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(54) **SILICONE ACRYLAMIDE COPOLYMER**

SILIKON-ACRYLAMID-COPOLYMER

COPOLYMÈRE DE SILICONE ET D'ACRYLAMIDE

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a silicone acrylamide copolymer, and the silicone acrylamide copolymer is especially suitably used for medical devices such as ophthalmic lenses, endoscopes, catheters, transfusion tubes, gas transport tubes, stents, sheaths, cuffs, tube connectors, access ports, drainage bags, blood circuits, wound covering materials and various kinds of medicine carriers, particularly contact lenses, intraocular lenses, artificial corneas.

10 BACKGROUND

[0002] In recent years, a silicone hydrogel has been known as a material of a contact lens for use in continuous wear. The silicone hydrogel is obtained by combining a silicone component with a hydrophilic component, and as one example thereof is known a silicone hydrogel obtained by polymerizing a polymerization mixture containing a silicone acrylamide monomer, and a hydrophilic acrylamide monomer, a hydrophilic methacrylate and an internal wetting agent for imparting wettability to a surface (US7396890 and US7214809).

[0003] However, the compositions described in US7396890 and US7214809 have at least one methacrylate as a component in a relatively large amount. The resulting mixed acrylate/methacrylamide systems display a reduction in the polymerization rate of the system compared to an all acrylamide system.

20 **[0004]** Japanese Patent Laid-Open No. H10-212355 and US4711943 disclose silicone hydrogels comprised of a silicone acrylamide monomer and a hydrophilic acrylamide monomer. Such silicone hydrogels have compositions mostly constituted by acrylamide monomers, and improvement of the polymerization rate of the whole system is expected. However, crosslinkers used in these documents have methacrylate group such as ethylene glycol dimethacrylate or tetraethylene glycol dimethacrylate. When such crosslinkers are copolymerized with a (meth)acrylamide monomer, the crosslinker is consumed early in the polymerization. This can lead to a heterogenous polymer network and optical distortion may occur when a contact lens is produced using such a polymer.

25 **[0005]** US4711943 also discloses a composition using a silicone bisacrylamide monomer as a main component of the polymer. Lenses formed from these monomers are hard, and wearer comfort is decreased.

[0006] Silicone containing bis (meth) acrylamide monomers having two (meth)acrylamide groups have also been disclosed.

30 **[0007]** WO 2010/147874 discloses Ma2D37 having a silicone segment with 37 repeating units in a silicone bis (meth) acrylamide monomer. However, the only silicone component disclosed to be polymerized with the silicon bis(meth)acrylamide is a mono-functional branched silicone (meth)acrylamide monomer. The resulting polymer displayed poor shape recovery. The composition disclosed in WO 2010/147874 also contains N-vinylpyrrolidone in a relatively large amount, which negatively effects the polymerization rate as well.

35 **[0008]** WO2010/071691 discloses silicone bis(meth)acrylamide monomers having molecular weights of 4500 and 11000. WO2010/071691 also discloses that it is critical to include a silicone-containing vinylic monomer having a tris(tri-alkylsilyloxy)silylalkyl group to eliminate optical defects. The polymers are disclosed to exhibit a "healing" effect (folding marks become transient), however, "shape recovery" , or the ability of a polymer to recover tensile strength after being released from polymer elongation, is not disclosed. Shape recovery is evaluated by measuring stress zero time. Stress zero time of the polymers in the reference is expected to be longer (worse shape recovery) than those in the present invention because mono-functional silicone acrylamide is not linear silicone.

40 **[0009]** US2011/0009519 discloses Ma2D37 as a silicone bis (meth) acrylamide monomer. Various monomers are polymerized with Ma2D37, but none are mono-functional (meth)acrylamide silicone monomers as presently disclosed. The closest monomer has -Si-CH₂-CH₂-Si- bond alternating with the -Si-O-Si- bonds and an undesirably high modulus.

[0010] European Patent No. 1956033 discloses a silicone bisacrylamide monomer in Synthesis Example 10. However, this monomer is only used as an intermediate for synthesizing a silicone tetraacrylamide compound in Example 10, and there are no descriptions of copolymerization with other silicone monomers, the modulus, transparency or any other properties of a copolymer obtained thereby.

50 **[0011]** N,N'-methylenebisacrylamide (hereinafter referred to as MBA) is a commercially available acrylamide crosslinker. Unfortunately when MBA is used as a crosslinker, undesirably high moduli are obtained. When the amount of crosslinker is decreased, the modulus is reduced, but the copolymer loses transparency before the modulus is sufficiently reduced, thus making it difficult to have both the low modulus and transparency. Furthermore, when an attempt was made to reduce the modulus by using various bisacrylamides having extended methylene chains, there was no significant difference in modulus compared to MBA, and when the amount of crosslinker was decreased, the transparency was reduced, thus making it difficult to have both low modulus and transparency. US2011237766 discloses a silicone hydrogel for contact lenses.

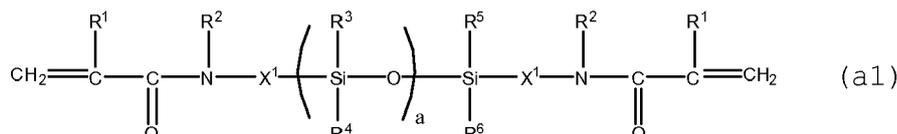
SUMMARY

[0012] The present invention provides a copolymer which has a high acrylamide monomer content, is transparent and has a low modulus.

[0013] The present invention relates to a copolymer comprising (A) a multi-functional (meth)acrylamide monomer having at least one siloxane bond and at least two (meth)acrylamide groups within a molecule and (B) a mono-functional linear silicone (meth)acrylamide monomer.

[0014] When the multi-functional (meth)acrylamide monomer comprises two (meth) acrylamide groups, it may in one embodiment be represented by formula (a1). Formula:

[Chemical Formula 1]



wherein

each R¹ is independently selected from hydrogen and methyl;

R² is independently selected from hydrogen, or an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms;

R³ to R⁶ are each an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms;

X¹ is independently selected from substituted or unsubstituted divalent organic groups having 1 to 20 carbon atoms; and

a represents an integer of 1 to 15.

DETAILED DESCRIPTION

[0015] The present invention provides a copolymer which has a high acrylamide monomer content, is transparent and has a low modulus. The copolymer is suitably used for various kinds of medical devices, particularly ophthalmic lenses such as a contact lens, an intraocular lens, an artificial cornea, and is especially suitable for a contact lens.

[0016] Copolymers of the present invention may be obtained by polymerizing a polymerization mixture comprising components (A) and (B) described below.

(A) is at least one multi-functional (meth)acrylamide monomer having at least one siloxane bond and at least two (meth)acrylamide groups within a molecule and (B) is at least one a mono-functional linear silicone (meth) acrylamide monomer.

[0017] In the present invention, siloxane bond refers to a Si-O-Si bond.

[0018] The term "lens" refers to ophthalmic devices that reside in or on the eye. These devices can provide optical correction, cosmetic enhancement, UV blocking and visible light or glare reduction, therapeutic effect, including wound healing, delivery of drugs or neutraceuticals, diagnostic evaluation or monitoring, or any combination thereof. The term lens includes, but is not limited to, soft contact lenses, hard contact lenses, intraocular lenses, overlay lenses, ocular inserts, and optical inserts.

[0019] "Multi-functional monomer" refers to a monomer having two or more radically polymerizable organic groups.

[0020] "Mono-functional monomer" refers to a monomer having one radically polymerizable organic group. The radically polymerizable organic group is preferably the (meth) acrylamide group.

[0021] The phrase "(meth)acrylamide group" refers to an acrylamide group or a methacrylamide group. In some embodiments the radically polymerizable organic group is preferably an acrylamide group because of the faster polymerization rate of acrylamide monomers.

[0022] As used herein "substituted" means hydroxyl, acid, ester, ether, thiol, and combinations thereof.

[0023] As used herein "parts by mass" in the present invention represents a mass ratio based on 98.8 parts by mass of the components of the polymerizable mixture excluding the multi-functional (meth)acrylamide monomer and polymerization solvent. For example, in the formulation of Example 1, the parts by mass is calculated based upon the polymerizable mixture components except the SiBA and t-amyl alcohol.

[0035] Each R² independently represents hydrogen, or a substituted or unsubstituted alkyl having 1 to 20 carbon atoms, or a substituted or unsubstituted aryl having 6 to 20 carbon atoms. The alkyl may be branched or linear. The substituted groups of the alkyl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, phenyl, and naphthyl. The substituted groups of the aryl are halogen(F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, C1-C6 alkyl, phenyl, and naphthyl. Examples of R² groups include hydrogen, methyl, ethyl, propyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, i-pentyl, s-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, icosyl, phenyl and naphthyl. If the number of carbon atoms of R² is too large, the silicone content may decrease, which reduces the oxygen permeability. Thus, in embodiments where oxygen permeabilities in excess of about 70 and in some cases about 80 barrers are desired, R² may be selected from hydrogen or an unsubstituted alkyl or unsubstituted aryl having 1 to 10 carbon atoms, or hydrogen or an unsubstituted alkyl having 1 to 4 carbon atoms, or hydrogen, ethyl or methyl.

[0036] R³ to R⁶ each independently represent an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms. The substituted groups of the alkyl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, phenyl, and naphthyl. The substituted groups of the aryl are halogen(F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, C1-C6 alkyl, phenyl, and naphthyl. If the number of carbon atoms of R³ to R⁶ is too large, the content of silicon atoms may relatively decrease, leading to a reduction in oxygen permeability. Thus, in embodiments where oxygen permeabilities in excess of about 70 and in some cases about 80 barrers are desired, R³ to R⁶ are selected from (a) unsubstituted alkyl groups having 1 to 10 carbon atoms or an unsubstituted aryl groups having 6 to 10 carbon atoms, (b) unsubstituted alkyl groups having 1 to 4 carbon atoms, or (c) methyl groups.

[0037] Each X¹ independently represents a divalent organic group which may be substituted and has 1 to 20 carbon atoms. The substituted groups of the divalent organic group are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, C1-C6 alkyl, phenyl, and naphthyl. Among the divalent organic group, alkylene and arylene groups are preferable. The alkylene and arylene group may be branched or linear. Examples thereof include methylene, ethylene, propylene, butylene, pentylene, octylene, decylene and phenylene. Among them, an alkylene having 1 to 10 carbon atoms is preferable, an alkylene having 1 to 5 carbon atoms is further preferable. When X¹ is propylene, copolymers having a low modulus can be easily obtained.

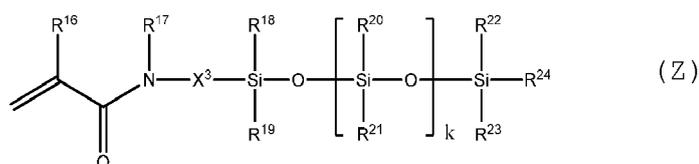
a represents an integer of 1 to 15. If the value of a is too large, the hydrophobicity of the multi-functional (meth)acrylamide monomer may increase making forming transparent copolymers, and particularly those containing polymeric wetting agents in the reactive mixture more difficult. Therefore in some embodiments a is preferably between 1 to 5. In embodiments where copolymers having oxygen permeabilities greater than about 80, and in some embodiments 100 barrers are desired a may have value of 7 to 13. Desirable molecular weights for the multi-functional (meth) acrylamide monomer include those up to 10, 000, and between about 300 and about 5000 weight average molecular weight.

[0038] The lower concentration of multi-functional (meth) acrylamide monomer which may be included in the reactive mixtures of the present application is about 0.1 part, more preferably about 1.0 part by mass, further preferably 1.5 parts by mass or greater as the shape and appearance may be impaired due to insufficient polymerization if concentration of multi-functional (meth) acrylamide monomer is too small. If the concentration of the multi-functional (meth) acrylamide monomer is too high the modulus of the resulting copolymer may be undesirably high. Accordingly, the upper concentration limits for the multi-functional (meth)acrylamide monomer are about 20 parts by mass, preferably 10 parts by mass, more preferably 5 parts by mass or less. The foregoing upper and lower ranges may be combined in any combination.

