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(54) **SILICONE HYDROGELS COMPRISING HIGH LEVELS OF POLYAMIDES**

SILIKONHYDROGELE MIT HOHEM GEHALT AN POLYAMIDEN

HYDROGELS DE SILICONE COMPRENANT DES TAUX ÉLEVÉS DE POLYAMIDES

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(73) Proprietor: **Johnson & Johnson Vision Care, Inc.**
Jacksonville, FL 32256 (US)

(72) Inventors:
• **ALLI, Azaam**
Jacksonville, Florida 32256 (US)

• **GUZMAN, Alexander**
Jacksonville, Florida 32256 (US)

(74) Representative: **Carpmaels & Ransford LLP**
One Southampton Row
London WC1B 5HA (GB)

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US-A1- 2010 296 049 US-A1- 2013 341 811

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Description**TECHNICAL FIELD**

[0001] The present invention relates to silicone hydrogels displaying improved biocompatibility. More specifically, the present invention relates to silicone hydrogels formed from a reactive mixture comprising a mixture of hydroxyl-substituted silicone components, at least one hydrophilic monomer, and at least about 15 wt% of at least one polyamide. The silicone hydrogels of the present invention display an excellent balance of physical, mechanical, and biological properties.

BACKGROUND

[0002] Contact lenses have been used commercially to improve vision since at least the 1950s. The first contact lenses were made of hard materials and as such were somewhat uncomfortable to users. Modern soft contact lenses are made of softer materials, typically hydrogels. Recently soft contact lenses made from silicone hydrogels have been introduced. Silicone hydrogel are water-swollen polymer networks that have high oxygen permeability. These lenses provide a good level of comfort to many lens wearers, but there are some users who experience discomfort and excessive ocular deposits leading to reduced visual acuity when using these lenses, in particular during extended periods of wear such as for several days in a row, for example, up to about 30 days. This discomfort and deposits has been attributed to the hydrophobic character of the surfaces of lenses and the interaction of those surfaces with the protein, lipids and mucin and the hydrophilic surface of the eye.

[0003] One way to increase the water content in a silicone hydrogel is to incorporate an internal wetting agent, such as a high molecular weight polymer, which creates more hydrophilic domains that retain more water. Incorporation of internal wetting agents also affects the surface lubricity of the silicone hydrogel depending on morphology and surface roughness. Poly(vinyl pyrrolidone) (PVP) has been used as an internal wetting agent in silicone hydrogels. For example, U.S. Patent Nos. 6,367,929, 6,822,016, and 7,052,131 disclose PVP present in the reactive monomer mixture in amounts between 1 and 15 weight percent. Poly(N-vinyl-N-methacrylamide) (PVMA) has been used as an internal wetting agent in non-ionic silicone hydrogels. For example, U.S. Patent Nos. 7,786,185 and 8,022,158 disclose PVMA present in the reactive monomer mixture in amounts between 1 and 15 weight percent. Compositions with higher concentrations of internal wetting agents, however, have not been disclosed. Contact lenses with higher concentrations of internal wetting agents and acceptable physical, mechanical, and biological properties have also not been disclosed. EP2258411 A1 discloses a silicone hydrogel contact lens comprises at least one oxygen permeable component, at least one compatibilizing component and a high molecular weight hydrophilic polymer. The amount of high molecular weight hydrophilic polymer is sufficient to provide said device, without a surface treatment, with tear film break up time after about one day of wear of at least about 7 seconds.

WO 2008/005147 A2 discloses contact lenses comprising at least one ionizable antimicrobial metal compound and a polymer formed from a reaction mixture comprising at least one hydrophobic component and hydrophilic components in a concentration to provide a hydrophilicity index of at least 42.

US 2013/341811 A1 discloses a contact lens formed from components including (i) at least one silicone component, (ii) at least one low molecular weight polyamide having a weight average molecular weight of less than 200,000, and (iii) at least one high molecular weight polyamide having a weight average molecular weight of greater than 200,000, wherein the low molecular weight polyamide does not contain a reactive group.

SUMMARY

[0004] Silicone hydrogels with high levels of polyamides have been prepared exhibiting an excellent balance of physical, mechanical, and biological properties.

[0005] The present invention relates to silicone hydrogels as defined by claim 1.

[0006] Additionally, the present invention provides a method as defined by claim 29 of making a silicone hydrogel.

[0007] These and other embodiments of the invention will become apparent from the following description which is illustrative of the invention. The description does not limit the scope of the invention, which is defined by the claims and equivalents thereof. Variations and modifications of the invention may be effected without departing from the spirit and scope of the novel contents of the disclosure.

DETAILED DESCRIPTION

[0008] Provided are silicone hydrogels formed from a reactive monomer mixture comprising: a hydroxyalkyl (meth)acrylate monomer; silicone-containing components; and at least one polyamide.

[0009] With respect to the terms used in this disclosure, the following definitions are provided. The polymer definitions

are consistent with those disclosed in the Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008, edited by: Richard G. Jones, Jaroslav Kahovec, Robert Stepto, Edward S. Wilks, Michael Hess, Tatsuki Kitayama, and W. Val Metanowski.

[0010] "About" refers to a range of $\pm 5\%$ of the number that is being modified. For example, the phrase "about 10" would include both 9.5 and 10.5.

[0011] The term "(meth)" designates optional methyl substitution. Thus, a term such as "(meth)acrylate" denotes both methacrylate and acrylate radicals.

[0012] Wherever chemical structures are given, it should be appreciated that alternatives disclosed for the substituents on the structure may be combined in any combination. Thus, if a structure contained substituents R^* and R^{**} , each of which contained three lists of potential groups, 9 combinations are disclosed. The same applies for combinations of properties.

[0013] When a subscript, such as "n" in the generic formula $[**]_n$, is used to depict the number of repeating units in a polymer's chemical formula, the formula should be interpreted to represent the number average molecular weight of the macromolecule.

[0014] A "macromolecule" is an organic compound having a molecular weight of greater than 1500, and may be reactive or non-reactive.

[0015] A "polymer" is a macromolecule of repeating chemical units linked together into a chain or network structure and is composed of repeating units derived from the monomers and macromers included in the reactive mixture.

[0016] A "homopolymer" is a polymer made from one monomer or macromer; a "copolymer" is a polymer made from two or more monomers, macromers or a combination thereof; a "terpolymer" is a polymer made from three monomers, macromers or a combination thereof. A "block copolymer" is composed of compositionally different blocks or segments. Diblock copolymers have two blocks. Triblock copolymers have three blocks. "Comb or graft copolymers" are made from at least one macromer.

[0017] A "repeating unit" or "repeating chemical unit" is the smallest repeating group of atoms in a polymer that result from the polymerization of monomers and macromers.

[0018] "Biomedical device" refers to any article that is designed to be used while either in or on mammalian tissues or fluid, and preferably in or on human tissue or fluids. Examples of these devices include but are not limited to wound dressings, sealants, tissue fillers, drug delivery systems, coatings, adhesion prevention barriers, catheters, implants, stents, and ophthalmic devices such as intraocular lenses and contact lenses. The biomedical devices may be ophthalmic devices, particularly contact lenses, most particularly contact lenses made from silicone hydrogels.

[0019] "Individual" includes humans and vertebrates.

[0020] "Ocular surface" includes the surface and glandular epithelia of the cornea, conjunctiva, lacrimal gland, accessory lacrimal glands, nasolacrimal duct and meibomian gland, and their apical and basal matrices, puncta and adjacent or related structures, including eyelids linked as a functional system by both continuity of epithelia, by innervation, and the endocrine and immune systems.

[0021] "Ophthalmic device" refers to any device which resides in or on the eye or any part of the eye, including the ocular surface. These devices can provide optical correction, cosmetic enhancement, vision enhancement, therapeutic benefit (for example as bandages) or delivery of active components such as pharmaceutical and nutraceutical components, or a combination of any of the foregoing. Examples of ophthalmic devices include, but are not limited to, lenses and optical and ocular inserts, including, but not limited to punctal plugs and the like. "Lens" includes soft contact lenses, hard contact lenses, hybrid contact lenses, intraocular lenses, and overlay lenses. The ophthalmic device may comprise a contact lens.

[0022] "Contact lens" refers to a structure, an ophthalmic device, that can be placed on the cornea of an individual's eye. The contact lens may provide corrective, cosmetic, therapeutic benefit, including wound healing, delivery of active components such as drugs or nutraceuticals, diagnostic evaluation or monitoring, or UV blocking and visible light or glare reduction, or a combination thereof. A contact lens can be of any appropriate material known in the art, and can be a soft lens, a hard lens, or a hybrid lens containing at least two distinct portions with different properties, such as modulus, water content, light absorbing characteristics or combinations thereof.

[0023] The biomedical devices, ophthalmic devices, and lenses of the present invention may be comprised of silicone hydrogels. These silicone hydrogels typically contain a silicone component and/or hydrophobic and hydrophilic monomers that are covalently bound to one another in the cured device.

[0024] "Silicone hydrogel contact lens" refers to a contact lens comprising at least one silicone hydrogel material. Silicone hydrogel contact lenses generally have increased oxygen permeability compared to conventional hydrogels. Silicone hydrogel contact lenses use both their water and polymer content to transmit oxygen to the eye.

[0025] A "polymeric network" is cross-linked macromolecule that can swell but cannot dissolve in solvents, because the polymeric network is essentially one macromolecule. "Hydrogel" or "hydrogel material" refers to a polymeric network that contains water in an equilibrium state. Hydrogels generally contain at least about 10 wt.% water, or at least about 15% water.

[0026] "Conventional hydrogels" refer to polymeric networks made from monomers without any siloxy, siloxane or carbosiloxane groups. Conventional hydrogels are prepared from monomeric mixtures predominantly containing hydrophilic monomers, such as 2-hydroxyethyl methacrylate ("HEMA"), N-vinyl pyrrolidone ("NVP"), N, N-dimethylacrylamide ("DMA"), or vinyl acetate. U.S. Patent Nos. 4,436,887, 4,495,313, 4,889,664, 5,006,622, 5,039,459, 5,236,969, 5,270,418, 5,298,533, 5,824,719, 6,420,453, 6,423,761, 6,767,979, 7,934,830, 8,138,290, and 8,389,597 disclose the formation of conventional hydrogels. Commercially available hydrogel formulations include, but are not limited to, etafilcon, polymacon, vifilcon, genfilcon, lenefilcon, hilafilcon, nesofilcon, and omafilcon, including all of their variants.

[0027] "Silicone hydrogel" refers to a hydrogel obtained by copolymerization of at least one silicone-containing component with at least one hydrophilic component. Hydrophilic components may also include non-reactive polymers. Each of the silicone-containing components and the hydrophilic components may be a monomer, macromer or combination thereof. A silicone-containing component contains at least one siloxane or carbosiloxane group. Examples of commercially available silicone hydrogels include balafilcon, aquafilcon, lotrafilcon, comfilcon, delefilcon, enfilcon, fanfilcon, formofilcon, galyfilcon, senofilcon, narafilecon, filcon II, asmoofilcon A, samfilcon, riofilcon, stenfilcon, somofilcon, as well as silicone hydrogels as prepared in US Patent No. 4,659,782, 4,659,783, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,998,498, 6,087,415, 5,760,100, 5,776,999, 5,789,461, 5,849,811, 5,965,631, 6,367,929, 6,822,016, 6,867,245, 6,943,203, 7,247,692, 7,249,848, 7,553,880, 7,666,921, 7,786,185, 7,956,131, 8,022,158, 8,273,802, 8,399,538, 8,470,906, 8,450,387, 8,487,058, 8,507,577, 8,637,621, 8,703,891, 8,937,110, 8,937,111, 8,940,812, 9,056,878, 9,057,821, 9,125,808, 9,140,825, 9,156,934, 9,170,349, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929 as well as WO 03/22321, WO 2008/061992, and US 2010/048847.

[0028] "Silicone-containing component" refers to a monomer, macromer, prepolymer, crosslinker, initiator, additive, or polymer that contains at least one silicon-oxygen bond, in the form of siloxane [-Si-O-Si] group or carbosiloxane group. Examples of silicone-containing components include, but are not limited to, silicone macromers, prepolymers, and monomers. Examples of silicone macromers include, but are not limited to, polydimethylsiloxane methacrylated with pendant hydrophilic groups. Examples of silicone-containing components which are useful in this invention may be found in U.S. Patent Nos. 3,808,178, 4,120,570, 4,136,250, 4,153,641, 4,740,533, 5,034,461, 5,962,548, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,760,100, 5,849,811, 5,962,548, 5,965,631, 5,998,498, 6,367,929, 6,822,016, and 5,070,215, and European Patent No. 080539.

[0029] "Reactive mixture" and "reactive monomer mixture" refer to the mixture of components (both reactive and non-reactive) which are mixed together and when subjected to polymerization conditions, form the silicone hydrogels and lenses of the present invention. The reactive mixture comprises reactive components such as monomers, macromers, prepolymers, cross-linkers, initiators, diluents, and additional components such as wetting agents, release agents, dyes, light absorbing compounds such as UV absorbers, pigments, dyes and photochromic compounds, any of which may be reactive or non-reactive but are capable of being retained within the resulting biomedical device, as well as active components, including pharmaceutical and nutraceutical compounds, and any diluents. It will be appreciated that a wide range of additives may be added based upon the biomedical device which is made, and its intended use. Concentrations of components of the reactive mixture are given in weight % of all components in the reaction mixture, excluding diluent. When diluents are used their concentrations are given as weight % based upon the amount of all components in the reaction mixture and the diluent.

[0030] "Monomer" is a molecule having non-repeating reactive groups, which can undergo chain growth polymerization, and in particular, free radical polymerization. Some monomers have di-functional impurities that can act as cross-linking agents. "Macromers" are linear or branched polymers having a repeating structure and at least one reactive group that can undergo chain growth polymerization. Monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight = 500-1500 g/mol) (mPDMS) and mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight = 500-1500 g/mol) (OH-mPDMS) are referred to as macromers. Typically, the chemical structure of the macromer is different than the chemical structure of the target macromolecule, that is, the repeating unit of the macromer's pendent group is different than the repeating unit of the target macromolecule or its mainchain.

[0031] "Reactive components" are the components in the reactive mixture which become part of the structure of the polymeric network of the resulting silicone hydrogel, by covalent bonding, hydrogen bonding or the formation of an interpenetrating network. Typically, the chemical structure of the macromer is different than the chemical structure of the target macromolecule, that is, the repeating unit of the macromer's pendent group is different than the repeating unit of the target macromolecule or its mainchain. Diluents and processing aids which do not become part of the structure of the polymer are not reactive components.

[0032] "Polymerizable" means that the compound comprises at least one reactive group which can undergo chain growth polymerization, such as free radical polymerization. Examples of reactive groups include the monovalent reactive groups listed below. "Non-polymerizable" means that the compound does not comprises such a polymerizable group.

[0033] "Monovalent reactive groups" are groups that can undergo chain growth polymerization, such as free radical and/or cationic polymerization. Non-limiting examples of free radical reactive groups include (meth)acrylates, styrenes,

vinyl ethers, (meth)acrylamides, *N*-vinyl lactams, *N*-vinylamides, O-vinyl carbamates, O-vinyl carbonates, and other vinyl groups. In one embodiment, the free radical reactive groups comprise (meth)acrylate, (meth)acrylamide, *N*-vinyl lactam, *N*-vinylamide, and styryl functional groups, or (meth)acrylates, (meth)acrylamides, and mixtures of any of the foregoing.

[0034] Examples of the foregoing include substituted or unsubstituted C₁₋₆alkyl(meth)acrylates, C₁₋₆alkyl(meth)acrylamides, C₂₋₁₂alkenyls, C₂₋₁₂alkenylphenyls, C₂₋₁₂alkenyl naphthyls, C₂₋₆alkenylphenylC₁₋₆alkyls, where suitable substituents on said C₁₋₆alkyls include ethers, hydroxyls, carboxyls, halogens and combinations thereof.

[0035] Other polymerization routes such as living free radical and ionic polymerization can also be employed. The device-forming monomers may form hydrogel copolymers. For hydrogels, the reactive mixture will typically include at least one hydrophilic monomer.

[0036] Hydrophilic components are those which yield a clear single phase when mixed with deionized water at 25°C at a concentration of 10 wt. %.

[0037] "Interpenetrating polymer networks" or "IPNs" are polymers comprising two or more polymeric networks which are at least partially interlaced on a molecular scale, but not covalently bonded to each other and cannot be separated unless chemical bonds are broken.

