A vinyl polymer containing silicons and preparation thereof.

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Proprietor: Nippon Paint Co., Ltd.
2-1-2, Oyodokita Oyodo-ku
Osaka-shi Osaka-fu(JP)

Inventor: Ohsugi, Hiroharu
1-1-111, Nishimakino 4-chome
Hirakata-shi Osaka-fu(JP)
Inventor: Eguchi, Yoshio
1-10-2, Sumiyoshi
Ikedashita Osaka-fu(JP)
Inventor: Urano, Satoshi
A36-301, Otokoyamakoro 6
Yawata-shi Kyoto-fu(JP)
Inventor: Mizuguchi, Ryuzo
42-6-301 Hashimoto-Kurigatan
Yawata-shi Kyoto-fu(JP)

Representative: Smulders, Theodorus A.H.J.,
Ir. et al
Vereenigde Octroibureaux Nieuwe Parklaan
97
NL-2587 BN 's-Gravenhage (NL)

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Description

The present invention relates to a novel silicon-containing vinyl copolymer. As a measure for giving the characteristics possessed by a siloxane resin as water resistance, weather resistance and the like to an acrylic resin or other resins, attempts have been made to fix an organosiloxane, through a chemical linkage, to a compound bearing radically polymerizable unsaturation bond. For example, Japanese Patent Application Kokai No. 61126/79 discloses methyl di (trimethyl siloxy) silyl propyl glycerol methacrylate which is prepared by the addition reaction of organo polysiloxane containing epoxy groups and methacrylic acid and is used as a monomer for a resin which is excellent in oxygen permeability and hydrophilic properties and hence is useful as a contact lens material; Japanese Patent Application Kokai No. 63200/79 discloses an organo polysiloxane containing acryloyloxy groups which has the characteristic of being cured in a short period of time under irradiation condition and which is prepared by the reaction of organo polysiloxane containing amino groups and glycidyl acrylate; Japanese Patent Application Kokai No. 22325/81 discloses a process for the preparation of polymerizable organo polysiloxane by the reaction of organo polysiloxane containing epoxy groups and acrylate; and Japanese Patent Application Kokai No. 1806/82 discloses a process for the preparation of polymerizable organosiloxane by the reaction of trialkyl chlorosilane and hydroxyalkyl acrylate. However, they are not always of satisfaction in respects of reaction speed and reaction yield and hence are not economical in an industrial scale of production of silicon modified monomers. Furthermore, in these methods, since the principal objects are mere introduction of hydrophobic siloxane bonds to polymerizable monomers, actual use of thus obtained monomers has been rather limited to narrow range as, for example, preparation of particular resins which are to be used in specific area requiring the characteristic properties of said siloxane bonds only, for example oxygen permeability in contact lens. Under the circumstances, the present inventors, having endeavored to find out a novel class of polymerizable silicon-containing monomers bearing functional groups or bonds as well as siloxane bonds, have succeeded in establishing a method for the preparation of class of monomers represented by the formula:

\[
R^1_m \left( CH_2=CH-A-NH-C-O-R^4 \right)_n SiO_{4-m-n} \]

wherein \( R^1 \) is a substituted or unsubstituted monovalent hydrocarbon residue; \( R^4 \) is a substituent directly bonded to silicon atom and is selected from a substituted or unsubstituted alkyne; \( R^3 \) is hydrogen or methyl; \( A \) is a direct bond,

\[
\begin{align*}
- & C-O-R^5^- , -C- , -C-NH-R^6^- , \\
\| & \quad \| \quad \| \\
O & \quad O \quad O
\end{align*}
\]

or a substituted or unsubstituted phenylene group; \( m \) and \( n \) each is a positive number which will fulfill the requirement of \( 2 \leq m + n \leq 4 \), comprising reacting a hydroxyl containing silicon compound of the formula:

\[
R^1_m (HOR^4)_n SiO_{4-m-n} \]

wherein \( R^1, R^4, m \) and \( n \) have the same meanings as defined hereinbefore, and a polymerizable isocyanate compound of the formula:
wherein $R^3$ and $A$ have the same meanings as defined hereinbefore, and have applied a patent on it at the same day with the present patent application (i.e. Japanese Patent Application No. 65425/81).

Such monomers are copolymerized with other vinyl monomers to provide various silicon-containing vinyl copolymers.

Finally, EP-A-0 127 321 discloses copolymers comprising an organopolysiloxane urethane acrylate and an ethylenically unsaturated comonomer. An example of an acrylate is a bis(urethane methacrylate) having formula VI shown hereinafter.