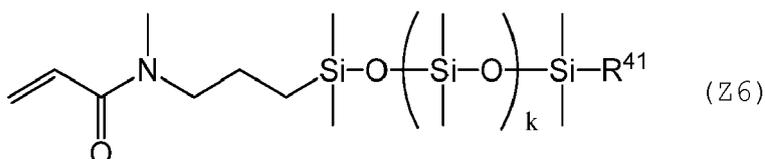
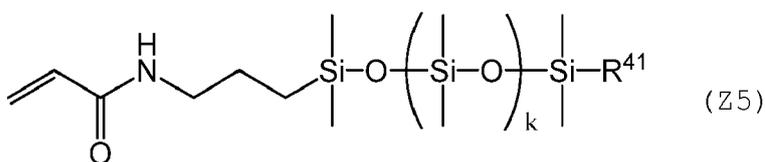
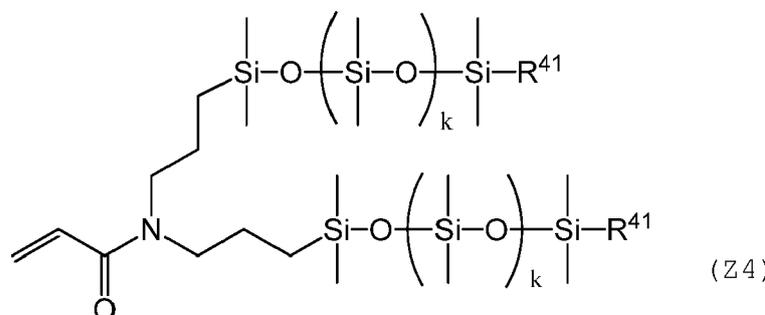
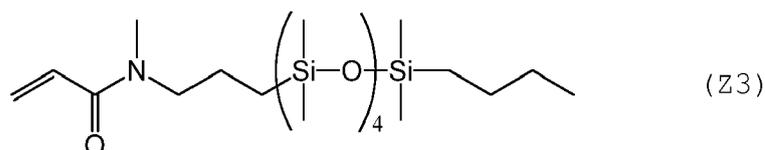
[0039] The oxygen permeability of the resulting copolymers may also be increased by including in the reactive mixture at least one mono-functional linear silicone (meth)acrylamide monomer. The inclusion of at least one mono-functional linear silicone (meth)acrylamide monomer increases the oxygen permeability of the resulting copolymer without increasing the modulus, as would be the case if additional multi-functional monomer was added instead. Furthermore, the use of a linear silicone (meth) acrylamide monomer can improve the shape recovery of the resulting polymer.

[0040] The mono-functional linear silicone (meth)acrylamide monomer comprises one (meth)acrylamide functional group and a at least one linear silicone group.

[0041] Suitable examples of the mono-functional linear silicone (meth)acrylamide monomer include monomers of formula (z)



Where R¹⁶ is selected from hydrogen and methyl. When R¹⁶ is hydrogen the copolymer systems display a faster

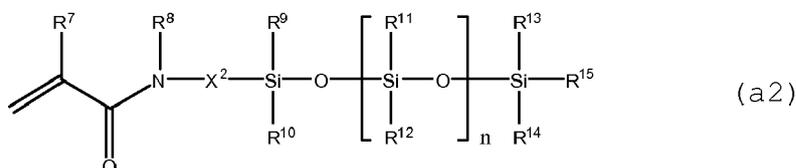


35 **[0048]** In formulae (Z4) to (Z6), k represents an integer of 3-12. R⁴¹ represents a C₁ to C₄ alkyl group.

[0049] Among monomers of the above formulae (Z1) to (Z6), more preferable are those of formulae (Z2) and (Z3) in a sense that compatibility can be easily obtained when the monomer is copolymerized with a hydrophilic component.

[0050] Where improved compatibility of the reactive mixture or transparency of the resulting copolymer is desired, mono-functional linear silicone (meth)acrylamide monomer comprising at least one hydroxyl group may be desirable. This may be particularly advantageous when the copolymer is used for an ophthalmic lens.

40 **[0051]** Suitable examples of the mono-functional linear silicone (meth)acrylamide monomer having at least one hydroxy group include monomers represented by the following general formula (a2) [Chemical Formula 6].



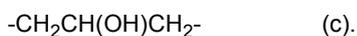
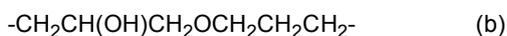
50 In formula (a2), R⁷ is one selected from hydrogen and methyl. When R⁷ is hydrogen the copolymer systems display a faster polymerization rate.

55 **[0052]** R⁸ represents hydrogen, or C₁ to C₂₀ alkyl group which may be substituted with a hydroxy group, or a C₆ to C₂₀ aryl group which may be substituted with a hydroxy. In some embodiments R⁸ is hydrogen, or a C₁-C₁₀ alkyl or C₆-C₁₀ aryl which may be substituted with a hydroxy group, and in another embodiment R⁸ is hydrogen or a C₁-C₄ alkyl which may be substituted with a hydroxy group. Specific examples of R⁸ include hydrogen, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2,3-dihydroxypropyl, 4-hydroxybutyl and 2-hydroxy-1,1-bis(hydroxymethyl)ethyl. A preferred example of R⁸, when X² has a hydroxy group, is hydrogen. A preferred example of R⁸, when X² has no hydroxy group, is 2,3-dihydroxypropyl.

[0053] R⁹ to R¹⁴ each independently represent a C₁ to C₂₀ alkyl which may be substituted, or a C₆ to C₂₀ aryl which may be substituted. The substituted groups of the alkyl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, phenyl, and naphthyl. The substituted groups of the aryl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, C1-C6 alkyl, phenyl, and naphthyl. If the number of carbon atoms of R⁹ to R¹⁴ is too large, the volume fraction of silicon atoms may relatively decrease, leading to a reduction in oxygen permeability of the copolymer. Thus in embodiments where oxygen permeabilities greater than about 80 or 100 barrers are desired, R⁹ to R¹⁴ are independently selected from C₁-C₁₀ alkyl groups or C₆-C₁₀ aryl groups, preferably C₁-C₄ alkyl groups, and in some embodiments R⁹ to R¹⁴ are methyl groups.

[0054] X² represents a C₁-C₂₀ alkylene group which may be substituted with a hydroxy group. The alkylene group may be branched or linear. If the number of carbon atoms of X² is too large, the ability of the mono-functional linear silicone (meth)acrylamide monomer to compatibilize with hydrophilic components may be reduced. Thus, where it is desirable for the mono-functional linear silicone (meth)acrylamide monomer to provide compatibilization to the reactive mixture, X² may be a C₁-C₁₀ alkylene which may be substituted with hydroxyl group. Examples of X², when R⁸ comprises at least one hydroxy group, include methylene, ethylene, propylene, butylene, pentalene, octalene, decylene and phenylene. X² may be propylene where a modulus less than about 100 psi is desired.

[0055] When R⁸ of the hydroxyl-substituted, mono-functional linear silicone (meth)acrylamide monomer does not contain at least one hydroxyl group, X² may contain at least one hydroxyl group. Examples of hydroxyl substituted X² groups include those of formula (b) and (c):



Among them, the structure of formula (b) will provide a more flexible polymer.

[0056] n represents a natural number of 1 to 1000. Polymer systems with a desirable balance of oxygen permeability and compatibility with hydrophilic monomers and polymers can be readily obtained when n is 1 to 50, preferably 2 to 30, 3 to 12. Any of the preferred lower limit values and any of the preferred upper limit values can be combined together. Furthermore, preferably n has no distribution in order to increase the reproducibility of the physical properties of the copolymer obtained. In the present invention, the phrase "no distribution" means that a single peak in the spectra accounts for at least 80% of the values of n, as measured by (a) GC the monomer can be measured using gas chromatography (GC) (FID analyzer), or (b) liquid chromatography (LC) (RI analyzer) for monomer having a high boiling point that cannot be measured using GC.

[0057] R¹⁵ represents a C₁ to C₂₀ alkyl which may be substituted, or a C₆ to C₂₀ aryl which may be substituted. The substituted groups of the alkyl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, phenyl, and naphthyl. The substituted groups of the aryl are halogen (F, Cl, Br, I), hydroxyl, amino, ether, carboxyl, ester, amide, sulfonyl, C1-C6 alkyl, phenyl, and naphthyl. As the number of carbons in the alkyl groups increase, the volume fraction of silicon atoms may relatively decrease, leading to a reduction in oxygen permeability of the copolymer. Thus, in embodiments where oxygen permeabilities greater than about 80 or 100 barrers are desired an alkyl having 1 to 10 carbon atoms or an aryl having 6 to 10 carbon atoms is more preferable, an alkyl having 1 to 6 carbon atoms is further preferable. When R¹⁵ is methyl, the polymers may display reduced stability, particularly when a carboxylic acid is included as a monomeric or polymeric component in the reaction mixture. In this embodiment R¹⁵ may be selected from C₂-C₄ alkyl groups.

[0058] Where the mono-functional linear silicone (meth)acrylamide monomer is selected to provide compatibility to a system comprising both hydrophilic and hydrophobic components, at least one of R⁸ and X² has at least one hydroxy group.

[0059] The minimum amount of mono-functional silicone (meth)acrylamide monomer used in the reactive mixtures of the present invention are about 30 parts by mass, 40 parts by mass, and in some embodiments 49 parts by mass. When the mono-functional silicone (meth)acrylamide monomer is present in amounts below those specified, the oxygen permeability of the resulting copolymer may be insufficient. If the amount of mono-functional silicone (meth) acrylamide monomer is too great, the hydrophilicity of the resulting copolymer may be undesirable. Accordingly, the upper amount of mono-functional silicone (meth) acrylamide monomer are 98 parts by mass, 80 parts by mass, and in some embodiments 65 parts by mass. The foregoing upper and lower ranges may be combined in any combination.

[0060] When copolymers comprising at least about 10 wt% water, and in some embodiments at least about 20% water are desired the reaction mixture of the present invention comprises at least one hydrophilic monomer.

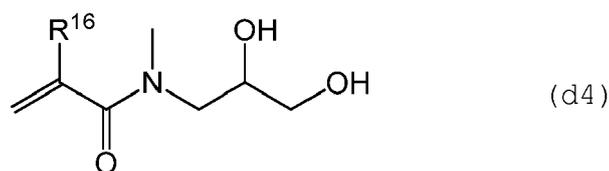
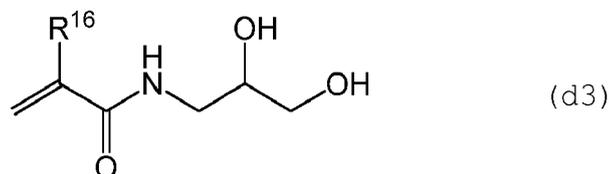
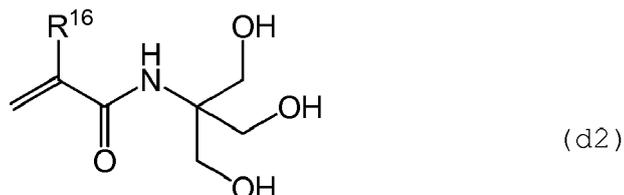
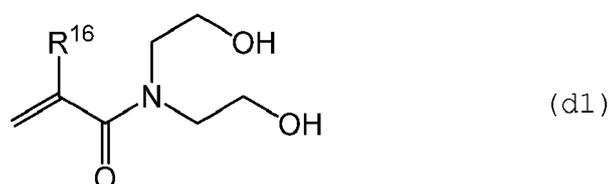
[0061] Examples of suitable hydrophilic monomers are known in the contact lens art and include (meth) acrylamide monomers such as acrylamide, methacrylamide, N,N-dimethyl acrylamide (hereinafter referred to as DMA), N,N-dimethyl methacrylamide, 2-hydroxyethyl methacrylamide, 2-hydroxyethyl acrylamide; (meth)acrylate monomers such as 2-hydroxyethyl acrylate, glycol methacrylate, polyethylene glycol monomethacrylate; N-vinyl carboxylic amides such as N-

vinylpyrrolidone (NVP), N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methylformamide, N-vinyl-N-ethylformamide, N-vinylacetamide, N-vinylformamide; N-vinyl carbamates such as N-2-hydroxyethylvinyl carbamate; N-vinyl esters such as N-carboxy-carboxy- β -alanine; hydrophilic N-vinyl carbonates; methacrylic acid, acrylic acid; a reactive polyethylene polyol, a hydrophilic oxazolone monomer, a hydrophilic oxazoline monomer and a combination thereof.