[0038] "Semi-interpenetrating polymer networks" or "semi-IPNs" are polymer comprising one or more polymer network(s) and one or more linear or branched polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched chains.

[0039] A "cross-linking agent" is a di-functional or multi-functional component which can undergo free radical polymerization at two or more locations on the molecule, thereby creating branch points and a polymeric network. Common examples are ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, methylene bisacrylamide, triallyl cyanurate, and the like.

[0040] The phrase "without a surface treatment" means that the exterior surfaces of the devices (e.g. silicone hydrogels, contact lenses) of the present invention are not separately treated to improve the wettability of the device. Treatments which may be foregone include, plasma treatments, grafting, coating, and the like. Coatings, however, which provide properties other than improved wettability, such as, but not limited to antimicrobial coatings and the application of color or other cosmetic enhancement may be applied to devices of the present invention.

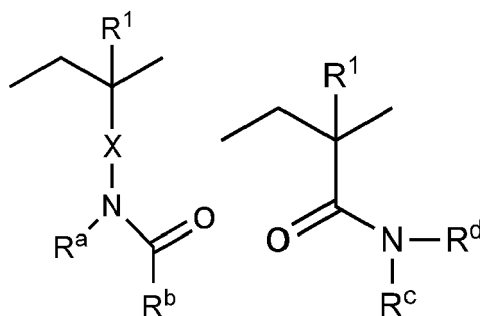
[0041] A silicone hydrogel may be formed from a reactive monomer mixture comprising at least one hydrophilic monomer, at least one hydroxyl-containing silicone component, at least one cross-linking agent, and at least one polyamide.

Polyamide

[0042] The reactive monomer mixture includes at least one polyamide. As used herein, the term "polyamide" refers to polymers and copolymers comprising repeating units containing amide groups. The polyamide may comprise cyclic amide groups, acyclic amide groups and combinations thereof, and may be any polyamide known to those of skill in the art.

[0043] Acyclic polyamides comprise pendant acyclic amide groups and are capable of association with hydroxyl groups. Cyclic polyamides comprise cyclic amide groups and are capable of association with hydroxyl groups.

[0044] Examples of suitable acyclic polyamides include polymers and copolymers comprising repeating units of Formula I or Formula II:



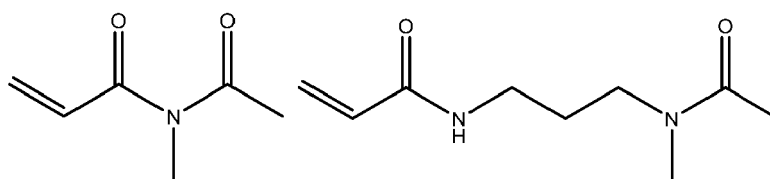
wherein the number of carbon atoms in R^a and R^b taken together is 8 or less, including 7, 6, 5, 4, 3, or less, and wherein the number of carbon atoms in R^c and R^d taken together is 8 or less, including 7, 6, 5, 4, 3, or less. The number of carbon atoms in R^a and R^b taken together may be 6 or less or 4 or less. The number of carbon atoms in R^c and R^d taken together may be 6 or less. As used herein substituted alkyl groups include alkyl groups substituted with an amine, amide, ether, hydroxyl, carbonyl, carboxy groups or combinations thereof.

[0045] R^a and R^b can be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. X may be a direct bond, and R^a and R^b may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups.

[0046] R^c and R^d can be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups, methyl, ethoxy, hydroxyethyl, and hydroxymethyl.

[0047] The acyclic polyamides of the present invention may comprise a majority of the repeating unit of Formula I or Formula II, or the acyclic polyamides can comprise at least about 50 mole % of the repeating unit of Formula I or Formula II, including at least about 70 mole %, and at least 80 mole %.

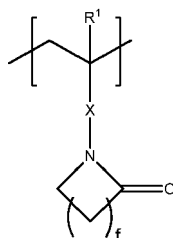
[0048] Specific examples of repeating units of Formula I and Formula II include repeating units derived from N-vinyl-N-methylacetamide, N-vinylacetamide, N-vinyl-N-methylpropionamide, N-vinyl-N-methyl-2-methylpropionamide, N-vinyl-2-methylpropionamide, N-vinyl-N,N'-dimethylurea, N, N-dimethylacrylamide, methacrylamide, and acyclic amides of Formulae IIIa and IIIb:



Formula IIIa

Formula IIIb

[0049] The acyclic polyamides may also be copolymers comprising both acyclic and cyclic amide repeating units. Examples of suitable cyclic amides that can be used to form the acyclic polyamides of include α -lactam, β -lactam, γ -lactam, δ -lactam, and ϵ -lactam. Examples of suitable cyclic amides include repeating units of Formula IV:



Formula IV

wherein R^1 is independently a hydrogen atom or methyl; f is a number from 1 to 10, X is a direct bond, $-(CO)-$, or $-(CO)-NH-R^e$, wherein R^e is a C_1 to C_3 alkyl group. In Formula IV, f may be 8 or less, including 7, 6, 5, 4, 3, 2, or 1. In Formula IV, f may be 6 or less, including 5, 4, 3, 2, or 1. In Formula IV, f may be from 2 to 8, including 2, 3, 4, 5, 6, 7, or 8. In Formula IV, f may be 2 or 3.

[0050] When X is a direct bond, f may be 2. In such instances, the cyclic polyamide may be poly(vinyl pyrrolidone) (PVP).

[0051] Specific examples of repeating units of Formula IV include repeating units derived from N-vinylpyrrolidone (NVP).

[0052] Additional repeating units may be formed from monomers selected from N-vinyl amides, acrylamides, hydroxyalkyl(meth)acrylates, alkyl(meth)acrylates and siloxane substituted acrylates or methacrylates. Specific examples of monomers which may be used to form the additional repeating units of the acyclic polyamides include as N-vinylpyrrolidone, N,N-dimethylacrylamide (DMA), 2-hydroxyethylmethacrylate, vinyl acetate, acrylonitrile, hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, methyl methacrylate and butyl methacrylate, hydroxybutyl methacrylate, MMA, PEGS, and the like and mixtures thereof. Ionic monomers may also be included. Examples of ionic monomers include acrylic acid, methacrylic acid, 2-methacryloyloxyethyl phosphorylcholine, 3-(dimethyl(4-vinylbenzyl)ammonio)propane-1-sulfonate (DMVBAPS), 3-((3-acrylamidopropyl)dimethylammonio)propane-1-sulfonate (AMPDAPS), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (MAMPDAPS), 3-((3-acryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (APDAPS), methacryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (MAPDAPS), 1-propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt (CBT, carboxybetaine; CAS

79704-35-1), 1-propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT, sulfo-betaine, CAS 80293-60-3), 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT, phosphobetaine, CAS 163674-35-9).

[0053] The at least one acyclic polyamide may be selected from the group consisting of polyvinylmethacrylamide (PVMA), polyvinylacetamide (PNVA), polydimethylacrylamide (PDMA), polyacrylamide and poly[N-vinyl N-alkyl acetamide] wherein the N-alkyl group is selected from the group consisting of linear and branched alkyl groups containing between one (C₁) and five (C₅) carbon atoms.

[0054] The reactive monomer mixture may comprise both an acyclic polyamide and a cyclic polyamide or copolymers thereof. The acyclic polyamide can be any of those acyclic polyamides described herein or copolymers thereof, and the cyclic polyamide can be formed from any combination of the repeating units of Formula V, either alone or with other repeating units. Examples of cyclic polyamides include PVP and PVP copolymers. Other polymeric internal wetting agents, such as poly(hydroxyethyl(meth)acrylamide), may also be included.

[0055] The total amount of all polyamides in the reactive mixture is greater than 15 weight percent, based upon the total weight of the reactive monomer mixture. The reactive monomer mixture may include the polyamide(s) in an amount in the range of between 15.1 weight percent and about 35 weight percent, including in the range of about 16 weight percent to about 30 weight percent, or the range of about 20 weight percent to about 30 weight percent, in all cases, based on the total weight of the reactive components of the reactive monomer mixture.

[0056] Without intending to be bound by theory, the polyamide functions as an internal wetting agent in the resulting silicone hydrogel. The polyamides of the present invention may be non-polymerizable, and in this case is incorporated into the silicone hydrogels as a semi-interpenetrating network. The non-polymerizable polyamide is "entrapped", or physically retained within a hydrogel matrix. Alternatively, the polyamides of the present invention may be polymerizable, for example as polyamide macromers, which are covalently incorporated into the silicone hydrogels. Reactive polyamides may be functionalized to contain at least one monovalent reactive group.

[0057] The polyamide(s) improve the wettability of the silicone hydrogel lens without a surface treatment. In silicone hydrogel formulations of the prior art, including wetting agents in amounts in excess of 15% was difficult, due to the inherent incompatibility of the silicone components, which are hydrophobic and the wetting agent, which is hydrophilic and has weight average molecular weights in excess of 100,000 and often 1,000,000 Daltons. This incompatibility is particularly challenging for formulations where oxygen permeabilities (Dk) of greater than about 80, 90, 100 or 120 barrers are desired. The silicone hydrogels may have Dk values between 80 and 170 barrers, between 90-170, 100-170 or 120- 170 barrers. The inventors have surprisingly found that including a mixture of at least two hydroxyl functional polydialkylsiloxanes, provides silicone hydrogels having very high concentrations of internal wetting agents, and desirable Dk values.

[0058] When the polyamides are incorporated into the reactive monomer mixture they have a weight average molecular weight of at least about 100,000 Daltons; greater than about 150,000; between about 150,000 to about 2,000,000 Daltons, between about 300,000 to about 1,800,000 Daltons.

[0059] The polyamides may also comprise at least one reactive group. For polyamides having molecular weights of 10,000 Daltons, a single reactive group may be included. For polyamides having molecular weights greater than about 10,000, greater than about 30,000, or greater than about 100,000 Daltons, more than one reactive group may be included. Mixtures of reactive and non-reactive polyamides may also be used.

[0060] The polyamides may be incorporated into the hydrogel by a variety of methods. For example, the polyamide may be added to the reaction mixture such that the hydrogel polymerizes "around" the polyamide, forming a semi-interpenetrating network.

Hydrophilic Component

[0061] The reactive monomer mixture may, in addition to the hydroxyalkyl (meth)acrylate monomers described below, include at least one additional hydrophilic component selected from hydrophilic monomers and macromers. Hydrophilic monomers can be any of the hydrophilic monomers known to be useful to make hydrogels. Examples of suitable families of hydrophilic monomers include *N*-vinyl amides, *N*-vinylimides, *N*-vinyl lactams, (meth)acrylates, (meth)acrylamides, styrenes, vinyl ethers, *O*-vinyl carbonates, *O*-vinyl carbamates, *N*-vinyl ureas, other hydrophilic vinyl compounds and mixtures thereof.

[0062] The hydrophilic monomers that may be used to make the polymers of this invention have at least one polymerizable double bond and at least one hydrophilic functional group. Such hydrophilic monomers may themselves be used as crosslinking agents, however, where hydrophilic monomers having more than one polymerizable functional group are used, their concentration should be limited as discussed above to provide a contact lens having the desired modulus. The term "vinyl-type" or "vinyl- containing" monomers refer to monomers containing the vinyl grouping (-CH=CH₂) and are generally highly reactive. Such hydrophilic vinylcontaining monomers are known to polymerize relatively easily.

[0063] "Acrylic-type" or "acrylic-containing" monomers are those monomers containing an acrylic group ($\text{CH}_2=\text{CRCOX}$) wherein R is H or CH_3 , and X is O or N, which are also known to polymerize readily, such as *N,N*-dimethyl acrylamide (DMA), 2-hydroxyethyl methacrylate (HEMA), glycerol methacrylate, 2-hydroxyethyl methacrylamide, polyethyleneglycol monomethacrylate, methacrylic acid, acrylic acid, mixtures thereof and the like.

[0064] Non-limiting examples of hydrophilic (meth)acrylate and (meth)acrylamide monomers include: acrylamide, *N*-isopropyl acrylamide, *N,N*-dimethylaminopropyl (meth)acrylamide, *N,N*-dimethyl acrylamide (DMA), *N*-(2-hydroxyethyl) (meth)acrylamide, *N,N*-bis(2-hydroxyethyl) (meth)acrylamide, *N*-(2-hydroxypropyl) (meth)acrylamide, *N,N*-bis(2-hydroxypropyl) (meth)acrylamide, *N*-(3-hydroxypropyl) (meth)acrylamide, *N*-(2-hydroxybutyl) (meth)acrylamide, *N*-(3-hydroxybutyl) (meth)acrylamide, *N*-(4-hydroxybutyl) (meth)acrylamide, vinyl acetate, acrylonitrile, and mixtures thereof.

[0065] Non-limiting examples of hydrophilic *N*-vinyl lactam and *N*-vinyl amide monomers include: *N*-vinyl pyrrolidone (NVP), *N*-vinyl-2-piperidone, *N*-vinyl-2-caprolactam, *N*-vinyl-3-methyl-2-caprolactam, *N*-vinyl-3-methyl-2-piperidone, *N*-vinyl-4-methyl-2-piperidone, *N*-vinyl-4-methyl-2-caprolactam, *N*-vinyl-3-ethyl-2-pyrrolidone, *N*-vinyl-4,5-dimethyl-2-pyrrolidone, *N*-vinyl acetamide (NVA), *N*-vinyl-*N*-methylacetamide (VMA), *N*-vinyl-*N*-ethyl acetamide, *N*-vinyl-*N*-ethyl formamide, *N*-vinyl formamide, *N*-vinyl-*N*-methylpropionamide, *N*-vinyl-*N*-methyl-2-methylpropionamide, *N*-vinyl-2-methylpropionamide, *N*-vinyl-*N,N'*-dimethylurea, 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-methyl-3-methylene-2-pyrrolidone; 1-ethyl-5-methylene-2-pyrrolidone, *N*-methyl-3-methylene-2-pyrrolidone, 5-ethyl-3-methylene-2-pyrrolidone, 1-*N*-propyl-3-methylene-2-pyrrolidone, 1-*N*-propyl-5-methylene-2-pyrrolidone, 1-isopropyl-3-methylene-2-pyrrolidone, 1-isopropyl-5-methylene-2-pyrrolidone, *N*-vinyl-*N*-ethyl acetamide, *N*-vinyl-*N*-ethyl formamide, *N*-vinyl formamide, *N*-vinyl isopropylamide, *N*-vinyl caprolactam, *N*-carboxyvinyl- β -alanine (VINAL), *N*-carboxyvinyl- α -alanine, *N*-vinylimidazole, and mixtures thereof

[0066] Non-limiting examples of hydrophilic *O*-vinyl carbamates and *O*-vinyl carbonates monomers include: *N*-2-hydroxyethyl vinyl carbamate and *N*-carboxy- β -alanine *N*-vinyl ester. Further examples of the hydrophilic vinyl carbonate or vinyl carbamate monomers are disclosed in U.S. Patent No. 5,070,215, and the hydrophilic oxazolone monomers are disclosed in U.S. Patent No. 4,910,277.

[0067] Other hydrophilic vinyl compounds include ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), allyl alcohol, 2-ethyl oxazoline, vinyl acetate, acrylonitrile, and mixtures thereof.

[0068] Other suitable hydrophilic monomers will be apparent to one skilled in the art.

[0069] The hydrophilic monomers of the present invention may be macromers of linear or branched polyethylene glycol, polypropylene glycol, or statistically random or block copolymers of ethylene oxide and propylene oxide. The macromers of these polyethers have one or more reactive group. Non-limiting examples of such reactive groups are acrylates, methacrylates, styrenes, vinyl ethers, acrylamides, methacrylamides, and other vinyl compounds. In one embodiment, the macromers of these polyethers comprise acrylates, methacrylates, acrylamides, methacrylamides, and mixtures thereof.

[0070] The hydrophilic monomers which may be incorporated into the polymers disclosed herein may be selected from *N,N*-dimethyl acrylamide (DMA), 2-hydroxyethyl acrylamide, 2-hydroxyethyl methacrylamide, *N*-hydroxypropyl methacrylamide, bis(2-hydroxyethyl) acrylamide, 2,3-dihydroxypropyl (meth)acrylamide, *N*-vinylpyrrolidone (NVP), *N*-vinyl-*N*-methyl acetamide, *N*-vinyl methacetamide (VMA), and polyethyleneglycol monomethacrylate.

[0071] The hydrophilic monomers may be selected from DMA, NVP, VMA, NVA, and mixtures thereof.