It is, therefore, an object of the invention to provide a novel class of silicon-containing copolymers bearing urethane bonds as well as siloxane bonds, which are derived from said polymerizable silicon-containing monomers and are specifically useful in paint, optical lens and various other industrial applications.

According to the invention, the abovesaid object can be attained with a silicon-containing vinyl copolymer, characterized in that said copolymer has in its molecule

- a constituent unit of formula (I):

\[
R^1 R^2 n SiO_{4-m-n} \quad 2
\]

wherein $R^1$ is a substituted or unsubstituted monovalent hydrocarbon residue; $R^2$ is

\[
\begin{align*}
& R^3 \\
& \text{CH}_2-C- \\
& \text{A-NH-B-R}^4-
\end{align*}
\]

$R^3$ is hydrogen or methyl; $R^4$ is a substituted or unsubstituted alkyene directly bonded to a silicon atom; $m$ and $n$ each is a positive number, which will fulfil the requirement of $2 \leq m + n \leq 4$;

$A$ is a direct bond,

\[-C-O-R^5-\ , \ -C-\ , \ -C-NH-R^6- ,\]

\[
\begin{array}{ccc}
\hline
\text{O} & \text{H} & \text{O} \\
\hline
\end{array}
\]

phenylene or a substituted phenylene; $B$ is

\[
\begin{align*}
& \text{C-O} \quad \text{or} \quad \text{C-N} \\
& \text{O} \quad \text{H}
\end{align*}
\]

or $R^5$ and $R^6$ each represents an alkyene; provided that when $A$ is
m + n is 2, said constituent unit of formula (I) being selected from formula (II), (III) or (IV):

$$\text{Y} \quad \text{Y}$$

$$\text{R}^2\text{Si} - \{\text{OSi}\}_n \text{O}$$

$$\text{Y}$$

(II)

$$\text{Z}_{\alpha}$$

$$\text{R}^2\text{Si} - \{\text{OSi}\}_n \text{Z}$$

$$\text{Y}$$

3-a

(III)

$$\text{Y}$$

$$\text{R}^2\text{Si}-\text{Y}$$

$$\text{Y}$$

(IV)

wherein $\text{R}^2$ has the same meaning as defined before, except for that $\alpha$ cannot be

$$\text{C}=\text{O} \text{R}^5 \quad \text{O}$$

in formula (III): $\text{Y}$ is $\text{R}^2$ or a monovalent hydrocarbon residue; $\text{Z}$ is a monovalent hydrocarbon residue; $n$ is a positive number of at least 2 in formula (II) and of at least 1 in formula (III); and $a$ is 1 or 2; and

- a constituent unit of at least one other $\alpha, \beta$-ethylenically unsaturated monomer.

The present silicon-containing vinyl copolymers may be advantageously prepared by either one of the following methods. For the sake of clarity there will be referred to constituent units of formula (I) and to precursors thereof as a genus for the species constituent units of formula (II), (III) and (IV) according to the invention, which will be discussed and exemplified further in the description.

That is, in the first method, a polymerizable monomer containing silicons represented by the formula (V):

$$\text{R}^3$$

$$\text{R}^1_m(\text{CH}_2=\text{C}-\text{A}-\text{NH}-\text{B}-\text{R}^4)\text{nSiO}_{4-m-n}^2$$

(V)
EP 0 320 537 B1

wherein \( R^1 \) is a substituted or unsubstituted monovalent hydrocarbon residue; \( R^2 \) is hydrogen or methyl; \( R^4 \) is a substituted or unsubstituted alkylene directly bonded to a silicon atom; \( m \) and \( n \) each is a positive number which will fulfill the requirement of \( 2 \leq m + n \leq 4 \); \( A \) is a direct bond,

\[
\begin{align*}
\text{\( -C-O-R^5_-, \quad -C-, \quad -C-NH-R^6_- \),} \\
\text{\( O \quad O \quad O \)}
\end{align*}
\]

or a substituted or unsubstituted phenylene; \( B \) is

\[
\begin{align*}
\text{\( -C-O- \quad \text{or} \quad -C-N- \),} \\
\text{\( O \quad O \quad H \)}
\end{align*}
\]

\( R^5 \) and \( R^6 \) each represents an alkylene, provided that when \( A \) is

\[
\begin{align*}
\text{\( -C-O-R^5_- \),} \\
\text{\( O \)}
\end{align*}
\]

\( m + n \) is 2, is copolymerized with at least one other \( \alpha,\beta \)-ethylenically unsaturated monomer.