Among them, the (meth)acrylamide monomers are preferable in terms of improvement of the polymerization rate. In some embodiments acrylamide monomers are more preferred, and the DMA is most preferable.

[0062] If the amount of the hydrophilic monomer that is used is too high, the oxygen permeability will be reduced, but if too low, the resulting copolymer will be too hard, and therefore the amount of the hydrophilic monomer in this embodiment is between about 1 and about 50 mass%, more preferably between about 10 and about 40 mass%, and most preferably between 15 and 35 mass%, based on the monomer and polymer component in the polymerization mixture. Lower limit values are about 1 mass%, about 10 mass%, and about 15 mass%. Upper limit values are about 50 mass%, about 40 mass%, and about 35 mass%. Any of the lower limit values and any of the upper limit values can be combined together.

[0063] If it is desired to improve the transparency of the resulting copolymer, a (meth)acrylamide monomer having two or more hydroxyl groups and no siloxanyl groups within a molecule may be included in the reaction mixture in addition to the hydrophilic monomer. These multihydroxy-containing (meth)acrylamide monomers may replace all or part of the hydrophilic monomer in the reaction mixture. Examples of suitable multihydroxy-containing (meth)acrylamide monomers include monomers represented by the following general formulae (d1) to (d4).



[0064] In formulae (d1) to (d4), R^{16} each independently represents hydrogen or methyl. In some embodiments, hydrogen may be preferable in terms of further improvement of the polymerization rate. Furthermore, among these monomers, most preferable are monomers represented by formula (d1) in terms of the transparency of the resulting copolymer.

[0065] The content of monomers having reactive functionality other than (meth)acrylamide functionality is preferably small to provide a faster polymerization rate overall and polymerization rates of copolymerization components which are equalized, to thereby obtain a copolymer having a uniform composition. The mass percent of radically polymerizable components having (meth)acrylamide functionality is preferably 90% by mass or greater, more preferably 95% by mass or greater, most preferably 97% by mass or greater based on the mass of all radically polymerizable components.

[0066] When the copolymer of the present invention is obtained by polymerization, at least one initiator may be added. Suitable initiators include thermal initiators and photoinitiators. When thermal polymerization is carried out, a thermal polymerization initiator having an optimum degradation characteristic at a desired reaction temperature is selected and

used. Generally, an azo initiator and a peroxide initiator having a ten-hour half-life temperature of 40°C to 120°C is preferred. Suitable examples of thermal initiators include peroxide and azo compounds such as lauroyl peroxide, benzoyl peroxide, isopropyl percarbonate, azobisisobutyronitrile.

[0067] In one embodiment, the reaction mixtures of the present invention comprise at least one photoinitiator. The use of photoinitiation provides desirable cure times (time to reach essentially complete cure) of less than about 30 minutes, less than about 20 minutes and in some embodiments less than about 15 minutes. The photoinitiators may include carbonyl compounds, peroxides, azo compounds, sulfur compounds, halogen compounds and metal salts. Suitable photoinitiator systems include aromatic alpha-hydroxy ketones, alkoxybenzoin, acetophenones, acylphosphine oxides, bisacylphosphine oxides, and a tertiary amine plus a diketone, mixtures thereof and the like. Illustrative examples of photoinitiators are 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (DMBAPO), bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide (Irgacure 819), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide and 2,4,6-trimethylbenzoyl diphenylphosphine oxide, benzoin methyl ester and a combination of camphorquinone and ethyl 4-(N,N-dimethylamino)benzoate. Commercially available visible light initiator systems include Irgacure 819, Irgacure 1700, Irgacure 1800, Irgacure 1850 (all from Ciba Specialty Chemicals) and Lucirin TPO initiator (available from BASF). Commercially available UV photoinitiators include Darocur 1173 and Darocur 2959 (Ciba Specialty Chemicals). These and other photoinitiators which may be used are disclosed in Volume III, Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition by J.V. Crivello & K. Dietliker; edited by G. Bradley; John Wiley and Sons; New York; 1998. The initiator is used in the reaction mixture in effective amounts to initiate photopolymerization of the reaction mixture, e.g., from about 0.1 to about 2 parts by weight per 100 parts of reactive monomer, and in some embodiments from about 0.1 to about 1 parts by weight per 100 parts of reactive monomer.

[0068] When the copolymer of the present invention is obtained by polymerization, a polymerization solvent may be used. As a solvent, various kinds of organic and inorganic solvents can be applied. Examples thereof include water, various kinds of alcohol solvents such as methanol, ethanol, propanol, 2-propanol, butanol, tert-butanol, tert-amyl alcohol, 3,7-dimethyl-3-octanol, various kinds of aromatic hydrocarbon solvents such as benzene, toluene and xylene, various kinds of aliphatic hydrocarbon solvents such as hexane, heptane, octane, decane, petroleum ether, kerosene, ligroin and paraffin, various kinds of ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, various kinds of ester solvents such as ethyl acetate, butyl acetate, methyl benzoate, dioctyl phthalate and ethylene glycol diacetate, and various kinds of glycol ether solvents such as diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dialkyl ether, diethylene glycol dialkyl ether, triethylene glycol dialkyl ether, tetraethylene glycol dialkyl ether, polyethylene glycol dialkyl ether, polyethylene glycol-polypropylene glycol block copolymers, polyethylene glycol-polypropylene glycol random copolymers, and they may be used alone or in mixture. Additional diluents useful for this invention are disclosed in US patent 6,020,445. Among them, alcohol solvents and glycol ether solvents are preferable in a sense that the solvent can be easily removed from the resulting copolymer by washing with water.

[0069] The copolymer of the present invention may be molded alone into a desired shape and used, or may be mixed with other materials and then molded. Furthermore, the copolymers of the present invention may also be coated on the surface of a molded product.

[0070] The reactive mixture may further comprise at least one reactive or non-reactive wetting agent; optionally 1 to 30% by weight wetting agent based upon total amount of reactive components; or 3 to 20% by weight wetting agent based upon total amount of reactive components. The wetting agent can be selected from the group consisting of poly-N-vinyl pyrrolidone, poly-N-vinyl-2-piperidone, poly-N-vinyl-2-caprolactam, poly-N-vinyl-3-methyl-2-caprolactam, poly-N-vinyl-3-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-caprolactam, poly-N-vinyl-3-ethyl-2-pyrrolidone, poly-N-vinyl-4,5-dimethyl-2-pyrrolidone, polyvinyl imidazole, poly-N-vinyl formamide, poly-N-vinyl (methyl)acetamide, poly-N-methyl-N-vinyl (methyl)acetamide, poly-N-vinyl-N-(methyl)propionamide, poly-N-vinyl-N-methyl-2-(methyl)propionamide, poly-N-vinyl-2-(methyl)propionamide, poly-N-vinyl-N,N'-dimethylurea, poly-N,N-dimethyl acrylamide, poly-N,N-diethyl acrylamide, poly-N-isopropyl acrylamide, polyvinyl alcohol, polyacrylate, polyethylene oxide, poly-2-ethyl oxazoline, heparine, polysaccharide, poly-acryloyl morpholine, and mixtures and copolymers thereof. The wetting agent may be selected from the group consisting of polyvinylpyrrolidone, poly-N,N-dimethyl acrylamide, polyacrylic acid, polyvinyl alcohol, poly-N-methyl-N-vinyl (methyl)acetamide and copolymers and mixtures thereof. The wetting agent may be selected from the group consisting of polyvinylpyrrolidone and poly-N,N-dimethyl acrylamide.

[0071] Applications of the copolymer of the present invention include ophthalmic lenses, endoscopes, catheters, trans-fusion tubes, gas transport tubes, stents, sheaths, cuffs, tube connectors, access ports, drainage bags, blood circuits, wound covering materials and various kinds of medicine carriers, but the copolymer of the present invention is particularly suitably used for ophthalmic lenses such as contact lenses, intraocular lenses, artificial corneas, cornea inlays and cornea onlays, and is most suitably for contact lenses.

[0072] When the copolymer of the present invention is molded and used as an ophthalmic lens, the following methods may be used as methods for polymerization and molding thereof: a method of molding the copolymer into a round bar or plate and processing the same into a desired shape by cutting, lathing or the like, a mold polymerization method and

a spin casting method.

[0073] A case where an ophthalmic lens comprised of the copolymer of the present invention is obtained by the mold polymerization method will now be described as an example.

[0074] A reactive mixture composition is dispensed in a gap formed between two molds halves having a lens shape. Photo polymerization or thermal polymerization is then carried out to form the composition into a lens shape. The molds may be made of resin, glass, ceramic, metal or the like but in the case of photo polymerization, an optically transparent material, usually resin or glass, is used. Subsequently, the filled molds are irradiated with visible light, UV light or a combination thereof, or placed in an oven or a liquid bath and heated to polymerize the reactive mixture. Photo polymerization may also be combined with thermal polymerization such that thermal polymerization is performed before or after photo polymerization. In the case of photo polymerization, the wavelength of the light source is selected based upon the activation wavelength of the initiator. When thermal polymerization is performed, conditions of gradually raising the temperature from around 23°C to 60°C to 200°C over several hours or several tens of hours are preferred as optical homogeneity and quality of the polymer are retained and repeatability is improved.

[0075] The copolymer of the present invention can be subjected to modification by various methods. When an ophthalmic lens is intended and no hydrophilic polymer is included internally, modification for improving the wettability of the surface may be carried out.

[0076] Specific modification methods may include irradiation of electromagnetic waves (including light), plasma irradiation, chemical vapor deposition processes such as vapor deposition and sputtering, heating, base treatments, acid treatments, use of other appropriate surface treatment agents and a combination thereof.

[0077] One example of the base treatment or acid treatment is a method of contacting a molded product with a basic or acidic solution, a method of contacting a molded product with a basic or acidic gas, or the like. More specific methods may include, for example, a method of immersing a molded product in a basic or acidic solution, a method of spraying a basic or acidic solution or a basic or acidic gas to a molded product, a method of coating a basic or acidic solution on a molded product by a knife or brush, and a spin coating method or dip coating method of applying a basic or acidic solution to a molded product. A method providing a significant modification effect in the simplest manner is the method of immersing a molded product in a basic or acidic solution.

[0078] The temperature at which the copolymer is immersed in a basic or acidic solution is not particularly limited, but is normally in the range of about -50°C to 300°C. When considering workability, the temperature may be in the range of -10°C to 150°C, or -5°C to 60°C.

[0079] Time for immersing the copolymer in a basic or acidic solution is, generally 100 hours or less, 24 hours or less, 12 hours or less or 4 hours or less although optimum time varies depending on the temperature. Too long contact time may not only deteriorate workability and productibility but also have detrimental effects such as a reduction of oxygen permeability and degradation in mechanical properties.

[0080] As a base, alkali metal hydroxides, alkali earth metal hydroxides, various kinds of carbonates, various kinds of borates, various kinds of phosphates, ammonia, various kinds of ammonium salts, various kinds of amines, polymer bases such as polyethyleneimine and polyvinylamine and the like can be used. Among them, alkali metal hydroxides are most preferable because of the low cost and high treatment effect.

[0081] As an acid, various kinds of inorganic acids such as sulfuric acid, phosphoric acid, hydrochloric acid and nitric acid, various kinds of organic acids such as acetic acid, formic acid, benzoic acid and phenol and various kinds of polymer acids such as polyacrylic acid and polystyrene sulfonic acid can be used. Among them, polymer acids are most preferable because of the high treatment effect and no detrimental effects on other properties.

[0082] As a solvent of a basic or acidic solution, various kinds of inorganic and organic solvents may be used. The solvents include, for example, water, various kinds of alcohols such as methanol, ethanol, propanol, 2-propanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and polyethylene glycol glycerine, various kinds of aromatic hydrocarbons such as benzene, toluene and xylene, various kinds of aliphatic hydrocarbons such as hexane, heptane, octane, decane, petroleum ether, kerosene, ligroin and paraffin, various kinds of ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, various kinds of esters such as ethyl acetate, butyl acetate, methyl benzoate and dioctyl phthalate, various kinds of ethers such as diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dialkyl ether, diethylene glycol dialkyl ether, triethylene glycol dialkyl ether, tetraethylene glycol dialkyl ether and polyethylene glycol dialkyl ether, various kinds of polar aprotic solvents such as dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, dimethyl imidazolidinone, hexamethyl phosphoric triamide and dimethyl sulfoxide, halogen solvents such as methylene chloride, chloroform, dichloroethane, trichloroethane and trichloroethylene. Among them, water is most preferable in terms of economic efficiency, easy handling, chemical stability and the like. As the solvent, a mixture of two or more substances can also be used.