[0072] Generally there are no particular restrictions with respect to the amount of the hydrophilic monomer present in the reactive monomer mixture. The amount of the hydrophilic monomers may be selected based upon the desired characteristics of the resulting hydrogel, including water content, clarity, contact angle, protein uptake, and the like. The hydrophilic monomer, when present, can be present in an amount in the range of up to about 40 wt. %, 30 wt. %, or 20 wt. %, or in the range of about 1 to about 40 wt. %, about 1 to about 30 wt. %, or about 1 to about 20 wt. %, based on the total weight of the reactive components in the reactive monomer mixture. It is a surprising effect of the present invention that silicone hydrogels with a desirable balance of wettability, water content and biocompatibility may be formed from reaction mixtures with less than about 30 wt. %, less than about 25 wt. %, 20 wt. % or even less than 10% hydrophilic monomers, and particularly hydrophilic amide monomers such as DMA, NVP and VMA.

Hydroxyl Containing Silicone Component

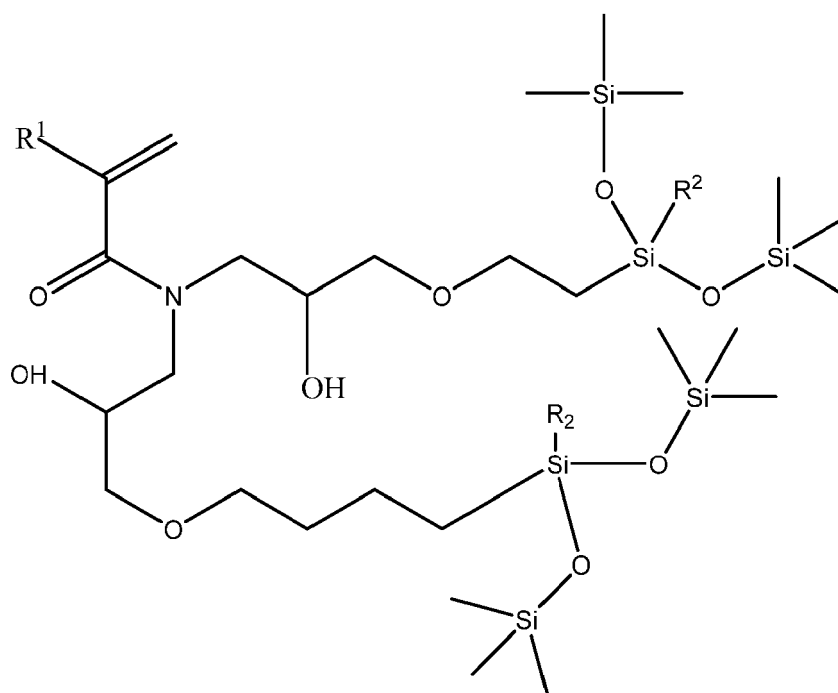
[0073] The reactive monomer mixture also includes a mixture of hydroxyl-containing silicone components of different molecular weights or different compositions. The first hydroxyl-containing silicone component may be selected from hydroxyl-containing silicone monomers, and hydroxyl containing polydisubstituted siloxanes having at least 4 polydisubstituted siloxane repeating units or 4-8 polydisubstituted siloxane repeating units; and at least one monovalent reactive group. When the first hydroxyl-containing silicone component is a hydroxyl-containing silicone monomer, the second hydroxyl-containing silicone component may be selected from hydroxyl substituted poly(disubstituted siloxane) having 4 to 8 siloxane repeating units, monofunctional hydroxyl substituted poly(disubstituted siloxane)s having 10 to 200, 10-100 or 10-20 siloxane repeating units and multifunctional hydroxyl substituted poly(disubstituted siloxane)s having

10 to 200, or 10 to 100 siloxane repeating units, and mixtures thereof. When the first hydroxyl-containing silicone component is a hydroxyl-substituted poly(disubstituted siloxane) having 4 to 8 siloxane repeating units, the second hydroxyl-containing silicone component may be selected from monofunctional hydroxyl substituted poly(disubstituted siloxane)s having 10 to 200, 10-100 or 10-20 siloxane repeating units and multifunctional hydroxyl substituted poly(disubstituted siloxane)s having 10 to 200, or 10 to 100 siloxane repeating units, and mixtures thereof.

[0074] Hydroxyl-containing silicone components having 4 polydisubstituted siloxane repeating units in the siloxane chain are not a distribution and have four repeating units in each monomer. For all hydroxyl-containing silicone components having more than four polydisubstituted siloxane repeating units in the siloxane chain the number of repeating units is a distribution, with the peak of the distribution centered around the listed number of repeat units.

[0075] The elemental Si content of the hydroxyl containing silicone component is greater than about 20 weight percent, to about 38 weight percent of the total molecular weight of the hydroxyl containing silicone component.

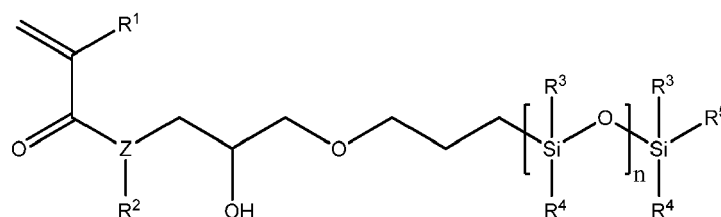
[0076] Examples of hydroxyl-containing silicone monomers include propenoic acid-2-methyl-2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propoxy]propyl ester ("SiGMA"), and 2-hydroxy-3-methacryloxypropyloxypropyltris(trimethylsiloxy)silane, and compounds of Formula V:



Formula V

wherein R^1 is a hydrogen atom or methyl group and R^2 is a linear, branched or cyclic alkyl groups containing 1 to 8 carbon atoms or a trimethylsiloxy group.

[0077] The hydroxyl-containing silicone components may be selected from monofunctional hydroxyl substituted, poly(disubstituted siloxane)s of Formula VI-1:



Formula VI-1

wherein Z is selected from O, N, S or NCH_2CH_2O , when Z is O or S R^2 is not present;
 R^1 is independently H or methyl;

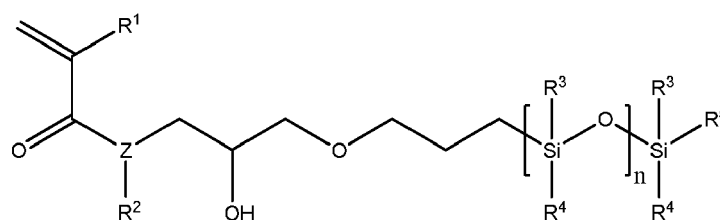
R^2 is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

R^3 and R^4 are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; R^3 and R^4 may be independently selected from methyl, ethyl or phenyl, or may be methyl;

n is the number of siloxane units and is from 4 to 8 for the first monofunctional hydroxyl substituted poly(disubstituted siloxane) monomer, and

R^5 is selected from straight or branched C_1 to C_8 alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, and combinations thereof. R^5 may be straight or branched C_4 alkyl, either of which may optionally be substituted with hydroxyl, or may be methyl.

[0078] The hydroxyl-containing silicone components may be selected from monofunctional hydroxyl substituted, poly(disubstituted siloxane)s of Formula VI-2:



Formula VI-2

wherein Z is selected from O, N, S or NCH_2CH_2O , when Z is O or S R^2 is not present;

R^1 is independently H or methyl;

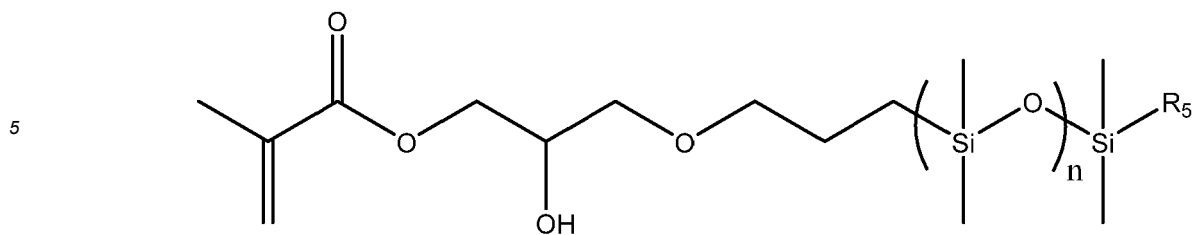
R^2 is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

R^3 and R^4 are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; R^3 and R^4 may be independently selected from methyl, ethyl or phenyl, or may be methyl;

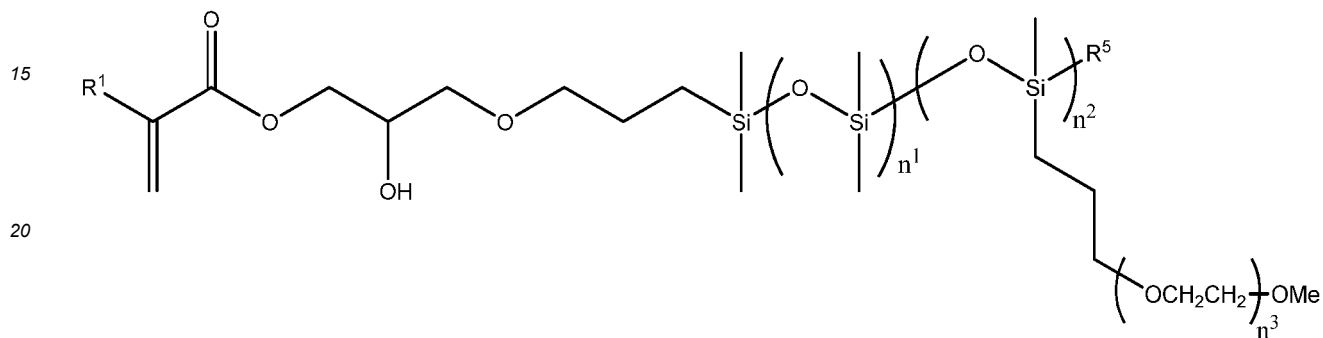
n is the number of siloxane units and is from 10 to 200, or 10-100, or 10-50, or 10-20, or 12-18 for the second monofunctional hydroxyl substituted poly(disubstituted siloxane), and

R^5 is selected from straight or branched C_1 to C_8 alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, and combinations thereof. R^5 may be straight or branched C_4 alkyl, either of which may optionally be substituted with hydroxyl, or may be methyl.

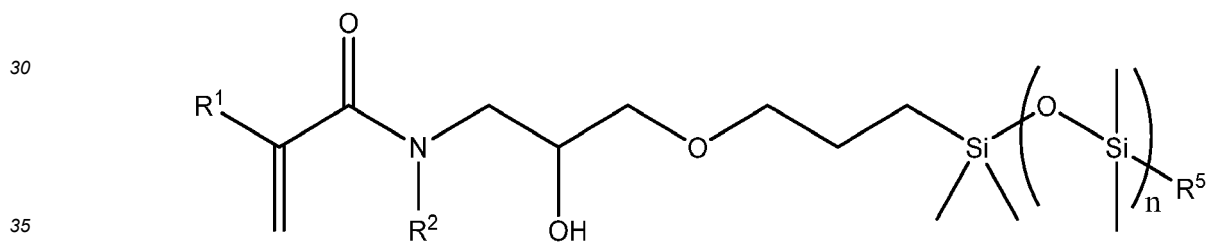
[0079] Examples of monofunctional hydroxyl containing silicone components include mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxanes (OH-mPDMS) as shown in Formula VIIa wherein n is between 4 and 30, 4-8 or 10-20; and polydimethylsiloxanes having the chemical structures as shown in Formulae VIIb through VIId, where n is between 4 and 30, 4 and 8 or 10 and 20; n^1 n^2 are independently between 4 to 100; 4 to 50; 4 to 25; n^3 is 1-50, 1-20, or 1-10; R^5 is selected from straight or branched C_1 to C_8 alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, polyhydroxyl groups selected from straight or branched C_1 to C_8 groups having a formula of $C_fH_g(OH)_h$ wherein $f=1-8$ and $g+h=2f+1$ and cyclic C_1 to C_8 groups having a formula of $C_fH_g(OH)_h$ wherein $f=1-8$ and $g+h=2f-1$, and combinations thereof; or R^5 may be selected from methyl, butyl or hydroxyl substituted C_2 - C_5 alkyl, including hydroxyl ethyl, hydroxyl propyl, hydroxyl butyl, hydroxyl pentyl and 2,3-dihydroxypropyl; and polycarbosiloxanes of Formula IX where a 4-8 for the first hydroxyl-containing silicone component and between 4-100 for the second hydroxyl-containing silicone component, and R^1 and R^5 are as defined above.



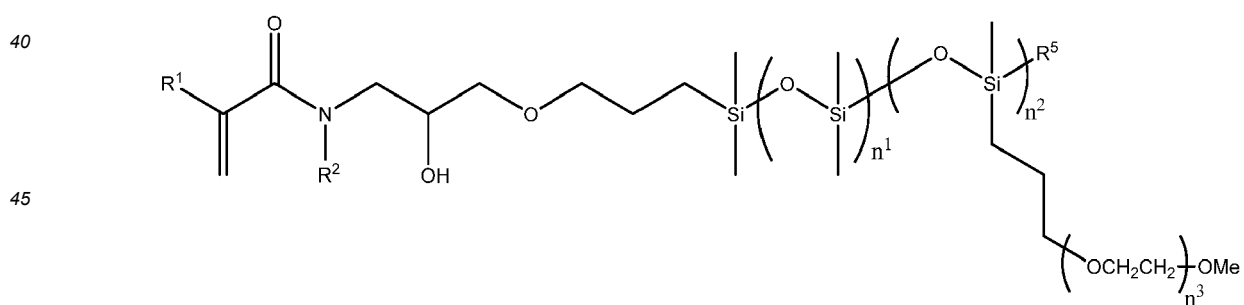
Formula VIIa



Formula VIIb



Formula VIIIa



Formula VIIIb



15



25



35



45

55



13

wherein in Formula X, Z is selected from O, N, S or $\text{NCH}_2\text{CH}_2\text{O}$; wherein R^1 is independently a hydrogen atom or methyl group; for $\text{Z} = \text{O}$ and S , R^2 is not required;

R^2 , R^6 , R^7 , R^8 , R^9 , R^{10} are independently selected from the group consisting of a hydrogen atom or any of the substituents defined for R^{11} through R^{14} ;

R^{11} , R^{12} , R^{13} , R^{14} are independently selected from the group consisting of

a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amido, ether, amino, carboxyl, carbonyl groups and combinations; a linear or branched alkyleneoxy group, specifically ethyleneoxy groups, $[\text{CH}_2\text{CH}_2\text{O}]_p$ wherein p is between 1 and 200, or 1 and 100, or 1 and 50, or 1 and 25, or 1 and 20, optionally substituted with one or more hydroxyl, amino, amido, ether, carbonyl, carboxyl, and combinations thereof;

a C_1 - C_6 linear or branched fluoroalkyl groups optionally substituted with one or more hydroxyl, amino, amido, ether, carbonyl, carboxyl, and combinations thereof;

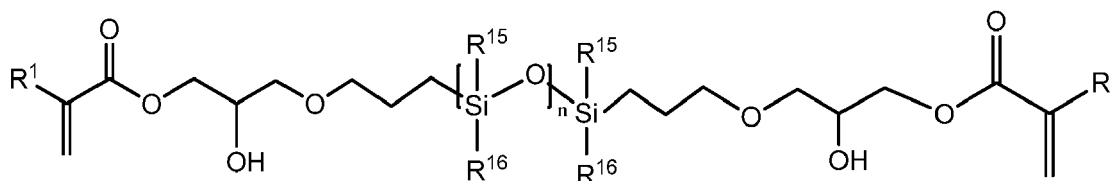
a substituted or un-substituted aryl groups, specifically phenyl groups, wherein the substituents are selected from halogen, hydroxyl, alkoxy, alkylcarbonyl, carboxy, and linear or branched or cyclic alkyl groups which may be further substituted with halogen, hydroxyl, alkoxy, alkylcarbonyl, and carboxyl groups, and combinations thereof; and

a, b, c, x, y and z are independently between 0 and 100, between 0 and 50, between 0 and 20, between 0 and 10, or between 0 and 5; and

n is the number of siloxane repeating units and is from 10 to 500; 10 to 200; 10 to 100; 10 to 50; 10 to 20.

the weight ratio of the first mono-functional hydroxyl-substituted poly(disubstituted siloxane) to the second hydroxyl-substituted poly(disubstituted siloxane) is in a range of 0.1 to 2, or 0.1 to 1.

