

## METHOD FOR PRODUCING SILICONE HYDROGEL CONTACT LENSES

The present invention is related to a method for producing silicone hydrogel contact lenses, in particular silicone hydrogel contact lenses having an inherently wettable surface.

### BACKGROUND OF THE INVENTION

In recent years, silicone hydrogel contact lenses become more and more popular because of their high oxygen permeability and comfort. Most commercially-available silicone hydrogel contact lenses are produced economically in large number in a manufacturing method which generally includes a molding process according to a conventional cast molding technique involving use of disposable plastic molds typically consisting of two mold halves and use of a mixture of vinylic monomers and at least one vinylic crosslinker. Following the molding process, molds are opened and the cast-molded lenses need to be removed from the molds and be subjected to various post-molding processes including extraction, hydration, packaging, and sterilization, etc.

Typically, after opening the disposable molds, each of the cast-molded silicone hydrogel contact lenses adheres to one of the two mold halves of each mold. The adhesion of a molded silicone hydrogel contact lens to a mold half can be quite strong. Removal (or delensing) of molded lenses from mold halves by force may cause damages to the molded lenses (e.g., completely or partial tears). Further, the lenses removed (delensed) from mold halves can adhere to itself (curl) and would be difficult to be handled. Consequently, those mold halves having a lens adhered thereon are subjected to extraction with an organic solvent in an extraction tank and subsequently to hydration in water in a hydration tank. Those hydrated lenses are then removed from those mold halves and further processed.

Because mold halves can take up valuable space in an extraction or hydration tank, it would be desirable to remove molded lenses from the lens-adhering mold halves before extraction and hydration processes. The U.S. Pat. Appl. Pub. No. 2018-0104919 A1 and the commonly-owned co-pending U.S. Pat. Appl. No. 15/841,647 disclose an apparatus and a method for removing molded lenses from mold halves by applying an ultrasonic vibrational energy to at least one area of the non-optical surface of a mold half having the molded silicone hydrogel contact lens adhered thereon. Although this approach can be used in removing silicone hydrogel contact lenses from mold halves, there are some limitations. For example, the higher level of ultrasonic vibrational energy might be required to remove silicone hydrogel contact lenses from mold halves. However, a higher ultrasonic vibrational energy could cause damages to the molded silicone

hydrogel contact lenses and lower the product yield. Further, it may not have adequate efficiency and consistency in removing silicone hydrogel contact lenses from mold halves.

Therefore, there is still a need for a delensing process which can remove silicone hydrogel contact lenses from mold halves in a relatively efficient and consistent manner and which can be easily implemented in a production environment.

#### SUMMARY OF THE INVENTION

The invention is directed to a method for producing silicone hydrogel contact lenses, comprising the step of: (1) obtaining a polymerizable composition which is clear at room temperature, wherein the polymerizable composition comprises (a) at least one siloxane-containing vinylic monomer, (b) at least one first polysiloxane vinylic crosslinker, (c) at least one hydrophilic N-vinyl amide monomer, (d) from about 5% to about 15% by weight of a hydrophobic acrylic monomer relative to the total weight of the polymerizable composition, wherein the hydrophobic acrylic monomer is capable of forming a homopolymer having a glass-transition temperature  $T_g$  of at least about 60°C, wherein the hydrophobic acrylic monomer is capable of dissolving components (a) to (c) to form a solution with a concentration of at least about 5% by weight, (e) from about 4% to about 16% by weight of at least one organic solvent having 2 to 8 carbon atoms relative to the total weight of the polymerizable composition, (f) at least one non-silicone vinylic crosslinker, and (g) at least one free radical initiator, wherein the sum of the amounts of components (a) to (c) is at least about 60% by weight relative to the total weight of the polymerizable composition, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.24 per 100 grams of the polymerizable composition; (2) introducing the polymerizable composition into a lens mold, wherein the lens mold comprises a male mold half having a first molding surface and a female mold half having a second molding surface, wherein the male and female mold halves are configured to receive each other such that a mold cavity is formed between the first and second molding surfaces when the mold is closed; (3) curing thermally or actinically the polymerizable composition in the lens mold to form an unprocessed silicone hydrogel lens precursor; (4) separating the mold into the male and female mold halves, with the unprocessed silicone hydrogel adhered on a lens-adhered mold half which is one of the male and female mold halves; (5) removing the unprocessed silicone hydrogel lens precursor from the lens-adhered mold half before the unprocessed silicone hydrogel lens precursor is contacted with water or any liquid, wherein the step of removing is performed by (a) bringing a ultrasonic horn in direct contact with at least one area of a non-optical surface of the lens-adhered mold half having the unprocessed silicone hydrogel lens

precursor attached thereon and (b) applying a ultrasonic vibrational energy of from about 0.2 to about 18 J to the at least one area of the non-optical surface of the lens-adhered mold half having the unprocessed silicone hydrogel lens precursor attached thereon so as to remove the unprocessed silicone hydrogel lens precursor from the lens-adhered mold half; and (6) subjecting the unprocessed silicone hydrogel lens precursor to one or more post-molding processes selected from the group consisting of extraction, hydration, packaging, sterilization, and combinations thereof.

The present invention provides the foregoing and other features, and the advantages of the invention will become further apparent from the following detailed description of the presently preferred embodiments, read in conjunction with the accompanying figures. The detailed description and figures are merely illustrative of the invention and do not limit the scope of the invention, which is defined by the appended claims and equivalents thereof.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a preferred mold.

FIG. 2 illustrates schematically a preferred process for separating the male and female mold halves of a mold.

FIG. 3 illustrates an ultrasonic welding system.

FIG. 4 illustrates a flat ultrasonic horn seated on extended flat edge surround the outer concave surface of the male mold half.

FIG. 5A and 5B illustrate a convex ultrasonic horn is seated within the outer concave portion of male half mold half.

FIG. 6 illustrates a flat ultrasonic horn is sized to be approximately the outer diameter of the female mold half.

FIG. 7A and 7B illustrate a concave ultrasonic horn seated within the outer convex portion of female half mold half.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Generally, the nomenclature used herein and the laboratory procedures are well known and commonly employed in the art. Conventional methods are used for these procedures, such as those provided in the art and various general references. Where a term is provided in the singular, the inventors also contemplate the plural of that term. The nomenclature used herein and the laboratory procedures

described below are those well-known and commonly employed in the art.

"About" as used herein in this application means that a number, which is referred to as "about", comprises the recited number plus or minus 1-10% of that recited number.

A "hydrogel" or "hydrogel material" refers to a crosslinked polymeric material which has three-dimensional polymer networks (i.e., polymer matrix), is insoluble in water, but can hold at least 10% by weight of water in its polymer matrix when it is fully hydrated (or equilibrated).

A "silicone hydrogel" refers to a silicone-containing hydrogel obtained by copolymerization of a polymerizable composition comprising at least one silicone-containing monomer or at least one silicone-containing macromer or at least one crosslinkable silicone-containing prepolymer.

As used in this application, the term "non-silicone hydrogel" refers to a hydrogel that is theoretically free of silicon.

"Hydrophilic," as used herein, describes a material or portion thereof that will more readily associate with water than with lipids.

The term "room temperature" refers to a temperature of about 21°C to about 27°C.

The term "soluble", in reference to a compound or material in a solvent, means that the compound or material can be dissolved in the solvent to give a solution with a concentration of at least about 0.5% by weight at room temperature.

The term "insoluble", in reference to a compound or material in a solvent, means that the compound or material can be dissolved in the solvent to give a solution with a concentration of less than 0.05% by weight at room temperature.

A "vinyl monomer" refers to a compound that has one sole ethylenically unsaturated group, is soluble in a solvent, and can be polymerized actinically or thermally.

As used in this application, the term "ethylenically unsaturated group" is employed herein in a broad sense and is intended to encompass any groups containing at least one  $>C=C<$  group. Exemplary ethylenically unsaturated groups include without limitation

(meth)acryloyl ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$  and/or  $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}=\text{CH}_2$ ), allyl, vinyl, styrenyl, or other  $C=C$  containing groups.

An "acrylic monomer" refers to a vinyl monomer having one sole (meth)acryloyl group. Examples of acrylic monomers includes (meth)acryloxy [or(meth)acryloyloxy] monomers and (meth)acrylamido monomers.

An "(meth)acryloxy monomer" or "(meth)acryloyloxy monomer" refers to a vinyl monomer having one sole group of  $-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$  or  $-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}=\text{CH}_2$ .

An "(meth)acrylamido monomer" refers to a vinyl monomer having one sole

group of  $-\text{NR}^0-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$  or  $-\text{NR}^0-\overset{\text{O}}{\text{C}}-\text{CH}=\text{CH}_2$  in which  $\text{R}^0$  is H or  $\text{C}_1\text{-C}_4$  alkyl.

The term “(meth)acrylamide” refers to methacrylamide and/or acrylamide.

The term “(meth)acrylate” refers to methacrylate and/or acrylate.

An “N-vinyl amide monomer” refers to an amide compound having a vinyl group ( $-\text{CH}=\text{CH}_2$ ) that is directly attached to the nitrogen atom of the amide group.

The term “terminal (meth)acryloyl group” refers to one (meth)acryloyl group at one of the two ends of the main chain (or backbone) of an organic compound as known to a person skilled in the art.

The term “(meth)acrylamide” refers to methacrylamide and/or acrylamide.

The term “(meth)acrylate” refers to methacrylate and/or acrylate.

As used herein, “actinically” in reference to curing, crosslinking or polymerizing of a polymerizable composition, a prepolymer or a material means that the curing (e.g., crosslinked and/or polymerized) is performed by actinic irradiation, such as, for example, UV/visible irradiation, ionizing radiation (e.g. gamma ray or X-ray irradiation), microwave irradiation, and the like. Thermal curing or actinic curing methods are well-known to a person skilled in the art.

A “hydrophilic vinylic monomer”, a “hydrophilic acrylic monomer”, a “hydrophilic (meth)acryloxy monomer”, or a “hydrophilic (meth)acrylamido monomer”, as used herein, respectively refers to a vinylic monomer, an acrylic monomer, a (meth)acryloxy monomer, or a (meth)acrylamido monomer, which typically yields a homopolymer that is water-soluble or can absorb at least 10 percent by weight of water.

A “hydrophobic vinylic monomer”, a “hydrophobic acrylic monomer”, a “hydrophobic (meth)acryloxy monomer”, or a “hydrophobic (meth)acrylamido monomer”, as used herein, respectively refers to a vinylic monomer, an acrylic monomer, a (meth)acryloxy monomer, or a (meth)acrylamido monomer, which typically yields a homopolymer that is insoluble in water and can absorb less than 10% by weight of water.

As used in this application, the term “vinylic crosslinker” refers to an organic compound having at least two ethylenically unsaturated groups. A “vinylic crosslinking agent” refers to a vinylic crosslinker having a molecular weight of 700 Daltons or less.

As used in this application, the term “polymer” means a material formed by polymerizing/crosslinking one or more monomers or macromers or prepolymers or combinations thereof.

As used in this application, the term “molecular weight” of a polymeric material (including monomeric or macromeric materials) refers to the number average molecular weight unless otherwise specifically noted or unless testing conditions indicate otherwise.

A "polysiloxane segment" refers to a polymer chain consisting of at least three consecutively- and directly-linked siloxane units (divalent radical) each independent of



one another having a formula of  $\begin{array}{c} \text{R}_1' \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{R}_2' \end{array}$  in which  $\text{R}_1'$  and  $\text{R}_2'$  are two substituents independently selected from the group consisting of  $\text{C}_1$ - $\text{C}_{10}$  alkyl,  $\text{C}_1$ - $\text{C}_4$ -alkyl- or  $\text{C}_1$ - $\text{C}_4$ -alkoxy-substituted phenyl,  $\text{C}_1$ - $\text{C}_{10}$  fluoroalkyl,  $\text{C}_1$ - $\text{C}_{10}$  fluoroether,  $\text{C}_6$ - $\text{C}_{18}$  aryl radical,  $-\text{alk}-(\text{OC}_2\text{H}_4)_{\gamma 1}-\text{OR}^\circ$  (in which alk is  $\text{C}_1$ - $\text{C}_6$  alkyl diradical,  $\text{R}^\circ$  is H or  $\text{C}_1$ - $\text{C}_4$  alkyl and  $\gamma 1$  is an integer from 1 to 10), a  $\text{C}_2$ - $\text{C}_{40}$  organic radical having at least one functional group selected from the group consisting of hydroxyl group ( $-\text{OH}$ ), carboxyl group ( $-\text{COOH}$ ),  $-\text{NR}_3'\text{R}_4'$ , amino linkages of  $-\text{NR}_3'-$ , amide linkages of  $-\text{CONR}_3'-$ , amide of  $-\text{CONR}_3'\text{R}_4'$ , urethane linkages of  $-\text{OCONH}-$ , and  $\text{C}_1$ - $\text{C}_4$  alkoxy group, or a linear hydrophilic polymer chain, in which  $\text{R}_3'$  and  $\text{R}_4'$  independent of each other are hydrogen or a  $\text{C}_1$ - $\text{C}_{15}$  alkyl.

A "polysiloxane vinylic crosslinker" refers to a compound comprising at least one polysiloxane segment and at least two ethylenically-unsaturated groups.

A "linear polysiloxane vinylic crosslinker" refers to a compound comprising a main chain which includes at least one polysiloxane segment and is terminated with one ethylenically-unsaturated group at each of the two ends of the main chain.

A "chain-extended polysiloxane vinylic crosslinker" refers to a compound comprising at least two ethylenically-unsaturated groups and at least two polysiloxane segments each pair of which are linked by one divalent radical.

The term "fluid" as used herein indicates that a material is capable of flowing like a liquid.

As used in this application, the term "clear" in reference to a polymerizable composition means that the polymerizable composition is a transparent solution or liquid mixture (i.e., having a light transmissibility of 85% or greater, preferably 90% or greater in the range between 400 to 700 nm).

The term "alkyl" refers to a monovalent radical obtained by removing a hydrogen atom from a linear or branched alkane compound. An alkyl group (radical) forms one bond with one other group in an organic compound.

The term "alkylene divalent group" or "alkylene diradical" or "alkyl diradical" interchangeably refers to a divalent radical obtained by removing one hydrogen atom from an alkyl. An alkylene divalent group forms two bonds with other groups in an organic compound.

The term "alkoxy" or "alkoxyl" refers to a monovalent radical obtained by removing the hydrogen atom from the hydroxyl group of a linear or branched alkyl alcohol. An

alkoxy group (radical) forms one bond with one other group in an organic compound.

In this application, the term “substituted” in reference to an alkyl diradical or an alkyl radical means that the alkyl diradical or the alkyl radical comprises at least one substituent which replaces one hydrogen atom of the alkyl diradical or the alkyl radical and is selected from the group consisting of hydroxyl (-OH), carboxyl (-COOH), -NH<sub>2</sub>, sulfhydryl (-SH), C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> alkylthio (alkyl sulfide), C<sub>1</sub>-C<sub>4</sub> acylamino, C<sub>1</sub>-C<sub>4</sub> alkylamino, di-C<sub>1</sub>-C<sub>4</sub> alkylamino, and combinations thereof.

A free radical initiator can be either a photoinitiator or a thermal initiator. A “photoinitiator” refers to a chemical that initiates free radical crosslinking/polymerizing reaction by the use of light. A “thermal initiator” refers to a chemical that initiates free radical crosslinking/polymerizing reaction by the use of heat energy.

“Post-curing surface treatment”, in reference to a silicone hydrogel bulk material or a SiHy contact lens, means a surface treatment process that is performed after the silicone hydrogel bulk material or the SiHy contact lens is formed by curing (i.e., thermally or actinically polymerizing) a SiHy lens formulation. A “SiHy lens formulation” refers to a polymerizable composition that comprises all necessary polymerizable components for producing a SiHy contact lens or a SiHy lens bulk material as well known to a person skilled in the art.

A “non-optical surface of a mold half” refers to mold half surface which does not contact the lens forming material during cast molding of a contact lens.