[0083] The basic or acidic solution for use in the present invention may contain components other than a basic or acidic substance and a solvent.

[0084] After the copolymer is subjected to a base treatment or acid treatment, a basic or acidic substance can be removed by washing.

[0085] As a washing solvent, various kinds of inorganic and organic solvents maybe used. The solvents include, for example, water, various kinds of alcohols such as methanol, ethanol, propanol, 2-propanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol and glycerine, various kinds of aromatic hydrocarbons such as benzene, toluene and xylene, various kinds of aliphatic hydrocarbons such as hexane, heptane, octane, decane, petroleum ether, kerosene, ligroin and paraffin, various kinds of ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, various kinds of esters such as ethyl acetate, butyl acetate, methyl benzoate and dioctyl phthalate, various kinds of ethers such as diethyl ether, tetrahydrofuran, dioxane, ethylene glycol dialkyl ether, diethylene glycol dialkyl ether, triethylene glycol dialkyl ether, tetraethylene glycol dialkyl ether and polyethylene glycol dialkyl ether, various kinds of polar aprotic solvents such as dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, dimethyl imidazolidinone, hexamethyl phosphoric triamide and dimethyl sulfoxide, halogen solvents such as methylene chloride, chloroform, dichloroethane, trichloroethane and trichloroethylene, and fluoro solvents.

[0086] As the washing solvent, a mixture of two or more solvents can also be used. The washing solvent may contain components other than a solvent, for example, inorganic salts, surfactants and washing agents. Aqueous washing solvents containing at least about 50%, 75% or 90% water may be used.

[0087] The abovementioned modification may be applied to the entire copolymer or may be applied to a part of the copolymer such as, for example, only the surface. When the modification is applied to only the surface, only the wettability of the surface can be improved without significantly changing the properties of the entire copolymer.

[0088] The water content of the copolymer of the present invention is desirably 20 weight% or greater, preferably 25 weight% or greater, more preferably 30 weight% greater. If the water content is too high, the article may dehydrate from an article, such as a contact lens, during use. In these embodiments, depending upon the other components it may be desirable for the water content to be less than 75 weight%, less than about 60 wt. These ranges may be combined in any combination.

[0089] Here, the water content is given by

$$\left[\frac{(\text{mass in wet state}) - (\text{mass in dry state})}{(\text{mass in wet state})} \right] \times 100$$

[0090] In this description, the wet state refers to a state after immersing a sample in pure water or a borate buffer at room temperature (23°C) for 24 hours or longer. Measurements of physical properties in the wet state are made as soon as possible after the sample is taken out from pure water or a borate buffer.

[0091] In the description, the dry state refers to a state after drying in a vacuum drier at 40°C for 16 hours or longer.

[0092] When an ophthalmic lens, particularly a soft contact lens is intended, the Young's modulus of the copolymer of the present invention is about 150 psi or less, about 110 psi or less, about 100 psi or less, 95 psi or less for affording good comfort.

[0093] The elasticity (elongation) of the copolymer of the present invention is generally about 250% or greater, about 270% or greater, or about 300% or greater as the copolymer is hard to be broken if the elasticity is high.

[0094] The elastic modulus and elasticity are measured on a hydrated sample using the following method. A sample is cut from the center of a -1.00 lens, where the width of the narrowest section is 5 mm, and then stretching at a rate of 100 mm/minute and a temperature of 25 C using a tensile tester until it breaks . The initial gauge length of the sample (Lo) and sample length at break (Lf) are measured. Twelve specimens of each composition are measured and the average is reported. Tensile modulus is measured at the initial linear portion of the stress/strain curve . Percent elongation is = [(Lf - Lo)/Lo]x 100.

[0095] In the present invention, low "formulation stability" means that, when the amount of crosslinker is changed slightly (0.1 part by mass change), mechanical properties such as modulus and elongation change substantially, for example by more than about 11 psi change in modulus, or 40% change in elongation with. Copolymers with low formulation stability display poor reproducibility of mechanical properties, and are thus not suitable for commercial production of medical devices, such as contact lenses.

[0096] Copolymers of the present invention having high formulation stability will have absolute values of the slope of modulus/ parts by mass of crosslinker (hereinafter referred to as SMC value) of 90 or lower, 70 or lower, or 50 or lower.

[0097] Alternatively, high formulation stability copolymers of the present invention may be characterized by the absolute value of the slope of elongation/ parts by mass (hereinafter referred to as SEC value) of crosslinker of the copolymer. Desirable SEC values include 220 or lower, 200 or lower, or 150 or lower.

[0098] Examples of component ranges which provide copolymers having desirable SMC and SEC values are shown in Table 1, below.

Table 1

Component	Parts by mass		
mono-functional linear silicone (meth)acrylamide monomer	40-80	49-65	50-60
non-silicone hydrophilic monomer	10-40	15-35	20-30
multihydroxyl-containing (meth)acrylamide monomer	2-30	3-20	4-10
Hydrophilic polymer	0-25	3-20	4-10
Initiator	0.1-2	0.1-1	0.1-0.5
UV absorber	0-4	0-3	0-2.5

[0099] The total parts by mass of the components described above is 98.8 parts by mass.

[0100] The formulations above may also include one or more polymerization solvents and optional components including one or more crosslinkers, medicinal agents, antimicrobial compounds, copolymerizable and nonpolymerizable dyes, including dyes and compounds which reversibly change color or reflect light when exposed to various wavelengths of light, polymeric wetting agents which may optionally contain at least one radically polymerizable group, release agents, reactive tints, pigments, combinations thereof.

[0101] When an ophthalmic lens is intended, the advancing contact angle of the copolymer of the present invention may be about 70° or less, about 60° or less, or 50° or less. The dynamic contact angle is measured in a sample in a wet state by a borate buffer with respect to the borate buffer.

[0102] For the oxygen permeability of the copolymer of the present invention, the oxygen permeability coefficient may be about 70×10^{-11} (cm²/sec) mL O₂ / (mL·hPa) or greater. The oxygen permeability coefficient is measured in a sample in a wet state by pure water.

[0103] For the transparency of the copolymer of the present invention, when an ophthalmic lens is intended, the transmissivity in a water-containing state of the ophthalmic lens is about 85% or greater, about 88% or greater, about 91% or greater.

[0104] For the transparency of the copolymer of the present invention by visual observations, in the case of the evaluation method described in examples below, A or B, of evaluation criteria A to D, is preferable, and A is more preferable.

[0105] For the shape of the copolymer of the present invention by visual observations, in the case of the evaluation method described in examples below, A or B, of evaluation criteria A to C, is preferable, and A is more preferable.

[0106] The copolymer of the present invention is suitable as a material for medical device and more specifically, especially suitable for medical devices such as ophthalmic lenses, endoscopes, catheters, transfusion tubes, gas transport tubes, stents, sheaths, cuffs, tube connectors, access ports, drainage bags, blood circuits, wound covering materials and various kinds of medicine carriers, particularly contact lenses, intraocular lenses, artificial corneas.

[Example]

[0107] The present invention will now be described in detail by examples, but the present invention is not thereby limited.

Measurement Methods

[0108] In this description, the borate buffer refers to the "salt solution" described in Example 1 of National Publication of International Patent Application No. 2004-517163. Specifically, the borate buffer is an aqueous solution prepared by dissolving 8.48 g of sodium chloride, 9.26 g of boric acid, 1.0 g of sodium borate (sodium tetraborate decahydrate) and 0.10 g of ethylene diamine tetraacetic acid in pure water to make up 1000 mL volume.

(1) Transmissivity

[0109] Measurements were made using SM Color Computer (Model SM-7-CH manufactured by Suga Test Instruments Co., Ltd.). Water on a lens-shaped sample was lightly wiped off and the sample was set on an optical path to make a measurement. The thickness was measured using ABC Digimatic Indicator (ID-C112 manufactured by Mitutoyo Corporation), and samples having a thickness of 0.14 to 0.15 mm were used for the measurement.

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(2) Elastic modulus, tensile elongation (rupture elongation)

5 [0110] A hydrated sample (in borate buffer) was used to make a measurement. A specimen having a width (minimum part) of 5 mm, a length of 14 mm and a thickness of 0.2 mm was cut out from a contact lens-shaped sample using a cutting die. With the specimen, a tensile test was carried out at 25 °C using RTG-1210 Model Tester (Load Cell UR-10N-D Model) manufactured by Orientec Co., Ltd. The tensile speed was 100 mm/minute and the distance between grips (initial) was 5 mm. Furthermore, in the case of a film-shaped sample, a measurement was made in the same manner using a specimen having a size of about 5 mm × 20 mm × 0.1 mm.

10 (3) Water content

15 [0111] A contact lens-shaped specimen was used. The specimen was immersed in a borate buffer and left standing in a temperature-controlled room at 23°C for 24 hours or longer to absorb water, followed by wiping off surface water with a wiping cloth ("Kimwipes" (registered trademark) manufactured by NIPPON PAPER CRECIA Co., LTD.) and measuring the mass (Ww). Thereafter, the specimen was dried in a vacuum drier at 40°C for 16 hours, and the mass (Wd) was measured. The water content was determined from the following equation. Water content (% by mass) = $100 \times (Ww - Wd) / Ww$

20 (4) Dynamic contact angle

25 [0112] A measurement was made with a sample in a wet state by a borate buffer. Using as a dynamic contact angle a film-shaped specimen having a size of about 5 mm × 10 mm × 0.1 mm, which was cut out from a sample molded in a film form or a strip-shaped specimen having a width of 5 mm, which was cut out from a contact lens-shaped sample, the dynamic contact angle at advance with respect to a borate buffer was measured at 25°C. The immersion rate was 0.1 mm/sec and the immersion depth was 7 mm.

(5) Stress zero time

30 [0113] A measurement was made with a sample in a wet state by a borate buffer. A strip-shaped sample having a width of 5 mm and a length of about 1.5 cm was cut out from a lens at or near its center, and a measurement was made using Rheometer CR-500 DX manufactured by Sun Scientific Co., Ltd.). The sample was attached to a chuck with a width set to 5 mm and drawn over a distance of 5 mm at a speed of 100 mm/minute, followed by returning the sample to an initial length (5 mm) at the same speed. The measurement was repeated three times. The length of time between a time point at which the stress became zero in the course of returning the sample to the initial length at the second repetition and a time point at which the stress emerged (no longer zero) after starting drawing at the third repetition was determined and designated as a stress zero time. It is shown that the shorter the stress zero time, the better the shape recovery of a silicone hydrogel, and the stress zero time is preferably 2 seconds or less, more preferably 1.5 seconds or less, most preferably 1.2 seconds or less.

40 (6) Transparency

[0114] The transparency of a sample in a hydrated state (borate buffer) was visually observed, and was evaluated according to the following criteria.

- 45 A: transparent with no turbidness
B: white turbidness at some midpoint between A and C
C: translucent with slight turbidness
D: no transparency with white turbidness

50 (7) Shape

[0115] The shape of a sample in a wet state by a borate buffer was visually observed, and was evaluated according to the following criteria.

- 55 A: good shape with no distortion
B: distortion at some midpoint between A and C
C: poor shape with distortion

(8) SMC value

[0116] At least two data points of modulus (psi) which are less than 300 psi are plotted versus parts by mass of crosslinker in a graph. A line is made between the two data points if two data points were plotted, or a line is made by least mean squares method if three or more data points were plotted. The preferred number of data points is two to four, and more preferred number is three. The absolute value of slope of the line is SMC value.

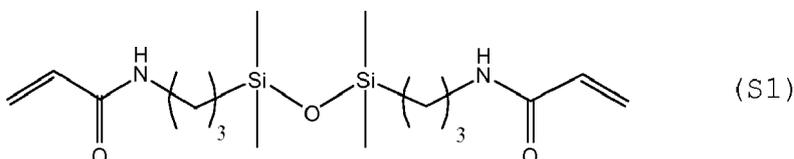
(9) SEC value

[0117] At least two data points of elongation (%) which are more than 50% are plotted versus parts by mass of crosslinker in a graph. A line is made between the two data points if two data points were plotted, or a line is made by least mean squares method if three or more data points were plotted. The preferred number of data points is two to four, and more preferred number is three. The absolute value of slope of the line is SEC value.