In the second method, a polymerizable isocyanate compound of the formula (VI):

\[
\begin{align*}
\text{\( R^3 \)} \\
\text{\( \text{CH}_2=\text{C-A-NCO} \) (VI)}
\end{align*}
\]

wherein \( R^3 \) is hydrogen or methyl; \( A \) is a direct bond,

\[
\begin{align*}
\text{\( -C-O-R^5_-, \quad -C-, \quad -C-NH-R^6_- \),} \\
\text{\( O \quad O \quad O \)}
\end{align*}
\]

or a substituted or unsubstituted phenylene; \( R^5 \) and \( R^6 \) each represents an alkylene, and at least one other \( \alpha,\beta \)-ethylenically unsaturated monomer bearing no functional group reactive to said isocyanate group, are copolymerized together and the thus obtained copolymer is then reacted with an organosilicon compound containing hydroxyl groups of the formula (VII):

\[
\begin{align*}
\text{\( R^1_m(\text{HO-R^4}^n)^{\text{SiO}_4-m-n} \)} \\
\text{\( \frac{2}{2} \) (VII)}
\end{align*}
\]

wherein \( R^1 \) is a substituted or unsubstituted monovalent hydrocarbon residue; \( R^4 \) is a substituted or unsubstituted alkylene directly bonded to a silicon atom; \( m \) and \( n \) each represents a positive number which
will fulfill the requirement of $2 \leq m+n \leq 4$, provided that when A of the aforesaid formula (VII) is

$$-\text{C} \equiv \text{O} - \text{R}_5^-,$$

$m+n$ is 2.

The polymerizable silicon-containing monomers of the formula (V) used in the preparation of the present vinyl copolymers having a constituent unit of the formula (I) are, as stated hereinafter, novel compounds first prepared by the inventors by the reaction of organosilicon compounds containing hydroxyl groups of the formula (VII)

$$R^1_m (\text{HOR}^4)_n \text{SiO}_{4-m-n} \quad \frac{2}{m+n}$$

(VII)

and polymerizable isocyanate compounds of the formula (VI)

$$R^3 \quad \text{CH}_2 = \text{C} \equiv \text{A} \equiv \text{NCO}$$

(VI)

wherein $R^1$, $R^2$, $m$, $n$, $R^3$ and A each has the same meaning as defined hereinbefore.

As the organosilicon compounds containing hydroxyl groups of the formula (VII), any of linear or cyclic siloxanes or silanes having one and more silicon atoms may be satisfactorily used, providing having at least one hydroxy alkyl group attached to silicon atoms. Preferable members are the compounds of the formula (VII) in which $R^1$ represents substituted or unsubstituted $C_1$ to $C_4$ alkyl or alkenyl group and $R^4$ represents substituted or unsubstituted lower alkylene. More specifically, particularly preferable members are 1,3,5,7-tetramethyl-3,5,7-triethyl-1-(γ-hydroxypropyl)cycloctrasiloxane, bis(trimethylsiloxy)-methyl-3-hydroxypropyl silane, 1,3,5,7-tetramethyl-3,7-dipropyl-1,5-bis(γ-hydroxypropyl) cycloctrasiloxane, 1,1,3,3,3-pentamethyl-1-(γ-hydroxypropyl) disiloxane, tris-(trimethylsiloxy)-γ-hydroxypropyl silane and 1,3,5,7-tetramethyl-3,5,7-triethyl-1-γ-(β-hydroxyethoxy)-propyl cyclotetra siloxane.

Examples of isocyanate compounds having $\alpha, \beta$-ethylenically unsaturated bonds represented by the formula (VI) are methacryloyl isocyanate, 2-isocyanate ethyl methacrylate, 2-isocyanate methyl methacrylate, 2-isocyanate ethyl acrylate, 2-isocyanate propyl methacrylate, 2-isocyanate octyl acrylate, $\pi$-isopropenyl-$\alpha, \alpha$-dimethyl benzyl isocyanate, $\pi$-isobutynyl-$\alpha, \alpha$-dimethyl benzyl isocyanate, $\pi$-ethyl-$\alpha, \alpha$-dimethyl benzyl isocyanate and vinyl isocyanate. Particularly preferable member from the standpoint of higher reactivity toward active hydrogen bearing group is methacryloyl isocyanate.

