	50	70	50	70				
SAT350									50	70
EPOLIGHT-4000	50	30					50	30		
EPIKOTE-191P			50	30						
EPIKOTE-828					50	30			50	30
EPIKOTE-806										
#918	0.5	0.7	0.5	0.7	0.5	0.7	0.5	0.7	0.5	0.7
ANCAMINE K54	5	3	5	3	5	3	5	3	5	3
A-1122	1	1	1	1	1	1	1	1	1	1
IRGANOX 1010	1	1	1	1	1	1	1	1	1	1
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Strength at break (MPa)										
Initial	8.9	4.8	11.7	3.7	26.9	7.4	6.9	5.0	8.5	11.8
After 70 hours	8.4	5.0	11.1	3.8	22.7	7.5	9.9	4.3	1.2	1.4
After 160 hours	9.8	4.9	14.2	6.2	21.6	8.7	9.5	4.9	0.2	0.1
After 350 hours		4.6	14.5		12.5	8.0	10.6		0.1	0.3
After 710 hours			11.9	4.8	13.1	7.8	8.2		0.0	0.0

The curable compositions and the cured products obtained from the curable compositions were all found having good heat

resistance.

(Examples 26 and 27 and Comparative Example 8)

Mixtures of the polymers [polymers P1 and P2] obtained
5 in the above-mentioned Synthesis Examples and the respective
kinds of components containing the respective epoxy resins were
mixed and stirred sufficiently by hands to give curable
compositions. According to durability test standardized in
JIS A 1439, the curable compositions were processed into
10 specimens with a size of 30 x 12 x 12 mm (adherends were float
glass with a size of 30 x 50 x 5 mm). The processed products
were kept still for 7 days at a room temperature and further
for 7 days at 50°C to give cured and aged specimens for the test.
The specimens were exposed to light irradiation for 3600 hours
15 by a xenon weatherometer according to the artificial exposure
test standardized in JIS A 1439 (Suga Test Instruments' SX120
model, radiation intensity 180 W; black panel temperature 63°C,
raining for 18 minutes during 2 hour irradiation). The
mechanical and physical properties before and after the
20 irradiation were compared by a tensile test (using Autograph
manufactured by Shimadzu Corporation, measurement
temperature: 23°C; pulling speed: 200 mm/sec.). The
respectively added components, the number of their addition
parts, and the respective results are shown in Table 5.

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Table 5

Tensile property	Example 26	Example 27	Comparative Example 8
Polymer P1	60		
Polymer P2		60	
SAT350			60
EPOLIGHT-4000	40		
EPIKOTE-191P		40	
EPIKOTE-828			40
EPIKOTE-806			
#918	1.0	1.0	1.0
ANCAMINE K54	6	6	6
A-1122	1	1	1
Water	0.5	0.5	0.5
Initial mechanical property			
Strength at break (MPa)	3.6	6.5	3.7
Elongation at break(%)	50	40	220
Mechanical property after 3620 hours-light irradiation by xenon weatherometer			
Strength at break (MPa)	4.2	2.8	0.4
Elongation at break(%)	60	20	20

The curable compositions and the cured products obtained from the curable compositions were all found having good weather resistance.

(Examples 28 to 35 and Comparative Examples 9 and 10)

Mixtures of the polymers [polymers P1 and P2] obtained in the above-mentioned Synthesis Examples and the respective kinds of components containing the respective epoxy resins were mixed and stirred sufficiently by hands to give curable compositions. Under heating condition and reduced pressure, the obtained curable compositions were applied to form about 2 mm-thick sheet-like coatings and the sheet-like coatings were kept still for 3 days at a room temperature and further for 4

days at 50°C for curing and aging. After curing and aging, the cured products were immersed in a prescribed oil (ASTM No. 1, IRM 903) at 150°C for 70 hours and the weight increase ratio to the initial weight was measured. The respectively added components, the number of their addition parts, and the respective results are shown in Table 6.