Synthesis Examples

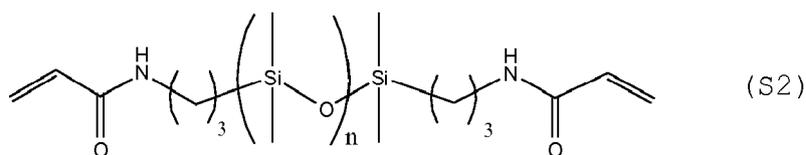
Synthesis Example 1

[0118] In a 200 mL three-necked flask, 2g of 1,3-bis(3-aminopropyl)tetramethyl siloxane (8.0 mmol, product name: LS-7430) manufactured by Shin-Etsu Chemical Co., Ltd., 1.62 g (16 mmol) of triethylamine and 50 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 1.45 g (16 mmol) of acryloyl chloride and 50 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for 2 hours and 30 minutes. The reaction was traced by gas chromatography with the dropping termination time as a start point. Disappearance of a raw material siloxane peak was observed at a reaction time of 0 hour, and therefore the reaction was terminated. By filtration using a Kiriya funnel (Kiriya glass works Co), a precipitate deposited in the reaction was removed while washing with ethyl acetate. The filtrate was concentrated in a water bath thermally controlled to 30°C for about 10 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: hexane/ethyl acetate (1/3) mixed solvent (v/v)) to obtain a bisacrylamide (SiBA) represented by the following formula (S1)



Synthesis Example 2

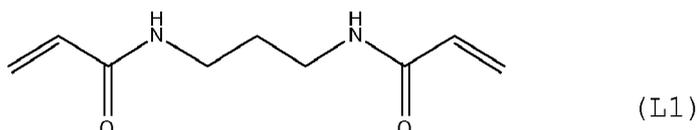
[0119] In a 200 mL three-necked flask, 5 g of amino-modified silicone oil (5.8 mmol, dual-end type, product name: KF-8010, reactive group equivalent weight 430 g/mol) manufactured by Shin-Etsu Chemical Co., Ltd., 1.17g (11.6 mmol) of triethylamine and 60 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 1.05 g (11.6 mmol) of acryloyl chloride and 60 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for 3 hours. Thereafter, the mixture was stirred at 0°C to 5°C for 3 hours. A deposited precipitate was removed by filtration while washing with ethyl acetate. Ethyl acetate was distilled away by a rotary evaporator for 5 minutes. Hexane was added to the resulting mixed solution, and the mixture was separately washed total six times with 100 mL of pure water (2X), 100 mL of aqueous sodium hydrogen carbonate solution (2X) and 100 mL of saturated aqueous sodium chloride solution (2X) in this order. It was confirmed by a pH indicator paper that an organic layer obtained by separate washing was neutral, and the organic layer was transferred to an Erlenmeyer flask. The organic layer was dehydrated by adding an appropriate amount of anhydrous sodium sulfate thereto, and anhydrous sodium sulfate was removed by filtration, followed by concentrating the organic layer in a water bath thermally controlled to 30°C for about 10 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: hexane/ethyl acetate (1/1, 1/3) mixed solvent (v/v)) to obtain a bisacrylamide (SiBA 1000) represented by the following formula (S2)



[0120] Here, n in formula (S2) is a natural number, and the average molecular weight of the compound was about 1000.

Synthesis Example 3

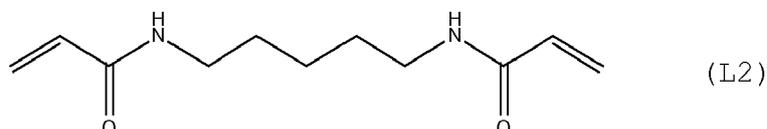
[0121] In a 200 mL three-necked flask, 2 g (27 mmol) of 1,3-propanediamine manufactured by Wako Pure Chemical Industries, Ltd., 6.01 g (59.4 mmol) of triethylamine and 30 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 5.38 g (59.4 mmol) of acryloyl chloride and 30 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for 3 hours and 30 minutes. The reaction was traced by GC with the dropping termination time point as a start point. A 1,3-propanediamine peak almost disappeared at a reaction time of 3 hours, and therefore the reaction was terminated. By filtration using a Kiriya funnel, a precipitate was removed while washing with ethyl acetate. 3, 5-dibutyl-4-hydroxytoluene was added to the filtrate, and the mixture was concentrated in a water bath thermally controlled to 30°C for about 20 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: ethanol/ethyl acetate (1/20, 1/10) mixed solvent (v/v)) to obtain a bisacrylamide (C3) represented by the following formula (L1) [Chemical Formula 10].



Synthesis Example 4

[0122] In a 200 mL three-necked flask, 2 g (19.6 mmol) of 1,5-diaminopentane manufactured by Wako Pure Chemical Industries, Ltd., 4.35 g (43.0 mmol) of triethylamine, 50 mL of ethyl acetate and 10 mL of IPA were each weighed and mixed. In a dropping funnel, 3.89 g (43.0 mmol) of acryloyl chloride and 40 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for an hour and 20 minutes. The reaction was traced by GC with the dropping termination time as a start point. A 1,5-diaminopentane peak almost disappeared at a reaction time of 4 hours, and therefore the reaction was terminated. By filtration using a Kiriya funnel, a precipitate was removed while washing with ethyl acetate.

[0123] 3,5-dibutyl-4-hydroxytoluene was added to the filtrate, and the mixture was concentrated in a water bath thermally controlled to 30°C for about 20 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: ethanol/ethyl acetate (1/20, 1/10) mixed solvent (v/v)) to obtain a bisacrylamide (C5) represented by the following formula (L2)



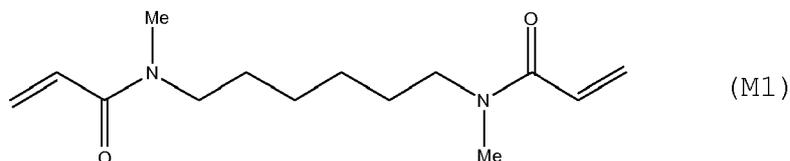
Synthesis Example 5

[0124] In a 200 mL three-necked flask, 2 g (13.9 mmol) of N,N'-dimethyl-1,6-hexanediamine manufactured by Tokyo Chemical Industry Co., Ltd., 2.81 g (27.8 mmol) of triethylamine and 30 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 2.52 g (27.8 mmol) of acryloyl chloride and 50 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for 2 hours and 30 minutes. The reaction was traced by GC with the dropping termination time as a start point. A N,N'-dimethyl-1,6-hexanediamine peak almost disappeared at a reaction time of 4 hours, and therefore the reaction was terminated. By filtration using a Kiriya funnel, a precipitate was removed while washing with ethyl acetate. 3,5-dibutyl-4-hydroxytoluene was added to the filtrate, and the mixture was concentrated in a water bath thermally controlled to 30°C for about 20 minutes using a rotary

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evaporator. The resulting crude product was purified by a silica gel column (column solvent: chloroform/ethyl acetate (30/1, 20/1, 10/1.5/1) mixed solvent (v/v)) to obtain a bisacrylamide (Me-C6) represented by the following formula (M1) [Chemical Formula 12].

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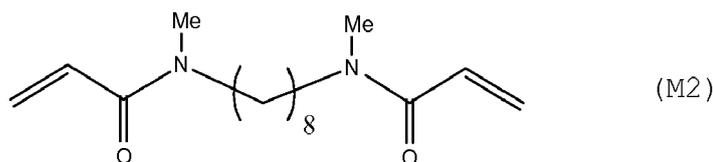


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Synthesis Example 6

[0125] In a 200 mL three-necked flask, 0.8 g (4.64 mmol) of N,N'-dimethyl-1,8-octanediamine manufactured by Sigma-Aldrich Corporation, 1.01 g (10 mmol) of triethylamine and 50 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 0.91 g (10 mmol) of acryloyl chloride and 50 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for an hour. The reaction was traced by GC with the dropping termination time as a start point. Disappearance of an N,N'-dimethyl-1,8-octanediamine peak was observed at a reaction time of 0 hour, and therefore the reaction was terminated. By filtration using a Kiriya funnel, a precipitate was removed while washing with ethyl acetate. 3,5-dibutyl-4-hydroxytoluene was added to the filtrate, and the mixture was concentrated in a water bath thermally controlled to 30°C for about 10 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: ethanol/ethyl acetate (1/20, 1/10) mixed solvent (v/v)) to obtain a bisacrylamide (Me-C8) represented by the following formula (M2) [Chemical Formula 13].

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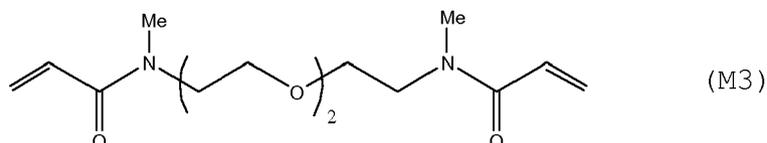


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Synthesis Example 7

[0126] In a 200 mL three-necked flask, 1g (5.67 mmol) of 1,8-bis(methylamino)-3,6-dioxaoctane manufactured by Acros Organics, 1.15 g (11.34 mmol) of triethylamine and 15 mL of ethyl acetate were each weighed and mixed. In a dropping funnel, 1.03 g (11.34 mmol) of acryloyl chloride and 15 mL of ethyl acetate were weighed and mixed. The flask was set in an ice salt bath and the mixture was added dropwise at -5 to 0°C for an hour. The reaction was traced by GC with the dropping termination time as a start point. A 1,8-bis(methylamino)-3,6-dioxaoctane peak almost disappeared at a reaction time of an hour, and therefore the reaction was terminated. By filtration using a Kiriya funnel, a precipitate was removed while washing with ethyl acetate. 3,5-dibutyl-4-hydroxytoluene was added to the filtrate, and the mixture was concentrated in a water bath thermally controlled to 30°C for about 10 minutes using a rotary evaporator. The resulting crude product was purified by a silica gel column (column solvent: ethanol/ethyl acetate (1/3, 1/5) mixed solvent (v/v)) to obtain a bisacrylamide (Me-3G) represented by the following formula (M3)

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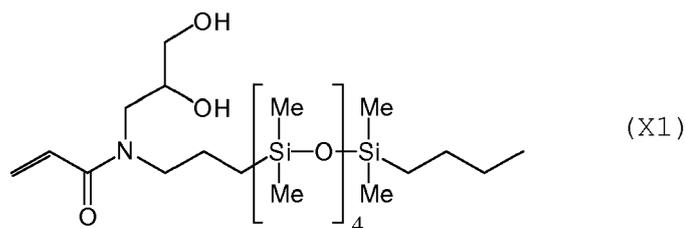
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Example 1

[0127] The bisacrylamide SiBA (0.016 g, 2.0 parts by mass) obtained in Synthesis Example 1, a mono-functional linear silicone acrylamide monomer represented by the following formula (X1)

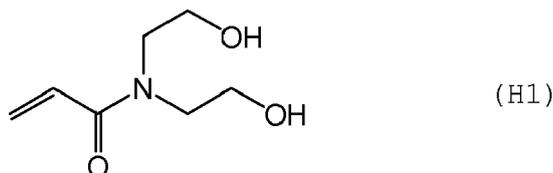
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10 (0.462 g, 56.06 parts by weight), DMA (0.208 g, 25.27 parts by weight), a non-silicone acrylamide monomer represented by the following formula (H1)

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20 (0.058 g, 7 parts by weight), polyvinyl pyrrolidone (PVP K90, 0.066 g, 8 parts by mass), a UV absorber 2-(2'-hydroxy-5'-methacryloyloxyethylphenyl)-2H-benzotriazole (0.018 g, 2.22 parts by mass), t-amyl alcohol (TAA, 0.681 g) and a photoinitiator Irgacure 819 (0.002 g, 0.25 part by mass) were mixed and stirred. The resulting monomer mixture was degassed in argon environment. In a glove box in a nitrogen environment, the monomer mixture was filled in a gap of
 25 a mold made of transparent resin having a lens shape (front curve side: ZEONOR, base curve side: polypropylene), and irradiated with light (Philips TL 03, 1.6 mW/cm², 15 minutes) and thereby photo-polymerized to obtain a lens. The lens obtained was immersed in a 70% (volume ratio) 2-propanol (IPA) aqueous solution at 23°C for 70 minutes to thereby demold the lens from the mold and extract impurities such as residual monomers. The lens was immersed in water for 10 minutes, and thereafter immersed in a borate buffer (pH 7.1 to 7.3) in a 5 mL vial, and the vial was placed in an autoclave and boiled at 120°C for 30 minutes.