The aforesaid compound (VII) and compound (VI) are generally reacted in an equimolar ratio of hydroxyl group in said compound (VII) : isocyanate group in said compound (VI). When a highly reactive isocyanate compound is selected, the urethane reaction can be proceeded very quickly without using a catalyst and at a room temperature, and however, when a less reactive isocyanate compound is used, an appropriate catalyst as dibutyl tin dilaurate is usually employed and the reaction may be advantageously carried out at an elevated temperature, e.g. 70 °C to 110 °C, for 2 to 4 hours. In either case, the reaction yield is excellent. The said polymerizable silicon containing monomers may also be prepared by the combination of steps of reacting an organosilicon compound containing hydroxyl groups of formula (VII)
wherein \( R^1, R^4, m \) and \( n \) are as defined above, with an isocyanate compound containing haloethyl group of the formula (VIII):

\[
\frac{R^1_m(\text{IIOR}^4)_nSiO_{4-m-n}}{2}
\]

(VII)

wherein \( X \) represents a halogen atom; \( R^3 \) is hydrogen or methyl group; \( A \) is a direct bond,

\[
\begin{array}{cccc}
\text{R}^3 & \text{X} & \text{CH}_2 & \text{CH-A-NCO} \\
\text{H} & \text{C} & \text{O} & \text{O} & \text{O}
\end{array}
\]

(VIII)

or a substituted or unsubstituted phenylene; \( R^5 \) and \( R^6 \) each represents an alkylene, to obtain a compound of the formula (IX):

\[
\frac{R^1_m(X-\text{CH}_2-\text{CH-A-N-C-O-R}^4)_nSiO_{4-m-n}}{2}
\]

(IX)

in which \( R^1, R^4, R^3, m, n, X \) and \( A \) are as defined above, and of reacting the abovementioned compound (IX) with a dehydrohalogenation agent.

Examples of the isocyanate compounds of the formula (VIII) are \( \alpha \)-chloromethyl propionyl isocyanate and \( \beta \)-chloropropionyl isocyanate, and examples of dehydrohalogenation agent are sodium hydroxide, potassium hydroxide, potassium alcooxide potassium alcooxide, alkali carbonate, pyridine, dialkyl amines and trialkyl amines as triethyl amine.

Since the both reactions of Step 1 and Step 2 are proceeded very effectively and quickly, this alternative method is also quite useful for the production of the polymerizable silicon containing monomers.

Though the polymerizable silicon containing monomers used in the present invention are most conveniently expressed by means of the aforesaid formula (V), more specific representatives shall be given below by using the structural formula, respectively.
cyclic siloxane monomers

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CH}_2=\text{C} \\
R^3 & \quad R^3 \\
-\text{A}-\text{N}-\text{C}-\text{O}-R^4 & \quad -\text{A}-\text{N}-\text{C}-\text{O}-R^4 \\
\mid & \quad \mid \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\{\text{OSi}_n\}_\text{Y} & \quad \{\text{OSi}_n\}_\text{Y} \\
\text{Y} & \quad \text{Y} \\
\end{align*}
\]

wherein \( Y \) is

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CH}_2=\text{C} \\
R^3 & \quad R^3 \\
-\text{A}-\text{N}-\text{C}-\text{O}-R^4 & \quad -\text{A}-\text{N}-\text{C}-\text{O}-R^4 \\
\mid & \quad \mid \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

or a monovalent hydrocarbon residue; \( R^3, R^4 \) and \( A \) are as defined hereinbefore; \( n \) is a positive number of 2 and more.

linear (non-cyclic) siloxane monomers

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CH}_2=\text{C} \\
R^3 & \quad R^3 \\
-\text{A}-\text{N}-\text{C}-\text{O}-R^4 & \quad -\text{A}-\text{N}-\text{C}-\text{O}-R^4 \\
\mid & \quad \mid \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\{\text{OSi}_n\}_\text{Y} & \quad \{\text{OSi}_n\}_\text{Y} \\
\text{Z} & \quad \text{Z} \\
\end{align*}
\]

wherein \( R^3, R^4 \) and \( A \) are as defined above; \( Y \) represents

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CH}_2=\text{C} \\
R^3 & \quad R^3 \\
-\text{A}-\text{N}-\text{C}-\text{O}-R^4 & \quad -\text{A}-\text{N}-\text{C}-\text{O}-R^4 \\
\mid & \quad \mid \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

or a monovalent hydrocarbon residue; \( Z \) is a monovalent hydrocarbon residue; \( a \) is 1 or 2 and \( n \) is a positive number of 1 and more.
silicon-containing monomers

\[ \text{CH}_2=\text{C} - \text{A} - \text{N} - \text{C} - \text{O} - \text{R}^4 - \text{S}^1 - \text{Y} \]

wherein \( R^3, R^4, \) and \( \text{A} \) are as defined above, and \( \text{Y} \) is a monovalent hydrocarbon residue or

\[ \text{CH}_2=\text{C} - \text{A} - \text{N} - \text{C} - \text{O} - \text{R}^4 - \text{H} - \text{O} \]

As the \( \alpha,\beta \)-ethylenically unsaturated monomers to be additionally polymerized with said silicon containing polymerizable monomers in the invention, any of the members customarily used in the preparation of vinyl resins may be satisfactorily used. They may be either mono functional or poly functional compounds.