Table 6

	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34	Example 35	Comparative Example 9	Comparative Example 10
Polymer P1	10	30	50	60	80				100	
Polymer P2						50	70	90		
SAT350										67
EPOLIGHT-4000	90	70	50	40	20					
EPIKOTE-191P						50	30	10		
EPIKOTE-828										33
EPIKOTE-806										
#918	0.1	0.3	0.5	0.6	0.8	0.5	0.7	0.9	1.0	0.7
ANCAMINE K54	9	7	5	4	2	5	3	1	0	3
A-1122	1	1	1	1	1	1	1	1	1	1
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Weight increase ratio after immersing in prescribed oil at 150° C for 70 hours (%)										
ASTM No.1	-6	-6	-4	-3	2	-6	-3	-2	7	14
IRM903	2	15	36	49	100	0	4	10	206	172

The curable compositions and the cured products obtained from the curable compositions were all found having good oil resistance.

(Examples 36 to 40)

Mixtures of the polymers [polymers P2 and P3] obtained in the above-mentioned Synthesis Examples, epoxy resins, and also the respective kinds of components including, as the polyether polymer containing at least one crosslinkable silyl group on average, a commercialized product, that is, modified silicone polymer (SAT 350, manufactured by KANEKA CORPORATION)

were mixed and stirred sufficiently by hands to give curable compositions. The stirred curable compositions were centrifuged by a centrifugal separator for removing almost all foams and further defoamed under heating condition and reduced pressure, and subjected to form about 3 mm-thick sheet-like coatings. The sheet-like coatings were kept still for 2 days at a room temperature and further for 3 days at 50°C for curing and aging. After curing and aging, No. 3 type dumbbell form specimens defined in JIS K 6251 were punched out from the cured products and subjected to a tensile test (using Autograph manufactured by Shimadzu Corporation, measurement temperature: 23°C; pulling speed: 200 mm/sec.).

The respectively added components, the number of their addition parts, and the respective results are shown in Table 7.

(Hardness)

The hardness was measured according to JIS K 6253. Practically, the measurement of the hardness of the sheet specimens was carried out by keeping the respective sheets for 1 hour at a thermostat (23°C), then laminating three of each sheet, and measuring the hardness by a hardness meter (Durometer Type A, manufactured by Shimadzu Corporation).

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Table 7

	Example 36	Example 37	Example 38	Example 39	Example 40
Polymer P1					
5 Polymer P2	60				
Polymer P3		60	42	30	18
SAT350			18	30	42
EPOLIGHT-4000	40	40	40	40	40
EPIKOTE-191P					
10 EPIKOTE-828					
EPIKOTE-806					
#918	0.6	0.6	0.6	0.6	0.6
ANCAMINE K54	4	4	4	4	4
A-1122	1	1	1	1	1
15 Water	0.5	0.5	0.5	0.5	0.5
Strength at break (MPa)	7.4	4.5	4.9	5.8	4.3
Elongation at break(%)	90	130	170	300	290
Hardness(Shore A)	80	52	56	60	53

20 The curable compositions of Examples and the cured products obtained from the curable compositions were all found transparent and having rubber elasticity by improvement of the hard and brittle properties of the epoxy resins. They also had sufficient strength at break and elongation at break. Further,

25 addition of the polyether polymer containing at least one crosslinkable silyl group on average was found effective to increase the elongation while keeping the hardness of the cured products to a certain level.

30 BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a transmittance electron microscopic photograph of a cured product obtained by curing the curable composition of Example 2.

35 Fig. 2 is a transmittance electron microscopic photograph of a cured product obtained by curing the curable composition

of Example 7.

INDUSTRIAL APPLICABILITY

The curable composition of the invention, although having
5 low viscosity itself, gives a cured product, when being cured,
which has wide range of elasticity, from hard to soft, which
is excellent in weather resistance and/or heat resistance, and
the hardness and brittleness (characteristic to epoxy resins)
of which have been improved to have rubber elasticity, and which
10 has high adhesion strength and is transparent.

When being used for adhering or sealing a transparent
material such as glass, polycarbonates, and acrylic resins, the
curable composition of the invention is usable for treatment
with sufficiently retaining the transparency, which is an
15 aesthetic characteristic. In the case of using the curable
composition of the invention for a coating agent or a lining
agent, the design of an under-layer material can be utilized
well and cracks etc. in a joint and/or the like parts can be
easily found to make quick repairing possible.

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CLAIMS

1. A curable composition comprising a vinyl polymer (I)
containing at least one crosslinkable silyl group on average
5 and an epoxy resin (II),

which gives a transparent cured product when the mixture
of the vinyl polymer (I) and the epoxy resin (II) is cured.