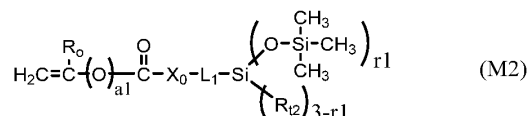
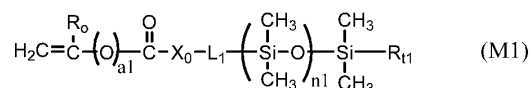
The invention is generally related to a contact lens manufacturing method comprising a process for removing unprocessed molded silicone hydrogel contact lenses from mold halves in a relatively efficient and consistent manner. The invention is partly based on the discovery that in combination with use of a relatively low ultrasonic vibration energy for delensing, higher efficiency and consistency in removing unprocessed molded silicone hydrogel contact lenses from mold halves can be achieved by using a hydrophobic acrylic monomer as a blending vinylic monomer (i.e., a reactive diluent) and an organic solvent (i.e., a non-reactive diluent) in such a way that weight ratio of the hydrophobic acrylic monomer (reactive diluent) over the sum of the hydrophobic acrylic monomer (reactive diluent) and the organic solvent (non-reactive diluent) is at least 0.24 per gram of the polymerizable composition. This method of the invention can be easily implemented in a production environment for enhancing the production yield.

The present invention provides a method for producing silicone hydrogel contact lenses, comprising the step of: (1) obtaining a polymerizable composition which is clear at room temperature, wherein the polymerizable composition comprises (a) at least one siloxane-containing vinylic monomer, (b) at least one first polysiloxane vinylic crosslinker,

(c) at least one hydrophilic N-vinyl amide monomer, (d) from about 5% to about 15% (preferably from about 6% to about 14%, more preferably from about 7% to about 13%, even more preferably from about 8% to about 12%) by weight of at least one hydrophobic acrylic monomer relative to the total weight of the polymerizable composition, wherein the hydrophobic acrylic monomer is capable of forming a homopolymer having a glass-transition temperature  $T_g$  of at least about 60°C (preferably at least about 70°C, more preferably at least about 80°C, even more preferably at least about 90°C), wherein the hydrophobic acrylic monomer is capable of dissolving components (a) to (c) to form a solution with a concentration of at least about 5% by weight, (e) from about 4% to about 16% (preferably from about 5% to about 15%, more preferably from about 6% to about 14%, even more preferably from about 6% to 12%) by weight of at least one organic solvent having 2 to 8 carbon atoms (preferably having 3 to 5 carbon atoms) relative to the total weight of the polymerizable composition, (f) at least one non-silicone vinyl crosslinker, and (g) at least one free radical initiator, wherein the sum of the amounts of components (a) to (c) is at least about 60%, (preferably at least about 65%, more preferably at least about 70%, even more preferably at least about 75%) by weight relative to the total weight of the polymerizable composition, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.24 (preferably at least 0.35, more preferably at least 0.45, even more preferably at least 0.55) per 100 grams of the polymerizable composition; (2) introducing the polymerizable composition into a lens mold, wherein the lens mold comprises a male mold half having a first molding surface and a female mold half having a second molding surface, wherein the male and female mold halves are configured to receive each other such that a mold cavity is formed between the first and second molding surfaces when the mold is closed; (3) curing thermally or actinically the polymerizable composition in the lens mold to form an unprocessed silicone hydrogel lens precursor within the lens mold; (4) separating the mold into the male and female mold halves, with the unprocessed silicone hydrogel adhered on a lens-adhered mold half which is one of the male and female mold halves; (5) removing the unprocessed silicone hydrogel lens precursor from the lens-adhered mold half before the unprocessed silicone hydrogel lens precursor is contacted with water or any liquid, wherein the step of removing is performed by (a) bringing an ultrasonic horn in direct contact with at least one area of a non-optical surface of the lens-adhered mold half having the unprocessed silicone hydrogel lens precursor attached thereon and (b) applying an ultrasonic vibrational energy of from about 0.2 to about 18 J to the at least one area of the non-optical surface of the lens-adhered mold half having the unprocessed silicone hydrogel lens precursor attached thereon so as to remove the unprocessed

silicone hydrogel lens precursor from the lens-adhered mold half; and (6) subjecting the unprocessed silicone hydrogel lens precursor to one or more post-molding processes selected from the group consisting of extraction, hydration, packaging, sterilization, and combinations thereof.

In accordance with the invention, a siloxane-containing vinylic monomer can be any vinylic monomer of formula (M1) or (M2)



in which: a1 is zero or 1; R<sub>0</sub> is H or methyl; X<sub>0</sub> is O or NR<sub>1</sub>; L<sub>1</sub> is a C<sub>2</sub>-C<sub>8</sub> alkylene divalent radical or a divalent radical of -L<sub>1</sub>'-X<sub>1</sub>-L<sub>1</sub>"-, -(C<sub>2</sub>H<sub>4</sub>O)<sub>q1</sub>-L<sub>1</sub>"-, -(C<sub>2</sub>H<sub>4</sub>O)<sub>q1</sub>-CONH-L<sub>1</sub>"-, -L<sub>1</sub>'-NHCOO-(C<sub>2</sub>H<sub>4</sub>O)<sub>q1</sub>-L<sub>1</sub>"-, -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-X<sub>1</sub>'-(C<sub>2</sub>H<sub>4</sub>O)<sub>q2</sub>-L<sub>1</sub>"-, -L<sub>1</sub>'-X<sub>1</sub>'-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-L<sub>1</sub>"-, or -(C<sub>2</sub>H<sub>4</sub>O)<sub>q1</sub>-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-L<sub>1</sub>"-; L<sub>1</sub>' is a C<sub>2</sub>-C<sub>8</sub> alkylene divalent radical which has zero or one hydroxyl group; L<sub>1</sub>" is C<sub>3</sub>-C<sub>8</sub> alkylene divalent radical which has zero or one hydroxyl group; X<sub>1</sub> is O, NR<sub>1</sub>, NHCOO, OCONH, CONR<sub>1</sub>, or NR<sub>1</sub>CO; R<sub>1</sub> is H or a C<sub>1</sub>-C<sub>4</sub> alkyl having 0 to 2 hydroxyl group; R<sub>t1</sub> and R<sub>t2</sub> independent of each other are a C<sub>1</sub>-C<sub>4</sub> alkyl; X<sub>1</sub>' is O or NR<sub>1</sub>; q<sub>1</sub> is an integer of 1 to 20; q<sub>2</sub> is an integer of 0 to 20; n<sub>1</sub> is an integer of 3 to 25; and r<sub>1</sub> is an integer of 2 or 3.

Examples of preferred siloxane-containing vinylic monomers of formula (M1) include without limitation α-(meth)acryloxypropyl terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-(meth)acryloxy-2-hydroxypropyloxypropyl terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-(2-hydroxyl-methacryloxypropyloxypropyl)-ω-C<sub>1</sub>-C<sub>4</sub>-alkyl-decamethylpentasiloxane, α-[3-(meth)acryloxyethoxy-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxy-propyloxy-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxyisopropyloxy-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxybutyloxy-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxyethylamino-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxypropylamino-2-hydroxypropyloxypropyl]-terminated ω-C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, α-[3-(meth)acryloxy-

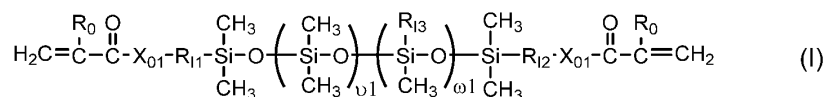
butylamino-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(meth)acryloxy(polyethylenoxy)-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyloxy-ethoxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyl-N-ethylaminopropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyl-aminopropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyloxy-(polyethylenoxy)propyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(meth)acryloylamidopropyloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -N-methyl-(meth)acryloylamidopropyloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidoethoxy-2-hydroxypropyloxy-propyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidopropyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidoisopropoxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidobutyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloylamido-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl polydimethylsiloxane,  $\alpha$ -[3-[N-methyl-(meth)acryloylamido]-2-hydroxypropyloxypropyl] terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, N-methyl-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilane) (meth)acrylamide, N-(2,3-dihydroxypropane)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilane) (meth)acrylamide, (meth)acryloylamidopropyltetra(dimethylsiloxy)dimethylbutylsilane,  $\alpha$ -vinyl carbonate-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl-terminated polydimethylsiloxanes,  $\alpha$ -vinyl carbamate-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl-terminated polydimethylsiloxane, those disclosed in U.S. Pat. Nos. 9097840 and 9103965, and mixtures thereof. The above preferred polysiloxanes vinylic monomers of formula (M1) can be obtained from commercial suppliers (e.g., Shin-Etsu, Gelest, etc.) or prepared according to procedures described in patents, e.g., U.S. Pat. Nos. 5070215, 6166236, 6867245, 8415405, 8475529, 8614261, and 9217813, or by reacting a hydroxyalkyl (meth)acrylate or (meth)acrylamide or a (meth)acryloxypolyethylene glycol with a mono-epoxypropyloxypropyl-terminated polydimethylsiloxane, by reacting glycidyl (meth)acrylate with a mono-carbinol-terminated polydimethylsiloxane, a mono-aminopropyl-terminated polydimethylsiloxane, or a mono-ethylaminopropyl-terminated polydimethylsiloxane, or by reacting isocyanatoethyl (meth)acrylate with a mono-carbinol-terminated polydimethylsiloxane according to coupling reactions well known to a person skilled in the art.

Examples of preferred siloxane-containing vinylic monomers of formula (M2) include without limitation tris(trimethylsilyloxy)silylpropyl (meth)acrylate, [3-(meth)acryloxy-2-hydroxypropyloxy]propylbis(trimethylsilyloxy)methylsilane, [3-(meth)acryloxy-2-hydroxypropyloxy]propylbis(trimethylsilyloxy)butylsilane, 3-(meth)acryloxy-2-(2-hydroxyethoxy)-propyloxypropylbis(trimethylsilyloxy)methylsilane, 3-(meth)acryloxy-2-hydroxypropyloxypropyltris(trimethylsilyloxy)silane, N-[tris(trimethylsilyloxy)silylpropyl]-(meth)acrylamide, N-(2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)propyl)-2-methyl (meth)acrylamide, N-(2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)-propyl) (meth)acrylamide, N-(2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)propyloxy)propyl)-2-methyl acrylamide, N-(2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)propyloxy)propyl) (meth)acrylamide, N-[tris(dimethylpropylsilyloxy)silylpropyl]-(meth)acrylamide, N-[tris(dimethylphenylsilyloxy)silylpropyl] (meth)acrylamide, N-[tris(dimethylethylsilyloxy)silylpropyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)propyl]-2-methyl (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)-propyloxy)propyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)-propyloxy)propyl]-2-methyl (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(tris(trimethylsilyloxy)-silyl)propyloxy)propyl] (meth)acrylamide, N-[2-hydroxy-3-(3-(t-butyl dimethylsilyl)propyloxy)-propyl]-2-methyl (meth)acrylamide, N-[2-hydroxy-3-(3-(t-butyl dimethylsilyl)propyloxy)propyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(t-butyl dimethylsilyl)propyloxy)propyl]-2-methyl (meth)acrylamide, N-2-(meth)acryloxyethyl-O-(methyl-bis-trimethylsiloxy-3-propyl)silyl carbamate, 3-(trimethylsilyl)propylvinyl carbonate, 3-(vinyl oxycarbonylthio)propyl-tris(trimethyl-siloxy)silane, 3-[tris(trimethylsiloxy)silyl]propylvinyl carbamate, 3-[tris(trimethylsiloxy)silyl] propyl allyl carbamate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, those disclosed in U.S. Pat. Nos. 9097840, 9103965 and 9475827, and mixtures thereof. The above preferred siloxane-containing vinylic monomers can be obtained from commercial suppliers or can be prepared according to procedures described in U.S. Pat. Nos. 5070215, 6166236, 7214809, 8475529, 8658748, 9097840, 9103965, and 9475827.

Any suitable polysiloxane vinylic crosslinkers can be used in the invention. Examples of preferred polysiloxane vinylic crosslinkers are di-(meth)acryloyl-terminated polydimethylsiloxanes; di-vinyl carbonate-terminated polydimethylsiloxanes; di-vinyl carbamate-terminated polydimethylsiloxane; N,N,N',N'-tetrakis(3-methacryloxy-2-hydroxypropyl)-alpha,omega-bis-3-aminopropyl-polydimethylsiloxane; polysiloxane-containing macromer selected from the group consisting of Macromer A, Macromer B,

Macromer C, and Macromer D described in U.S. Pat. No. 5760100; polysiloxane-containing macromers disclosed in U.S. Pat. Nos. 4136250, 4153641, 4182822, 4189546, 4343927, 4254248, 4355147, 4276402, 4327203, 4341889, 4486577, 4543398, 4605712, 4661575, 4684538, 4703097, 4833218, 4837289, 4954586, 4954587, 5010141, 5034461, 5070170, 5079319, 5039761, 5346946, 5358995, 5387632, 5416132, 5451617, 5486579, 5962548, 5981675, 6039913, 6762264, 4259467, 4260725, and 4261875.

One class of preferred polysiloxane vinylic crosslinkers are di-(meth)acryloyloxy-terminated polysiloxane vinylic crosslinkers each having dimethylsiloxane units and hydrophilized siloxane units each having one methyl substituent and one monovalent C<sub>4</sub>–C<sub>40</sub> organic radical substituent having 2 to 6 hydroxyl groups as disclosed in U.S. Pat. App. Pub. No. 2017-0166673 A1, more preferably a polysiloxane vinylic crosslinker of formula (I)



in which:

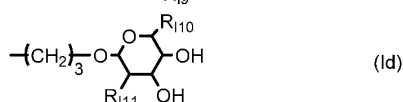
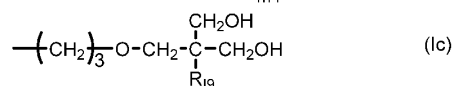
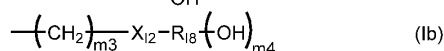
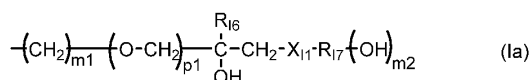
$\omega 1$  is an integer of from 30 to 500 and  $\omega 1$  is an integer of from 1 to 75, provided that  $\omega 1/\omega 1$  is from about 0.035 to about 0.15 (preferably from about 0.040 to about 0.12, even more preferably from about 0.045 to about 0.10);

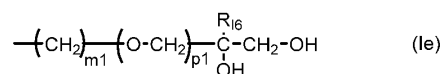
X<sub>01</sub> is O or NR<sub>N</sub> in which R<sub>N</sub> is hydrogen or C<sub>1</sub>–C<sub>10</sub>-alkyl;

R<sub>0</sub> is hydrogen or methyl;

R<sub>11</sub> and R<sub>12</sub> independently of each other are a substituted or unsubstituted C<sub>1</sub>–C<sub>10</sub> alkylene divalent radical or a divalent radical of –R<sub>14</sub>–O–R<sub>15</sub>– in which R<sub>14</sub> and R<sub>15</sub> independently of each other are a substituted or unsubstituted C<sub>1</sub>–C<sub>10</sub> alkylene divalent radical;

R<sub>13</sub> is a monovalent radical of any one of formula (Ia) to (Id)





$p_1$  is zero or 1;  $m_1$  is an integer of 2 to 4;  $m_2$  is an integer of 1 to 5;  $m_3$  is an integer of 3 to 6;  $m_4$  is an integer of 2 to 5;

$R_{16}$  is hydrogen or methyl;

$R_{17}$  is a  $C_2$ - $C_6$  hydrocarbon radical having  $(m_2+1)$  valencies;

$R_{18}$  is a  $C_2$ - $C_6$  hydrocarbon radical having  $(m_4+1)$  valencies;

$R_{19}$  is ethyl or hydroxymethyl;

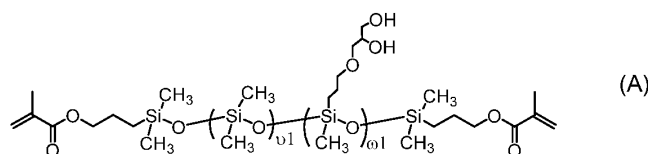
$R_{110}$  is methyl or hydromethyl;

$R_{111}$  is hydroxyl or methoxy;

$X_{11}$  is a sulfur linkage of  $\text{---S---}$  or a tertiary amino linkage of  $\text{---NR}_{112}\text{---}$  in which  $R_{112}$  is  $C_1$ - $C_1$  alkyl, hydroxyethyl, hydroxypropyl, or 2,3-dihydroxypropyl; and

$X_{12}$  is an amide linkage of  $\text{---NR}_{113}\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---}$  or  $\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---NR}_{113}\text{---}$  in which  $R_{113}$  is hydrogen or  $C_1$ - $C_{10}$  alkyl.