Examples of mono functional monomers are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, iso-butyl acrylate, iso-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethyl hexyl acrylate, 2-ethyl hexyl methacrylate, isononyl acrylate, isononyl methacrylate, lauryl acrylate, lauryl methacrylate, acrylic acid, methacrylic acid, 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, tri-butyl tin acrylate, tri-butyl tin methacrylate, acrylamide, N-butoxymethyl acrylamide, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-butoxyethyl acrylate, acid phosphoryl ethyl methacrylate, 3-chloro-2-acid phosphoxy propyl methacrylate, acid phosphoxy propyl methacrylate, ethyleneglycol mono acrylate, ethyleneglycol mono methacrylate and 2-isocyanate ethyl methacrylate, methacryloyl isocyanate; styrene, vinyl toluene, dibutyl fumarate, diethyl fumarate, and N-vinyl pyrrolidone.

Examples of polyfunctional monomers are ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, diethyleneglycol diacrylate, diethyleneglycol dimethacrylate, triethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol diacrylate, 1,4-butylene glycol dimethacrylate, 1,6-hexanediol diacrylate and 1,6-hexanediol dimethacrylate.

The polymerization of said polymerizable monomer (V) and at least one other polymerizable vinyl monomer abovementioned may be carried out, following a conventional addition polymerization technique, in the presence of an appropriate polymerization initiator as azobis series compounds and in an appropriate reaction medium, and no specific means are required.

The present vinyl polymers may also be advantageously prepared by the combination steps of effecting an addition polymerization of a polymerizable isocyanate compound (VI):

\[ \text{CH}_2=\text{C} - \text{A} - \text{NCO} \]  

(VI)

with at least one other \( \alpha,\beta \)-ethylenically unsaturated monomer bearing no functional group reactive to said isocyanate group, e.g. hydroxyl, amino and reacting thus obtained product with an organosilicon compound containing hydroxyl groups of the formula (VIII). In either method, a novel vinyl copolymer containing silicones having in its molecule a constituent unit of the formula (I):
can be easily prepared.

The particular polymerizable monomer used is selected in such a way that the present vinyl copolymer contains in its molecule at least one constituent unit of either one of the following:

\[
\frac{R_1^1 R_2^2 \text{SiO}_{d-m-n}}{2}
\]

wherein \( Y \) is \( R^2 \) or a monovalent hydrocarbon residue; \( Z \) is a monovalent hydrocarbon residue; \( n \) is a positive number of at least 2 in formula (II) and of at least 1 in formula (III); \( a \) is 1 or 2; and \( R^2 \) has the same meaning as defined hereinbefore, including the exception made for \( A \) which cannot be

\[
-\text{C-O-R}^5^-
\]

in formula (III).

The present methods are quite suitable for the industrial scale production of the present vinyl copolymers because the required materials are easily available or prepared as desired and reaction speed and reaction yield are excellent in each reaction step involve.

Furthermore, the present vinyl copolymers thus obtained have unique combination of properties of excellent water resistance, weather resistance and oxygen permeability derived from the presence of siloxane-silicon bonding, excellent adhesion toward various substrate materials due to the presence of urethane bonding, and desired properties coming from the exaggerated cohesive power. Therefore, the present vinyl polymers are quite useful in various technical fields including lens and other molding products, paints and various industrial resins.

The invention shall be now more fully explained in the following examples. Unless otherwise being stated, all parts and % are by weight.
Manufacturing Example 1

Into a 4-necked flask fitted with a stirrer, a reflux condenser and a dropping funnel, were placed 424 parts of 1,3,5,7-tetramethyl-3,5,7-tripropyl-1-(γ-hydroxypropyl) cyclotetrasiloxane and 60 parts of butyl acetate and the mixture was maintained at 20-25°C.

To this, were dropwise added 111 parts of methacryloyl isocyanate at a constant speed in 30 minutes and after completion of said addition, the mixture was maintained at a room temperature for 3 hours and then stirred at 50°C under 5 mmHg pressure for 1 hour to remove butyl acetate out of the system. Thus obtained product was confirmed to be of the structure A:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2=\text{C} & \quad \text{C}_3\text{H}_7 \\
\text{C-N-C-O-} & \quad \text{Si-\{OSi(CH}_3\}_3\text{O}} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

from infra-red absorption spectrum analysis and mass spectrum analysis thereof, and was a slightly viscous, clear liquid; the purity determined by quantitative analysis by gas chromatography means 98.8%; refractive index n\text{o}^25 = 1.454; and the viscosity 1.8 x 10^{-1} Pa.s.