[0081] The hydroxyl-containing silicone components may comprise a mixture of a first mono-functional hydroxyl-substituted poly(disubstituted siloxane) of Formula VI, or VIIa-IX where n is from 4 to 8 and a second hydroxyl-substituted poly(disubstituted siloxane) selected from the group consisting of a mono-functional hydroxyl-substituted poly(disubstituted siloxane) of Formula VI or VIIa to IX, wherein n is from 10-200, 10-100 or 10 to 20 and a di-functional hydroxyl-substituted poly(disubstituted siloxane) of Formula XI



Formula XI

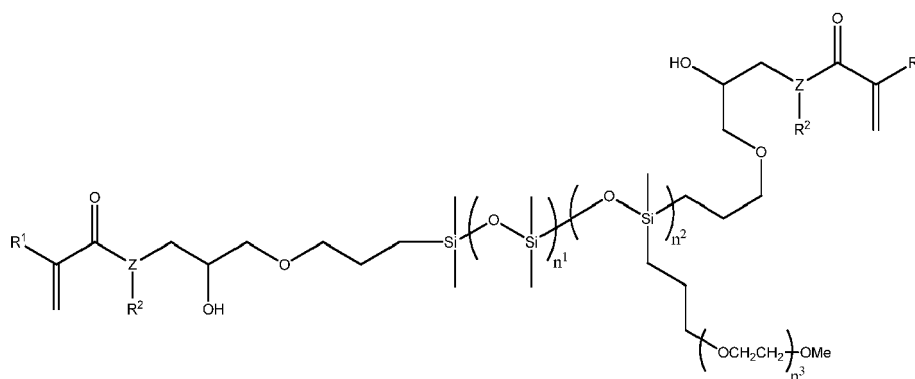
wherein

R^1 is independently a hydrogen atom or methyl group;

R^{15} and R^{16} are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amido, ether, amino, carboxyl, carbonyl groups and combinations thereof; or are independently selected from unsubstituted C_{1-4} alkyl groups and C_{1-4} alkyl groups substituted with hydroxyl or ether; or are selected from methyl, ethyl or $-(\text{CH}_2\text{CH}_2\text{O})_m\text{OCH}_3$;

n is selected from is 4 to 100; 4 to 50; or 4 to 25; and m is 1-50, 1-20, and 1-10.

[0082] Examples of multifunctional hydroxyl containing silicones include α -(2-hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-decamethylpentasiloxane and those of Formula XII:



Formula XII

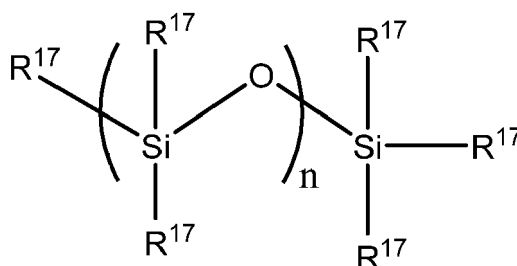
wherein Z is selected from O, N, S or $\text{NCH}_2\text{CH}_2\text{O}$, when Z is O or S, R^2 is not present; R^1 is independently H or methyl; R^2 is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; and n^1 and n^2 are independently between 4 to 100; 4 to 50; 4 to 25; n^3 is 1-50, 1-20, or 1-10.

[0083] The ratio of the first hydroxyl-containing silicone component to any of the above described second hydroxyl substituted, poly(disubstituted siloxane) can be in a range of 0.2-1.3, 0.4-1 and 0.6-1.

[0084] The hydroxyl containing silicone components are present in the reactive mixture in amounts between about 40 and about 70 wt% or about 45 to about 70 wt%.

Silicone-Containing Compounds without Hydroxyl Functionality

[0085] Additional silicone-containing compounds without hydroxyl functionality may also be included. Suitable examples include those of Formula XIII:



Formula XIII

wherein:

at least one R^{17} is a monovalent reactive group, and the remaining R^{17} are independently selected from monovalent reactive groups, monovalent alkyl groups, or monovalent aryl groups, any of the foregoing which may further comprise functionality selected from hydroxy, amino, oxa, carboxy, alkyl carboxy, alkoxy, amido, carbamate, carbonate, halogen or combinations thereof;

fluoroalkyl alkyl or aryl groups; partially fluorinated alkyl or aryl groups; halogens; linear, branched or cyclic alkoxy or aryloxy groups; linear or branched polyethyleneoxyalkyl groups, polypropyleneoxyalkyl groups, or poly(ethyleneoxy-co-propyleneoxyalkyl groups; and

monovalent siloxane chains comprising between 1-100 siloxane repeat units which may further comprise functionality selected from alkyl, alkoxy, hydroxy, amino, oxa, carboxy, alkyl carboxy, alkoxy, amido, carbamate, halogen or combinations thereof;

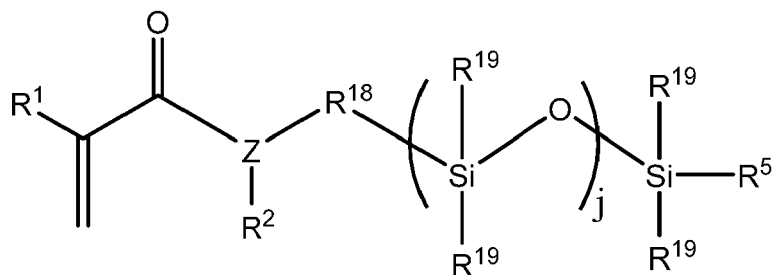
wherein n is 0 to 500 or 0 to 200, or 0 to 100, or 0 to 20, where it is understood that when n is other than 0, n is a distribution having a mode equal to a stated value

[0086] In Formula XIII from one to three R^{17} may comprise monovalent reactive groups.

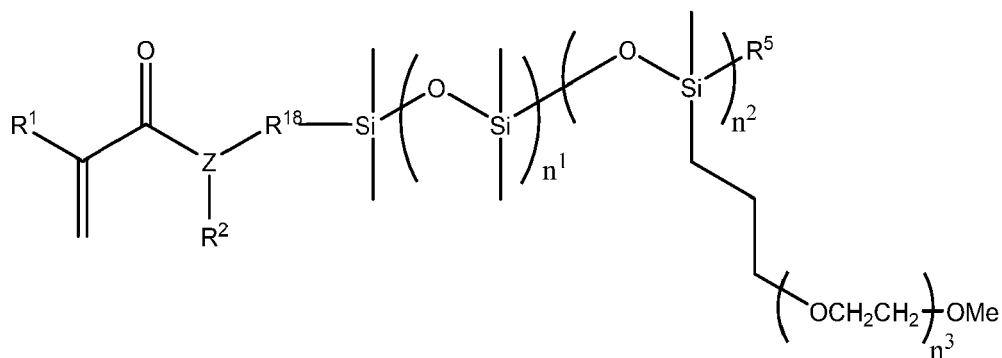
[0087] Suitable monovalent alkyl and aryl groups include

unsubstituted and substituted monovalent linear, branched or cyclic C₁ to C₁₆ alkyl groups, or unsubstituted monovalent C₁ to C₆ alkyl groups, such as substituted and unsubstituted methyl, ethyl, propyl, butyl, substituted or unsubstituted C₆-C₁₄ aryl groups, or a substituted or unsubstituted C₆ aryl group, wherein the substituents include amido, ether, amino, halo, hydroxyl, carboxyl, carbonyl groups; or a phenyl or benzyl group, combinations thereof and the like.

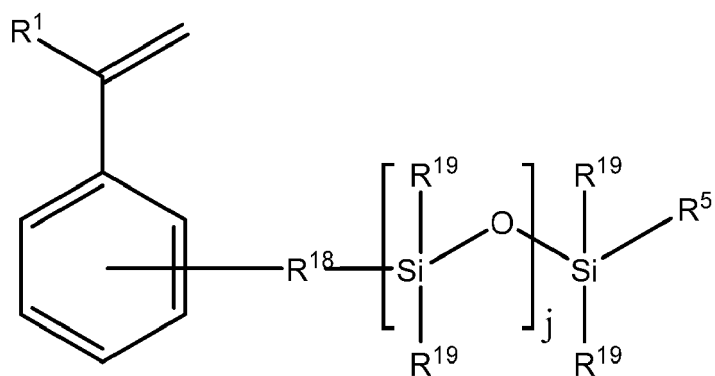
[0088] When one R¹⁷ is a monovalent reactive group, the additional silicone containing compounds may be selected from the polydisubstituted siloxane macromer of Formulae XIVa or XIVb; the styryl polydisubstituted siloxane macromer of Formula XVa or XVb or the carbosilane of Formula XVC:



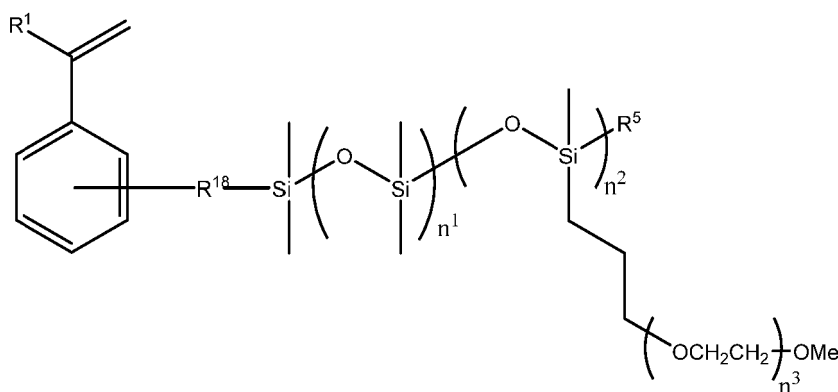
Formula XIVa



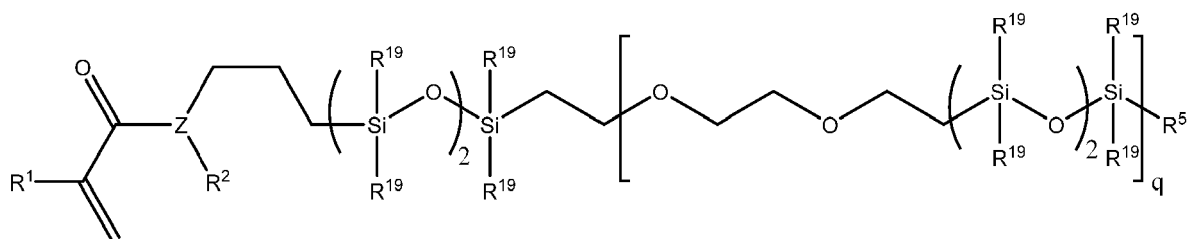
Formula XIVb



Formula XVa



Formula XVb



Formula XVc

wherein R¹ is a hydrogen atom or methyl;

Z is selected from O, N, S or NCH₂CH₂O; when Z = O or S, R² is not required;

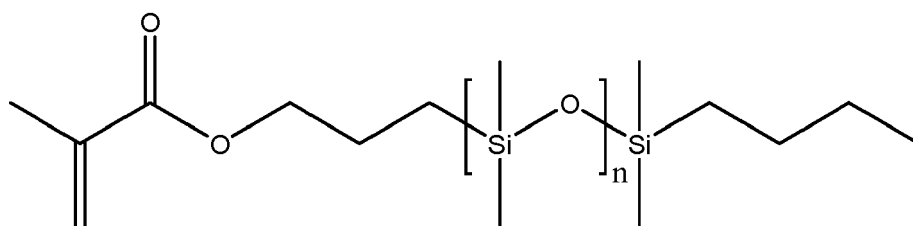
wherein j is a whole number between 1 and 20; n¹ and n² are between 4 to 100; 4 to 50; or 4 to 25; n³ is 1-50, 1-20, or 1-10; q is up to 50, 5-30 or 10-25;

wherein R¹⁸ is a substituted or unsubstituted C₁₋₆, C₁₋₄ or C₂₋₄ alkylene segment of formula (CH₂)_r, wherein each methylene group may optionally be independently substituted with ethers, amines, carbonyls, carboxylates, carbamates and combinations thereof; or an oxyalkylene segment (OCH₂)_k wherein k is a whole number from one to three, or wherein R¹⁸ may be a mixture of alkylene and oxyalkylene segments and the sum of r and k is between 1 and 9;

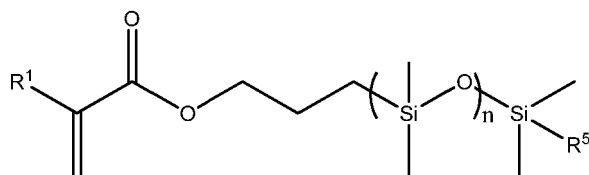
wherein each R¹⁹ is independently a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethyleneoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof;

wherein R⁵ is a substituted or un-substituted linear or branched alkyl group having 1 to eight carbon atoms, or 1 to 4 carbon atoms, or methyl or butyl; or an aryl group, any of which may be substituted with one or more fluorine atoms.

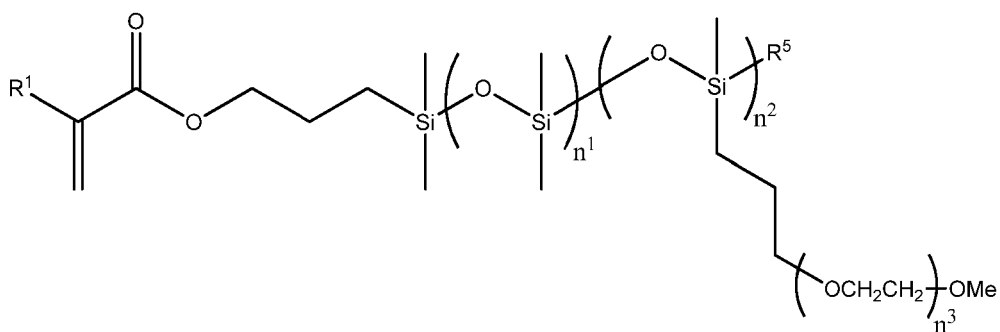
[0089] When Z is O, non-limiting examples of polysiloxane macromers include monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxanes (mPDMS) as shown in Formula XVI wherein n is between 3 and 15; mono-methacryloxypropyl terminated mono-n-alkyl terminated polydimethylsiloxanes, mono-n-alkyl terminated, polydimethyl, polyethylene glycol siloxanes as shown in Formulae XVIIa and XVIIb wherein n is 4-100, 4-20, or 3-15; n¹ and n² are between 4 to 100; 4 to 50; or 4 to 25; n³ is 1-50, 1-20, or 1-10; and macromers having the chemical structures as shown in formulae XVIIIa through XXIIb wherein R¹ is hydrogen or a methyl group; R² is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; n¹ and n² are between 4 to 100; 4 to 50; or 4 to 25; n³ is 1-50, 1-20, or 1-10; and R⁵ may be C₁-C₄ alkyl or methyl or butyl.