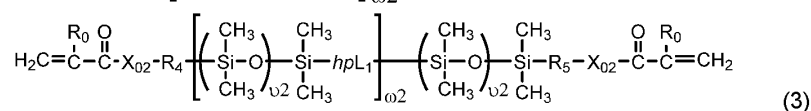
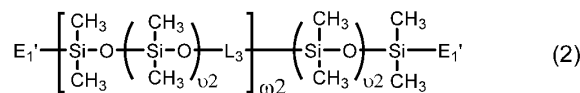
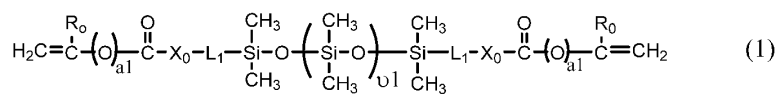
In a particularly preferred embodiment, the monovalent radical  $R_{13}$  is a radical of formula (Ie) in which  $m_1$  is 3,  $p_1$  is 1, and  $R_{16}$  is hydrogen. Such a preferred polysiloxane vinylic crosslinker is represented by formula (A)

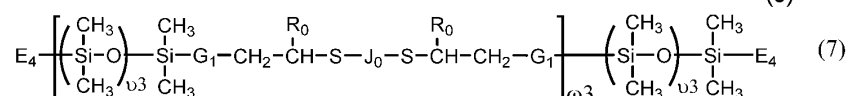
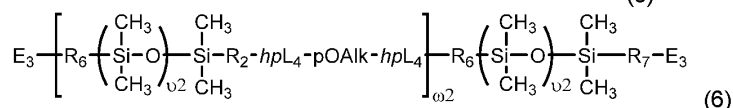
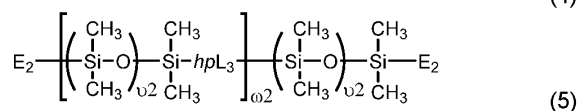
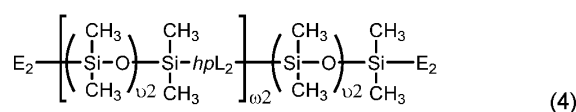


in which  $v_1$  and  $\omega_1$  are as defined above.

A polysiloxane vinylic crosslinker of formula (I) can be prepared according to procedures described in U.S. Pat. Appl. Pub. No. 2017-0166673 A1.

Other classes of preferred polysiloxane vinylic crosslinkers are vinylic crosslinkers of any one of formula (1) to (7)





in which:

$\nu 1$  is an integer of from 30 to 500;

$\nu 2$  is an integer of from 5 to 50;

$\nu 3$  is an integer of from 5 to 100;

$\omega 2$  and  $\omega 3$  independent of each other are an integer of from 1 to 15;

$a_1$  and  $g_1$  independent of each other is zero or 1;

$h_1$  is an integer of 1 to 20 and  $h_2$  is an integer of 0 to 20;

$m_1$  and  $m_3$  independent of each other is 0 or 1,  $m_2$  is an integer of 1 to 6,  $m_4$  is an integer of 1 to 5,  $m_5$  is 2 or 3;

$q_1$  is an integer of 1 to 20,  $q_2$  is an integer of 0 to 20,  $q_3$  is an integer of 0 to 2,  $q_4$  is an integer of 2 to 50,  $q_5$  and  $q_6$  independent of each other are a number of 0 to 35, provided that  $(q_4 + q_5 + q_6)$  is an integer of 2 to 50;

$x + y$  is an integer of from 10 to 30;

$e_1$  is an integer of 5 to 100,  $p_1$  and  $b_1$  independent of each other are an integer of 0 to 50, provided that  $(e_1 + p_1 + b_1) \geq 10$  and  $\frac{e_1}{(p_1 + b_1)} \geq 2$  (preferably from about 2:1 to about 10:1, more preferably from about 3:1 to about 6:1) when  $(p_1 + b_1) \geq 1$ ;

$R_0$  is H or methyl;

$R_1$ ,  $R_{1n}$ ,  $R_{2n}$ ,  $R_{3n}$ , and  $R_{4n}$  independent of one another are H or a  $C_1$ - $C_4$  alkyl having 0 to 2 hydroxyl group;

$R_{n5}$  is H or a  $C_1$ - $C_{10}$  alkyl;

$R_2$  is a  $C_4$ - $C_{14}$  hydrocarbon divalent radical;

$R_3$  is a  $C_2$ - $C_6$  alkylene divalent radical;

$R_4$  and  $R_5$  independent of each other are a  $C_1$ - $C_6$  alkylene divalent radical or a  $C_1$ - $C_6$  alkylene-oxy- $C_1$ - $C_6$  alkylene divalent radical;

$R_6$  and  $R_7$  independent of each other are a  $C_1$ - $C_6$  alkylene divalent radical or a  $C_1$ - $C_6$

alkoxy-C<sub>1</sub>-C<sub>6</sub> alkylene divalent radical;

R<sub>8</sub> and R<sub>9</sub> independent of each other are a substituted or unsubstituted C<sub>1</sub>-C<sub>12</sub> alkylene divalent radical;

X<sub>0</sub>, X<sub>1</sub>', X<sub>01</sub>, X<sub>02</sub>, and X<sub>03</sub> independent of one another are O or NR<sub>1</sub>;

X<sub>1</sub> is O, NR<sub>1</sub>, NHCOO, OCONH, CONR<sub>1</sub>, or NR<sub>1</sub>CO;

X<sub>04</sub> is -COO- or -CONR<sub>n5</sub>-;

X<sub>05</sub> and X<sub>07</sub> independent of each other are a direct bond, -COO- or -CONR<sub>n5</sub>-;

X<sub>06</sub> is a direct bond, a C<sub>1</sub>-C<sub>6</sub> alkylene divalent radical, a C<sub>1</sub>-C<sub>6</sub> alkylenoxy divalent radical, -COO-, or -CONR<sub>n5</sub>-;

X<sub>08</sub> is a direct bond or -COO-;

X<sub>09</sub> is O or NR<sub>n5</sub>;

X<sub>10</sub> is a direct bond, a C<sub>1</sub>-C<sub>6</sub> alkylene divalent radical, -COO-, or -CONR<sub>n5</sub>-;

E<sub>1</sub>' is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}_{01}-\text{L}_4-$ ;

E<sub>2</sub> is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Z}_7-$ ;

E<sub>3</sub> is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}_{03}-$ ;

E<sub>4</sub> is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}_{11}-\text{G}_2-$  or  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{G}_3-$ ;

L<sub>1</sub> is a C<sub>2</sub>-C<sub>8</sub> alkylene divalent radical or a divalent radical of -L<sub>1</sub>'-X<sub>1</sub>-L<sub>1</sub>"-,

$-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{L}_1'-$ ,  $-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{CONH}-\text{L}_1"-$ ,  $-\text{L}_1'-\text{NHCOO}-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{L}_1"-$ ,

$-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{X}_1'-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_1"-$ ,  $-\text{L}_1'-\text{X}_1'-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{L}_1"-$ , or

$-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{L}_1"-$ ;

L<sub>1</sub>' is a C<sub>2</sub>-C<sub>8</sub> alkylene divalent radical which has zero or one hydroxyl group;

L<sub>1</sub>" is C<sub>3</sub>-C<sub>8</sub> alkylene divalent radical which has zero or one hydroxyl group;

L<sub>3</sub> is a divalent radical of

$-\text{L}_3'-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{CONH}-\text{R}_2-(\text{NHCO}-\text{PE}-\text{CONH}-\text{R}_2)_{g1}-\text{NHCO}-(\text{OC}_2\text{H}_4)_{q2}-\text{O}-\text{L}_3'-$  in which PE

is a divalent radical of

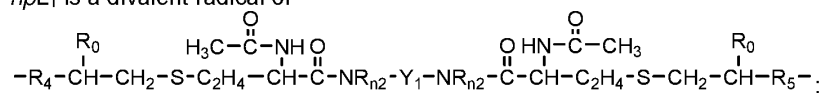
$-(\text{CH}_2\text{CH}_2\text{O})_{q3}-\text{Z}_0-\text{CF}_2-(\text{OCF}_2)_x-(\text{OCF}_2\text{CF}_2)_y-\text{OCF}_2-\text{Z}_0-(\text{OCH}_2\text{CH}_2)_{q3}-$  or

$-\text{Z}_0-(\text{CH}_2\text{CH}_2\text{O})_{q4}-\left(\text{CH}_2-\overset{\text{CH}_3}{\underset{\cdot}{\text{CH}}}-\text{O}\right)_{q5}-\left(\text{CH}_2-\overset{\text{C}_2\text{H}_5}{\underset{\cdot}{\text{CH}}}-\text{O}\right)_{q6}-\text{Z}_0-$ ;

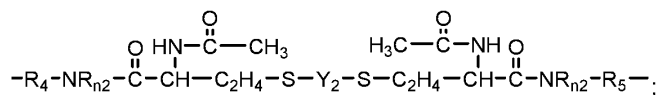
L<sub>3</sub>' is C<sub>3</sub>-C<sub>8</sub> alkylene divalent radical;

$L_4$  is a divalent radical of  $-\text{C}_2\text{H}_4-\text{NHCO}-\text{O}-\left(\text{C}_2\text{H}_4\text{O}\right)_{q_2}-\text{L}_3'-$ ,  
 $\left(\text{C}_2\text{H}_4\text{O}\right)_{q_1}-\text{CONH}-\text{R}_2-\text{NHCO}-\text{O}-\left(\text{C}_2\text{H}_4\text{O}\right)_{q_2}-\text{L}_3'-$ ,  
 $-\text{R}_3-\text{O}-\text{CONH}-\text{R}_2-\text{NHCO}-\text{O}-\left(\text{C}_2\text{H}_4\text{O}\right)_{q_2}-\text{L}_3'-$ ,  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\left(\text{C}_2\text{H}_4\text{O}\right)_{q_2}-\text{L}_3'-$ , or  
 $-\left(\text{C}_2\text{H}_4\text{O}\right)_{q_2}-\text{L}_3'-$ ;

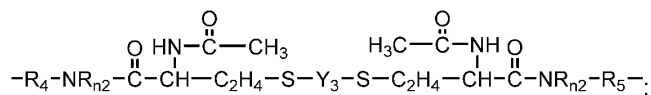
$hpl_1$  is a divalent radical of



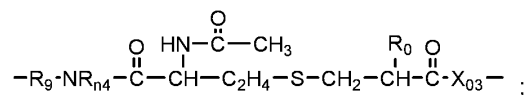
$hpl_2$  is a divalent radical of



$hpl_3$  is a divalent radical of



$hpl_4$  is a divalent radical of  $-\text{X}_{03}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}_0}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{S}-\text{C}_2\text{H}_4-\overset{\text{H}_3\text{C}-\overset{\text{O}}{\parallel}}{\underset{|}{\text{C}}}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}_{n4}-\text{R}_8-$  or



$p\text{OAlk}$  is a divalent radical of  $-(\text{EO})_{c1}(\text{PO})_{p1}(\text{BO})_{b1}-$  in which EO is an oxyethylene

unit  $(-\text{CH}_2\text{CH}_2\text{O}-)$ , PO is an oxypropylene unit  $(-\text{CH}_2-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{O}-)$ , and BO is an

oxybutylene unit  $(-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}}-\text{O}-)$ ;

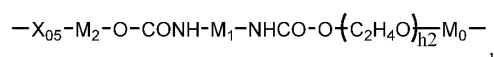
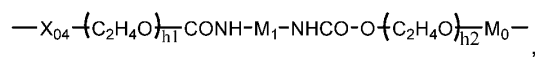
$M_0$  is  $\text{C}_3$ - $\text{C}_8$  alkylene divalent radical;

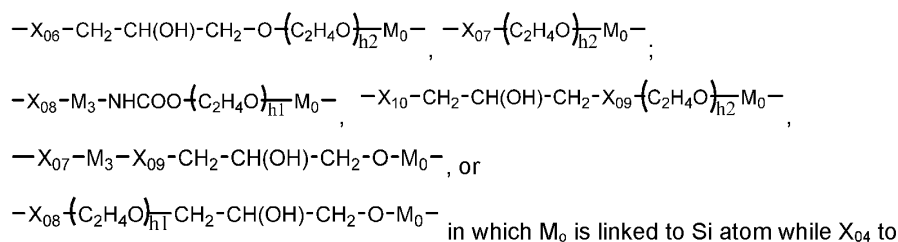
$M_1$  is a  $\text{C}_4$ - $\text{C}_{14}$  hydrocarbon divalent radical;

$M_2$  and  $M_3$  independent of each other are a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical;

$J_0$  is a  $\text{C}_1$ - $\text{C}_{12}$  hydrocarbon radical having 0 to 2 hydroxyl or carboxyl groups;

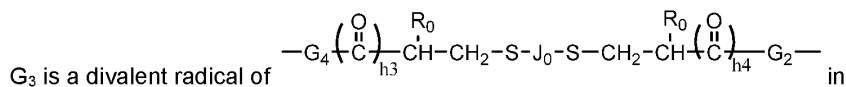
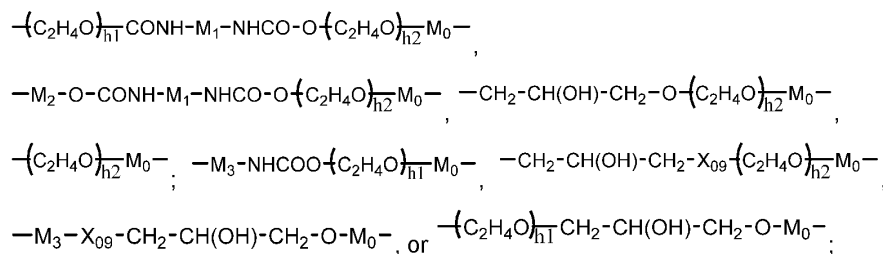
G1 is a direct bond, a  $\text{C}_1$ - $\text{C}_4$  alkylene divalent radical, or a divalent radical of





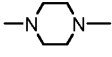
$X_{10}$  are linked to the group of  $-CH_2-$  in formula (7) and at least one of  $J_0$  and  $G_1$  in formula (7) comprises at least one moieties selected from the group consisting of hydroxyl groups, urethane linkage of  $-OCONH-$ , amino groups of  $-NHR^0$ , amino linkages of  $-NH-$ , amide linkages of  $-CONH-$ , carboxyl groups, and combinations thereof;

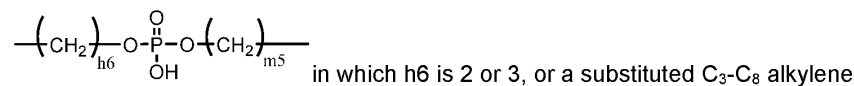
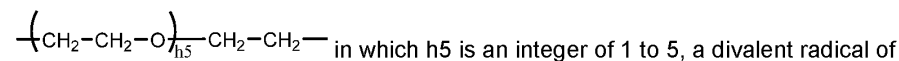
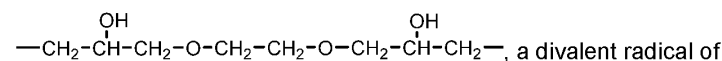
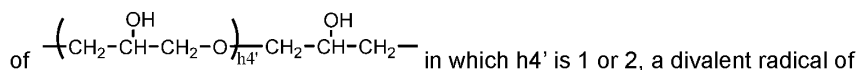
$G_2$  is a  $C_1$ - $C_4$  alkylene divalent radical or a bivalent radical of



which  $h_3$  and  $h_4$  independent of each other are 1 or 0;

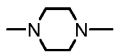
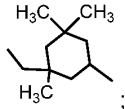
$G_4$  is a divalent radical of any one of (a)  $-NR_3'-$  in which  $R_3'$  is hydrogen or  $C_1$ - $C_3$

alkyl, (b) , (c)  $-NR_0-G_5-NR_0-$  in which  $G_5$  is a  $C_1$ - $C_6$  alkylene divalent radical, 2-hydroxypropylene divalent radical, 2-(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical, 2,3-dihydroxybutylene divalent radical, and (d)  $-O-G_6-O-$  in which  $G_6$  is a  $C_1$ - $C_6$  alkylene divalent radical, a divalent radical

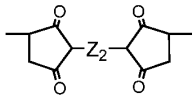


divalent radical having a hydroxyl group or phosphonyloxy group;

$Y_1$  is a  $C_1$ - $C_6$  alkylene divalent radical, 2-hydroxypropylene divalent radical, 2-(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical, a

divalent radical of , or a divalent radical of ;

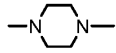
$Y_2$  is a divalent radical of  $-\text{CH}_2-\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Z}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\text{CH}_2-$ ;

$Y_3$  is a divalent radical of  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{S}}-(\text{Z}_1-\overset{\text{O}}{\parallel}{\text{S}})_{m1}-\text{CH}_2-\text{CH}_2-$  or ;