Manufacturing Example 2

Into a similar reaction vessel as used in Example 1, were placed 280 parts of bis (trimethylsiloxy)methyl-3-hydroxypropyl silane and maintained at 20-25°C. To this, were dropwise added 111 parts of methacryloyl isocyanate in 30 minutes at a constant speed under oxygen stream and the mixture was then maintained at 20-25°C for 1 hour to obtain the reaction product, which was confirmed by infra-red spectrum analysis to be silicon-containing polymerizable monomer of the formula (B):

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2=\text{C} & \quad \text{O} \\
\text{C-N-C-O-} & \quad \text{Si-\{OSi(CH}_3\}_3\text{O}} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

The product was a slightly viscous, clear liquid; the purity confirmed by gas chromatography 98.5%; and the viscosity 4.5 x 10^{-1} Pa.s.

Manufacturing Example 3

Into a similar reaction vessel as used in Manufacturing Example 1, were placed 424 parts of 1,3,5,7-tetramethyl-3,5,7-tripropyl-1-(γ-hydroxypropyl) cyclotetrasiloxane, 0.5 part of dibutyl tin dilaurate and 100 parts of xylene and the mixture was maintained at 80-85°C.

To this, was dropwise added under oxygen stream and at a constant speed a mixture of 155 parts of methacrylic acid 2-isocyanate ethyl and 0.06 part of 2,6-dimethyl-4-methylphenol in 30 minutes and the mixture was maintained at 80-85°C for 1 hour and then stirred at 80°C under 0.67 kPa pressure for 1 hour to remove xylene off.

Thus obtained product was confirmed by infra-red spectrum analysis to be the polymerizable monomer (c) of the following formula:
and was a slightly viscous, clear liquid; the purity confirmed by gas chromatography 99.1%; the refractive index $n_5^{20} = 1.4424$; and the viscosity $2.0 \times 10^{-1}$ Pa.s.

Example 1

Into a reaction vessel fitted with a stirrer, a thermometer, a reflux condenser, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 40 parts of the polymerizable monomer (A) obtained in Manufacturing Example 1, and the mixture was heated, under $N_2$ stream, to 90 °C. To this, a mixture (a) of 100 parts of methyl methacrylate, 60 parts of n-butyl acrylate and 3.0 parts of 2,2'-azobisisobutyronitrile was dropwise added from the dropping funnel at a constant speed in 3 hours. After completion of said addition, the combined mixture was maintained at 90 °C for 30 minutes and then added dropwise with a mixture of 1 part of t-butyl peroxy-2-ethyl hexanoate and 10 parts of xylene.

Thereafter, the mixture was maintained at 90 °C for 5 hours to obtain a resinous solution (I).

Using a benzene-methanol purification method, a sample of purified copolymer was obtained from said resinous solution (I) and subjected to $^{1}H$-NMR analysis. The monomer composition was as follows:

Polymerizable silicon-containing monomer (A) : methyl methacrylate : n-butyl acrylate = 18.4:52.8:28.8 (weight % calculation).

Molecular weight of said copolymer was analyzed by GPC means, and the result was as follows:

| number average molecular weight | 10100 |
| weight average molecular weight | 59300 |

Example 2

Into a similar reaction vessel as used in Example 1, were placed 100 parts of xylene and 10 parts of methacryloyl isocyanate and the mixture was heated under $N_2$ stream to 90 °C. To this, a mixture (b) of 60 parts of methyl methacrylate, 30 parts of n-butyl acrylate and 1.5 parts of 2,2'-azobisisobutyronitrile was dropwise added from the dropping funnel in 3 hours and the combined mixture was then maintained at 90 °C for 5 hours. Thereafter, 76.4 parts of 1,3,5,7-tetramethyl-3,5,7-tri(propyl-1-(γ-hydroxypropyl) cyclotetrasiloxane were dropwise added in 1 hour and the combined mixture was maintained at a room temperature for 2 hours. IR spectrum showed no presence of isocyanate groups in the reaction mixture.

From a part of thus obtained resinous solution (II), purified copolymer was recovered and analyzed as in Example 1.