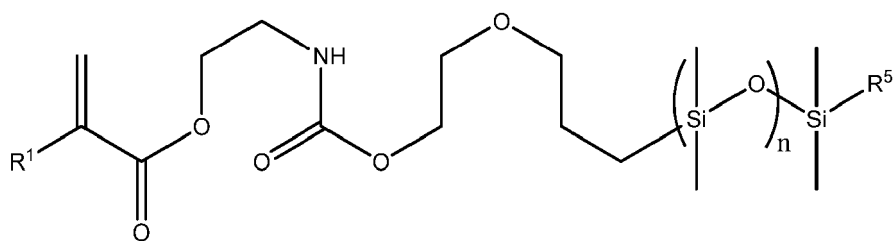
Formula XVI



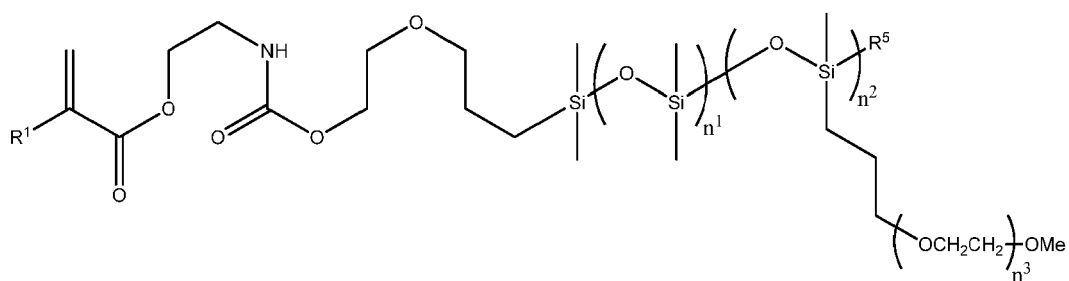
Formula XVIIa



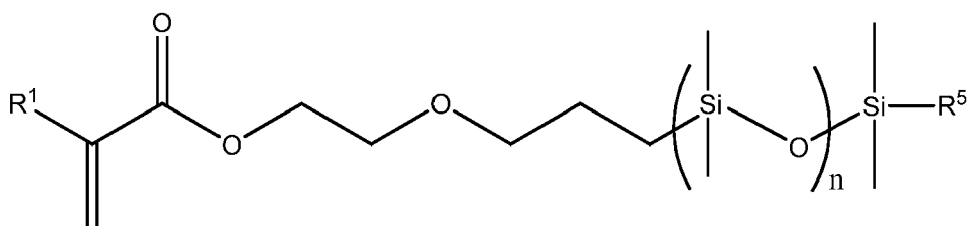
Formula XVIIb



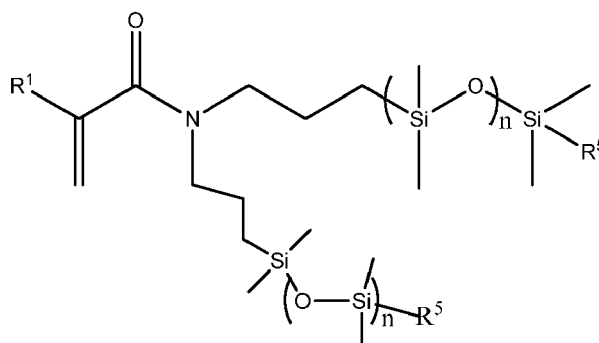
Formula XVIIIa



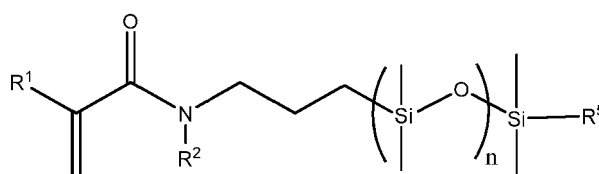
Formula XVIIIb



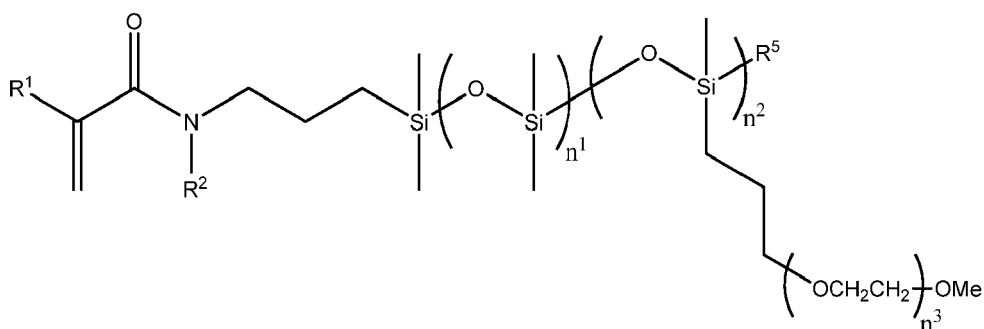
Formula XIX



Formula XX



Formula XXIa



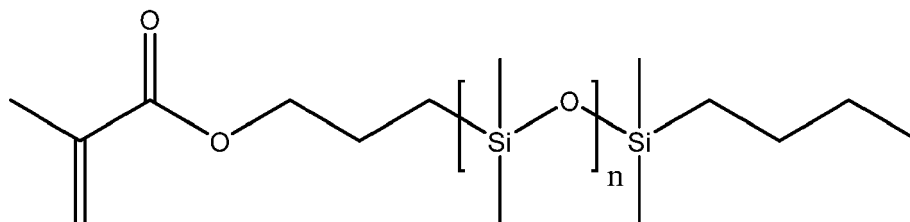
Formula XXIb

[0090] Examples of suitable mono(meth)acryloxyalkylpolydisubstituted siloxanes include mono(meth)acryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, mono(meth)acryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane, mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane, mono(meth)acrylamidoalkylpolydialkylsiloxanes mono(meth)acryloxyalkyl terminated monoalkyl polydiarylsiloxanes, and mixtures thereof.

[0091] In Formula XIII, when n is zero, one R¹⁸ may be a monovalent reactive group, and at least 3 R¹⁸ are selected from monovalent alkyl groups having 1 to 16, 1 to 6 or 1-4 carbon atoms. Non-limiting examples of silicone components include, 3-methacryloxypropyltris(trimethylsiloxy)silane (TRIS), 3-methacryloxypropylbis(trimethylsiloxy)methylsilane, and 3-methacryloxypropylpentamethyl disiloxane.

[0092] The number of siloxane repeating units, n, may also be 2 to 50, 3 to 25, or 3 to 15; wherein at least one terminal R¹⁷ comprises a monovalent reactive group and the remaining R¹⁷ are selected from monovalent alkyl groups having

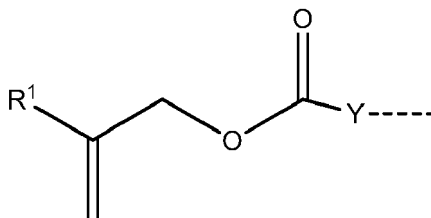
1 to 16 carbon atoms, or from monovalent alkyl groups having 1 to 6 carbon atoms. Non-hydroxyl containing silicone compounds may also include those where n is 3 to 15, one terminal R¹⁷ comprises a monovalent reactive group, the other terminal R¹⁷ comprises a monovalent alkyl group having 1 to 6 carbon atoms and the remaining R¹⁷ comprise monovalent alkyl group having 1 to 3 carbon atoms. Non-limiting examples of silicone components include monomethacryloxypropyl n-butyl terminated polydimethylsiloxanes (M_n=800-1000), (mPDMS, as shown in XXII).



Formula XXII

[0093] Formula XIII may also include compounds where n is 5 to 400 or from 10 to 300, both terminal R¹⁷ comprise monovalent reactive groups and the remaining R¹⁷ are independently of one another selected from monovalent alkyl groups having 1 to 18 carbon atoms which may have ether linkages between carbon atoms and may further comprise halogen.

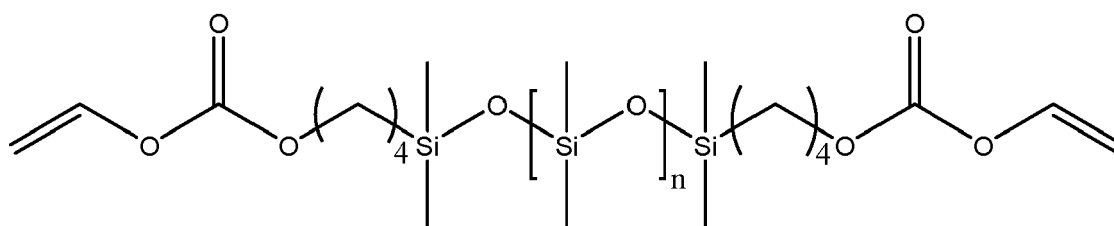
[0094] One to four R¹⁷ in Formula XIII may comprise a vinyl carbonate or vinyl carbamate of Formula XXIIIa:



Formula XXIIIa

wherein Y denotes O-, S- or NH-; R¹ denotes a hydrogen atom or methyl.

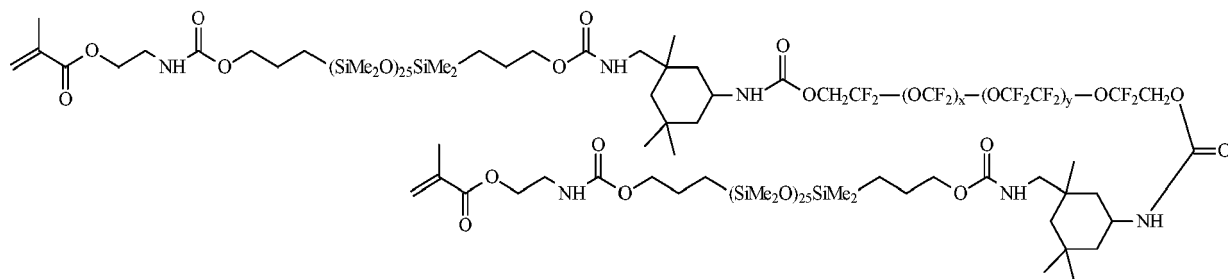
[0095] The silicone-containing vinyl carbonate or vinyl carbamate monomers specifically include: 1,3-bis[4-(vinyl-oxycarbonyloxy)but-1-yl]tetramethyl-disiloxane; 3-(vinyl-oxycarbonylthio) propyl-[tris (trimethylsiloxy)silane]; 3-[tris(trimethylsiloxy)silyl] propyl allyl carbamate; 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbamate; trimethylsilylethyl vinyl carbonate; trimethylsilylmethyl vinyl carbonate, and the crosslinking agent of Formula XXIIIb.



Formula XXIIIb

[0096] Where biomedical devices with moduli below about 200 psi are desired, only one R¹⁷ comprises a monovalent reactive group and no more than two of the remaining R¹⁷ groups comprise monovalent siloxane groups.

[0097] Another suitable silicone-containing macromer is compound of Formula XXIV in which the sum of x and y is a number in the range of 10 to 30. The silicone containing macromer of Formula XXIV is formed by the reaction of fluoroether, hydroxy-terminated polydimethylsiloxane, isophorone diisocyanate and isocyanatoethylmethacrylate.



Formula XXIV

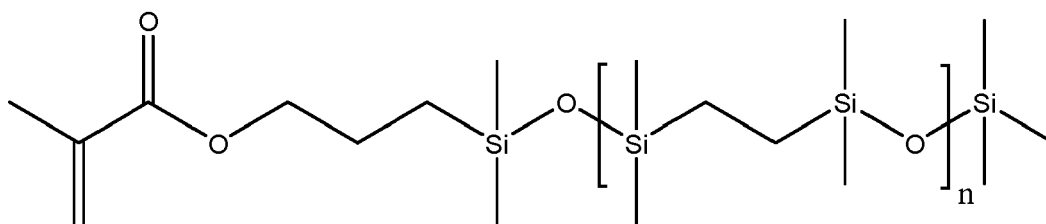
[0098] The non-hydroxyl containing silicone-containing component may be selected from non-hydroxyl containing acrylamide silicones of U.S. Patent No. 8,415,405. Other silicone components suitable for use in this invention include those described in WO 96/31792 such as macromers containing polysiloxane, polyalkylene ether, diisocyanate, polyfluorinated hydrocarbon, polyfluorinated ether and polysaccharide groups. Another class of suitable silicone-containing components includes silicone-containing macromers made via GTP, such as those disclosed in U.S. Patent Nos. 5,314,960, 5,331,067, 5,244,981, 5,371,147, and 6,367,929. U.S. Patent Nos. 5,321,108, 5,387,662, and 5,539,016 describe polysiloxanes with a polar fluorinated graft or side group having a hydrogen atom attached to a terminal difluorosubstituted carbon atom. US 2002/0016383 describes hydrophilic siloxanyl methacrylates containing ether and siloxanyl linkages and crosslinkable monomers containing polyether and polysiloxanyl groups. Any of the foregoing polysiloxanes can also be used as the silicone-containing component in this invention.

[0099] In one embodiment where a modulus of less than about 120 psi is desired, the majority of the mass fraction of the silicone-containing components used in the lens formulation should contain only one polymerizable functional group.

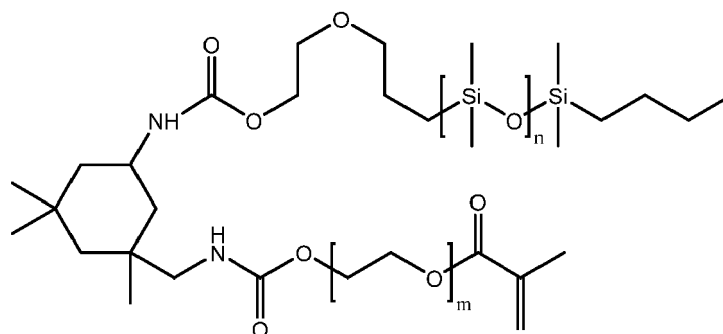
[0100] The non-hydroxyl containing silicone component may be selected from the group consisting of monomethacryloxypropyl terminated, mono-n-alkyl terminated linear polydisubstituted siloxane; methacryloxypropyl-terminated linear polydisubstituted siloxane; and mixtures thereof.

[0101] The non-hydroxyl containing silicone component may also be selected from monomethacrylate terminated, C₁-C₄ alkyl terminated, linear polydimethylsiloxanes; and mixtures thereof.

[0102] In some instances, the non-hydroxyl functionalized silicone-containing component may be used in amounts up to about 10 wt%. Examples include those selected from mPDMS of Formula XXII where R⁵ is methyl or butyl, compounds of Formulae XVIa, XVIIb through XVIIIb, XX, XXIa, XXIb and the macromers shown in Formula XXV or XXVI where n is 1-50 and m is 1-50, 1-20 or 1-10:



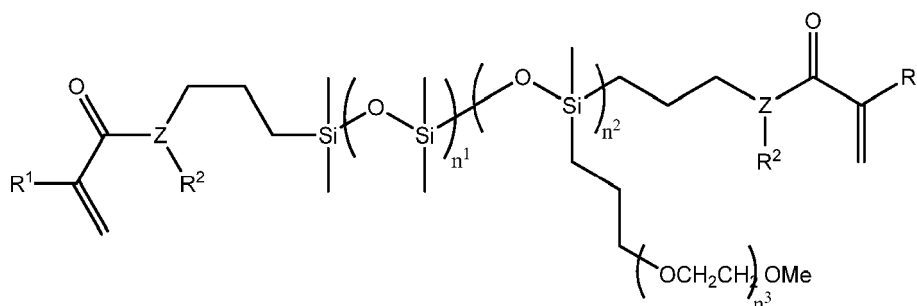
Formula XXV



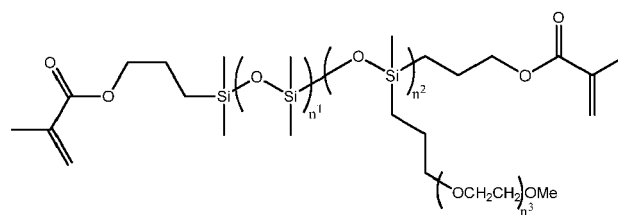
Formula XXVI

[0103] Specific examples of non-hydroxyl functionalized silicone-containing components include mPDMS of Formula XVIIa, compounds of Formulae XVIII or XIX where R¹ is methyl and R⁵ is selected from methyl or butyl and the macromers shown in Formula XXV where n is 1-50 or 4-40, 4-20.

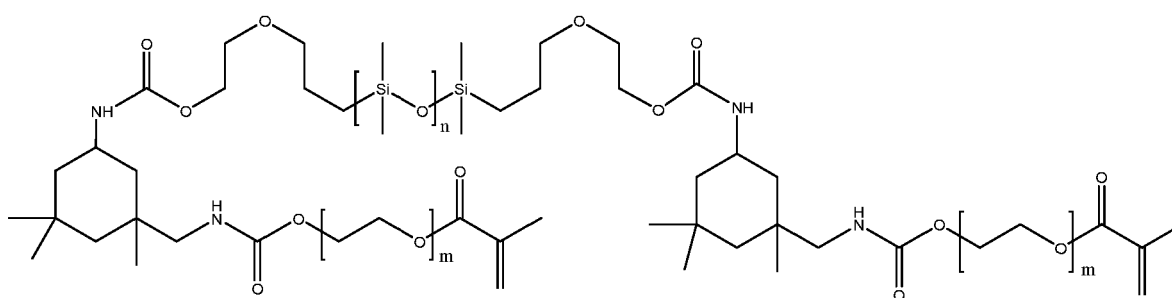
[0104] Specific examples of silicone containing crosslinkers include bismethacryloxypropyl polydimethyl siloxane, where n may be 4-200, or 4-150, and the following compounds of Formula XXVIa-XXVIc, wherein n¹ and n² are independently selected from 4 to 100; 4 to 50; or 4 to 25; n³ is 1-50, 1-20 or 1-10, m is 1-100, 1-50, 1-20 or 1-10, and q is up to 50, 5-30 or 10-25; wherein R¹ is a hydrogen atom or methyl; wherein Z is selected from O, N, S or NCH₂CH₂O; when Z = O or S, R² is not required; R² is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; and wherein each R¹⁹ is independently a linear, branched, or cyclic alkyl group containing between one and six carbon atoms, a linear, branched, or cyclic alkoxy group containing between one and six carbon atoms, a linear or branched polyethyleneoxyalkyl group, a phenyl group, a benzyl group, a substituted or un-substituted aryl group, a fluoroalkyl group, a partially fluorinated alkyl group, a perfluoroalkyl group, a fluorine atom, or combinations thereof.