$Z_0$  is a direct bond or a  $C_1$ - $C_{12}$  alkylene divalent radical;

$Z_1$  is a  $C_1$ - $C_6$  alkylene divalent radical, a hydroxyl- or methoxy-substituted  $C_1$ - $C_6$  alkylene divalent radical, or a substituted or unsubstituted phenylene divalent radical,

$Z_2$  is a  $C_1$ - $C_6$  alkylene divalent radical, a hydroxyl- or methoxy-substituted  $C_1$ - $C_6$  alkylene divalent radical, a dihydroxyl- or dimethoxy-substituted  $C_2$ - $C_6$  alkylene divalent radical, a divalent radical of  $-\text{C}_2\text{H}_4-(\text{O}-\text{C}_2\text{H}_4)_{m2}-$ , a divalent radical of  $-\text{Z}_4-\text{S}-\text{S}-\text{Z}_4-$ , a hydroxyl- or methoxy-substituted  $C_1$ - $C_6$  alkylene divalent radical, or a substituted or unsubstituted phenylene divalent radical,

$Z_3$  is a divalent radical of any one of (a)  $-\text{NR}_{n3}-$ , (b) , (c)  $-\text{NR}_0-\text{Z}_5-\text{NR}_0-$ , and (d)  $-\text{O}-\text{Z}_6-\text{O}-$ ,

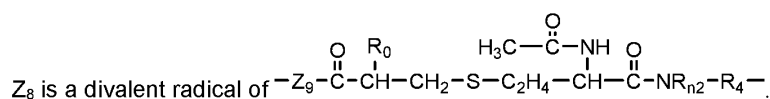
$Z_4$  is a  $C_1$ - $C_6$  alkylene divalent radical,

$Z_5$  is a  $C_1$ - $C_6$  alkylene divalent radical, 2-hydroxypropylene divalent radical, 2-(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical, 2,3-dihydroxybutylene divalent radical,

$Z_6$  is (a) a  $C_1$ - $C_6$  alkylene divalent radical, (b) a divalent radical of

$-(\text{CH}_2-\overset{\text{OH}}{\underset{\cdot}{\text{C}}}-\text{CH}_2-\text{O})_{m3}-\text{CH}_2-\overset{\text{OH}}{\underset{\cdot}{\text{C}}}-\text{CH}_2-$ ,  $-\text{CH}_2-\overset{\text{OH}}{\underset{\cdot}{\text{C}}}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\overset{\text{OH}}{\underset{\cdot}{\text{C}}}-\text{CH}_2-$ ,  $-(\text{CH}_2-\text{CH}_2-\text{O})_{m4}-\text{CH}_2-\text{CH}_2-$ ,  $-(\text{CH}_2)_{m5}-\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{OH})-\text{O}-(\text{CH}_2)_{m5}-$ , or (c) a substituted  $C_3$ - $C_8$  alkylene divalent radical having a hydroxyl group or phosphonyloxy group,

$Z_7$  is a divalent radical of  $-\text{Z}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}_0}{\underset{\cdot}{\text{C}}}-\text{CH}_2-\text{S}-\text{C}_2\text{H}_4-\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}_{n2}-\text{R}_4-$ ; and



Polysiloxane vinylic crosslinkers of formula (1) can be obtained from commercial suppliers, or prepared by reacting glycidyl (meth)acrylate (meth)acryloyl chloride with a di-amino-terminated polydimethylsiloxane or a di-hydroxyl-terminated polydimethylsiloxane, reacting isocyanatoethyl (meth)acrylate with di-hydroxyl-terminated polydimethylsiloxanes, reacting an amino-containing acrylic monomer with di-carboxyl-terminated polydimethylsiloxane in the presence of a coupling agent (a carbodiimide); reacting a carboxyl-containing acrylic monomer with di-amino-terminated polydimethylsiloxane in the presence of a coupling agent (a carbodiimide). Or reacting a hydroxyl-containing acrylic monomer with a di-hydroxy-terminated polydisiloxane.

Preferred examples of polysiloxane vinylic crosslinkers of formula (1) include without limitation  $\alpha,\omega$ -bis[3-(meth)acrylamidopropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxyethoxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxy-isopropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxybutyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidoethoxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidopropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidoisopropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidobutyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxyethylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxybutylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acrylamidoethylamino-2-hydroxypropyloxy-propyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidopropylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamide-butylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyloxy-ethoxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyl-N-ethylaminopropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -

bis[(meth)acryloxy-2-hydroxypropyl-aminopropyl]-polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyloxy-(polyethylenoxy)propyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxyethylamino-carbonyloxy-ethoxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxyethylamino-carbonyloxy-(polyethylenoxy)propyl]-terminated polydimethylsiloxane, combinations thereof.

Chain-extended polysiloxane vinylic crosslinkers of formula (2) can be prepared according to the procedures described in U.S. Pat. Nos. 5034461, 5416132, 5449729, 5760100, 7423074, and 8529057. Chain-extended polysiloxane vinylic crosslinkers of formula (3), (4) or (5) can be prepared according to the procedures described in detail in U.S. Pat. App. Pub. No. 2018-0100053 A1. Chain-extended polysiloxane vinylic crosslinkers of formula (6) can be prepared according to the procedures described in detail in U.S. Pat. App. Pub. No. 2018-0100038 A1. Chain-extended polysiloxane vinylic crosslinkers of formula (7) can be prepared according to the procedures described in U.S. Pat. No. 8993651.

Another class of preferred chain-extended polysiloxane vinylic crosslinkers are those which each comprise at least two polysiloxane segments and dangling hydrophilic polymer chains each covalently attached to a divalent radical separating each pair of adjacent polysiloxane segments and having at least two pendant hydrophilic groups and/or chains as disclosed in U.S. Pat. Appl. Pub. No. 2012-0088843 A1; those which each comprise at least two polysiloxane segments and dangling hydrophilic polymer chains each covalently attached to a divalent radical separating each pair of adjacent polysiloxane segments as disclosed in U.S. Pat. Appl. Pub. No. 2012-0088844 A1.

In accordance with the invention, any suitable N-vinyl amide monomers can be used in the invention. Examples of preferred N-vinyl amide monomers include without limitation N-vinylpyrrolidone, N-vinyl piperidone, N-vinyl caprolactam, N-vinyl-N-methyl acetamide, N-vinyl formamide, N-vinyl acetamide, N-vinyl isopropylamide, N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, and mixtures thereof. Preferably, the N-vinyl amide monomer is N-vinylpyrrolidone, N-vinyl-N-methyl acetamide, or combinations thereof.

Any hydrophobic acrylic monomer can be used in the invention, provided that it can form a homopolymer with a  $T_g$  of at least about 60°C (preferably at least about 70°C, more preferably at least about 80°C, even more preferably at least about 90°C) and that it can dissolve components (a) to (c) to form a solution with a concentration of at least about 5% by weight. It is believed that such a hydrophobic acrylic monomer can increase a  $T_g$  of the dominant phase of a resultant silicone hydrogel material above the room temperature and may make the unprocessed silicone hydrogel lens precursor more rigid.

Examples of such hydrophobic acrylic monomers includes methyl methacrylate ( $T_g=105^\circ\text{C}$  of homopolymer), ethyl methacrylate ( $T_g=65^\circ\text{C}$  of homopolymer), isopropyl methacrylate ( $T_g=81^\circ\text{C}$  of homopolymer), sec-butyl methacrylate ( $T_g=60^\circ\text{C}$  of homopolymer), tert-butyl methacrylate ( $T_g=107^\circ\text{C}$  of homopolymer), cyclohexyl methacrylate ( $T_g=83^\circ\text{C}$  of homopolymer), isobornyl acrylate ( $T_g=94^\circ\text{C}$  of homopolymer), isobornyl methacrylate ( $T_g=110^\circ\text{C}$  of homopolymer), phenyl methacrylate ( $T_g=110^\circ\text{C}$  of homopolymer), 4-tert-butylstyrene ( $T_g=132^\circ\text{C}$  of homopolymer), 2-methylstyrene ( $T_g=120^\circ\text{C}$  of homopolymer), styrene ( $T_g=100^\circ\text{C}$  of homopolymer), 4-ethoxystyrene ( $T_g=86^\circ\text{C}$  of homopolymer), 2,4-dimethylstyrene ( $T_g=112^\circ\text{C}$  of homopolymer), 2,5-dimethylstyrene ( $T_g=143^\circ\text{C}$  of homopolymer), 3,5-dimethylstyrene ( $T_g=104^\circ\text{C}$  of homopolymer), and combinations thereof. More preferably, methyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, or a combination thereof is used in the invention. Even more preferably, methyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, or a combination thereof is used in the invention.

Examples of preferred organic solvents having 2 to 8 carbon atoms include without limitation, alcohols having 2 to 8 carbon atoms (e.g., ethanol, 1-propanol, isopropanol, 1-butanol, sec-butanol, isobutanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-1-butanol, 2,2-dimethyl-1-propanol, tert-amyl alcohol, 2-hexanol, 3-hexanol, 2-heptanol, 2-octanol, 2-nonanol, 2-decanol, 3-octanol, 2-methyl-2-pentanol, 2,3-dimethyl-2-butanol, 3-methyl-3-pentanol, 2-methyl-2-hexanol, 3-methyl-3-hexanol, 3-methyl-3-heptanol, 4-methyl-4-heptanol, 2-methyl-2-heptanol, 3-ethyl-3-hexanol, 3-methyl-3-heptanol, 2,4-dimethyl-2-pentanol, 3-ethyl-3-pentanol, 1-methoxy-2-propanol, 3-ethoxy-1-propanol, 1-ethoxy-2-propanol, 1-isobutoxy-2-propanol, 3-methoxy-1-butanol, 1-methoxy-2-butanol, norborneol, 1-methylcyclohexanol, 1-methylcyclopentanol, 1-ethylcyclopentanol, 1-ethylcyclopentanol, 4-hydroxy-4-methyl-1-cyclopentanol, or combinations thereof), dipropylene glycol methyl ether, ethylene glycol n-butyl ether, acetone, methyl ethyl ketone, diethylene glycol n-butyl ether, diethylene glycol methyl ether, propylene glycol methyl ether, propylene glycol methyl ether acetate, propylene glycol n-propyl ether, propylene glycol n-butyl ether, ethyl acetate, butyl acetate, amyl acetate, methyl lactate, ethyl lactate, propyl lactate, 1-methyl-2-pyrrolidone, N,N-dimethylpropionamide, dimethyl formamide, dimethyl acetamide, dimethyl propionamide, N-methyl pyrrolidinone, and mixtures thereof. Preferably, the organic solvent is an alcohol having 3 to 5 carbon atoms (e.g., 1-propanol, isopropanol, 1-butanol, sec-butanol, isobutanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-1-butanol, 2,2-dimethyl-1-propanol, tert-amyl alcohol, 1-methoxy-2-

propanol, 3-ethoxy-1-propanol, 1-ethoxy-2-propanol, or combinations thereof).

In accordance with the invention, a polymerizable composition can comprise about 1.5% or less (preferably about 1.2% or less, more preferably from about 0.1% to about 1.0%) by weight of one or more non-silicone vinylic crosslinkers relative to the total weight of all polymerizable components in the polymerizable composition.

Examples of preferred non-silicone vinylic cross-linking agents include without limitation ethyleneglycol di-(meth)acrylate, diethyleneglycol di-(meth)acrylate, triethyleneglycol di-(meth)acrylate, tetraethyleneglycol di-(meth)acrylate, glycerol di-(meth)acrylate, 1,3-propanediol di-(meth)acrylate, 1,3-butanediol di-(meth)acrylate, 1,4-butanediol di-(meth)acrylate, glycerol 1,3-diglycerolate di-(meth)acrylate, ethylenebis[oxy(2-hydroxypropane-1,3-diyl)] di-(meth)acrylate, bis[2-(meth)acryloxyethyl] phosphate, trimethylolpropane di-(meth)acrylate, and 3,4-bis[(meth)acryloyl]tetrahydrofuran, diacrylamide (i.e., N-(1-oxo-2-propenyl)-2-propenamide), dimethacrylamide (i.e., N-(1-oxo-2-methyl-2-propenyl)-2-methyl-2-propenamide), N,N-di(meth)acryloyl-N-methylamine, N,N-di(meth)acryloyl-N-ethylamine, N,N'-methylene bis(meth)acrylamide, N,N'-ethylene bis(meth)acrylamide, N,N'-dihydroxyethylene bis(meth)acrylamide, N,N'-propylene bis(meth)acrylamide, N,N'-2-hydroxypropylene bis(meth)acrylamide, N,N'-2,3-dihydroxybutylene bis(meth)acrylamide, 1,3-bis(meth)acrylamide-propane-2-yl dihydrogen phosphate (i.e., N,N'-2-phosphonyloxypropylene bis(meth)acrylamide), piperazine diacrylamide (or 1,4-bis(meth)acryloyl piperazine), tetraethyleneglycol divinyl ether, triethyleneglycol divinyl ether, diethyleneglycol divinyl ether, ethyleneglycol divinyl ether, triallyl isocyanurate, triallyl cyanurate, trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, bisphenol A dimethacrylate, and combinations thereof. A preferred non-silicone vinylic cross-linking agent is tetra(ethyleneglycol) di-(meth)acrylate, tri(ethyleneglycol) di-(meth)acrylate, ethyleneglycol di-(meth)acrylate, di(ethyleneglycol) di-(meth)acrylate, tetraethyleneglycol divinyl ether, triethyleneglycol divinyl ether, diethyleneglycol divinyl ether, ethyleneglycol divinyl ether, triallyl isocyanurate, triallyl cyanurate, or a combination thereof.

Any suitable thermal polymerization initiators, known to the skilled artisan, can be used in the invention. Examples of thermal polymerization initiators includes without limitation peroxides, hydroperoxides, azo-bis(alkyl- or cycloalkylnitriles), persulfates, percarbonates or mixtures thereof. Examples of thermal free radical initiators are benzoylperoxide, tert.-butyl peroxide, di-tert.-butyl-diperoxyphthalate, tert.-butyl hydroperoxide, azo-bis(isobutyronitrile) (AIBN), 1,1'-azodiisobutyramidine, 1,1'-azo-bis (1-cyclohexanecarbonitrile), 2,2'-azo-bis(2,4-dimethylvaleronitrile) and the like. The

polymerization is carried out conveniently in an above-mentioned solvent at elevated temperature, for example at a temperature of from 25 to 100°C and preferably 40 to 80°C. The reaction time may vary within wide limits, but is conveniently, for example, from 1 to 24 hours or preferably from 2 to 12 hours. It is advantageous to previously degas the components and solvents used in the polymerization reaction and to carry out said copolymerization reaction under an inert atmosphere, e.g., under N<sub>2</sub> or Ar atmosphere.

Suitable photoinitiators are benzoin methyl ether, diethoxyacetophenone, a benzoylphosphine oxide, 1-hydroxycyclohexyl phenyl ketone and Darocur and Irgacur types, preferably Darocur 1173® and Darocur 2959®, Germane-based Norrish Type I photoinitiators. Examples of benzoylphosphine initiators include 2,4,6-trimethylbenzoyldiphenylphosphine oxide; bis-(2,6-dichlorobenzoyl)-4-N-propylphenylphosphine oxide; and bis-(2,6-dichlorobenzoyl)-4-N-butylphenylphosphine oxide. Reactive photoinitiators which can be incorporated, for example, into a macromer or can be used as a special monomer are also suitable. Examples of reactive photoinitiators are those disclosed in EP 632 329, herein incorporated by reference in its entirety. The polymerization can then be triggered off by actinic radiation, for example light, in particular UV light or visible light of a suitable wavelength. The spectral requirements can be controlled accordingly, if appropriate, by addition of suitable photosensitizers.

In accordance with a preferred embodiment of the invention, a polymerizable composition of the invention can further comprise (but preferably comprises) one or more UV-absorbing vinylic monomers and optionally (but preferably) one or more UV/HEVL-absorbing vinylic monomers. The term "UV/HEVL-absorbing vinylic monomer" refers to a vinylic monomer that can absorb UV light and high-energy-violet-light (i.e., light having wavelength between 380 nm and 440 nm). Examples of UV-absorbing vinylic monomers and UV/HEVL-absorbing vinylic monomers are known to a person skilled in the art and are disclosed in the patents and patent application publications, e.g., US 9,315,669, US 2018-0081197 A1, etc.

In accordance with the invention, a polymerizable composition of the invention can further comprise one or more hydrophilic acrylic monomers, preferably in an amount of about 10% or less (more preferably about 8% or less, even more preferably about 5% or less) by weight relative to the total weight of the polymerizable composition.