Monomer composition:

polymerizable silicon-containing monomer : methyl methacrylate : n-butyl acrylate = 32.3:45.1:22.6 (weight % calculation)

| number average molecular weight | 13600 |
| weight average molecular weight | 88700 |
Example 3

Into a test tube, were placed 50g of polymerizable monomer containing silicones (A) obtained in Manufacturing Example 1, 25g of methyl methacrylate, 10g of ethyleneglycol monomethacrylate, 5g of ethyleneglycol dimethacrylate, 10g of ethyl methacrylate and 0.1g of azobisisobutyronitrile and after purging air with nitrogen gas, the tube was sealed. The content was polymerized by UV irradiation at 40°C for 18 hours and then by heating at 110°C for 6 hours to obtain colorless, solid stick, silicon-containing vinyl copolymer

Example 4

Into a similar reaction vessel as used in Example 1, were placed 100 parts of xylene and the content was, while introducing N₂ gas, heated to 90°C. To this, the following mixture (c) was dropwise added in 4 hours.

<table>
<thead>
<tr>
<th>polymerizable monomer containing silicones (B) obtained in Manufacturing Example 2</th>
<th>60 parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl methacrylate</td>
<td>100</td>
</tr>
<tr>
<td>2-ethyl hexyl acrylate</td>
<td>40</td>
</tr>
<tr>
<td>t-butyleroxy-2-hexanoate</td>
<td>3</td>
</tr>
</tbody>
</table>

After completion of said addition, the mixture was maintained at 90°C for 30 minutes and treated as in Example 1 to obtain a resinous solution (III). The contained copolymer was purified and analyzed as in Example 1.

Monomer composition:

polymerizable silicon-containing monomer (B) : methyl methacrylate : 2-ethyl hexyl acrylate = 28.5:51.8:19.7 (weight % calculation)

<table>
<thead>
<tr>
<th>number average molecular weight</th>
<th>15700</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight average molecular weight</td>
<td>88800</td>
</tr>
</tbody>
</table>

Example 5

Into a similar reaction vessel as used in Example 1, were placed 100 parts of xylene and the content was, while introducing N₂ gas, heated to 90°C. To this, the following mixture (d) was dropwise added in 3 hours.

Mixture (d):

<table>
<thead>
<tr>
<th>polymerizable silicon-containing monomer (C) obtained in Manufacturing Example 3</th>
<th>60 parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl methacrylate</td>
<td>100</td>
</tr>
<tr>
<td>butyl acrylate</td>
<td>40</td>
</tr>
<tr>
<td>2,2’-azobisisobutyronitrile</td>
<td>3.0</td>
</tr>
</tbody>
</table>

After completion of said addition, the combined mixture was maintained at 90°C for 30 minutes and thereafter treated in the same way as in Example 1 to obtain a resinous solution (IV). The contained copolymer was purified and analyzed as in Example 1. The results are as follows:

polymerizable silicon-containing monomer (C) : methyl : methacrylate : butyl acrylate = 27.9:52.1:20.0

(weight % calculation)
Claims

1. A silicon-containing vinyl copolymer, characterized in that said copolymer has in its molecule
   - a constituent unit of formula (I):

   \[
   \frac{R_1^m R_2^n SiO_{4-m-n}}{2}
   \]

   (I)

   wherein \( R_1^1 \) is a substituted or unsubstituted monovalent hydrocarbon residue; \( R_2^2 \) is

   \[
   \begin{array}{c}
   \text{R}^3 \\
   -\text{CH}_2-\text{C}- \\
   \text{A-NH-B-R}^4- \end{array}
   \]

   \( R_3^3 \) is hydrogen or methyl; \( R_4^4 \) is a substituted or unsubstituted alkylene directly bonded to a silicon
   atom; \( m \) and \( n \) each is a positive number, which will fulfill the requirement of \( 2 \leq m + n \leq 4 \);
   \( A \) is a direct bond,

   \[
   \begin{array}{c}
   \text{O C-O-R}^5- \\
   \text{O C-} \\
   \text{O C-NH-R}^6- \\
   \text{O} \end{array}
   \]

   phenylene or a substituted phenylene; \( B \) is

   \[
   \begin{array}{c}
   \text{O OH} \\
   \text{O C-O-} \\
   \text{O C-N-} \end{array}
   \]

   \( R_5^5 \) and \( R_6^6 \) each represents an alkylene;
   provided that when \( A \) is

   \[
   \begin{array}{c}
   \text{O C-O-R}^5- \\
   \text{O} \end{array}
   \]

   \( m + n \) is 2, said constituent unit of formula (I) being selected from formula (II), (III) or (IV):
WHEREIN \( R^2 \) HAS THE SAME MEANING AS DEFINED BEFORE, EXCEPT THAT \( A \) CANNOT BE

\[ \sigma - \frac{\alpha}{\beta} \]
R³
\begin{align*}
| & \text{-CH₂-C-} \\
\text{A-NH-B-R⁴-} & \\
\end{align*}

steht, worin
R³ für Wasserstoff oder Methyl steht;
R⁴ für einen substituierten oder unsubstituierten Alkylen-rest steht, der direkt an ein Siliciumatom gebunden ist;
m und n jeweils für eine positive Zahl stehen, die das Kriterium 2 ≤ m + n ≤ 4 erfüllen;
A für eine Direktbindung,

\begin{align*}
-\text{C-O-R⁵}, & \quad -\text{C-}, \quad -\text{C-NH-R⁶-}, \\
\text{O} & \quad \text{O} & \quad \text{O}
\end{align*}