30 **[0128]** The transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1, and lenses well extendable with a low modulus were obtained.

[Table 1]

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[0129]

Table 1

		bisac crylamide		transmissivity (%)	water content (%)	modulus (psi)	elongation (%)	stress zero time (sec)	transparency	shape
		parts by mass	mass average molecular weight							
Example 1	Formula (S1)	2.00	356	91.2	39.1	92.3	272.5	1.01	A	A
Example 2	Formula (S1)	1.80	356	91.1	39.6	90.7	274.7	0.99	B	B
Example 3	Formula (S1)	2.20	356	91.5	39.2	109.3	253	1.01	A	A
Example 4	Formula (S2)	3.50	1000	92.5	38.7	106.1	292	0.88	A	A
Example 5	Formula (S2)	2.50	1000	91.2	39.5	83.9	433.7	0.90	B	A
Example 6	Formula (S2)	3.00	1000	92.3	38.5	94.5	312.4	0.91	B	A
Comparative Example 1	Formula (L1)	1.10	182	91.4	38.5	124.3	187.4	0.84	A	A
Comparative Example 2	Formula (L1)	0.90	182	92.5	39.6	102.1	267.7	0.85	A	C
Comparative Example 3	Formula (L1)	1.00	182	92.2	39.5	112.2	214.2	0.94	A	B
Comparative Example 4	Formula (L2)	0.90	210	90.2	42.1	71.2	346	0.96	B	C
Comparative Example 5	Formula (L2)	1.10	210	90.9	39.4	91.2	235.6	0.92	A	B
Comparative Example 6	Formula (L2)	1.50	210	90.9	37.6	126.9	191.3	0.89	A	A
Comparative Example 7	Formula (M1)	0.90	252	91.5	38.5	91.8	275.8	1.07	B	C

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(continued)

		bisac crylamide		transmissivity (%)	water content (%)	modulus (psi)	elongation (%)	stress zero time (sec)	transparency	shape
		parts by mass	mass average molecular weight							
Comparative Example 8	Formula (M1)	1.10	252	91.6	37.9	121.7	215.6	0.94	A	B
Comparative Example 9	Formula (M1)	1.80	252	91.9	35.5	186.1	137.4	0.91	A	A

Examples 2 and 3

5 [0130] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Example 4

10 [0131] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that SiBA 1000 obtained in Synthesis Example 2 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Examples 5 and 6

15 [0132] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 4 except that the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

20 Comparative Example 1

25 [0133] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that C3 obtained in Synthesis Example 3 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Comparative Examples 2 and 3

30 [0134] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 1 except that the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Comparative Example 4

35 [0135] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that C5 obtained in Synthesis Example 4 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

40 Comparative Examples 5 and 6

45 [0136] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 4 except that the composition was changed as in Table 1. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Comparative Example 7

50 [0137] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that Me-C6 obtained in Synthesis Example 5 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Comparative Examples 8 and 9

55 [0138] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 7 except that the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 1.

Comparative Example 10

[0139] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that Me-C8 obtained in Synthesis Example 6 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

[Table 2]

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[0140]

Table 2

	bisacrylamide			transmissivity (%)	water content (%)	modulus (psi)	elongation (%)	stress zero time (sec)	transparency	shape
	Formula	parts by mass	mass average molecular weight							
Comparative Example 11	Formula (M2)	1.00	280	92.3	39.7	94.7	241.8	0.89	A	B
Comparative Example 12	Formula (M2)	1.10	280	91.5	39	100.7	228.9	0.95	A	B
Comparative Example 13	Formula (M2)	2.00	280	92.0	36.8	232	106.4	0.82	A	A
Comparative Example 14	Formula (M3)	1.10	284	91.1	39.5	79.4	280.8	1.03	C	C
Comparative Example 15	Formula (M3)	1.30	284	89.1	38.5	99.2	304	0.89	B	C
Comparative Example 16	Formula (M3)	1.50	284	90.2	37.6	117.2	277	0.95	B	B
Comparative Example 17	Formula (Y1)	1.10	154	91.3	37.9	141	176.2	1.01	A	A
Comparative Example 18	Formula (Y2)	0.80	224	91.5	39	90.7	322.7	0.95	B	C
Comparative Example 19	Formula (Y2)	1.10	224	91.7	37.4	115.7	225	0.93	A	B
Comparative Example 20	Formula (Y3)	0.90	200	83.4	52.2	not analyzed	not analyzed	not analyzed	D	C
Comparative Example 21	Formula (Y3)	1.10	200	83.1	52.3	not analyzed	not analyzed	not analyzed	D	B
Comparative Example 22	Formula (Y3)	1.40	200	83.1	51.6	not analyzed	not analyzed	not analyzed	D	B

Comparative Examples 11 to 13

5 **[0141]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 10 except that the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

Comparative Example 14

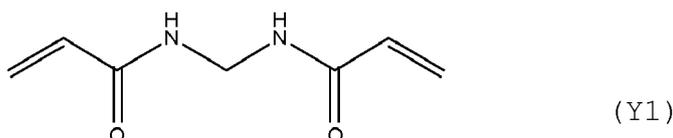
10 **[0142]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that Me-3G obtained in Synthesis Example 7 was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

Comparative Examples 15 and 16

15 **[0143]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 14 except that the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

Comparative Example 17

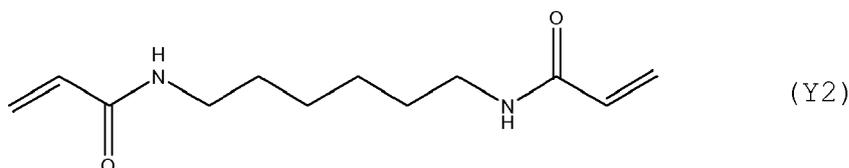
20 **[0144]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that a monomer represented by the following formula (Y1)



was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

Comparative Example 18

35 **[0145]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that a monomer represented by the following formula (Y2)



was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

Comparative Example 19

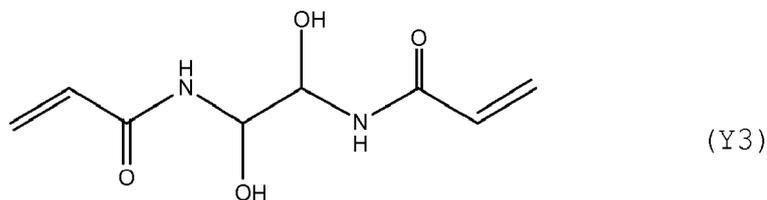
50 **[0146]** A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 18 except that the composition was changed as in Table 2. The appearance, transmissivity, water content, modulus, elasticity and stress zero time of the obtained lens-shaped sample were as shown in Table 2.

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Comparative Example 20

[0147] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Example 1 except that a monomer represented by the following formula (Y3)

[Chemical Formula 19]



was used as a bisacrylamide monomer instead of SiBA obtained in Synthesis Example 1 and the composition was changed as in Table 2. The physical properties of the obtained sample were as shown in Table 2.

Comparative Examples 21 and 22

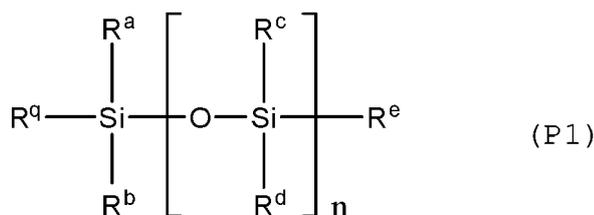
[0148] A lens-shaped sample was obtained by carrying out polymerization in the same manner as in Comparative Example 20 except that the composition was changed as in Table 2. The physical properties of the obtained sample were as shown in Table 2.

INDUSTRIAL APPLICABILITY

[0149] The present invention relates to a silicone hydrogel, and the silicone hydrogel is especially suitably used for contact lenses, intraocular lenses, artificial corneas.

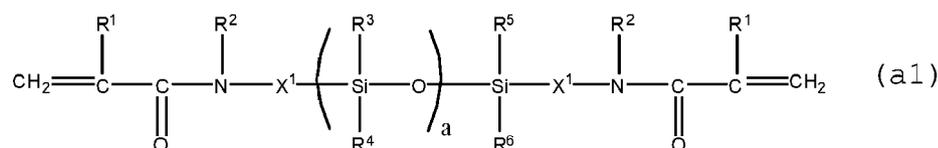
Claims

1. A copolymer formed from a reactive mixture comprising radically polymerizable components comprising (A) a multi-functional (meth)acrylamide monomer having at least one siloxane bond and at least two (meth)acrylamide groups within a molecule and (B) a mono-functional linear silicone (meth)acrylamide monomer of formula (P1)



Where R^q comprises a (meth)acrylamide group containing no silicon atom; R^a to R^e contain no silicon atoms, and may be independently selected from substituted or unsubstituted alkyl groups having 1 to 20 carbon atoms, or substituted or unsubstituted aryl groups having 6 to 20 carbon atoms, and n represents an integer of 1 or greater; wherein; the multi-functional (meth)acrylamide monomer is present in an amount of 0.1 part by mass to 20 parts by mass.

2. The copolymer according to claim 1, wherein the multi-functional (meth)acrylamide monomer has two (meth)acrylamide groups.
3. The copolymer according to claim 2, wherein the multi-functional (meth)acrylamide monomer is represented by Formula (a1) :



wherein R¹ is independently selected from hydrogen and methyl;

R² is independently selected from hydrogen, or an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms;

R³ to R⁶ are each an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms;

X¹ is independently selected from substituted or unsubstituted divalent organic groups having 1 to 20 carbon atoms; and

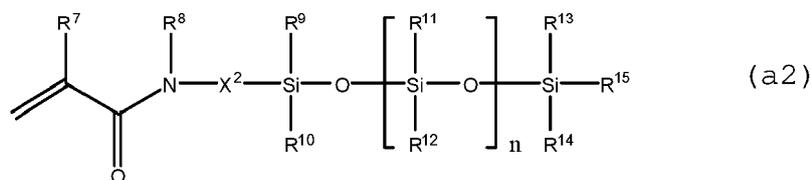
a represents an integer of 1 to 15.

4. The copolymer according to any of claims 1 to 3, wherein the mass average molecular weight of the multi-functional (meth)acrylamide monomer is 1500 or less.

5. The copolymer according to any of claims 1 to 4, wherein the mono-functional linear silicone (meth)acrylamide monomer has at least one hydroxy group.

6. The copolymer according to any of claims 1 to 5, wherein the mono-functional linear silicone (meth)acrylamide monomer is represented by formula (a2). Formula:

[Chemical Formula 2]



[in formula (a2), R⁷ is one selected from hydrogen and methyl]; R⁸ is hydrogen, an alkyl which may be substituted with a hydroxy group and has 1 to 20 carbon atoms, or an aryl which may be substituted with a hydroxy group and has 6 to 20 carbon atoms; R⁹ to R¹⁴ are each an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms; X² represents a C₁-C₂₀ alkylene group which may be substituted with a hydroxy group; n is 1 to 1000; R¹⁵ is an alkyl which may be substituted and has 1 to 20 carbon atoms, or an aryl which may be substituted and has 6 to 20 carbon atoms; with the proviso that any of R⁸ and X² has at least one hydroxy group.

7. The copolymer according to claim 6, wherein

a) R⁷ in general formula (a2) is hydrogen; and/or

b) the X² in general formula (a2) is a propylene or a structure represented by the following formula (b):

-CH₂CH(OH)CH₂OCH₂CH₂CH₂-. (b); and/or

c) at least one of R⁹ to R¹⁴ is methyl; and/or

d) R¹⁵ is methyl or n-butyl; and/or

e) n is an integer of 1 to 6 and has no distribution; and/or

f) R⁸ in general formula (a2) is hydrogen or an alkyl which is substituted with a hydroxy group and has 1 to 20 carbon atoms; or R⁸ is a 2,3-dihydroxypropyl.