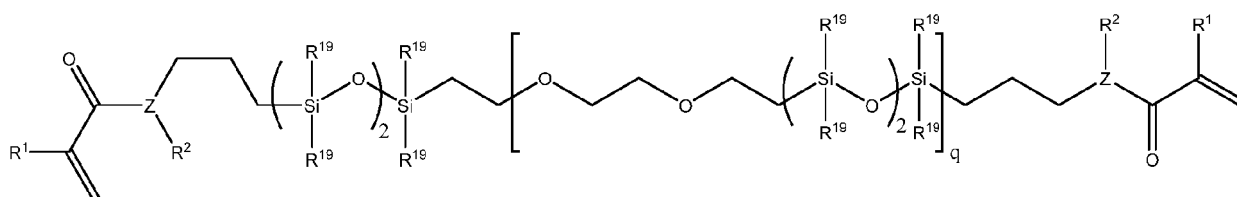
Formula XXVIa



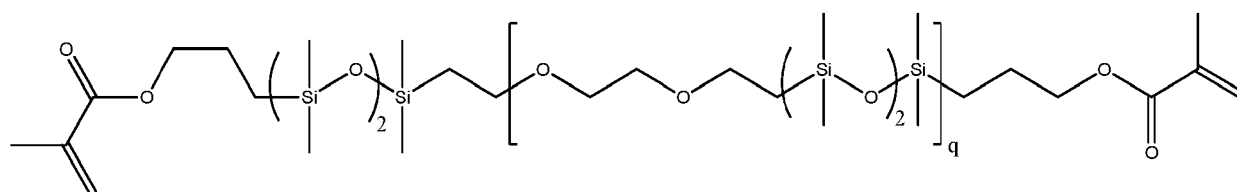
Formula XXVIb



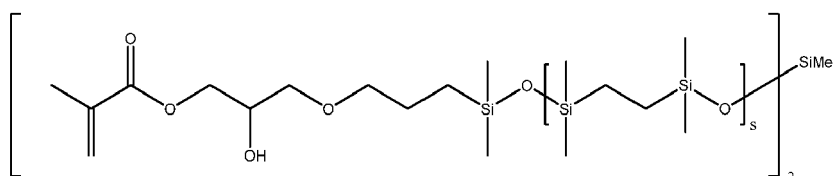
Formula XXVIc



Formula XXVIIa



Formula XXVIIb



Formula XXVIIc

[0105] The non-hydroxyl containing silicone component may have an average molecular weight of from about 400 to about 4000 Daltons.

[0106] If present, the non-hydroxyl containing silicone components may be present in amounts which do not degrade the properties of the resulting lenses, including haze. The non-hydroxyl containing silicone components may be present in amounts up to about 15 wt% or up to about 10wt%. The reactive monomer mixture may be free from non-hydroxyl containing silicone components. The silicone-containing component(s) (both hydroxyl and non-hydroxyl containing) may be present in amounts up to about 80 weight %, or from about 10 and about 80, from about 20 and about 75 weight %, or from about 20 and about 70 weight %, based upon all reactive components of the reactive mixture (e.g., excluding diluents).

Charged Reactive Component

[0107] The reactive monomer mixture may further comprise at least one reactive component which is charged under physiological conditions. The charged monomer may be selected from anions, cations, zwitterions, betaines, and mixtures thereof.

[0108] The charged monomers, when incorporated into the silicone hydrogels of the present invention, provide a net negative charge distribution. Anionic monomers comprise at least one anionic group and at least one reactive group. Specifically, the anionic group can include, but is not limited to, carboxylate groups, phosphates, sulfates, sulfonates, phosphonates, borates, and mixtures thereof. The anionic groups may comprise from three to ten carbon atoms, or from three to eight carbon atoms. The anionic groups may comprise carboxylic acid groups. Specifically, the charged monomer may be a carboxylic acid monomer selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, cinnamic acid, vinylbenzoic acid, monoesters of fumaric acid, maleic acid, and itaconic acid, and mixtures thereof.

[0109] The charged monomer can be a zwitterionic monomer. Zwitterionic monomers comprise at least one zwitterionic group and at least one reactive group. As used herein, the term "zwitterion" refers to a neutral chemical compound with both a positive and negative electrical charge. Zwitterionic monomers include betaine monomers.

[0110] The charged monomer can be a betaine monomer. Betaine monomers comprise at least one betaine group and at least one reactive group. As used herein, the term "betaine" refers to a neutral chemical compound with a positively charged cationic functional group such as a quaternary ammonium or phosphonium cation which bears no hydrogen atom and with negatively charged functional group such as a carboxylate group which may not be adjacent to the cationic

site.

[0111] The charged monomer contains at least one polymerizable group, or reactive group. Reactive groups include groups that can undergo free radical polymerization. Non-limiting examples of free radical reactive groups include (meth)acrylates, styryls, vinyls, vinyl ethers, C₁₋₆ alkyl(meth)acrylates, (meth)acrylamides, C₁₋₆ alkyl (meth)acrylamides, N-vinyl lactams, N-vinylamides, C₂₋₁₂ alkenyls, C₂₋₁₂ alkenylphenyls, C₂₋₁₂ alkenylnaphthyls, C₂₋₆ alkenylphenyl, C₁₋₆ alkyls, O-vinylcarbamates, and O-vinylcarbonates.

[0112] Examples of "charged monomers" include (meth)acrylic acid, N-[(ethenoxy)carbonyl]-β-alanine (VINAL, CAS #148969-96-4), 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopropanoic acid (ACA2), 3-acrylamido-3-methylbutanoic acid (AMBA), 2-(methacryloyloxy)ethyl trimethylammonium chloride (Q Salt or METAC), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 1-propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt (CBT, carboxybetaine; CAS 79704-35-1), 1-propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT, sulfobetaine, CAS 80293-60-3), 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT, phosphobetaine, CAS 163674-35-9, 2-methacryloyloxyethyl phosphorylcholine, 3-(dimethyl(4-vinylbenzyl)ammonio)propane-1-sulfonate (DMVBAPS), 3-((3-acrylamidopropyl)dimethylammonio)propane-1-sulfonate (AMPDAPS), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (MAMPDAPS), 3-((3-(acryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (APDAPS), methacryloyloxypropyl)dimethylammonio)propane-1-sulfonate (MAPDAPS).

The charged monomer may be selected from (meth)acrylic acid, 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopropanoic acid (ACA2), and mixtures thereof..

[0113] The charged monomer can be present in an amount up to about 10 weight percent (wt. %), based on the total weight of the reaction monomer mixture, including a range of about 0.5 to about 5 wt.%, about 0.5 to about 3 wt.%, about 0.5 to about 2 wt.%, about 1 to about 10 wt.%, about 1 to about 5 wt.%, about 1 to about 3 wt.%, and about 1 to about 2 wt.%.

Hydroxyalkyl (meth)acrylate monomer

[0114] The reactive mixtures of the present invention further comprise at least one hydroxyalkyl (meth)acrylate where the hydroxyl alkyl group may be selected from C₂-C₄ mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; or is selected from 2-hydroxyethyl, 2,3-dihydroxypropyl, or 2-hydroxypropyl.

[0115] Examples of suitable hydroxyalkyl (meth)acrylate monomer include 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 1-hydroxypropyl-2-(meth)acrylate, 2-hydroxy-2-methyl-propyl (meth)acrylate, 3-hydroxy-2,2-dimethyl-propyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycerol (meth)acrylate, polyethyleneglycol monomethacrylate, and mixtures thereof.

[0116] The hydroxyalkyl monomer may also be selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxypropyl methacrylate, hydroxybutyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, and mixtures thereof. The hydroxyalkyl monomer may comprise 2-hydroxyethyl methacrylate, 3-hydroxy-2,2-dimethylpropyl methacrylate, hydroxybutyl methacrylate or glycerol methacrylate.

[0117] Hydroxyl containing (meth)acrylamides are generally too hydrophilic to be included as compatibilizing hydroxyalkyl monomers, and when included are hydrophilic monomers.

[0118] The lower amount of hydroxyalkyl monomers may be selected to provide a haze value to the final lens of less than about 50% or less than about 30%.

[0119] It will be appreciated that the amount of hydroxyl component will vary depending upon a number of factors, including, the number of hydroxyl groups on the hydroxyalkyl monomer, the amount, molecular weight and presence of hydrophilic functionality on the silicone containing components. The hydrophilic hydroxyl component may be present in the reactive mixture in amounts up to about 15%, up to about 10 wt%, between about 1 and about 15 wt%, about 3 and about 15 wt%, or about 5 and about 15 wt%.

Cross-linking Agent

[0120] Cross-linking agents, also referred to as cross-linking monomers, may be included in the reactive mixture. The cross-linking agents may be selected from bifunctional cross-linkers, trifunctional cross-linkers, tetrafunctional cross-linkers, and mixtures thereof, including silicone-containing and non-silicone containing cross-linking agents. Non-silicone-containing crosslinking agents include ethylene glycol dimethacrylate (EGDMA), diethyleneglycol dimethacrylate, tetraethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate ("TMPTMA"), glycerol trimethacrylate, 1,3-propanediol dimethacrylate; 2,3-propanediol dimethacrylate; 1,6-hexanediol dimethacrylate; 1,4-butanediol dimethacrylate, triallyl cyanurate (TAC), glycerol trimethacrylate, methacryloxyethyl vinylcarbonate (HEMAVc), allylmethacrylate, methylene bisacrylamide (MBA), polyethylene glycol dimethacrylate (wherein the polyethylene glycol has a molecular weight up to, e.g., about 5000 Daltons). The cross-linking agents may be used in the usual amounts, e.g., from

about 0.000415 to about 0.0156 mole per 100 grams of reactive components in the reaction mixture. Alternatively, if the hydrophilic monomers and/or the silicone-containing components are multifunctional by molecular design or because of impurities, the addition of a cross-linking agent to the reaction mixture is optional. Examples of hydrophilic monomers and macromers which can act as the cross-linking agent and when present do not require the addition of an additional cross-linking agent to the reaction mixture include (meth)acrylate and (meth)acrylamide endcapped polyethers.

Further Constituents

[0121] The reactive monomer mixture may contain additional components such as, but not limited to, diluents, wetting agents, light absorbing compounds, including UV absorbers, and photochromic compounds; tints, pigments, dyes, any of which may be reactive or non-reactive but capable of being retained in the biomedical device, and medicinal agents, antimicrobial compounds, pharmaceutical compounds, nutraceutical compounds, release agents, and combinations thereof.

[0122] Classes of suitable diluents for silicone hydrogel reaction mixtures include alcohols having 2 to 20 carbon atoms, amides having 10 to 20 carbon atoms derived from primary amines and carboxylic acids having 8 to 20 carbon atoms. The diluents may be primary, secondary and tertiary alcohols.

[0123] Generally the reactive components are mixed in a diluent to form a reaction mixture. Suitable diluents are known in the art. For silicone hydrogels suitable diluents are disclosed in WO 03/022321 and US6020445.

[0124] Classes of suitable diluents for silicone hydrogel reaction mixtures include alcohols having 2 to 20 carbons, amides having 10 to 20 carbon atoms derived from primary amines, and carboxylic acids having 8 to 20 carbon atoms. Primary and tertiary alcohols may be used. Preferred classes include alcohols having 5 to 20 carbons and carboxylic acids having 10 to 20 carbon atoms.

[0125] Specific diluents which may be used include 1-ethoxy-2-propanol, diisopropylaminoethanol, isopropanol, 3,7-dimethyl-3-octanol, 1-decanol, 1-dodecanol, 1-octanol, 1-pentanol, 2-pentanol, 1-hexanol, 2-hexanol, 2-octanol, 3-methyl-3-pentanol, tert-amyl alcohol, tert-butanol, 2-butanol, 1-butanol, 2-methyl-2-pentanol, 2-propanol, 1-propanol, ethanol, 2-ethyl-1-butanol, (3-acetoxy-2-hydroxypropyloxy)-propylbis(trimethylsiloxy) methylsilane, 1-tert-butoxy-2-propanol, 3,3-dimethyl-2-butanol, tert-butoxyethanol, 2-octyl-1-dodecanol, decanoic acid, octanoic acid, dodecanoic acid, 2-(diisopropylamino)ethanol mixtures thereof and the like.

[0126] Preferred diluents include 3,7-dimethyl-3-octanol, 1-dodecanol, 1-decanol, 1-octanol, 1-pentanol, 1-hexanol, 2-hexanol, 2-octanol, 3-methyl-3-pentanol, 2-pentanol, t-amyl alcohol, tert-butanol, 2-butanol, 1-butanol, 2-methyl-2-pentanol, 2-ethyl-1-butanol, ethanol, 3,3-dimethyl-2-butanol, 2-octyl-1-dodecanol, decanoic acid, octanoic acid, dodecanoic acid, mixtures thereof and the like.

[0127] More preferred diluents include 3,7-dimethyl-3-octanol, 1-dodecanol, 1-decanol, 1-octanol, 1-pentanol, 1-hexanol, 2-hexanol, 2-octanol, 1-dodecanol, 3-methyl-3-pentanol, 1-pentanol, 2-pentanol, t-amyl alcohol, tert-butanol, 2-butanol, 1-butanol, 2-methyl-2-pentanol, 2-ethyl-1-butanol, 3,3-dimethyl-2-butanol, 2-octyl-1-dodecanol, mixtures thereof and the like.

[0128] Mixtures of diluents may be used. The diluents may be used in amounts up to about 55% by weight of the total of all components in the reaction mixture. More preferably the diluent is used in amounts less than about 45% and more preferably in amounts between about 15 and about 40% by weight of the total of all components in the reaction mixture.

[0129] If a diluent is present, generally there are no particular restrictions with respect to the amount of diluent present. When diluent is used, the diluent may be present in an amount in the range of about 2 to about 70 weight percent, including in the range of about 5 to about 50 weight percent, and in the range of about 15 to about 40 weight percent, based on the total weight of the reactive mixtures (including reactive and nonreactive components).

[0130] A polymerization initiator may be used in the reaction mixture. The polymerization initiator can include at least one of lauryl peroxide, benzoyl peroxide, iso-propyl percarbonate, azobisisobutyronitrile, and the like, that generate free radicals at moderately elevated temperatures, and photoinitiator systems such as aromatic alpha-hydroxy ketones, alkoxyoxybenzoin, 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 (DM-BAPO), bis(2,4,6-trimethylbenzoyl)-phenyl phosphineoxide (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.

[0131] Commercially available visible light initiator systems include Irgacure[®] 819, Irgacure[®] 1700, Irgacure[®] 1800, Irgacure[®] 819, Irgacure[®] 1850 (all from Ciba Specialty Chemicals) and Lucrin[®] 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. Polymerization of the reaction mixture can be initiated using the appropriate choice of heat or visible or ultraviolet light or other means depending on the polymerization initiator used. Alternatively, initiation can be conducted without a photoinitiator using, for example, e-beam. However, when a photoinitiator is used, the preferred initiators are bisacylphosphine oxides, such as bis(2,4,6-tri-methylbenzoyl)-phenyl phosphine oxide (Irgacure® 819) or a combination of 1-hydroxycyclohexyl phenyl ketone and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (DMBAPO), or the method of polymerization initiation is via visible light activation.

[0132] Polymerization of the reaction mixture can be initiated using the appropriate choice of heat or visible or ultraviolet light or other means depending on the polymerization initiator used. Alternatively, initiation can be conducted without a photoinitiator using, for example, e-beam.

Curing of Silicone Polymer/Hydrogel and Manufacture of Lens

[0133] The reactive mixtures of the present invention can be formed by any of the methods known in the art, such as shaking or stirring, and used to form polymeric articles or devices by known methods. The reactive components (hydrophilic monomer, hydroxyl-containing silicone component, cross-linking agent, polyamide, etc.) are mixed together either with or without a diluent to form the reactive mixture.

[0134] For examples, the silicone hydrogels may be prepared by mixing reactive components, and, optionally, diluent(s), with a polymerization initiator and curing by appropriate conditions to form a produce that can be subsequently formed into the appropriate shape by lathing, cutting, and the like. Alternatively, the reaction mixture may be placed in a mold and subsequently cure into the appropriate article.