Examples of preferred hydrophilic acrylic monomers include without limitation N,N-dimethyl (meth)acrylamide, (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N-hydroxypropyl (meth)acrylamide, hydroxyethyl methacrylate, glycerol methacrylate (GMA), polyethylene glycol (meth)acrylate having a number average molecular weight of

up to 1500, polyethylene glycol C<sub>1</sub>-C<sub>4</sub>-alkyl ether (meth)acrylate having a number average molecular weight of up to 1500, *N*-[tris(hydroxymethyl)methyl]-acrylamide, (meth)acrylic acid, ethylacrylic acid, and combinations thereof. Preferably, the hydrophilic vinylic monomer is *N,N*-dimethyl (meth)acrylamide, hydroxyethyl (meth)acrylate, *N*-hydroxyethyl (meth)acrylamide, glycerol methacrylate (GMA), or combinations thereof.

A polymerizable composition of the invention can also comprise other necessary components known to a person skilled in the art, such as, for example, a visibility tinting agent (e.g., one or more polymerizable dyes, pigments, or mixtures thereof), antimicrobial agents (e.g., preferably silver nanoparticles), a bioactive agent, leachable lubricants, leachable tear-stabilizing agents, and mixtures thereof, as known to a person skilled in the art.

A polymerizable composition of the invention can be prepared by dissolving and blending all of the desirable components in a mixture of components (d) and (e).

Methods of manufacturing mold sections for cast molding a contact lens are generally well known to those of ordinary skill in the art. The process of the present invention is not limited to any particular method of forming a mold. In fact, any method of forming a mold can be used in the present invention. However, for illustrative purposes, the following discussion has been provided as one embodiment of forming a mold.

In general, a mold comprises at least two mold halves (or mold sections), one male half and one female mold half. The male mold half has a first molding (or optical) surface which is in direct contact with a polymerizable composition for cast molding of a contact lens and defines the posterior (concave) surface of a molded contact lens; and the female mold half has a second molding (or optical) surface which is in direct contact with the polymerizable composition and defines the anterior (convex) surface of the molded contact lens. The male and female mold halves are configured to receive each other such that a lens-forming cavity is formed between the first molding surface and the second molding surface.

FIG. 1 schematically illustrates a preferred mold **100** used in the methods of the invention. The mold **100** comprises a female mold half **1** and male mold half **2**.

The male mold half **2** comprises a base **61**, a substantially cylindrical body **25** which extends upward from base **61**, a posterior molding surface defining the posterior (concave) surface of a molded contact lens, and an annular shoulder **65** which surrounds the posterior molding surface. The posterior molding surface protrudes outward from the top of body **25**. The annular shoulder **65** shown is flat. It is understood that the annular shoulder **65** can have any suitable surface, such as, e.g., a tilted surface.

The female mold half **1** comprises a base **51**, a substantially cylindrical body **15**

which extends upward from base **51**, an anterior molding surface defining the anterior (convex) surface of a molded contact lens, and a collar **4**. The anterior molding surface recesses downward from the top of the body **15**. Collar **4** (or up-protruding flange) is preferably integral part of the female mold half **1** and protrudes upward from the top of the body **15**. A circumferential groove (or recess) **11** is formed on top of the body **15** between the anterior molding surface and the collar **4** and functions as an overflow for any excess unpolymerized lens-forming material.

The term "collar" as used herein refers to a peripheral circular part which protrudes upward from the top of body of one of the two mating mold halves. A collar can be attached to or preferably integral part of that mold half and which can encircle the other mold half to provide a tight seal between the two mold halves. It is understood that the collar can be provided on either of the male and female mold halves.

The female mold half **1** and a male mold half **2** are configured to receive each other such that a contact lens forming cavity **12** is formed between the anterior and posterior molding surfaces. The collar **4** encircles the body **25** of the male mold half **2** to provide a tight seal **5** between the female and male mold halves when the mold is closed. Typically, there is no lens material in the seal.

In operation, mold halves **1** and **2** can be first injection molded from a plastic resin in an injection molding apparatus, as well known to a person skilled in the art. A specific amount of a polymerizable lens-forming material is typically dispensed into the female mold half **1** by means of a dispensing device and then the male mold half **2** is put on and the mold **100** is closed (FIG. 1). As the mold **100** closes, any excess unpolymerized lens-forming material is pressed into an overflow **11** provided on the female mold half **1**. Subsequently, the polymerizable composition in the closed mold **100** is cured thermally in an oven or actinically with UV/visible irradiation.

The mold halves can be formed through various techniques, such as injection molding. Methods of manufacturing mold halves for cast-molding a contact lens are generally well known to those of ordinary skill in the art. The process of the present invention is not limited to any particular method of forming a mold. In fact, any method of forming a mold can be used in the present invention. The mold halves can be formed through various techniques, such as injection molding or lathing. Examples of suitable processes for forming the mold halves are disclosed in U.S. Patent Nos. 4,444,711; 4,460,534; 5,843,346; and 5,894,002, which are also incorporated herein by reference.

Virtually all materials known in the art for making molds can be used to make molds for making contact lenses. For example, polymeric materials, such as polyethylene, polypropylene, polystyrene, PMMA, Topas® COC grade 8007-S10 (clear amorphous

copolymer of ethylene and norbornene, from Ticona GmbH of Frankfurt, Germany and Summit, New Jersey), or the like can be used. Other materials that allow UV light transmission could be used, such as quartz glass and sapphire.

In accordance with the invention, the polymerizable composition can be introduced (dispensed) into a cavity formed by a mold according to any known methods. A specific amount of a polymerizable lens-forming material is typically dispensed into a female mold half by means of a dispensing device and then a male mold half is put on and the mold is closed. As the mold closes, any excess unpolymerized lens-forming material is pressed into an overflow provided on the female mold half (or alternatively on the male mold half).

The closed mold containing the polymerizable composition subsequently is cured (i.e., polymerized) thermally or actinically to produce a molded unprocessed silicone hydrogel lens precursor.

Subsequently, applying a force to non-optical surface of the female mold at a location about the center area of non-optical molding surface at an angle of less than about 30 degrees, preferably less than about 10 degrees, most preferably less than about 5 degrees (i.e., in a direction substantially normal to center area of non-optical molding surface) relative to the axis of the mold to deform the female mold half which breaks the bonds between the optical molding surface of the female mold half and the molded lens, as shown in FIG. 2. Various ways of applying a force to non-optical surface of the female mold half at a location about the center area of non-optical molding surface along the axis of the mold to deform the female mold half which breaks the bonds between the optical molding surface of the female mold half and the molded lens. It is understood that the mold-opening device can have any configurations known to a person skilled in the art for performing the function of separating two mold halves from each other. For example, referring to FIG. 2, the demolding assembly comprises a pin **70** positionable against the center area of non-optical molding surface of the female mold half. The pin **70** has a flat free end **70a** to enable a surface contact between the free end **70a** and the center area of non-optical molding surface of the female mold half. It will be appreciated that the scope of the invention is not limited to such a particular flat configuration of the pin end **70a**, for example the pin may have a rounded free end. In the present embodiment, the pin **70** is movable and the female mold half remains stationary by applying a restraining force to the female mold half with a first prying finger **32** for maintaining the female mold half in a fixed position. However, it is possible to arrange the assembly so that the female mold half is movable and the pin **70** remains stationary, or so that both the pin **70** and the female mold half can be moved relative to each other.

In use, during the demolding operation, the free end **70a** of the pin **70** applies a longitudinally directed force to the central portion of the non-optical surface of the female mold half. The first prying finger **32** applies a counteractive force against the end face **51a** of the flange **51** of the female mold half **1**. Consequently, the female mold half is compressed between the free end **70a** of the pin **70** and the first finger **32**. The compression force deforms the curved part of the female mold half and breaks the adhesive bond between the molding surface of the female mold half **1** and the anterior surface of the molded lens **12**.

Then, apply a vertical lifting movement to the male mold half with a second prying finger (while maintaining the restraints on the female mold so as to effectuate gradual separation between the female mold and the male mold).

After breaking the bond between the optical molding surface of the female mold half and the molded lens, the mold is separated, the molded unprocessed contact lens adheres to the male mold half **2**. It is surprising to find out that, according to the present invention, the molded contact lens adhering to the male mold half even though the molding surfaces of the female mold and male mold are not treated before or after dispensing a specific amount of a polymerizable lens-forming material into one of the mold halves to render the molded contact lens preferentially adhered to the female mold or male mold when separating the mold.

According to the present application as mentioned above, the lens typically remains adhered to the male mold section. However, by using similar principle, the compression can be applied to the applying a force to non-optical surface of the male mold half at a location about the center area of non-optical molding surface along the longitudinal axis of the mold to deform the male mold half to compress the female mold half between the pin and the first set of pry fingers so as to break the bonds between the optical molding surface of the male mold half and the molded lens, thereby the molded lens adheres to the female mold half after separating the mold.

According to the present application, an ultrasonic welding system is used not to welding two pieces of plastic material together, but instead to separate molded silicone hydrogel contact lens from the lens-adhered mold half. An ultrasonic welding system as illustrated in FIG. 3 comprises: a power supply **300** which provides a high power AC signal with frequency matching the resonance frequency of the ultrasonic stack. An ultrasonic stack composed of a converter **310**, a booster **320** and a horn **330**. All three elements of the stack are specifically tuned to resonate at the same exact ultrasonic frequency (Typically 15, 20, 30, 35, 40 or 70 kHz). The converts the electrical signal into a mechanical vibration. The booster modifies the amplitude of the vibration. The horn can

also define the amplitude of vibration and apply the mechanical vibration to the parts to be contacted. However, any kind of mechanical system which transfers the vibrational energy from the converter to the mold half can be used.

FIG. 4 illustrates an embodiment of the invention wherein an ultrasonic horn **330** having a flat surface **340** is sized to be approximately the outer diameter of the male mold half **2** and seated on extended flat edge surround the outer concave surface **35** (or back surface of the annular shoulder **65** of the male mold half. The male mold half **2** proximate the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens **85** is attached thereon so that a relative motion at the frequency of the acoustic energy takes place between back surface of the annular shoulder **65** of the male mold half and the contact lens attached thereon. The male mold half and the contact lens attached thereon is held stationary by a position holder **75**. A person skilled in the art knows which device can be used as a position holder, for example, a level metal or a cup having an attached level metal. The cup can be used to collect the lens separated from the male mold half. Furthermore, the cup can be attached a vacuum source and the vacuum can assist the separation of the lens from the male mold half.

FIG. 5A and 5B show an embodiment wherein an ultrasonic horn **330** having a convex surface **340** is of a size that allows it to extend within the outer concave portion of male half mold half **2**. The male mold half and the contact lens **85** attached thereon is held stationary by a position holder **75**. FIG. 5A illustrates that the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens is attached thereon so that a relative motion at the frequency of the acoustic energy takes place through contact surface between inside of the outer concave portion of male half mold half **2** and the contact lens attached thereon. FIG. 5B illustrates that the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens is attached thereon so that a relative motion at the frequency of the acoustic energy takes place through contact points between edges of the outer concave portion of male half mold half **2** and the contact lens attached thereon.

FIG. 6 illustrates an embodiment of the invention is shown wherein an ultrasonic horn **330** having a flat surface **340** is sized to be approximately the outer diameter of the female mold half **1** to contact the center area of the outer convex portion of the female mold half. The female mold half and the contact lens **85** attached thereon is held stationary by a position holder **75**. The center portion of back surface (non-optical surface) of the female mold half **1** proximate the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens is attached thereon so that a

relative motion at the frequency of the acoustic energy takes place between the female mold half and the contact lens attached thereon.

FIG. 7A and 7B show an embodiment wherein an ultrasonic horn **330** having a concave surface **340** is of a size that allows it to extend within the outer convex portion of female half mold half **1** to contact the center area of the outer convex portion of the female mold half. The female mold half and the contact lens **85** attached thereon is held stationary by a position holder **75**. FIG. 7A illustrates that the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens is attached thereon so that a relative motion at the frequency of the acoustic energy takes place through contact surface between inside of the outer convex portion of female half mold half **1** and the contact lens attached thereon. 7B illustrates that the ultrasonic horn vibrates with the acoustical energy emitted from the ultrasonic horn **330** while the contact lens is attached thereon so that a relative motion at the frequency of the acoustic energy takes place through contact points between edges of the outer concave portion of female half mold half **1** and the contact lens attached thereon.

According to the present invention, the modification to the output part of the horn and the preferred parameters associated with operating the system are given in the following.

The ultrasonic welding system is comprised of a power supply **300** which generates a frequency range from 15 kHz to 70 kHz by the use of solid state power devices. This high frequency electrical energy is supplied to a converter **320**. This component changes the electrical energy into ultrasonic mechanical vibratory energy at the frequency of the converted electrical energy supply which is typically 15 kHz to 70 kHz. The vibratory ultrasonic acoustical energy is then transmitted through an amplitude modifying device called a booster **320**. The booster is a passive (i.e., non-powered) device which is used to modify the output amplitude of the converter before it reaches the horn **330**. The horn is shaped to have a flat surface, convex surface, a concave surface, or the like **340** which is an acoustical tool that transfers the vibratory energy directly to the non-optical surface of a mold half.

The present invention is practiced with the above described apparatus as follows: an ultrasonic welding apparatus as described above, the specific system being used for the investigation is a Dukane iQ Series ES Servo Ultrasonic Welding Press System with a 30 kHz generator, 2:1 booster. The generator creates a user settable, high voltage (~1000 Vrms), 30 kHz signal that is applied to the transducer. The transducer expands and contract with this applied voltage and creates a mechanical vibration at the face of the transducer. This vibration is amplified by the booster and horn assembly. To

maximize the effectiveness of the mechanical vibration on the part, the vibration needs to be applied in a prescribed manner.

To operate the Dukane Servo system, the ultrasonic horn is lowered to a point in space, where it begins to look for a reaction force equal to the trigger force set by the user. It will continue to move downward at prescribed speed over a short distance looking for that reaction force. When that force is achieved, the system will fire the ultrasonics. Once fired, the horn will seek to move to maintain that constant force. Force mode was chosen to deal with the normal positional variation you would encounter with different parts placed slightly differently from the previous part, as well as slight geometry variations from part to part. The generator output energy equals to the time integral of power. Example process settings are shown in the following table.

| Process Parameter   | Setting      |
|---------------------|--------------|
| Generator Frequency | 30 or 40 kHz |
| Booster             | 2:1          |
| Horn                | 2:1          |
| Trigger Force       | 100 N        |
| Energy              | 0.1-40J      |

According to the present invention, Generator Frequency is operated between 15 kHz to 70 kHz, preferably between 20 kHz to 40 kHz, more preferably between 30 kHz to 40 kHz. Trigger Force is operated between 1.0 N to 150N, preferably between 20 N to 120N, more preferably between 40 N to 110N, still more preferably between 80 N to 100N. Energy is operated between 0.1J to 40J, preferably between 0.5J to 30J, still more preferably between 1.0J to 20J. The duration of applying the ultrasonic vibration energy necessary to separate the molded hydrogel contact lens from the female mold half or the male mold half attached thereon is typically less than 10 seconds, preferably less than 5.0 seconds, more preferably less than 2.0 seconds, still more preferably less than 1.0 second.