2. A curable composition comprising a vinyl polymer (I)
10 containing at least one crosslinkable silyl group on average
and an epoxy resin (II),

which gives a cured product having a modulated structure
when being cured.

15 3. The curable composition according to Claim 1 or 2
wherein a vinyl monomer constituting the main chain of
the vinyl polymer (I) is mainly selected from the group
consisting of (meth)acrylic monomers, acrylonitrile monomers,
aromatic vinyl monomers, fluorine-containing vinyl monomers
20 and silicon-containing vinyl monomers.

4. The curable composition according to Claim 3
wherein the main chain of the vinyl polymer (I) is a
(meth)acrylic polymer.

25 5. The curable composition according to Claim 4
wherein the main chain of the vinyl polymer (I) is an
acrylic polymer.

30 6. The curable composition according to Claim 5
wherein the main chain of the vinyl polymer (I) is an
acrylic ester polymer.

7. The curable composition according to any one of Claims
35 1 to 6

wherein the main chain of the vinyl polymer (I) is a polymer or a copolymer having higher polarity than that of a butyl acrylate homopolymer.

5 8. The curable composition according to any one of Claims 1 to 7

wherein the main chain of the vinyl polymer (I) is a polymer or a copolymer having a repeating unit structure represented by the general formula 1:

10 $-\text{[CH}_2\text{-CR(COOR')]}-$ (1)

(wherein, R represents a hydrogen atom or a methyl group; R' may be same or different and each represents an alkoxyalkyl group or an alkyl group having 1 to 3 carbon atoms.)

15 9. The curable composition according to any one of Claims 1 to 8

wherein the vinyl polymer (I) has a molecular weight distribution of less than 1.8.

20 10. The curable composition according to any one of Claims 1 to 9

wherein the crosslinkable silyl group is represented by the general formula 2:

$-\text{[Si(R}^1\text{)}_{2-b}\text{(Y)}_b\text{O]}_m\text{-Si(R}^2\text{)}_{3-a}\text{(Y)}_a$ (2)

25 {wherein, R¹ and R² may be same or different and each is an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms or a triorganosiloxy group represented by (R'')₃SiO- (in which R'' is a univalent hydrocarbon group containing 1 to 20 carbon atoms and a plurality of R' groups may be the same or different) and, when there are two or more R¹ or R² groups, they may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different; a represents 0, 1, 2 or 3,
30
35 b represents 0, 1 or 2, and m is an integer of 0 to 19, provided

that the relation $a + mb \geq 1$ should be satisfied.}

11. The curable composition according to any one of Claims
1 to 10

5 wherein the main chain of the vinyl polymer (I) is
produced by living radical polymerization.

12. The curable composition according to Claim 11
wherein the main chain of the vinyl polymer (I) is
10 produced by atom transfer radical polymerization.

13. The curable composition according to any one of Claims
1 to 12

15 wherein the crosslinkable silyl group of the vinyl
polymer (I) is at the molecular terminus.

14. The curable composition according to any one of Claims
1 to 13

20 wherein the epoxy resin (II) is an epoxy resin (II)
containing no aromatic rings.

15. The curable composition according to any one of Claims
1 to 14

25 wherein the epoxy resin (II) is an alicyclic epoxy resin.

16. The curable composition according to Claim 15
wherein the alicyclic epoxy resin (II) is selected from
the group consisting of a hydrogenated bisphenol A epoxy resin
and a glycidyl ester epoxy resin.

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17. The curable composition according to any one of Claims
1 to 16

which further comprises a polyether polymer (III).

35 18. The curable composition according to Claim 17

wherein the main chain of the polyether polymer (III) is substantially polypropylene oxide.

19. The curable composition according to Claim 17 or 18
5 wherein the polyether polymer (III) contains at least one crosslinkable silyl group on average.

20. The curable composition according to Claim 1 or 2
10 wherein the total luminous transmittance of the cured product with a thickness of about 2 mm obtained by curing the above-mentioned mixture is 50% or higher.

21. The curable composition according to Claim 1 or 20
15 wherein the parallel luminous transmittance of the cured product with a thickness of about 2 mm obtained by curing the above-mentioned mixture is 10% or higher.

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Figures: _____

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