8. The copolymer according to any of claims 1 to 7, further comprising a non-silicone hydrophilic monomer as a copolymerization component.

9. The copolymer according to claim 8, wherein the non-silicone hydrophilic monomer is selected from the group

consisting of N,N-dimethyl acrylamide (DMA), N-vinylpyrrolidone (NVP), 2-hydroxyethyl acrylate, glycerol methacrylate, 2-hydroxyethyl methacrylamide, polyethylene glycol monomethacrylate, methacrylic acid, acrylic acid, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-ethylformamide, N-vinylformamide, N-2-hydroxyethylvinyl carbamate, N-carboxy-β-alanine N-vinyl ester, a reactive polyethylene polyol, a hydrophilic vinyl carbonate, a vinyl carbamate monomer, a hydrophilic oxazolone monomer, a hydrophilic oxazoline monomer and a combination thereof.

10. The copolymer according to any of claims 1 to 9, wherein

- a) the mass of the (meth)acrylamide monomer component is 90% by mass or greater based on the mass of all monomer components; and/or
- b) the mono-functional linear silicone (meth)acrylamide monomer is present in an amount of 30 parts by mass to 98 parts by mass.

11. The copolymer of any preceding claim comprising a modulus of less than 100 psi; and/or comprising a water content of 20 to 75%.

12. A material for medical device comprised of the copolymer according to any of claims 1 to 11; optionally wherein the material for medical device is any one selected from a contact lens, an endoscope, a catheter, a transfusion tube, a gas transport tube, a stent, a sheath, a cuff, a tube connector, an access port, a drainage bag, a blood circuit, a wound covering material and a medicine carrier.

13. An ophthalmic lens or a contact lens comprised of the copolymer according to any of claims 1 to 11.

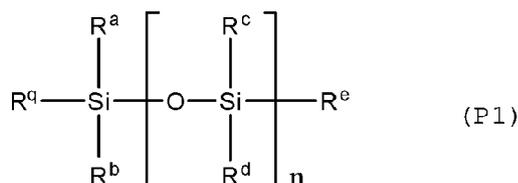
14. The copolymer of any of claims 1-9 wherein the reactive mixture further comprises at least one reactive or nonreactive wetting agent;

- optionally 1 to 30% by weight wetting agent based upon total amount of reactive components; or
- 3 to 20% by weight wetting agent based upon total amount of reactive components.

15. The copolymer of claim 14 wherein the wetting agent is selected from the group consisting of poly-N-vinyl pyrrolidone, poly-N-vinyl-2-piperidone, poly-N-vinyl-2-caprolactam, poly-N-vinyl-3-methyl-2-caprolactam, poly-N-vinyl-3-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-piperidone, poly-N-vinyl-4-methyl-2-caprolactam, poly-N-vinyl-3-ethyl-2-pyrrolidone, poly-N-vinyl-4,5-dimethyl-2-pyrrolidone, polyvinyl imidazole, poly-N-vinyl formamide, poly-N-vinyl (methyl)acetamide, poly-N-methyl-N-vinyl (methyl)acetamide, poly-N-vinyl-N-(methyl)propionamide, poly-N-vinyl-N-methyl-2-(methyl)propionamide, poly-N-vinyl-2-(methyl)propionamide, poly-N-vinyl-N,N'-dimethylurea, poly-N,N-dimethyl acrylamide, poly-N,N-diethyl acrylamide, poly-N-isopropyl acrylamide, polyvinyl alcohol, polyacrylate, polyethylene oxide, poly-2-ethyl oxazoline, heparine, polysaccharide, poly-acryloyl morpholine, and mixtures and copolymers thereof; or wherein the wetting agent is selected from the group consisting of polyvinylpyrrolidone, poly-N,N-dimethyl acrylamide, polyacrylic acid, polyvinyl alcohol, poly-N-methyl-N-vinyl (methyl)acetamide and copolymers and mixtures thereof; or wherein the wetting agent is selected from the group consisting of polyvinylpyrrolidone and poly-N,N-dimethyl acrylamide.

Patentansprüche

1. Copolymer, gebildet aus einer reaktiven Mischung, umfassend radikalisch polymerisierbare Komponenten, umfassend (A) ein multifunktionelles (Meth)-acrylamidmonomer mit mindestens einer Siloxanbindung und mindestens zwei (Meth)acrylamidgruppen in einem Molekül und (B) ein monofunktionelles lineares Silikon(meth)acrylamidmonomer der Formel (P1)

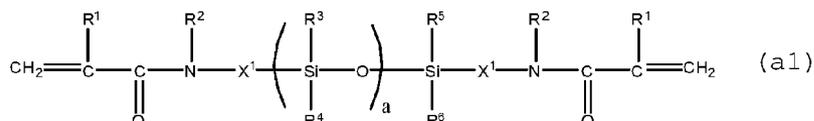


wobei R^q eine (Meth)acrylamidgruppe, die kein Siliciumatom enthält, umfasst; R^a bis R^e keine Siliciumatome enthalten und unabhängig aus substituierten oder unsubstituierten Alkylgruppen mit 1 bis 20 Kohlenstoffatomen oder substituierten oder unsubstituierten Arylgruppen mit 6 bis 20 Kohlenstoffatomen ausgewählt sein können und n für eine ganze Zahl mit einem Wert von 1 oder mehr steht; wobei

das multifunktionelle (Meth)acrylamidmonomer in einer Menge von 0,1 Masseteilen bis 20 Masseteilen vorliegt.

2. Copolymer nach Anspruch 1, wobei das multifunktionelle (Meth)acrylamidmonomer zwei (Meth)-acrylamidgruppen aufweist.

3. Copolymer nach Anspruch 2, wobei das multifunktionelle (Meth)acrylamidmonomer durch Formel (a1) wiedergegeben wird:



wobei R¹ unabhängig aus Wasserstoff und Methyl ausgewählt ist;

R² unabhängig aus Wasserstoff oder einem Alkyl, das substituiert sein kann und 1 bis 20 Kohlenstoffatome aufweist, oder einem Aryl, das substituiert sein kann und 6 bis 20 Kohlenstoffatome aufweist, ausgewählt ist; R³ bis R⁶ jeweils für ein Alkyl, das substituiert sein kann und 1 bis 20 Kohlenstoffatome aufweist, oder ein Aryl, das substituiert sein kann und 6 bis 20 Kohlenstoffatome aufweist, stehen;

X¹ unabhängig aus substituierten oder unsubstituierten zweiwertigen organischen Gruppen mit 1 bis 20 Kohlenstoffatomen ausgewählt ist und a für eine ganze Zahl von 1 bis 15 steht.

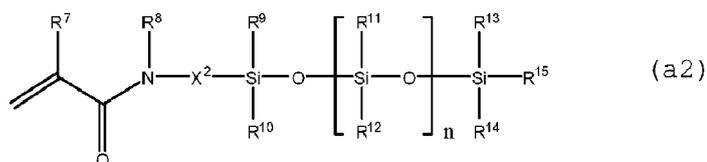
4. Copolymer nach einem der Ansprüche 1 bis 3, wobei das massenmittlere Molekulargewicht des multifunktionellen (Meth)acrylamidmonomers 1500 oder weniger beträgt.

5. Copolymer nach einem der Ansprüche 1 bis 4, wobei das monofunktionelle lineare Silikon(meth)-acrylamidmonomer mindestens eine Hydroxygruppe aufweist.

6. Copolymer nach einem der Ansprüche 1 bis 5, wobei das monofunktionelle lineare Silikon(meth)-acrylamidmonomer durch Formel (a2) wiedergegeben wird.

Formel:

[Chemisch Formel 2]



[in Formel (a2) ist R⁷ aus Wasserstoff und Methyl ausgewählt; steht R⁸ für Wasserstoff, ein Alkyl, das mit einer Hydroxygruppe substituiert sein kann und 1 bis 20 Kohlenstoffatome aufweist, oder ein Aryl, das mit einer Hydroxygruppe substituiert sein kann und 6 bis 20 Kohlenstoffatome aufweist; stehen R⁹ bis R¹⁴ jeweils für ein Alkyl, das substituiert sein kann und 1 bis 20 Kohlenstoffatome aufweist, oder ein Aryl, das substituiert sein kann und 6 bis 20 Kohlenstoffatome aufweist; steht X² für eine C₁-C₂₀-Alkylengruppe, die mit einer Hydroxygruppe substituiert sein kann; steht n für 1 bis 1000; steht R¹⁵ für ein Alkyl, das substituiert sein kann und 1 bis 20 Kohlenstoffatome aufweist, oder ein Aryl, das substituiert sein kann und 6 bis 20 Kohlenstoffatome aufweist; mit der Maßgabe, dass ein beliebiges von R⁸ und X² mindestens eine Hydroxygruppe aufweist.

7. Copolymer nach Anspruch 6, wobei

a) R⁷ in der allgemeinen Formel (a2) für Wasserstoff steht und/oder

b) das X² in der allgemeinen Formel (a2) für ein Propylen oder eine durch die folgende Formel (b) wiedergegebene Struktur steht:

-CH₂CH(OH)CH₂OCH₂CH₂CH₂-. (b) und/oder

c) mindestens eines von R⁹ bis R¹⁴ für Methyl steht und/oder

d) R¹⁵ für Methyl oder n-Butyl steht und/oder

e) n für eine ganze Zahl von 1 bis 6 steht und keine Verteilung aufweist und/oder

f) R⁸ in der Formel (a2) für Wasserstoff oder ein Alkyl, das mit einer Hydroxygruppe substituiert ist und 1 bis 20 Kohlenstoffatome aufweist, steht oder R⁸ für 2,3-Dihydroxypropyl steht.

8. Copolymer nach einem der Ansprüche 1 bis 7, ferner umfassend ein hydrophiles Nichtsilikonmonomer als Copolymerisationskomponente.

9. Copolymer nach Anspruch 8, wobei das hydrophile Nichtsilikonmonomer aus der Gruppe bestehend aus N,N-Dimethylacrylamid (DMA), N-Vinylpyrrolidon (NVP), 2-Hydroxyethylacrylat, Glycerinmethacrylat, 2-Hydroxyethylmethacrylamid, Polyethylenglykolmonomethacrylat, Methacrylsäure, Acrylsäure, N-Vinyl-N-methylacetamid, N-Vinyl-N-ethylacetamid, N-Vinyl-N-ethylformamid, N-Vinylformamid, N-2-Hydroxyethylvinylcarbamid, N-Carboxy-β-alanin-N-vinylester, einem reaktiven Polyethylenpolyol, einem hydrophilen Vinylcarbonat, einem Vinylcarbamidmonomer, einem hydrophilen Oxazolmonomer, einem hydrophilen Oxazolinmonomer und einer Kombination davon ausgewählt ist.

10. Copolymer nach einem der Ansprüche 1 bis 9, wobei

a) die Masse der (Meth)acrylamidmonomer-Komponente 90 Masse-% oder mehr, bezogen auf die Masse aller Monomerkomponenten, beträgt und/oder

b) das monofunktionelle lineare Silikon(meth)-acrylamidmonomer in einer Menge von 30 Masseteilen bis 98 Masseteilen vorliegt.

11. Copolymer nach einem der vorhergehenden Ansprüche mit einem Modul von weniger als 100 psi und/oder einem Wassergehalt von 20 bis 75 %.

12. Material für eine medizinische Vorrichtung, bestehend aus dem Copolymer nach einem der Ansprüche 1 bis 11; gegebenenfalls wobei es sich bei dem Material für eine medizinische Vorrichtung um eines handelt, das aus einer Kontaktlinse, einem Endoskop, einem Katheter, einem Transfusionsschlauch, einem Gastransportschlauch, einem Stent, einem Schaft, einer Manschette, einer Schlauchverbindung, einer Zugangsöffnung, einem Ausflussbeutel, einem Blutkreislauf, einem Wundbedeckungsmaterial und einem Medizinträger ausgewählt ist.

13. Ophthalmische Linse oder Kontaktlinse, bestehend aus dem Copolymer nach einem der Ansprüche 1 bis 11.

14. Copolymer nach einem der Ansprüche 1-9, wobei die reaktive Mischung ferner mindestens ein reaktives oder unreaktives Netzmittel; gegebenenfalls 1 bis 30 Gew.-% Netzmittel, bezogen auf die Gesamtmenge an reaktiven Komponenten; oder 3 bis 20 Gew.-% Netzmittel, bezogen auf die Gesamtmenge an reaktiven Komponenten; umfasst.