[0135] The reactive mixture of the present invention may be cured via any known process for molding the reaction mixture in the production of contact lenses, including spincasting and static casting. Spincasting methods are disclosed in U.S. Patents Nos. 3,408,429 and 3,660,545, and static casting methods are disclosed in U.S. Patents Nos. 4,113,224 and 4,197,266. The contact lenses of this invention may be formed by the direct molding of the silicone hydrogels, which is economical, and enables precise control over the final shape of the hydrated lens. For this method, the reaction mixture is placed in a mold having the shape of the final desired silicone hydrogel and the reaction mixture is subjected to conditions whereby the monomers polymerize, to thereby produce a polymer in the approximate shape of the final desired product.

[0136] After curing, the lens may be subjected to extraction to remove unreacted components and release the lens from the lens mold. The extraction may be done using conventional extraction fluids, such organic solvents, such as alcohols or may be extracted using aqueous solutions.

[0137] Aqueous solutions are solutions which comprise water. The aqueous solutions of the present invention may comprise at least about 30 weight % water, or at least about 50 weight % water, or at least about 70% water, or at least about 90 weight % water. Aqueous solutions may also include additional water soluble components such as release agents, wetting agents, slip agents, pharmaceutical and nutraceutical components, combinations thereof and the like. Release agents are compounds or mixtures of compounds which, when combined with water, decrease the time required to release a contact lens from a mold, as compared to the time required to release such a lens using an aqueous solution that does not comprise the release agent. The aqueous solutions may comprise less than about 10 weight %, or less than about 5 weight % organic solvents such as isopropyl alcohol, or may be free from organic solvents. The aqueous solutions may not require special handling, such as purification, recycling or special disposal procedures.

[0138] In various embodiments, extraction can be accomplished, for example, via immersion of the lens in an aqueous solution or exposing the lens to a flow of an aqueous solution. In various embodiments, extraction can also include, for example, one or more of: heating the aqueous solution; stirring the aqueous solution; increasing the level of release aid in the aqueous solution to a level sufficient to cause release of the lens; mechanical or ultrasonic agitation of the lens; and incorporating at least one leach aid in the aqueous solution to a level sufficient to facilitate adequate removal of unreacted components from the lens. The foregoing may be conducted in batch or continuous processes, with or without the addition of heat, agitation or both.

[0139] Some embodiments can also include the application of physical agitation to facilitate leach and release. For example, the lens mold part to which a lens is adhered can be vibrated or caused to move back and forth within an aqueous solution. Other embodiments may include ultrasonic waves through the aqueous solution.

[0140] The lenses may be sterilized by known means such as, but not limited to autoclaving.

[0141] The contact lenses of the present invention display desirable combination of both mechanical and biological properties including water content, haze, contact angle, modulus, oxygen permeability, lipid uptake, lysozyme uptake and PQ1 uptake, as shown in the following table. All values are prefaced by "about", and the ophthalmic devices of the present invention may have any combination of the listed properties.

	[H ₂ O] %	>20	>30	>40	20-60	30-60
	% haze	>50	>30			
5	DCA (°)	>90	>70	≥50	≥40	≥20
	Modulus (psi)	>120	>110	50-120	50-110	
	Dk (barrers)	>80	80-200	90-180	100-160	
	Lipid uptake (μg/lens)	<20	<10	<5		
10	Lysozyme uptake (μg/lens)	>50	>100	>200	>500	>700
	PQ1 uptake (%)	<10	<5			

[0142] When the contact lenses of the present invention contain at least one charged component the lysozyme uptake may also be at least about 800 or between 50 and 1500, 100-1500 or 200-1500 μg/lens.

Test Methods

[0143] It will be appreciated that all of the tests specified herein have a certain amount of inherent error. Accordingly, the results reported herein are not to be taken as absolute numbers, but numerical ranges based upon the precision of the particular test.

[0144] Haze was measured by placing a hydrated test lens in borate buffered saline in a clear glass cell at ambient temperature above a flat black background, illuminating from below with a fiber optic lamp (Dolan-Jenner PL-900 fiber optic light with 0.5 inch diameter light guide) at an angle of 66° normal to the lens cell, and capturing an image of the test lens from above, normal to the glass cell with a video camera (DVC 1310C RGB camera or equivalent equipped with a suitable zoom camera lens) placed 14 cm above the lens holder. The background scatter is subtracted from the scatter of the test lens by subtracting an image of a blank cell with borate buffered saline (baseline) using EPIX XCAP V 3.8 software. The subtracted scattered light image is quantitatively analyzed by integrating over the central 10 mm of the test lens and then compared to a frosted glass standard.

[0145] The light intensity/power setting was adjusted to achieve a mean grayscale value in the range of 900-910 for the frosted glass standard; at this setting, the baseline mean grayscale value was in the range of 50-70. The mean grayscale values of the baseline and frosted glass standard are recorded and used to create a scale from zero to 100, respectively. In the grayscale analysis, the mean and standard deviations of the baseline, frosted glass, and every test lens was recorded. For each lens, a scaled value was calculated according to the equation: scaled value equals the mean grayscale value (lens minus baseline) divided by the mean grayscale value (frosted glass minus baseline) times by 100. Three to five test lenses are analyzed, and the results are averaged.

[0146] Water content was measured gravimetrically. Lenses were equilibrated in packing solution for 24 hours. Each of three test lens are removed from packing solution using a sponge tipped swab and placed on blotting wipes which have been dampened with packing solution. Both sides of the lens are contacted with the wipe. Using tweezers, the test lens are placed in a tared weighing pan and weighed. The two more sets of samples are prepared and weighed. All weight measurements were done in triplicate, and the average of those values used in the calculations. The wet weight is defined as the combined weight of the pan and wet lenses minus the weight of the weighing pan alone.

[0147] The dry weight was measured by placing the sample pans in a vacuum oven which has been preheated to 60°C for 30 minutes. Vacuum was applied until the pressure reaches at least 1 inch of Hg is attained; lower pressures are allowed. The vacuum valve and pump are turned off and the lenses are dried for at least 12 hours; typically overnight. The purge valve is opened allowing dry air or dry nitrogen gas to enter. The oven is allowed reach atmospheric pressure. The pans are removed and weighed. The dry weight is defined as the combined weight of the pan and dry lenses minus the weight of the weighing pan alone. The water content of the test lens was calculated as follows:

$$\% \text{ water content} = \frac{(\text{wet weight} - \text{dry weight})}{\text{wet weight}} \times 100$$

[0148] The average and standard deviation of the water content were calculated and the average value reported as the percent water content of the test lens.

[0149] The refractive index (RI) of a contact lens was measured by a Leica ARIAS 500 Abbe refractometer in manual

mode or by a Reichert ARIAS 500 Abbe refractometer in automatic mode with a prism gap distance of 100 microns. The instrument was calibrated using deionized water at 20°C (+/- 0.2 °C). The prism assembly was opened and the test lens placed on the lower prism between the magnetic dots closest to the light source. If the prism is dry, a few drops of saline were applied to the bottom prism. The front curve of the lens was against the bottom prism. The prism assembly was then closed. After adjusting the controls so that the shadow line appeared in the reticle field, the refractive index was measured. The RI measurement was made on five test lenses. The average RI calculated from the five measurements was recorded as the refractive index as well as its standard deviation.

[0150] Oxygen permeability (Dk) was determined by the polarographic method generally described in ISO 9913-1:1996 and ISO 18369-4:2006, but with the following modifications. The measurement was conducted at an environment containing 2.1% oxygen created by equipping the test chamber with nitrogen and air inputs set at the appropriate ratio, for example, 1800 mL/min of nitrogen and 200 mL/min of air. The t/Dk is calculated using the adjusted oxygen concentration. Borate buffered saline was used. The dark current was measured by using a pure humidified nitrogen environment instead of applying MMA lenses. The lenses were not blotted before measuring. Four lenses were stacked instead of using lenses of various thickness (t) measured in centimeters. A curved sensor was used in place of a flat sensor; radius was 7.8 mm. The calculations for a 7.8 mm radius sensor and 10% (v/v) air flow are as follows:

$$Dk/t = (\text{measured current} - \text{dark current}) \times (2.97 \times 10^{-8} \text{ mL O}_2/(\mu\text{A} \cdot \text{sec} \cdot \text{cm}^2 \cdot \text{mm Hg}))$$

[0151] The edge correction was related to the Dk of the material.

[0152] For all Dk values less than 90 barrers:

$$t/Dk (\text{edge corrected}) = [1 + (5.88 \times t)] \times (t/Dk)$$

[0153] For Dk values between 90 and 300 barrers:

$$t/Dk (\text{edge corrected}) = [1 + (3.56 \times t)] \times (t/Dk)$$

[0154] For Dk values greater than 300 barrers:

$$t/Dk (\text{edge corrected}) = [1 + (3.16 \times t)] \times (t/Dk)$$

[0155] Non-edge corrected Dk was calculated from the reciprocal of the slope obtained from the linear regression analysis of the data wherein the x variable was the center thickness in centimeters and the y variable was the t/Dk value. On the other hand, edge corrected Dk was calculated from the reciprocal of the slope obtained from the linear regression analysis of the data wherein the x variable was the center thickness in centimeters and the y variable was the edge corrected t/Dk value. The resulting Dk value was reported in barrers.

[0156] Wettability of lenses was determined by a Wilhelmy plate method using a Cahn DCA-315 instrument at room temperature and using deionized water as the probe solution. The experiment was performed by dipping the lens specimen of known parameter into the packing solution of known surface tension while measuring the force exerted on the sample due to wetting by a sensitive balance. The advancing contact angle of the packing solution on the lens is determined from the force data collected during sample dipping. The receding contact angle is likewise determined from force data while withdrawing the sample from the liquid. The Wilhelmy plate method is based on the following formula: $F_g = \gamma p \cos \theta - B$, wherein F = the wetting force between the liquid and the lens (mg), g = gravitational acceleration (980.665 cm/sec²), γ = surface tension of probe liquid (dyne/cm), p = the perimeter of the contact lens at the liquid/lens meniscus (cm), θ = the dynamic contact angle (degree), and B = buoyancy (mg). B is zero at the zero depth of immersion. Four test strips were cut from the central area of the contact lens. Each strip was approximately 5 mm in width and equilibrated in packing solution. Then, each sample was cycled four times, and the results were averaged to obtain the advancing and receding contact angles of the lens.

[0157] The mechanical properties of the contact lenses were measured by using a tensile testing machine such as an Instron model 1122 or 5542 equipped with a load cell and pneumatic grip controls. Minus one diopter lens is the

preferred lens geometry because of its central uniform thickness profile. A dog-bone shaped sample cut from a -1.00 power lens having a 0.522 inch length, 0.276 inch "ear" width and 0.213 inch "neck" width was loaded into the grips and elongated at a constant rate of strain of 2 inches per minute until it breaks. The center thickness of the dog-bone sample was measured using an electronic thickness gauge prior to testing. The initial gauge length of the sample (L_0) and sample length at break (L_f) were measured. At least five specimens of each composition were measured, and the average values were used to calculate the percent elongation to break: percent elongation = $[(L_f - L_0)/L_0] \times 100$.

[0158] The tensile modulus was calculated as the slope of the initial linear portion of the stress-strain curve; the units of modulus are pounds per square inch or psi. The tensile strength was calculated from the peak load and the original cross-sectional area: tensile strength = peak load divided by the original cross-sectional area; the units of tensile strength are psi.

[0159] Toughness was calculated from the energy to break and the original volume of the sample: toughness = energy to break divided by the original sample volume; the units of toughness are in-lbs/in³.

[0160] PQ1 uptake was measured chromatographically. The HPLC was calibrated using a series of standard PQ1 solutions having concentrations 2, 4, 6, 8, 12 and 15 µg/mL. Lenses were placed into polypropylene contact lens cases with 3 mL of Optifree Replenish or similar lens solution (PQ1 concentration = 10 micrograms/mL) which is commercially available from Alcon. A control lens case, containing 3 mL of solution, but no contact lens was also prepared. The lenses and control solutions were stored at room temperature for 72 hours. 1 mL of solution was removed from each of the samples and controls and mixed with trifluoroacetic acid (10 µL). The analysis was conducted using HPLC/ELSD and a Phenomenex Luna C5 (4.6 mm x 5 mm; 5 µm particle size) column with the following equipment and conditions: Agilent 1200 HPLC or equivalent with an ELSD operating at $T = 100^\circ\text{C}$, Gain = 12, Pressure = 4.4 bar, Filter = 3s; ELSD parameters may vary from instrument to instrument; using mobile phase A of water (0.1% TFA) and mobile phase B of acetonitrile (0.1% TFA), a column temperature of 40°C and an injection volume of 100 µL. An elution profile was used and listed in Table A. A calibration curve was created by plotting the peak area value as a function of the concentration of the PQ1 standard solutions. The concentration of PQ1 in a sample was then calculated by solving the quadratic equation representing the calibration curve. Three lenses were run for each analysis, and the results were averaged. PQ1 uptake was reported as the percentage loss of PQ1 after soak with lens compared to the PQ1 present in the control without lens.

Table A. HPLC Elution Profile

Time (minutes)	% A	% B	Flow Rate (mL/min)
0.00	100	0	1.2
1.00	100	0	1.2
5.00	0	100	1.2
8.50	0	100	1.2
8.60	100	0	1.2
11.00	100	0	1.2

[0161] The amount of cholesterol absorbed by a contact lens was determined by a LC-MS method (lipid uptake in the data tables). Lenses were soaked in a cholesterol solution and then extracted with dichloromethane. The dichloromethane extract was evaporated and reconstituted with a heptane/isopropanol mixture with subsequent analysis by LC-MS. The results were reported as micrograms of cholesterol per lens. A deuterated cholesterol internal standard was used to improve accuracy and precision of the method.

[0162] A cholesterol stock solution was prepared by placing 15.0 ± 0.5 milligrams of cholesterol into a wide-mouth 10 mL glass volumetric flask followed by dilution with isopropanol.

[0163] A cholesterol soak solution was prepared by placing 0.430 ± 0.010 grams of lysozyme (purity = 93%), 0.200 ± 0.010 grams of albumin, and 0.100 ± 0.010 grams of β -lactoglobulin into a 200 mL glass volumetric flask, adding approximately 190 milliliters of PBS to the flask, and swirling to dissolve the contents. 2 Milliliters of the cholesterol stock solution was then added and diluted to volume with PBS. The volumetric flask was capped and shaken well. The concentration of the cholesterol soak solution was approximately 15 µg/mL. Note: The mass of these components may be adjusted to account for lot-to-lot purity variability so that the target concentrations can be achieved.

[0164] Six contact lenses were removed from their packages and blotted with lint-free paper towels to remove excess packing solution. The lenses were placed into six separate 8 mL glass vials (one lens per vial), and 3.0 mL of the cholesterol soak solution was added to each vial. The vials were capped and placed into a New Brunswick Scientific incubator-shaker for 72 hours at 37°C and 100 rpm. After incubation, each lens was rinsed three times with PBS in 100

mL beakers and placed into a 20-mL scintillation vial.

[0165] To each lens-containing scintillation vial, 5 mL of dichloromethane and 100 µL of the internal standard solution were added. After a minimum of 16 hours of extraction time, the supernatant liquid was transferred into a 5 mL disposable glass culture tube. The tube was placed into the Turbopap and the solvent completely evaporated. Place 1 mL of the diluent into the culture tube and re-dissolve the contents. The aforementioned diluent was a 70:30 (v/v) mixture of heptane and isopropanol. The diluent was also the mobile phase. The resulting solution was carefully transferred into an autosampler vial and ready for LC-MS analysis.

[0166] An internal standard stock solution was prepared by weighing approximately 12.5 + 2 mg of deuterated cholesterol (2,2,3,4,4,6-d6-cholesterol) in a 25 mL volumetric flask followed by dilution with the diluent. The concentration of the internal standard stock solution was approximately 500 µg/mL.

[0167] An internal standard solution was prepared by placing 1.0 mL of the internal standard stock solution in a 50mL volumetric flask followed by dilution to volume with diluent. The concentration of this intermediate internal standard solution is approximately 10 µg/mL.

[0168] A reference standard stock solution was prepared by weighing approximately 50 + 5 mg of cholesterol in a 100 mL volumetric flask followed by dilution with diluent. The concentration of the cholesterol in this reference stock solution is approximately 500 µg/mL.

[0169] Working standard solutions were then made according to Table 2 by placing the appropriate amount of standard solutions into the listed 25-mL, 50-mL or 100-mL volumetric flasks. After the standard solutions were added to the volumetric flasks, the mixture was diluted to volume with diluent and swirled well.