Although various embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those skilled in the art without departing from the spirit or scope of the present invention, which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged either in whole or in part or can be combined in any manner and/or used together, as illustrated below:

1. A method for producing silicone hydrogel contact lenses, comprising the steps of:

- (1) obtaining a polymerizable composition which is clear at room temperature, wherein the polymerizable composition comprises (a) at least one siloxane-containing vinylic monomer, (b) at least one polysiloxane vinylic crosslinker, (c) at least one hydrophilic N-vinyl amide monomer, (d) from about 5% to about 15% by weight of at least one hydrophobic acrylic monomer relative to the total weight of the polymerizable composition, wherein the hydrophobic acrylic monomer is capable of forming a homopolymer having a glass-transition temperature  $T_g$  of at least about 60°C, wherein the hydrophobic acrylic monomer is capable of dissolving components (a) to (c) to form a solution with a concentration of at least about 5% by weight, (e) from about 4% to about 16% by weight of at least one organic solvent having 2 to 8 carbon atoms relative to the total weight of the polymerizable composition, (f) at least one non-silicone vinylic crosslinker, and (g) at least one free radical initiator, wherein the sum of the amounts of components (a) to (c) is at least about 60% by weight relative to the total weight of the polymerizable composition, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.24 (preferably at least 0.35, more preferably at least 0.45, even more preferably at least 0.55) per 100 grams of the polymerizable composition;
- (2) introducing the polymerizable composition into a lens mold, wherein the lens mold comprises a male mold half having a first molding surface and a female mold half having a second molding surface, wherein the male and female mold halves are configured to receive each other such that a mold cavity is formed between the first and second molding surfaces when the mold is closed;
- (3) curing thermally or actinically the polymerizable composition in the lens mold to form an unprocessed silicone hydrogel lens precursor within the lens mold;
- (4) separating the mold into the male and female mold halves, with the unprocessed silicone hydrogel adhered on a lens-adhered mold half which is one of the male and female mold halves;
- (5) removing the unprocessed silicone hydrogel lens precursor from the lens-adhered mold half before the unprocessed silicone hydrogel lens precursor is contacted with water or any liquid, wherein the step of removing is performed by (a) bringing an ultrasonic horn in direct contact with at least one area of a non-optical surface of the lens-adhered mold half having the unprocessed silicone hydrogel lens precursor attached thereon and (b) applying an ultrasonic vibrational energy of from about 0.2 to about 18 J to the at least one area of the non-optical surface of the lens-adhered mold half having the unprocessed

silicone hydrogel lens precursor attached thereon so as to remove the unprocessed silicone hydrogel lens precursor from the lens-adhered mold half; and

- (6) subjecting the unprocessed silicone hydrogel lens precursor to one or more post-molding processes selected from the group consisting of extraction, hydration, packaging, sterilization, and combinations thereof.
2. The method of embodiment 1, wherein the polymerizable composition comprises from about 6% to about 14% by weight of the hydrophobic acrylic monomer relative to the total weight of the polymerizable composition.
  3. The method of embodiment 1, wherein the polymerizable composition comprises from about 7% to about 13% by weight of the hydrophobic acrylic monomer relative to the total weight of the polymerizable composition.
  4. The method of embodiment 1, wherein the polymerizable composition comprises from about 8% to about 12% by weight of the hydrophobic acrylic monomer relative to the total weight of the polymerizable composition.
  5. The method of any one of embodiments 1 to 4, wherein the hydrophobic acrylic monomer is methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, phenyl methacrylate, 4-tert-butylstyrene, 2-methylstyrene, styrene, 4-ethoxystyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, 3,5-dimethylstyrene, or a combination thereof.
  6. The method of any one of embodiments 1 to 4, wherein the hydrophobic acrylic monomer is methyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, or a combination thereof.
  7. The method of any one of embodiments 1 to 4, wherein the hydrophobic acrylic monomer is methyl methacrylate, tert-butyl methacrylate, or a combination thereof.
  8. The method of any one of embodiments 1 to 7, wherein the homopolymer of the hydrophobic acrylic monomer has a glass-transition temperature  $T_g$  of at least about 70°C.
  9. The method of any one of embodiments 1 to 7, wherein the homopolymer of the hydrophobic acrylic monomer has a glass-transition temperature  $T_g$  of at least about 80°C.
  10. The method of any one of embodiments 1 to 7, wherein the homopolymer of the hydrophobic acrylic monomer has a glass-transition temperature  $T_g$  of at least about 90°C.
  11. The method of any one of embodiments 1 to 10, wherein the polymerizable

composition comprises from about 5% to about 15% by weight of the organic solvent relative to the total weight of the polymerizable composition.

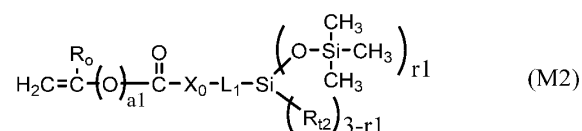
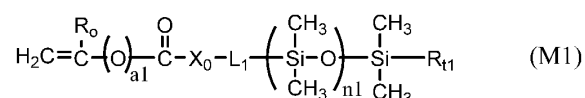
12. The method of any one of embodiments 1 to 10, wherein the polymerizable composition comprises from about 6% to about 14% by weight of the organic solvent relative to the total weight of the polymerizable composition.
13. The method of any one of embodiments 1 to 10, wherein the polymerizable composition comprises from about 6% to 12% by weight of the organic solvent relative to the total weight of the polymerizable composition.
14. The method of any one of embodiments 1 to 13, wherein the organic solvent has 3 to 5 carbon atoms.
15. The method of any one of embodiments 1 to 13, wherein the organic solvent is 1-propanol, isopropanol, 1-butanol, sec-butanol, isobutanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-1-butanol, 2,2-dimethyl-1-propanol, tert-amyl alcohol, 1-methoxy-2-propanol, 3-ethoxy-1-propanol, 1-ethoxy-2-propanol, or a combination thereof.
16. The method of any one of embodiments 1 to 15, wherein the sum of the amounts of components (a) to (c) is at least about 65% by weight relative to the total weight of the polymerizable composition.
17. The method of any one of embodiments 1 to 15, wherein the sum of the amounts of components (a) to (c) is at least about 70% by weight relative to the total weight of the polymerizable composition.
18. The method of any one of embodiments 1 to 15, wherein the sum of the amounts of components (a) to (c) is at least about 75% by weight relative to the total weight of the polymerizable composition.
19. The method of any one of embodiments 1 to 18, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.35 per 100 grams of the polymerizable composition.
20. The method of any one of embodiments 1 to 18, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.45 per 100 grams of the polymerizable composition.
21. The method of any one of embodiments 1 to 18, wherein weight ratio of component (d) over the sum of components (d) and (e) is at least 0.55 per 100 grams of the polymerizable composition.
22. The method of any one of embodiments 1 to 21, wherein the polymerizable composition comprises about 1.5% or less by weight of at least one non-silicone vinylic crosslinker relative to the total weight of all polymerizable components in the

polymerizable composition.

23. The method of any one of embodiments 1 to 21, wherein the polymerizable composition comprises about 1.2% or less by weight of at least one non-silicone vinylic crosslinker relative to the total weight of all polymerizable components in the polymerizable composition.
24. The method of any one of embodiments 1 to 21, wherein the polymerizable composition comprises from about 0.1% to about 1.0% by weight of at least one non-silicone vinylic crosslinker relative to the total weight of all polymerizable components in the polymerizable composition.
25. The method of embodiment 24, wherein said at least non-silicone vinylic crosslinker is ethyleneglycol di-(meth)acrylate, diethyleneglycol di-(meth)acrylate, triethyleneglycol di-(meth)acrylate, tetraethyleneglycol di-(meth)acrylate, glycerol di-(meth)acrylate, 1,3-propanediol di-(meth)acrylate, 1,3-butanediol di-(meth)acrylate, 1,4-butanediol di-(meth)acrylate, glycerol 1,3-diglycerolate di-(meth)acrylate, ethylenebis[oxy(2-hydroxypropane-1,3-diyl)] di-(meth)acrylate, bis[2-(meth)acryloxyethyl] phosphate, trimethylolpropane di-(meth)acrylate, and 3,4-bis[(meth)acryloyl]tetrahydrofuran, diacrylamide (i.e., N-(1-oxo-2-propenyl)-2-propenamide), dimethacrylamide (i.e., N-(1-oxo-2-methyl-2-propenyl)-2-methyl-2-propenamide), N,N-di(meth)acryloyl-N-methylamine, N,N-di(meth)acryloyl-N-ethylamine, N,N'-methylene bis(meth)acrylamide, N,N'-ethylene bis(meth)acrylamide, N,N'-dihydroxyethylene bis(meth)acrylamide, N,N'-propylene bis(meth)acrylamide, N,N'-2-hydroxypropylene bis(meth)acrylamide, N,N'-2,3-dihydroxybutylene bis(meth)acrylamide, 1,3-bis(meth)acrylamide-propane-2-yl dihydrogen phosphate (i.e., N,N'-2-phosphonyloxypropylene bis(meth)acrylamide), piperazine diacrylamide (or 1,4-bis(meth)acryloyl piperazine), tetraethyleneglycol divinyl ether, triethyleneglycol divinyl ether, diethyleneglycol divinyl ether, ethyleneglycol divinyl ether, triallyl isocyanurate, triallyl cyanurate, trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, bisphenol A dimethacrylate, or combinations thereof.
26. The method of embodiment 24, wherein said at least non-silicone vinylic crosslinker is tetra(ethyleneglycol) di-(meth)acrylate, tri(ethyleneglycol) di-(meth)acrylate, ethyleneglycol di-(meth)acrylate, di(ethyleneglycol) di-(meth)acrylate, tetraethyleneglycol divinyl ether, triethyleneglycol divinyl ether, diethyleneglycol divinyl ether, ethyleneglycol divinyl ether, triallyl isocyanurate, triallyl cyanurate, or a combination thereof.
27. The method of any one of embodiments 1 to 26, wherein the step of curing is

carried out thermally.

28. The method of any one of embodiments 1 to 26, wherein the step of curing is carried out actnically.
29. The method of any one of embodiments 1 to 28, wherein the polymerizable composition further comprises about 10% or less by weight of at least one hydrophilic acrylic monomer, relative to the total weight of the polymerizable composition.
30. The method of any one of embodiments 1 to 28, wherein the polymerizable composition further comprises about 8% or less by weight of at least one hydrophilic acrylic monomer, relative to the total weight of the polymerizable composition.
31. The method of any one of embodiments 1 to 28, wherein the polymerizable composition further comprises about 5% or less by weight of at least one hydrophilic acrylic monomer, relative to the total weight of the polymerizable composition.
32. The method of any one of embodiments 29 to 31, wherein hydrophilic acrylic monomer is N,N-dimethyl (meth)acrylamide, (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N-hydroxypropyl (meth)acrylamide, hydroxyethyl methacrylate, glycerol methacrylate (GMA), polyethylene glycol (meth)acrylate having a number average molecular weight of up to 1500, polyethylene glycol C<sub>1</sub>-C<sub>4</sub>-alkyl ether (meth)acrylate having a number average molecular weight of up to 1500, N-[tris(hydroxymethyl)methyl]-acrylamide, (meth)acrylic acid, ethylacrylic acid, or a combination thereof.
33. The method of any one of embodiments 29 to 31, wherein hydrophilic acrylic monomer is N,N-dimethyl (meth)acrylamide, hydroxyethyl (meth)acrylate, N-hydroxyethyl (meth)acrylamide, glycerol methacrylate (GMA), or a combination thereof.
34. The method of any one of embodiments 1 to 33, wherein said at least one siloxane-containing vinylic monomer is a vinylic monomer of formula (M1) or (M2)



in which: a<sub>1</sub> is zero or 1; R<sub>0</sub> is H or methyl; X<sub>0</sub> is O or NR<sub>1</sub>; L<sub>1</sub> is a C<sub>2</sub>-C<sub>8</sub> alkylene

divalent radical or a divalent radical of  $-\text{L}_1'-\text{X}_1-\text{L}_1''-$ ,  $-(\text{C}_2\text{H}_4\text{O})_{\text{q1}}-\text{L}_1''-$ ,

$\text{-(C}_2\text{H}_4\text{O)}_{q1}\text{-CONH-L}_1\text{'-}$ ,  $\text{-L}_1\text{'-NHCOO-(C}_2\text{H}_4\text{O)}_{q1}\text{-L}_1\text{'-}$ ,  
 $\text{-CH}_2\text{-CH(OH)-CH}_2\text{-X}_1\text{'-(C}_2\text{H}_4\text{O)}_{q2}\text{-L}_1\text{'-}$ ,  $\text{-L}_1\text{'-X}_1\text{'-CH}_2\text{-CH(OH)-CH}_2\text{-O-L}_1\text{'-}$ , or  
 $\text{-(C}_2\text{H}_4\text{O)}_{q1}\text{-CH}_2\text{-CH(OH)-CH}_2\text{-O-L}_1\text{'-}$ ;  $\text{L}_1\text{'}$  is a  $\text{C}_2\text{-C}_8$  alkylene divalent radical which  
 has zero or one hydroxyl group;  $\text{L}_1\text{'}$  is  $\text{C}_3\text{-C}_8$  alkylene divalent radical which has zero  
 or one hydroxyl group;  $\text{X}_1$  is O,  $\text{NR}_1$ ,  $\text{NHCOO}$ ,  $\text{OCONH}$ ,  $\text{CONR}_1$ , or  $\text{NR}_1\text{CO}$ ;  $\text{R}_1$  is H  
 or a  $\text{C}_1\text{-C}_4$  alkyl having 0 to 2 hydroxyl group;  $\text{R}_{11}$  and  $\text{R}_{12}$  independent of each other  
 are a  $\text{C}_1\text{-C}_4$  alkyl;  $\text{X}_1\text{'}$  is O or  $\text{NR}_1$ ;  $q_1$  is an integer of 1 to 20;  $q_2$  is an integer of 0 to  
 20;  $n_1$  is an integer of 3 to 25; and  $r_1$  is an integer of 2 or 3.

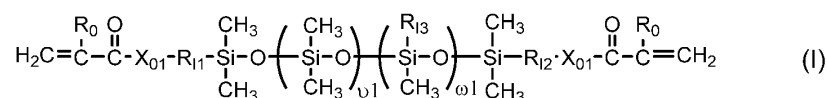
35. The method of any one of embodiments 1 to 33, wherein said at least one siloxane-containing vinylic monomer is tris(trimethylsilyloxy)silylpropyl (meth)acrylate, [3-(meth)acryloxy-2-hydroxypropyloxy]propylbis(trimethylsiloxy) methylsilane, [3-(meth)acryloxy-2-hydroxypropyloxy]propylbis(trimethylsiloxy)butylsilane, 3-(meth)acryloxy-2-(2-hydroxyethoxy)-propyloxy]propylbis(trimethylsiloxy)methylsilane, 3-(meth)acryloxy-2-hydroxypropyloxy]propyltris(trimethylsiloxy)silane, N-[tris(trimethylsiloxy)silylpropyl]-(meth)acrylamide, N-(2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)-propyl)-2-methyl (meth)acrylamide, N-(2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)-propyloxy)propyl) (meth)acrylamide, N-(2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)-propyloxy)propyl)-2-methyl acrylamide, N-(2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)-propyloxy)propyl) (meth)acrylamide, N-[tris(dimethylpropylsiloxy)silylpropyl]-(meth)acrylamide, N-[tris(dimethylphenylsiloxy)silylpropyl] (meth)acrylamide, N-[tris(dimethylethylsiloxy)silylpropyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)propyl]-2-methyl (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(bis(trimethylsilyloxy)methylsilyl)propyloxy)-propyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)propyloxy)-propyl]-2-methyl (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(tris(trimethylsilyloxy)silyl)propyloxy)propyl] (meth)acrylamide, N-[2-hydroxy-3-(3-(t-butylidimethylsilyl)-propyloxy)propyl]-2-methyl (meth)acrylamide, N-[2-hydroxy-3-(3-(t-butylidimethylsilyl)propyloxy)propyl] (meth)acrylamide, N,N-bis[2-hydroxy-3-(3-(t-butylidimethylsilyl)propyloxy)propyl]-2-methyl (meth)acrylamide, N-2-(meth)acryloxyethyl-O-(methyl-bis-trimethylsiloxy-3-propyl)silyl carbamate, 3-(trimethylsilyl)propylvinyl carbonate, 3-(vinyloxycarbonylthio)-propyl-tris(trimethylsiloxy)silane, 3-[tris(trimethylsiloxy)silyl]propylvinyl carbamate, 3-

[tris(trimethylsiloxy)silyl] propyl allyl carbamate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, or a combination thereof.

36. The method of any one of embodiments 1 to 33, wherein said at least one siloxane-containing vinylic monomer is  $\alpha$ -(meth)acryloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(meth)acryloxy-2-hydroxypropyloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(2-hydroxyl-methacryloxypropyloxypropyl)- $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl-decamethylpentasiloxane,  $\alpha$ -[3-(meth)acryloxyethoxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxy-propyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxyisopropyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxybutyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxyethylamino-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxypropylamino-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloxy-butylamino-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(meth)acryloxy(polyethylenoxy)-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyloxy-ethoxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyl-N-ethylaminopropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyl-aminopropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[(meth)acryloxy-2-hydroxypropyloxy-(polyethylenoxy)propyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -(meth)acryloylamidopropyloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -N-methyl-(meth)acryloylamidopropyloxypropyl terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidoethoxy-2-hydroxypropyloxy-propyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidopropyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidoisopropyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acrylamidobutyloxy-2-hydroxypropyloxypropyl]-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane,  $\alpha$ -[3-(meth)acryloylamido-2-hydroxypropyloxypropyl] terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl polydimethylsiloxane,  $\alpha$ -[3-[N-

methyl-(meth)acryloylamido]-2-hydroxypropyloxypropyl] terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl terminated polydimethylsiloxane, N-methyl-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilane) (meth)acrylamide, N-(2,3-dihydroxypropane)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilane) (meth)acrylamide, (meth)acryloylamidopropyltetra(dimethylsiloxy)dimethylbutylsilane,  $\alpha$ -vinyl carbonate-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl-terminated polydimethylsiloxanes,  $\alpha$ -vinyl carbamate-terminated  $\omega$ -C<sub>1</sub>-C<sub>4</sub>-alkyl-terminated polydimethylsiloxane, or a mixture thereof.