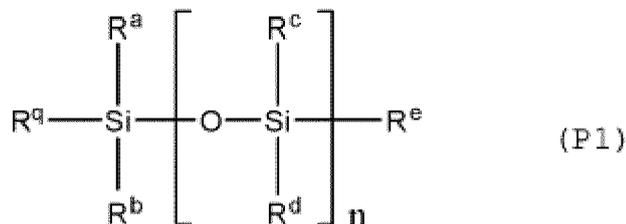
15. Copolymer nach Anspruch 14, wobei das Netzmittel aus der Gruppe bestehend aus Poly-N-vinylpyrrolidon, Poly-N-vinyl-2-piperidon, Poly-N-vinyl-2-caprolactam, Poly-N-vinyl-3-methyl-2-caprolactam, Poly-N-vinyl-3-methyl-2-piperidon, Poly-N-vinyl-4-methyl-2-piperidon, Poly-N-vinyl-4-methyl-2-caprolactam, Poly-N-vinyl-3-ethyl-2-pyrrolidon, Poly-N-vinyl-4,5-dimethyl-2-pyrrolidon, Polyvinylimidazol, Poly-N-vinylformamid, Poly-N-vinyl(methyl)acetamid, Poly-N-methyl-N-vinyl(methyl)acetamid, Poly-N-vinyl-N-(methyl)propionamid, Poly-N-vinyl-N-methyl-2-(methyl)propionamid, Poly-N-vinyl-2-(methyl)propionamid, Poly-N-vinyl-N,N'-dimethylharnstoff, Poly-N,N-dimethylacrylamid, Poly-N,N-diethylacrylamid, Poly-N-isopropylacrylamid, Polyvinylalkohol, Polyacrylat, Polyethylenoxid, Poly-2-ethylloxazolin, Heparin, Polysaccharid, Polyacryloylmorpholin und Mischungen und Copolymeren davon ausgewählt ist oder

wobei das Netzmittel aus der Gruppe bestehend aus Polyvinylpyrrolidon, Poly-N,N-dimethylacrylamid, Polyacrylsäure, Polyvinylalkohol, Poly-N-methyl-N-vinyl(methyl)acetamid und Copolymeren und Mischungen davon ausgewählt ist oder

wobei das Netzmittel aus der Gruppe bestehend aus Polyvinylpyrrolidon und Poly-N,N-dimethylacrylamid ausgewählt ist.

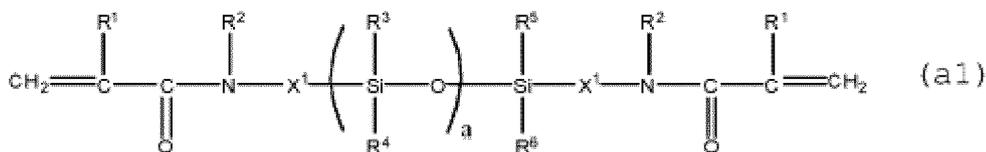
Revendications

1. Copolymère formé à partir d'un mélange réactif comprenant des composants polymérisables par voie radicalaire comprenant (A) un monomère de type (méth)acrylamide multifonctionnel possédant au moins une liaison siloxane et au moins deux groupes (méth)acrylamide dans une molécule et (B) un monomère de type (méth)acrylamide de silicone linéaire monofonctionnel de formule (P1)



dans laquelle R^q comprend un groupe (méth)acrylamide ne contenant pas d'atome de silicium ; R^a à R^e ne contiennent pas d'atomes de silicium, et peuvent être indépendamment choisis parmi des groupes alkyle substitués ou non substitués possédant 1 à 20 atomes de carbone, et des groupes aryle substitués ou non substitués possédant 6 à 20 atomes de carbone, et n représente un entier de 1 ou plus ; le monomère de type (méth)acrylamide multifonctionnel étant présent en une quantité de 0,1 partie en masse à 20 parties en masse.

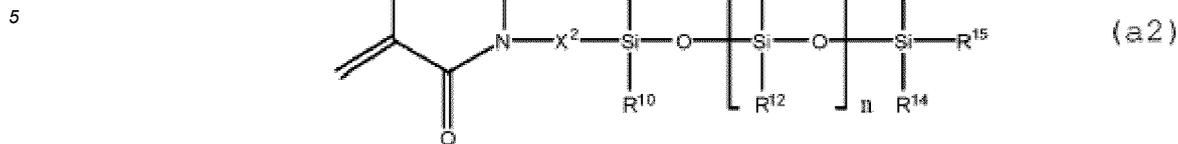
2. Copolymère selon la revendication 1, le monomère de type (méth)acrylamide multifonctionnel possédant deux groupes (méth)acrylamide.
3. Copolymère selon la revendication 2, le monomère de type (méth)acrylamide multifonctionnel étant représenté par la Formule (a1) :



R¹ étant indépendamment choisi parmi hydrogène et méthyle ;
 R² étant indépendamment choisi parmi hydrogène, un alkyle qui peut être substitué et possède 1 à 20 atomes de carbone, et un aryle qui peut être substitué et possède 6 à 20 atomes de carbone ;
 R³ à R⁶ étant chacun un alkyle qui peut être substitué et possède 1 à 20 atomes de carbone, ou un aryle qui peut être substitué et possède 6 à 20 atomes de carbone ;
 X¹ étant indépendamment choisi parmi des groupes organiques divalents substitués ou non substitués possédant 1 à 20 atomes de carbone ; et
 a représentant un entier de 1 à 15.

4. Copolymère selon l'une quelconque des revendications 1 à 3, le poids moléculaire moyen en masse du monomère de type (méth)acrylamide multifonctionnel étant de 1 500 ou moins.
5. Copolymère selon l'une quelconque des revendications 1 à 4, le monomère de type (méth)acrylamide de silicone linéaire monofonctionnel possédant au moins un groupe hydroxy.
6. Copolymère selon l'une quelconque des revendications 1 à 5, le monomère de type (méth)acrylamide de silicone linéaire monofonctionnel étant représenté par la formule (a2), Formule :

[Formule Chimique 2]



10 dans la formule (a2), R⁷ étant une choisie parmi hydrogène et méthyle ;
 R⁸ étant hydrogène, un alkyle qui peut être substitué par un groupe hydroxy et possède 1 à 20 atomes de
 carbone, ou un aryle qui peut être substitué par un groupe hydroxy et possède 6 à 20 atomes de carbone ; R⁹
 à R¹⁴ étant chacun un alkyle qui peut être substitué et possède 1 à 20 atomes de carbone, ou un aryle qui peut
 15 être substitué et possède 6 à 20 atomes de carbone ; X² représentant un groupe C₁₋₂₀ alkylène qui peut être
 substitué par un groupe hydroxy ; n étant 1 à 1 000 ; R¹⁵ étant un alkyle qui peut être substitué et possède 1
 à 20 atomes de carbone, ou un aryle qui peut être substitué et possède 6 à 20 atomes de carbone ; à la condition
 que l'un quelconque parmi R⁸ et X² possède au moins un groupe hydroxy.

20 7. Copolymère selon la revendication 6,

- a) R⁷ dans la formule générale (a2) étant hydrogène ; et/ou
 b) le X² dans la formule générale (a2) étant un propylène ou une structure représentée par la formule suivante (b) :
 25 -CH₂CH(OH)CH₂OCH₂CH₂CH₂-. (b); et/ou
 c) au moins l'un parmi R⁹ à R¹⁴ étant méthyle ; et/ou
 d) R¹⁵ étant méthyle ou n-butyle ; et/ou
 e) n étant un entier de 1 à 6 et ne possédant pas de distribution ; et/ou
 f) R⁸ dans la formule générale (a2) étant hydrogène ou un alkyle qui est substitué par un groupe hydroxy et
 possède 1 à 20 atomes de carbone ; ou R⁸ est un 2,3-dihydroxypropyle.

30 8. Copolymère selon l'une quelconque des revendications 1 à 7, comprenant en outre un monomère hydrophile non
 de silicone en tant que composant de copolymérisation.

35 9. Copolymère selon la revendication 8, le monomère hydrophile non de silicone étant choisi dans le groupe constitué
 par le N,N-diméthylacrylamide (DMA), la N-vinylpyrrolidone (NVP), l'acrylate de 2-hydroxyéthyle, le méthacrylate
 de glycérol, le 2-hydroxyéthyl-méthacrylamide, un monométhacrylate de polyéthylène glycol, l'acide méthacrylique,
 l'acide acrylique, le N-vinyl-N-méthylacétamide, le N-vinyl-N-éthylacétamide, le N-vinyl-N-éthylformamide, le N-
 vinylformamide, le N-2-hydroxyéthylvinyl-carbamate, l'ester de N-vinyle de la N-carboxy-β-alanine, un polyéthylène
 40 polyol réactif, un carbonate de vinyle hydrophile, un monomère de type carbamate de vinyle, un monomère de type
 oxazolone hydrophile, un monomère de type oxazoline hydrophile et une combinaison correspondante.

10. Copolymère selon l'une quelconque des revendications 1 à 9,

- 45 a) la masse du composant monomérique de type (méth)acrylamide étant de 90 % en masse ou plus sur la base
 de la masse de tous les composants monomériques ; et/ou
 b) le monomère de type (méth)acrylamide de silicone linéaire monofonctionnel étant présent en une quantité
 de 30 parties en masse à 98 parties en masse.

50 11. Copolymère selon une quelconque revendication précédente comprenant un module inférieur à 100 psi ; et/ou
 comprenant une teneur en eau de 20 à 75 %.

55 12. Matériau pour dispositif médical composé du copolymère selon l'une quelconque des revendications 1 à 11 ; éven-
 tuellement, le matériau pour dispositif médical étant l'un quelconque choisi parmi une lentille de contact, un endos-
 cope, un cathéter, un tube de transfusion, un tube de transport de gaz, un stent, une gaine, un manchon, un
 connecteur de tube, un orifice d'accès, un sac de drainage, un circuit de sang, un matériau de recouvrement de
 plaie et un véhicule médical.

13. Lentille ophtalmique ou lentille de contact composée du copolymère selon l'une quelconque des revendications 1

à 11.

14. Copolymère selon l'une quelconque des revendications 1 à 9, le mélange réactif comprenant en outre au moins un agent mouillant réactif ou non réactif ;

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éventuellement 1 à 30 % en poids d'agent mouillant sur la base de la quantité totale de composants réactifs ; ou 3 à 20 % en poids d'agent mouillant sur la base de la quantité totale de composants réactifs.

15. Copolymère selon la revendication 14, l'agent mouillant étant choisi dans le groupe constitué par poly-N-vinylpyrrolidone, poly-N-vinyl-2-pipéridone, poly-N-vinyl-2-caprolactame, poly-N-vinyl-3-méthyl-2-caprolactame, poly-N-vinyl-3-méthyl-2-pipéridone, poly-N-vinyl-4-méthyl-2-pipéridone, poly-N-vinyl-4-méthyl-2-caprolactame, poly-N-vinyl-3-éthyl-2-pyrrolidone, poly-N-vinyl-4,5-diméthyl-2-pyrrolidone, polyvinylimidazole, poly-N-vinylformamide, poly-N-vinyl(méthyl)acétamide, poly-N-méthyl-N-vinyl(méthyl)acétamide, poly-N-vinyl-N-(méthyl)propionamide, poly-N-vinyl-N-méthyl-2-(méthyl)propionamide, poly-N-vinyl-2-(méthyl)propionamide, poly-N-vinyl-N,N'-diméthylurée, poly-N,N-diméthylacrylamide, poly-N,N-diéthylacrylamide, poly-N-isopropylacrylamide, poly(alcool vinylique), polyacrylate, poly(oxyde d'éthylène), poly-2-éthylloxazoline, héparine, polysaccharide, poly-acryloylmorpholine, et des mélanges et des copolymères correspondants ; ou l'agent mouillant étant choisi dans le groupe constitué par polyvinylpyrrolidone, poly-N,N-diméthylacrylamide, poly(acide acrylique), poly(alcool vinylique), poly-N-méthyle-N-vinyl-(méthyl)acétamide et des copolymères et des mélanges correspondants ; ou l'agent mouillant étant choisi dans le groupe constitué par polyvinylpyrrolidone et poly-N,N-diméthylacrylamide.

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