Phenylen oder substituiertes Phenyl steht;
B für

\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{H} \\
\text{-C-O-} & \quad \text{oder} & \quad \text{-C-N-}
\end{align*}

steht;
R⁵ und R⁶ jeweils für Alkylen stehen;
mit der Maßgabe, daß, wenn A für

\begin{align*}
\text{-C-O-R⁵} \\
\text{O}
\end{align*}

steht und
und m + n für 2 steht, die Teileinheit der Formel (I) ausgewählt ist unter den Formeln (II), (III) oder (IV):
worin

\[ R^2 \text{ die oben angegebenen Bedeutungen besitzt, mit Ausnahme davon, daß } A \text{ nicht für } \]

\[ \text{C} = \text{O} = R^5 \]

in Formel (III) stehen kann;

- Y für R² oder für einen monovalenten Kohlenwasserstoffrest steht;

- Z für einen monovalenten Kohlenwasserstoffrest steht; n für

- eine positive Zahl von wenigstens 2 in Formel (II) und von wenigstens 1 in Formel (III) steht; und

- a für 1 oder 2 steht; und

- eine Teilleinheit von wenigstens einem anderen α,β-ethylenisch ungesättigten Monomer aufweist.

Reverdications

1. Un copolymère vinylique contenant du silicium, caractérisé en ce que ledit copolymère a dans sa molécule

- une unité de constitution de formule (I):

\[ R^1_m R^2_n SiO \frac{4-m-n}{2} \]

où R¹ est un résidu hydrocarbure monovalent substitué ou non substitué; R² est

\[ R^3 \]

\[ -CH_2-C- \]

\[ A-NH-B-R^4 - \]

R³ est un hydrogène ou un méthyle; R⁴ est un alkylène substitué ou non substitué directement lié à un atome de silicium; m et n sont chacun un nombre positif, dont la somme remplit la condition suivante : 2 ≤ m + n ≤ 4.
A est une liaison directe,

\[ \begin{array}{c}
\text{C} - \text{O} - \text{R}^5 \tau \\
\| \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{C} \quad \text{C} - \text{NH} - \text{R}^6 \tau \\
\| \\
\text{O} \quad \text{O}
\end{array} \]

un phényle ou un phényléne substitué; B est

\[ \begin{array}{c}
\text{O} \\
\| \\
-\text{C} - \text{O} - \\
\text{O} \\
\| \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{O} \\
\| \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{O} \\
\| \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{C} - \text{N} - \\
\|
\end{array} \]

\( R^5 \) et \( R^6 \) représentent chacun un alkylène;
pour autant que quand A est

\[ \begin{array}{c}
\text{C} - \text{O} - \text{R}^5 \tau \\
\| \\
\text{O}
\end{array} \]

\( m + n \) est égal à 2,
ladite unité de constitution de formule (I) étant sélectionnée à partir des formules (II), (III) ou (IV);

\[ \begin{array}{c}
\text{Y} \\
\| \\
\text{R}^2 - \text{Si} - (\text{O} \text{Si})^n \\
\| \\
\text{Y} \\
\text{O}
\end{array} \quad \text{(II)} \]

\[ \begin{array}{c}
\text{Z} \\
\| \\
\text{R}^2 - \text{Si} - (\text{O} \text{Si})^n - \text{Z} \\
\| \\
\text{Y} \\
\text{Z} \\
\| \\
\text{Y}
\end{array} \quad \text{(III)} \]

\[ \begin{array}{c}
\text{Y} \\
\| \\
\text{R}^2 - \text{Si} - \text{Y} \\
\| \\
\text{Y}
\end{array} \quad \text{(IV)} \]

où \( R^2 \) a la même signification que celle précédemment définie, excepté que A ne peut être
- C-CO-R^5

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
</table>

5
dans la formule (III);
Y est R^2 ou un résidu hydrocarbure monovalent; Z est un résidu hydrocarbure monovalent; n est un nombre positif au moins égal à 2 dans la formule (II) et au moins égal à 1 dans la formule (III);
et a est égal à 1 ou 2; et

10 - une unité de constitution d'au moins un autre monomère insaturé éthylénique α,β.