37. The method of any one of embodiments 1 to 36, wherein said at least one polysiloxane vinylic crosslinker is a vinylic crosslinker of formula (I)



in which:

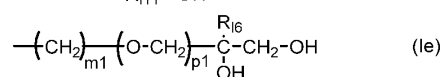
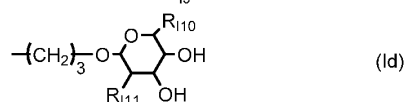
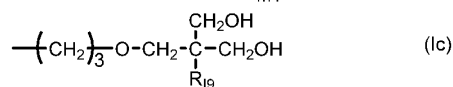
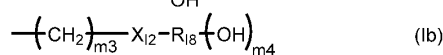
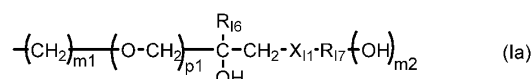
$\omega 1$  is an integer of from 30 to 500 and  $\omega 1$  is an integer of from 1 to 75, provided that  $\omega 1/\omega 1$  is from about 0.035 to about 0.15;

$\text{X}_{01}$  is O or  $\text{NR}_N$  in which  $\text{R}_N$  is hydrogen or C<sub>1</sub>-C<sub>10</sub>-alkyl;

$\text{R}_0$  is hydrogen or methyl;

$\text{R}_{11}$  and  $\text{R}_{12}$  independently of each other are a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkylene divalent radical or a divalent radical of  $-\text{R}_{14}-\text{O}-\text{R}_{15}-$  in which  $\text{R}_{14}$  and  $\text{R}_{15}$  independently of each other are a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkylene divalent radical;

$\text{R}_{13}$  is a monovalent radical of any one of formula (Ia) to (Ie)



$p1$  is zero or 1;  $m1$  is an integer of 2 to 4;  $m2$  is an integer of 1 to 5;  $m3$  is an integer of 3 to 6;  $m4$  is an integer of 2 to 5;

R<sub>16</sub> is hydrogen or methyl;

R<sub>17</sub> is a C<sub>2</sub>-C<sub>6</sub> hydrocarbon radical having (m<sub>2</sub>+1) valencies;

R<sub>18</sub> is a C<sub>2</sub>-C<sub>6</sub> hydrocarbon radical having (m<sub>4</sub>+1) valencies;

R<sub>19</sub> is ethyl or hydroxymethyl;

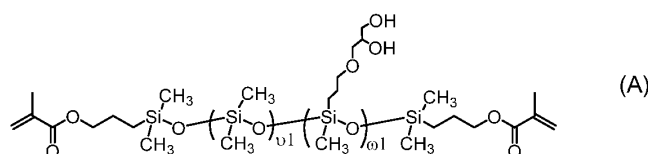
R<sub>110</sub> is methyl or hydromethyl;

R<sub>111</sub> is hydroxyl or methoxy;

X<sub>11</sub> is a sulfur linkage of -S- or a tertiary amino linkage of -NR<sub>112</sub>- in which R<sub>112</sub> is C<sub>1</sub>-C<sub>1</sub> alkyl, hydroxyethyl, hydroxypropyl, or 2,3-dihydroxypropyl; and

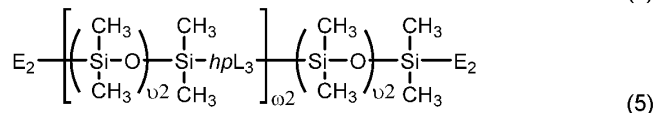
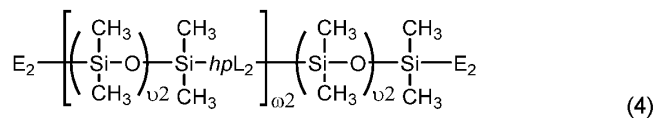
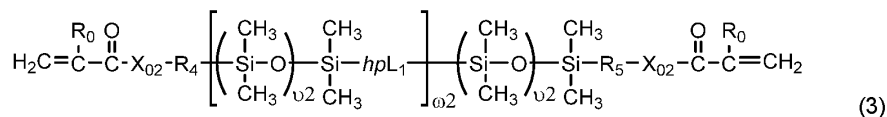
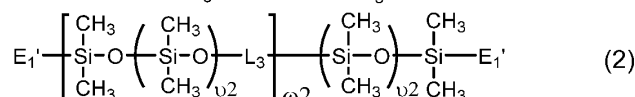
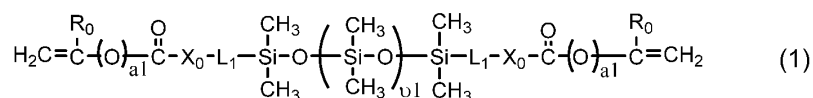
X<sub>12</sub> is an amide linkage of -NR<sub>113</sub>-C(=O)- or -C(=O)-NR<sub>113</sub>- in which R<sub>113</sub> is hydrogen or C<sub>1</sub>-C<sub>10</sub> alkyl.

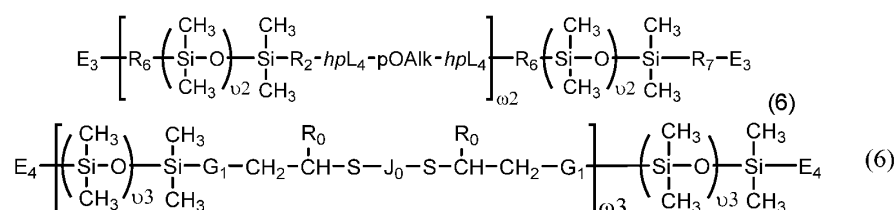
38. The method of any one of embodiments 1 to 36, wherein said at least one polysiloxane vinylic crosslinker is a vinylic crosslinker of formula (A)



in which ν<sub>1</sub> is an integer of from 30 to 500 and ω<sub>1</sub> is an integer of from 1 to 75, provided that ω<sub>1</sub>/ν<sub>1</sub> is from about 0.035 to about 0.15.

39. The method of any one of embodiments 1 to 36, wherein said at least one polysiloxane vinylic crosslinker is a vinylic crosslinker of any one of formula (1) to (7)





in which:

$\nu 1$  is an integer of from 30 to 500;

$\nu 2$  is an integer of from 5 to 50;

$\nu 3$  is an integer of from 5 to 100;

$\omega 2$  and  $\omega 3$  independent of each other are an integer of from 1 to 15;

$a_1$  and  $g_1$  independent of each other is zero or 1;

$h_1$  is an integer of 1 to 20 and  $h_2$  is an integer of 0 to 20;

$m_1$  and  $m_3$  independent of each other is 0 or 1,  $m_2$  is an integer of 1 to 6,  $m_4$  is an integer of 1 to 5,  $m_5$  is 2 or 3;

$q_1$  is an integer of 1 to 20,  $q_2$  is an integer of 0 to 20,  $q_3$  is an integer of 0 to 2,  $q_4$  is an integer of 2 to 50,  $q_5$  and  $q_6$  independent of each other are a number of 0 to 35, provided that  $(q_4+q_5+q_6)$  is an integer of 2 to 50;

$x+y$  is an integer of from 10 to 30;

$e_1$  is an integer of 5 to 100,  $p_1$  and  $b_1$  independent of each other are an integer of 0 to 50, provided that  $(e_1+p_1+b_1) \geq 10$  and  $\frac{e_1}{(p_1+b_1)} \geq 2$  when  $(p_1+b_1) \geq 1$ ;

$R_0$  is H or methyl;

$R_1$ ,  $R_{1n}$ ,  $R_{2n}$ ,  $R_{3n}$ , and  $R_{4n}$  independent of one another are H or a  $C_1$ - $C_4$  alkyl having 0 to 2 hydroxyl group;

$R_{n5}$  is H or a  $C_1$ - $C_{10}$  alkyl;

$R_2$  is a  $C_4$ - $C_{14}$  hydrocarbon divalent radical;

$R_3$  is a  $C_2$ - $C_6$  alkylene divalent radical;

$R_4$  and  $R_5$  independent of each other are a  $C_1$ - $C_6$  alkylene divalent radical or a  $C_1$ - $C_6$  alkylene-oxy- $C_1$ - $C_6$  alkylene divalent radical;

$R_6$  and  $R_7$  independent of each other are a  $C_1$ - $C_6$  alkylene divalent radical or a  $C_1$ - $C_6$  alkoxy- $C_1$ - $C_6$  alkylene divalent radical;

$R_8$  and  $R_9$  independent of each other are a substituted or unsubstituted  $C_1$ - $C_{12}$  alkylene divalent radical;

$X_0$ ,  $X_1$ ,  $X_{01}$ ,  $X_{02}$ , and  $X_{03}$  independent of one another are O or  $NR_1$ ;

$X_1$  is O,  $NR_1$ ,  $NHCOO$ ,  $OCONH$ ,  $CONR_1$ , or  $NR_1CO$ ;

$X_{04}$  is  $-COO-$  or  $-CONR_{n5}-$ ;

$X_{05}$  and  $X_{07}$  independent of each other are a direct bond,  $-\text{COO}-$  or  $-\text{CONR}_{n5}-$ ;

$X_{06}$  is a direct bond, a  $\text{C}_1\text{-C}_6$  alkylene divalent radical, a  $\text{C}_1\text{-C}_6$  alkylenoxy divalent radical,  $-\text{COO}-$ , or  $-\text{CONR}_{n5}-$ ;

$X_{08}$  is a direct bond or  $-\text{COO}-$ ;

$X_{09}$  is O or  $\text{NR}_{n5}$ ;

$X_{10}$  is a direct bond, a  $\text{C}_1\text{-C}_6$  alkylene divalent radical,  $-\text{COO}-$ , or  $-\text{CONR}_{n5}-$ ;

$E_1'$  is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{X}_{01}-\text{L}_4-$ ;

$E_2$  is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{Z}_7-$ ;

$E_3$  is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{X}_{03}-$ ;

$E_4$  is a monovalent radical of  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{X}_{11}-\text{G}_2-$  or  $\text{H}_2\text{C}=\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\text{C}}-\text{G}_3-$ ;

$\text{L}_1$  is a  $\text{C}_2\text{-C}_8$  alkylene divalent radical or a divalent radical of  $-\text{L}_1'-\text{X}_1-\text{L}_1''-$ ,

$-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{L}_1''-$ ,  $-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{CONH}-\text{L}_1''-$ ,  $-\text{L}_1'-\text{NHCOO}-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{L}_1''-$ ,

$-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{X}_1'-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_1''-$ ,  $-\text{L}_1'-\text{X}_1'-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{L}_1''-$ , or

$-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{L}_1''-$ ;

$\text{L}_1'$  is a  $\text{C}_2\text{-C}_8$  alkylene divalent radical which has zero or one hydroxyl group;

$\text{L}_1''$  is  $\text{C}_3\text{-C}_8$  alkylene divalent radical which has zero or one hydroxyl group;

$\text{L}_3$  is a divalent radical of

$-\text{L}_3'-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{CONH}-\text{R}_2-(\text{NHCO}-\text{PE}-\text{CONH}-\text{R}_2)_{g1}-\text{NHCO}-(\text{OC}_2\text{H}_4)_{q2}-\text{O}-\text{L}_3'-$  in which

PE is a divalent radical of

$-(\text{CH}_2\text{CH}_2\text{O})_{q3}-\text{Z}_0-\text{CF}_2-(\text{OCF}_2)_x-(\text{OCF}_2\text{CF}_2)_y-\text{OCF}_2-\text{Z}_0-(\text{OCH}_2\text{CH}_2)_{q3}-$  or

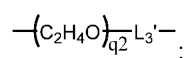
$-\text{Z}_0-(\text{CH}_2\text{CH}_2\text{O})_{q4}-\left(\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{O}\right)_{q5}-\left(\text{CH}_2-\overset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}}-\text{O}\right)_{q6}-\text{Z}_0-$ ;

$\text{L}_3'$  is  $\text{C}_3\text{-C}_8$  alkylene divalent radical;

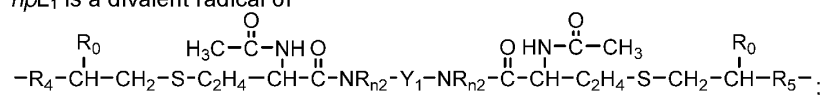
$\text{L}_4$  is a divalent radical of  $-\text{C}_2\text{H}_4-\text{NHCO}-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_3'-$ ,

$-(\text{C}_2\text{H}_4\text{O})_{q1}-\text{CONH}-\text{R}_2-\text{NHCO}-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_3'-$ ,

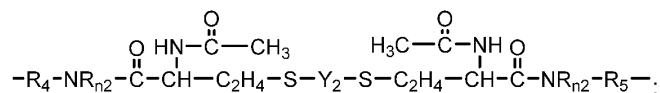
$-\text{R}_3-\text{O}-\text{CONH}-\text{R}_2-\text{NHCO}-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_3'-$ ,  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-(\text{C}_2\text{H}_4\text{O})_{q2}-\text{L}_3'-$ , or



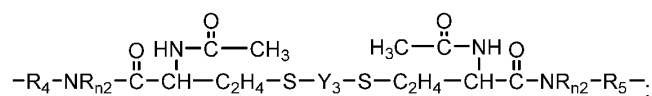
hpL<sub>1</sub> is a divalent radical of



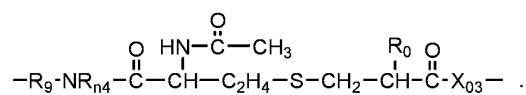
hpL<sub>2</sub> is a divalent radical of



hpL<sub>3</sub> is a divalent radical of



hpL<sub>4</sub> is a divalent radical of  $-X_{03}-\overset{O}{\underset{||}{C}}-\overset{R_0}{\underset{|}{CH}}-CH_2-S-C_2H_4-\overset{H_3C}{\underset{|}{CH}}-\overset{O}{\underset{||}{C}}-NR_{n4}-R_8-$  or



pOAlk is a divalent radical of  $-(EO)_{e1}(PO)_{p1}(BO)_{b1}-$  in which EO is an

oxyethylene unit ( $-CH_2CH_2O-$ ), PO is an oxypropylene unit ( $\begin{matrix} -CH_2-CH-O- \\ | \\ CH_3 \end{matrix}$ ), and

BO is an oxybutylene unit ( $\begin{matrix} -CH_2-CH-O- \\ | \\ C_2H_5 \end{matrix}$ );

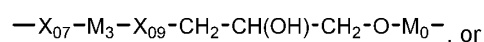
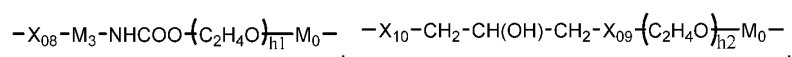
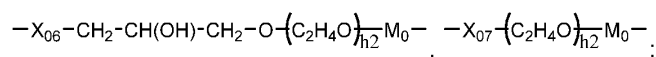
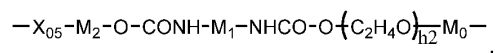
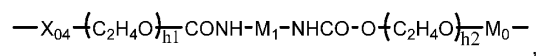
M<sub>0</sub> is C<sub>3</sub>-C<sub>8</sub> alkylene divalent radical;

M<sub>1</sub> is a C<sub>4</sub>-C<sub>14</sub> hydrocarbon divalent radical;

M<sub>2</sub> and M<sub>3</sub> independent of each other are a C<sub>1</sub>-C<sub>6</sub> alkylene divalent radical;

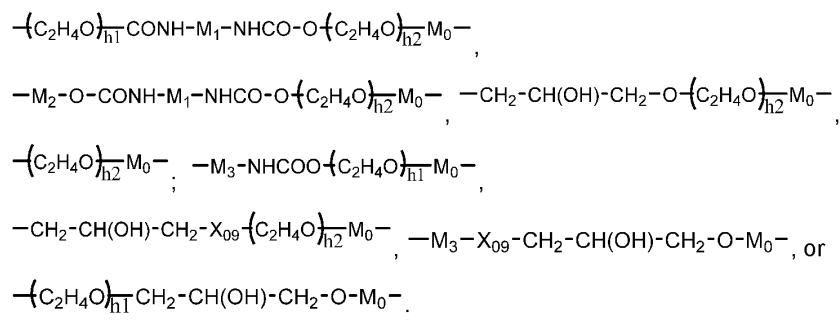
J<sub>0</sub> is a C<sub>1</sub>-C<sub>12</sub> hydrocarbon radical having 0 to 2 hydroxyl or carboxyl groups;

G<sub>1</sub> is a direct bond, a C<sub>1</sub>-C<sub>4</sub> alkylene divalent radical, or a divalent radical of



$-X_{08}-(C_2H_4O)_{h1}-CH_2-CH(OH)-CH_2-O-M_0-$  in which  $M_0$  is linked to Si atom while  $X_{04}$  to  $X_{10}$  are linked to the group of  $-CH_2-$  in formula (7) and at least one of  $J_0$  and  $G_1$  in formula (7) comprises at least one moieties selected from the group consisting of hydroxyl groups, urethane linkage of  $-OCONH-$ , amino groups of  $-NHR^0$ , amino linkages of  $-NH-$ , amide linkages of  $-CONH-$ , carboxyl groups, and combinations thereof;

$G_2$  is a  $C_1$ - $C_4$  alkylene divalent radical or a bivalent radical of



$G_3$  is a divalent radical of  $-G_4-\left(\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\right)_{h3}-\overset{\text{R}_0}{\text{CH}}-CH_2-S-J_0-S-CH_2-\overset{\text{R}_0}{\text{CH}}-\left(\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\right)_{h4}-G_2-$  in which  $h_3$  and  $h_4$  independent of each other are 1 or 0;

$G_4$  is a divalent radical of any one of (a)  $-NR_3'-$  in which  $R_3'$  is hydrogen or  $C_1$ - $C_3$

alkyl, (b)  $-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{N}-$ , (c)  $-NR_0-G_5-NR_0-$  in which  $G_5$  is a  $C_1$ - $C_6$  alkylene divalent radical, 2-hydroxylpropylene divalent radical, 2-(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical, 2,3-dihydroxybutylene divalent radical, and (d)  $-O-G_6-O-$  in which  $G_6$  is a  $C_1$ - $C_6$  alkylene divalent radical, a

divalent radical of  $-(CH_2-\overset{\text{OH}}{\underset{|}{\text{CH}}}-CH_2-O)_{h4'}-CH_2-\overset{\text{OH}}{\underset{|}{\text{CH}}}-CH_2-$  in which  $h_4'$  is 1 or 2, a

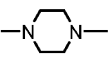
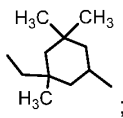
divalent radical of  $-CH_2-\overset{\text{OH}}{\underset{|}{\text{CH}}}-CH_2-O-CH_2-CH_2-O-CH_2-\overset{\text{OH}}{\underset{|}{\text{CH}}}-CH_2-$ , a divalent

radical of  $-(CH_2-CH_2-O)_{h5}-CH_2-CH_2-$  in which  $h_5$  is an integer of 1 to 5, a

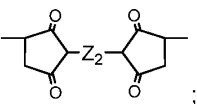
divalent radical of  $-(CH_2)_{h6}-O-\overset{\text{O}}{\underset{\text{||}}{\text{P}}}-O-(CH_2)_{m5}-$  in which  $h_6$  is 2 or 3, or a substituted  $C_3$ - $C_8$  alkylene divalent radical having a hydroxyl group or phosphonyloxy group;

$Y_1$  is a  $C_1$ - $C_6$  alkylene divalent radical, 2-hydroxylpropylene divalent radical, 2-

(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical,

a divalent radical of , or a divalent radical of ;

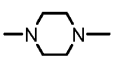
$Y_2$  is a divalent radical of  $-\text{CH}_2-\overset{\text{R}_0}{\underset{\text{O}}{\text{C}}}-\text{Z}_3-\overset{\text{O}}{\underset{\text{R}_0}{\text{C}}}-\text{CH}_2-$ ;

$Y_3$  is a divalent radical of  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}(\text{Z}_1-\overset{\text{O}}{\underset{\text{O}}{\text{S}}})_{m1}-\text{CH}_2-\text{CH}_2-$  or ;

$Z_0$  is a direct bond or a  $\text{C}_1$ - $\text{C}_{12}$  alkylene divalent radical;

$Z_1$  is a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, a hydroxyl- or methoxy-substituted  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, or a substituted or unsubstituted phenylene divalent radical,

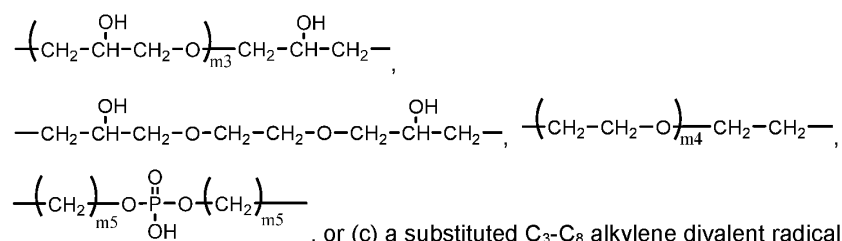
$Z_2$  is a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, a hydroxyl- or methoxy-substituted  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, a dihydroxyl- or dimethoxy-substituted  $\text{C}_2$ - $\text{C}_6$  alkylene divalent radical, a divalent radical of  $-\text{C}_2\text{H}_4-(\text{O}-\text{C}_2\text{H}_4)_{m2}-$ , a divalent radical of  $-\text{Z}_4-\text{S}-\text{S}-\text{Z}_4-$ , a hydroxyl- or methoxy-substituted  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, or a substituted or unsubstituted phenylene divalent radical,

$Z_3$  is a divalent radical of any one of (a)  $-\text{NR}_{n3}-$ , (b) , (c)  $-\text{NR}_0-\text{Z}_5-$   $\text{NR}_0-$ , and (d)  $-\text{O}-\text{Z}_6-\text{O}-$ ,

$Z_4$  is a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical,

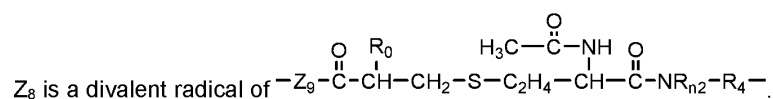
$Z_5$  is a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, 2-hydroxypropylene divalent radical, 2-(phosphonyloxy)propylene divalent radical, 1,2-dihydroxyethylene divalent radical, 2,3-dihydroxybutylene divalent radical,

$Z_6$  is (a) a  $\text{C}_1$ - $\text{C}_6$  alkylene divalent radical, (b) a divalent radical of



having a hydroxyl group or phosphonyloxy group,

$Z_7$  is a divalent radical of  $-\text{Z}_3-\overset{\text{O}}{\underset{\text{R}_0}{\text{C}}}-\text{CH}-\text{CH}_2-\text{S}-\text{C}_2\text{H}_4-\text{CH}-\overset{\text{O}}{\underset{\text{H}_3\text{C}-\text{C}-\text{NH}}{\text{C}}}-\text{NR}_{n2}-\text{R}_4-$ ; and



40. The method of any one of embodiments 1 to 36, wherein the polymerizable materials comprise at least one silicone-containing vinylic crosslinker which is  $\alpha,\omega$ -bis[3-(meth)acrylamidopropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxyethoxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxy-isopropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxybutyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidoethoxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidopropoxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidoisopropyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidobutyloxy-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxyethylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxypropylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acryloxybutylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acrylamidoethylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamidopropylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[3-(meth)acrylamide-butylamino-2-hydroxypropyloxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyloxy-ethoxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyl-N-ethylaminopropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyl-aminopropyl]-polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxy-2-hydroxypropyloxy-(polyethylenoxy)propyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxyethylamino-carbonyloxy-ethoxypropyl]-terminated polydimethylsiloxane,  $\alpha,\omega$ -bis[(meth)acryloxyethylamino-carbonyloxy-(polyethylenoxy)propyl]-terminated polydimethylsiloxane, or a combination thereof.
41. The method of any one of embodiments 1 to 40, wherein said at least one

hydrophilic N-vinyl amide monomer is N-vinylpyrrolidone, N-vinyl piperidone, N-vinyl caprolactam, N-vinyl-N-methyl acetamide, N-vinyl formamide, N-vinyl acetamide, N-vinyl isopropylamide, N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, or a mixture thereof.

42. The method of any one of embodiments 1 to 40, wherein said at least one hydrophilic N-vinyl amide monomer is N-vinylpyrrolidone, N-vinyl-N-methyl acetamide, or a combination thereof.
43. The method of any one of embodiments 1 to 42, wherein the polymerizable composition further comprises from about 1% to about 10% by weight of at least one hydrophilic acrylic monomer relative to the total weight of the polymerizable composition.
44. The method of any one of embodiments 1 to 42, wherein the polymerizable composition further comprises from about 1% to about 8% by weight of at least one hydrophilic acrylic monomer relative to the total weight of the polymerizable composition.
45. The method of any one of embodiments 1 to 42, wherein the polymerizable composition further comprises from about 1% to about 5% by weight of at least one hydrophilic acrylic monomer relative to the total weight of the polymerizable composition.
46. The method of any one of embodiments 43 to 45, wherein said at least one hydrophilic acrylic monomer is N,N-dimethyl (meth)acrylamide, (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N-hydroxypropyl (meth)acrylamide, hydroxyethyl methacrylate, glycerol methacrylate (GMA), polyethylene glycol (meth)acrylate having a number average molecular weight of up to 1500, polyethylene glycol C<sub>1</sub>-C<sub>4</sub>-alkyl ether (meth)acrylate having a number average molecular weight of up to 1500, *N*-[tris(hydroxymethyl)methyl]-acrylamide, (meth)acrylic acid, ethylacrylic acid, or a combination thereof.
47. The method of any one of embodiments 43 to 45, wherein said at least one hydrophilic acrylic monomer is N,N-dimethyl (meth)acrylamide, hydroxyethyl (meth)acrylate, N-hydroxyethyl (meth)acrylamide, glycerol methacrylate (GMA), or a combination thereof.
48. The method of any one of embodiments 1 to 47, wherein the ultrasonic horn has a convex surface which is in contact with the lens-adhered mold half.
49. The method of any one of embodiments 1 to 47, wherein the ultrasonic horn has a concave surface which is in contact with the lens-adhered mold half.
50. The method of any one of embodiments 1 to 47, wherein the ultrasonic horn has a

flat surface which is in contact with the lens-adhered mold half.

The previous disclosure will enable one having ordinary skill in the art to practice the invention. Various modifications, variations, and combinations can be made to the various embodiment described herein. In order to better enable the reader to understand specific embodiments and the advantages thereof, reference to the following examples is suggested. It is intended that the specification and examples be considered as exemplary.

### Example 1

#### Chemicals

The following abbreviations are used in the following examples: NVP represents N-vinylpyrrolidone; MMA represents methyl methacrylate; TEGDMA represent triethyleneglycol dimethacrylate; VAZO 64 represents 2,2'-dimethyl-2,2'-azodipropiononitrile; Nobloc is 2-[3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate from Aldrich; UV28 represents 2-{2'-Hydroxy-3'-*tert*-butyl-5'-[3'-methacryloyloxypropoxy]phenyl}-5-chloro-2*H*-benzotriazole; RB247 is Reactive Blue 247; PrOH represents 1-propanol; PBS represents a phosphate-buffered saline which has a pH of  $7.2 \pm 0.2$  at 25°C and contains about 0.044 wt.%  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , about 0.388 wt.%  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , and about 0.79 wt.% NaCl and; wt.% represents weight percent; D9 represents monobutyl-terminated monomethacryloxypropyl-terminated polydimethylsiloxane ( $M_w \sim 984$  g/mol from Shin-Etsu); "G4" macromer represents a dimethacryloyloxypropyl-terminated polysiloxane ( $M_n \sim 13.5\text{K}$  g/mol, OH content  $\sim 1.8$  meq/g) of formula (A) shown above.

#### Preparation of Polymerizable Compositions

All polymerizable compositions (i.e., "formulations") are prepared at room temperature in air using 5-30 minutes of stirring. 1-propanol (PrOH) is used as non-reactive diluent. MMA is used as reactive diluent. Eight polymerizable compositions are prepared by dissolving and blending: 33 weight part units of D9; 10 weight part units of G4; 46 weight part units of NVP; 1.5 weight part units of Nobloc; 33 weight part units of D9; 0.01 weight part unit of RB247; 0.4 weight part unit of UV28; 0.5 weight part unit of Vazo-64; and various amounts (weight part units shown in Table 1) of TEGDMA; in various amounts (weight part units shown in Table 1) of PrOH and various amounts (weight part units shown in Table 1) of MMA. These eight polymerizable compositions are designed according to 3 factor DOE (Design of Experiment) using Minitab version 17.

Table 1

| Formulation # | PrOH              | MMA | TEGDMA | $\frac{[MMA]}{[MMA] + [PrOH]}$ (per 100 g of formulation) |
|---------------|-------------------|-----|--------|-----------------------------------------------------------|
|               | Weight Part Units |     |        |                                                           |
| 1             | 6                 | 5   | 0.1    | 0.44                                                      |
| 2             | 6                 | 10  | 0.1    | 0.58                                                      |
| 3             | 6                 | 5   | 0.8    | 0.44                                                      |
| 4             | 6                 | 10  | 0.8    | 0.58                                                      |
| 5             | 14                | 5   | 0.1    | 0.24                                                      |
| 6             | 14                | 10  | 0.1    | 0.36                                                      |
| 7             | 14                | 5   | 0.8    | 0.24                                                      |
| 8             | 14                | 10  | 0.8    | 0.36                                                      |

### Cast Molding

Approximately 30-35 mg of a formulation prepared above is introduced into a polypropylene molds. Then, the molds are dosed and thermally cured in an even under nitrogen using the following temperature conditions: at 55°C for 40 minutes; at 80°C for 40 minutes; and at 100°C for 40 minutes.

### Mold Separation

Lens molds each with a molded silicone hydrogel contact lens precursor therein are mechanically opened as illustrated by FIG. 2 and described above. The molded unprocessed silicone hydrogel contact lens precursors adhere to the male mold halves.

### Removing Lens Precursors from Lens-Adhered Mold Halves

Molded unprocessed silicone hydrogel contact lens precursors are removed (i.e., “delensed”) from lens-adhered male mold halves by using an ultrasonic welding apparatus as illustrated in FIG. 3. An ultrasonic horn made of stainless steel and having a shape shown in FIGs 4 and 5.

Lens molds each with a molded silicone hydrogel contact lens precursor therein are mechanically opened as illustrated by FIG. 2 and described above. The molded unprocessed silicone hydrogel contact lens precursors adhere to the male mold halves. The following energy settings shown in Table 2 are used for each group.

Table 2

| Condition | Energy (J) | Trigger force (N) | Ramp up time (ms) |
|-----------|------------|-------------------|-------------------|
| 2J        | 2          | 56                | 100               |
| 18J       | 18         | 56                | 20                |

For the milder 2J condition, a slower ramp-up time is employed to make the overall condition even milder for the lens mold interface. Lenses removed with this condition are regarded as having weaker surface bonding. Five lenses per condition per formulation are tested. E.g., for formulation 8, 5 lenses are tested under the 2J condition while 5 lenses are tested under the 18J condition. The results are reported in Table 3.

Table 3

| Formulation | [PrOH] | [MMA] | [TEGDMA] | $\frac{[MMA]}{[MMA] + [PrOH]}$ * | Delensing% |          |
|-------------|--------|-------|----------|----------------------------------|------------|----------|
|             |        |       |          |                                  | With 2J    | with 18J |
| 1           | 6      | 5     | 0.1      | 0.44                             | 0          | 40       |
| 2           | 6      | 10    | 0.1      | 0.58                             | 40         | 100      |
| 3           | 6      | 5     | 0.8      | 0.44                             | 0          | 100      |
| 4           | 6      | 10    | 0.8      | 0.58                             | 100        | 100      |
| 5           | 14     | 5     | 0.1      | 0.24                             | 0          | 20       |
| 6           | 14     | 10    | 0.1      | 0.36                             | 20         | 80       |
| 7           | 14     | 5     | 0.8      | 0.24                             | 0          | 0        |
| 8           | 14     | 10    | 0.8      | 0.36                             | 0          | 100      |

\* per 100 grams of formulation

All the publications, patents, and patent application publications, which have been cited herein above, are hereby incorporated by reference in their entireties.