Table B. Working Standard Solution Formulations

Working Standard Name	Volume of Internal Standard Solution (mL)	Volume of Reference Standard Stock Solution (µL)	Final Volume (mL)	Approximate Cholesterol Concentration (µg/mL)
Std 1	10	20	100	0.10
Std 2	5	25	50	0.25
Std 3	5	50	50	0.50
Std 4	5	100	50	1.00
Std 5	2.5	125	25	2.50
Std 6	2.5	250	25	5.00

[0170] The following LC-MS analysis was performed:

(1) Make 6 injections of the "Std4" to evaluate system suitability. The RSD% of the peak areas for the working standards and the internal standards must be < 5% and RSD(%) of their peak area ratios must be < 7% to pass system suitability.

(2) Inject working standards 1-6 to create a calibration curve. The square of the correlation coefficient (r^2) must be > 0.99.

(3) Inject test samples followed by a bracketing standard (Std4). The peak area ratio of the bracketing standard must be within $\pm 10\%$ of the averaged peak area ratio from the system suitability injections.

[0171] A calibration curve was constructed by plotting the peak area ratio (reference std/internal std) value that corresponds to the concentration of each working standard solution. The concentration of cholesterol in sample is calculated by solving a quadratic equation. Typical equipment and their settings for the LC-MS analysis are listed below and shown in Tables C and D. The values for the instrument tune parameters may change each time the mass spectrometer is tuned.

Turbopap Conditions:

[0172]

Temperature: 45°C

Time: 30 minutes or more to dryness

Gas: nitrogen @ 5psi

HPLC Conditions:**[0173]**

HPLC: Thermo Accela HPLC Instrument or equivalent
HPLC Column: Agilent Zorbax NH₂ (4.6 mm x 150 mm; 5 µm particle size)
Mobile Phase: 70% heptane and 30% isopropanol
Column Temperature: 30 °C
Injection Volume: 25 µL
Flow Rate: 1000 µL/min

Table C. Mass Spectrometry Conditions

Thermo Finnigan TSQ Quantum Ultra	
MS Settings	Value
Ionization	APCI
Polarity	Positive
Scan type	SIM
APCI probe position	D
Mass (m/z) of Reference Standards	369.2
Mass (m/z) of Internal Standards	375.3
Mass width (m/z)	1.0
Scan time (s)	0.10
Data type	centroid
Peak Width Q3 (FWHM)	0.40
Skimmer Offset (V)	10

Table D. Tune Parameters

Instrument Tune Parameters	Value
Discharge Current (arbitrary units):	20
Capillary temperature (°C):	240
Vaporizer Temperature (°C):	500
Tube lens offset (V):	68
Sheath gas pressure (arbitrary units):	20
Auxiliary gas flow (arbitrary units):	15

[0174] The amount of lysozyme uptake by a contact lens was measured by a HPLC-UV method. Lysozyme uptake was determined as the difference of lysozyme content in phosphatebuffered saline solution (PBS) before contact lenses are immersed and the concentration in the test solution after 72 hours of lens immersion at 37°C.

[0175] A lysozyme soak solution was prepared by placing 0.215 ± 0.005 grams of lysozyme (purity = 93%) into a 100 mL volumetric flask followed by adding 50 mL of PBS to dissolve the lysozyme by swirling followed by dilution to volume with PBS. The resulting lysozyme soak solution was filtered/sterilized using a Millipore Stericup filtration device. The concentration of the lysozyme soak solution is approximately 2000 µg/mL. The mass of lysozyme may be adjusted to account for lot-to-lot purity variability so that a 2000 µg/mL concentration can be achieved.

[0176] Three contact lenses were removed from their packages and blotted with lint-free paper towel to remove excess packing solution. The lenses were placed into three separate 8 mL glass vials (one lens per vial). 1.5 mL of the lysozyme soak solution was added to each vial. The vials were capped and inspected to ensure each lens was completely immersed

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in the soak solution. As control samples, 1.5 mL of lysozyme soak solution were added into three separate 8 mL glass vials. The samples were then incubated on a New Brunswick Scientific incubator-shaker for 72 hours at 37°C and 100 rpm.

[0177] A diluent was prepared by mixing 900 mL water, 100 mL acetonitrile and 1 mL trifluoroacetic acid into a 1L glass bottle.

[0178] A lysozyme stock solution was prepared by placing 0.240 ± 0.010 grams of lysozyme (purity = 93%) into a 100 mL volumetric flask followed by dilution to volume with diluent. The concentration of the lysozyme stock solution is approximately 2200 µg/mL.

[0179] As shown in Table E, a series of working standard solutions was prepared by mixing the appropriate amounts of lysozyme stock solution with diluent using 5 mL volumetric flasks.

Table E. Working Standards

Working Standard Name	Volume of Stock Solution (mL)	Final Volume (mL)	Approximate Lysozyme Concentration (µg/mL)
Std 1	1.135	5	500
Std 2	1.815	5	800
Std 3	2.725	5	1200
Std 4	3.635	5	1600
Std 5	4.540	5	2000
Std 6 (stock)	-	-	2200

[0180] A 10% (v/v) solution was prepared by adding 1 mL of trifluoroacetic acid into a 10 mL glass volumetric flask followed by dilution with HPLC water. Samples for HPLC-UV analysis were prepared as follows: (1) by placing 1000 µL of test sample and 10 µL of the 10% TFA solution into an autosampler vial or (2) by placing 1000 µL of reference standard and 10 µL of reference standard diluent into an autosampler vial.

[0181] The analysis involved the following steps:

- (1) Perform 6 injections of the "Std4" to evaluate system suitability. The RSD% of the peak areas and retention times must be < 0.5% to pass system suitability.
- (2) Inject working standards 1-6 to create a calibration curve. The square of the correlation coefficient (r^2) must be > 0.99.
- (3) Inject test samples followed by a bracketing standard (Std4). The peak area of the bracketing standard must be $\pm 1\%$ of the averaged peak areas from the system suitability injections.

[0182] A calibration curve was constructed by plotting the peak area value that corresponds to the concentration of each lysozyme working standard solution. The concentration of lysozyme in the test samples was calculated by solving a linear equation. Typical equipment and their settings are listed below or shown in Table F.

Instrument: Agilent 1200 HPLC with UV detection (or equivalent HPLC-UV)
 Detection: UV @ 280 nm (5 nm bandwidth)
 HPLC Column: Phenomenex Luna C5 (50 x 4.6 mm) or Agilent PLRP-S (50 x 4.6 mm)
 Mobile Phase A: H₂O (0.1% TFA)
 Mobile Phase B: Acetonitrile (0.1% TFA)
 Column Temperature: 40 °C
 Injection Volume: 10 µL

Table F. HPLC Run Conditions

Time (minutes)	% A	% B	Flow Rate (mL/min)
0.0	95	5	1.2
4.0	5	95	1.2
4.1	95	5	1.2
6.5	95	5	1.2

[0183] Alternatively, lysozyme uptake was measured as follows. A lysozyme solution was prepared from chicken egg white (Sigma, L7651) at a concentration of 2 mg/mL in phosphate saline buffer supplemented by sodium bicarbonate at 1.37g/L and D-glucose at 0.1 g/L.

[0184] Three lenses for each test sample were tested using each protein solution, and three were tested using PBS as a control solution. The test lenses were blotted on sterile gauze to remove packing solution and aseptically transferred, using sterile forceps, into sterile 24 well cell culture plates (one lens per well) each well containing 2 mL of the lysozyme solution. Each lens was fully immersed in the solution. As controls, 2 mL of the lysozyme solution was placed in wells without a contact lens.

[0185] The plates were sealed using parafilm to prevent evaporation and dehydration and placed onto an orbital shaker and incubated at 35°C with agitation at 100 rpm for 72 hours. After the 72 hour incubation period, the lenses were rinsed 3 to 5 times by dipping lenses into 200 mL of PBS. The lenses were blotted on a paper towel to remove excess PBS and transferred into sterile conical tubes (1 lens per tube), each tube containing a volume of PBS determined based upon an estimate of lysozyme uptake expected based upon on each lens composition. The lysozyme concentration in each tube to be tested must be within the albumin standards range as described by the manufacturer (0.05 micrograms to 30 micrograms). Samples known to uptake a level of lysozyme lower than 100 µg per lens were diluted 5 times. Samples known to uptake levels of lysozyme higher than 500 µg per lens were diluted 20 times.

[0186] Lysozyme uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer and was calculated by subtracting the optical density measured on PBS soaked lenses from the optical density determined on lenses soaked in lysozyme solution. The optical density was measured using a Synergy II Micro-plate reader capable of reading optical density at 562 nm.

[0187] The invention is now described with reference to the following examples. Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0188] The following abbreviations will be used throughout the Examples and have the following meanings:

BC: back curve plastic mold

FC: front curve plastic mold

NVP: N-vinylpyrrolidone (Acros or Aldrich)

DMA: N, N-dimethylacrylamide (Jarchem)

HEMA: 2-hydroxyethyl methacrylate (Bimax)

NMMA: N-methyl methacrylamide (Monomer Polymer)

VMA: N-vinyl N-methyl acetamide (Aldrich)

AA: acrylic acid

MAA: methacrylic acid (Acros)

VINAL: N-[(ethenyloxy)carbonyl]-β-alanine; CAS #148969-96-4

ACA1: 3-acrylamidopropanoic acid

ACA2: 5-acrylamidopropanoic acid

CBT: 1-Propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt; carboxy-betaine; CAS 79704-35-1

SBT: 1-Propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt; sulfobetaine; CAS 80293-60-3

PBT: 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI); phosphobetaine; CAS 163674-35-9

Q Salt or METAC: 2-(methacryloyloxy)ethyl trimethylammonium chloride

AMPS: 2-acrylamido-2-methylpropane sulfonic acid

HPMA: 2-hydroxypropyl methacrylate

HEAA: 2-hydroxyethyl acrylate

Bis-HEAA: N,N-bis(2-hydroxyethyl) acrylamide

GMMA: 2,3-dihydroxypropyl methacrylate

HBMA: 2-hydroxybutyl methacrylate

Blue HEMA: 1-amino-4-[3-(4-(2-methacryloyloxy-ethoxy)-6-chlorotriazin-2-ylamino)-4-sulfophenylamino]anthraquinone-2-sulfonic acid, as described in US Patent No. 5,944,853

pVMA: poly(N-vinyl N-methyl acetamide) M_w = 570KDa or 628KDa

PVP: poly(N-vinylpyrrolidone) (ISP Ashland) K90

EGDMA: ethylene glycol dimethacrylate (Esstech)

TEGDMA: tetraethylene glycol dimethacrylate (Esstech)

TMPTMA: trimethylolpropane trimethacrylate (Esstech)

TAC: Triallyl Cyanurate (Polysciences)

MBA: methylene bisacrylamide (Aldrich)

Tegomer V-Si 2250: diacryloxypolydimethylsiloxane (Evonik)

Irgacure 819: bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (BASF or Ciba Specialty Chemicals)

Irgacure 1870: blend of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphineoxide and 1-hydroxy-cyclohexyl-phenyl-ketone (BASF or Ciba Specialty Chemicals)

mPDMS: monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (800-1000 MW) (Gelest)

HO-mPDMS: mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (400-1000 MW) (Ortec or DSM-Polymer Technology Group)

TRIS: 3-methacryloxypropyl tris(trimethylsiloxy)silane

SiMAA: 2-propenoic acid, 2-methyl-2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (Toray)

SA2: N-(2,3-dihydroxypropyl) N-(3-tetra(dimethylsiloxy)dimethylbutylsilane)propyl acrylamide

mPEG 950 : polyethylene glycol mono-methacrylate (Aldrich)

D3O: 3,7-dimethyl-3-octanol (Vigon)

TAM: t-amyl alcohol (BASF)

3E3P: 3-ethyl 3-pentanol

DI water: deionized water

IPA: isopropyl alcohol

Norbloc: 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole (Janssen)

PP: polypropylene which is the homopolymer of propylene

TT: Tuftec which is a hydrogenated styrene butadiene block copolymer (Asahi Kasei Chemicals)

Z: Zeonor which is a polycycloolefin thermoplastic polymer (Nippon Zeon Co Ltd)

EXAMPLES

[0189] Preparation of Poly(N-vinyl N-methyl acetamide) (pVMA): 380 mL (3.48 mol) of distilled N-vinyl-N-methyl acetamide and 187 mg (1.14 mmol) of azobisisobutyronitrile were added to a 3-neck round bottom flask fitted with reflux condenser, magnetic stirring bar and thermocouple and purged of oxygen gas for 2 hours by bubbling nitrogen gas through the reaction mixture. Then, the reaction mixture was heated at 75°C for 24 hours during which time the reaction mixture solidified. The reaction product was quenched in air and isolated by work-up procedure 1 or work-up procedure 2. Work-up Procedure 1: The reaction product was dissolved in 800 mL of methylene chloride at 40°C and cooled to room temperature. The solution was poured into 2L of cold diethyl ether with manual stirring to afford a white solid after decanting off the solvents. The solid product was air dried followed by vacuum drying overnight at 50°C. The precipitated product was ground into a fine white powder and vacuum dried overnight at 50°C (85% yield). Work-up Procedure 2: The reaction product was dissolved in water and dialyzed extensively in dialysis membrane tubing (Spectra Pore MWCO 3500) and freeze dried (LABCONCO, Freezone® Triad™ freeze dry system, Model # 7400030) or spray dried (BUCHI mini spray dryer, Model # B-290). The molecular weight was determined by Size Exclusion Chromatography with Multi-Angle Light Scattering (SEC-MALS). The SEC-MALS setup employed methanol (with 10 mM LiBr) as the mobile phase at a flow rate of 0.6 mL/min at 50 °C. Three Tosoh Biosciences TSK-gel columns in series were used [SuperAW3000 4 µm, 6.0 mm ID x 15 cm (PEO/DMF Exclusion Limit = 60,000 g/mole), SuperAW4000 6 µm, 6.0 mm ID x 15 cm (PEO/DMF Exclusion Limit = 400,000 g/mole) and a SuperAW5000 7 µm, 6.0 mm ID x 15 cm (PEO/DMF Exclusion Limit = 4,000,000 g/mole)] with an online Agilent 1200 UV/VIS diode array detector, a Wyatt Optilab rEX interferometric refractometer, and a Wyatt miniDAWN Treos multiangle laser scattering (MALS) detector ($\lambda=658\text{nm}$). A $d\eta/dc$ value of 0.1829 mL/g at 30 °C ($\lambda=658\text{ nm}$) was used for absolute molecular weight determination. Absolute molecular weights and polydispersity data were calculated using the Wyatt ASTRA 6.1.1.17 SEC/LS software package. The weight average molecular weight typically varied from about 500 KDa to about 700 KDa, and the polydispersity varied from about 1.8 to about 2.8.

Examples 1-15

[0190] Each reactive mixture was formed by mixing the reactive components listed in Tables 1 and 2, filtering through a 3 µm filter using a heated or unheated stainless steel or glass syringe, and then degassed by applying vacuum at ambient temperature for about 10-20 minutes. In a glove box with a nitrogen gas atmosphere and less than 0.1 percent oxygen gas, about 75-100 µL of the reactive mixture were dosed using an Eppendorf pipet at room temperature into the FC made of Zeonor. The BC made of a 55:45 (w/w) blend of Z:PP was then placed onto the FC. The molds were equilibrated for at least twelve hours in the glove box prior to dosing. Eight trays, each containing eight such mold

assemblies, were placed on a mirrored metallic plate and quartz plates were placed on top of the trays to maintain proper fit and alignment. The plate was transferred into an adjacent glove box maintained at 60-65°C, and the lenses were cured from the top for 20 minutes using TL03 lights having intensity of 4-5 mW/cm². Reactive monomer mixtures exhibiting high viscosities at room temperature were dosed into molds in the heated glove box. The light source was about six inches above the trays. A detailed description of the curing process and apparatus can be found in US Patent No. 8,937,110.

[0191] The lenses were manually de-molded with most lenses adhering to the FC and released by suspending about 64-112 lenses in about one liter of 70% IPA for about one hour, followed by washing with 25% IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasted between 10 and 30 minutes. Lab scale lens release is typically performed in jars on a laboratory roller. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all of the lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were transferred into vials and subsequently sterilized by autoclaving at 122°C for 30 minutes. The physical and mechanical properties of the sterile lenses were measured and listed in Table 3.

TABLE 1

Component	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
OH-mPDMS (n=15)	30	30	30	30	30	30
OH-mPDMS (n=4)	28	28	28	28	0	28
[OH-mPDMS (n=4)] : [OH-mPDMS (n=15)]	0.93	0.93	0.93	0.93	0	0.93
SiMAA	0	0	0	0	28	0
[SiMAA]: [OH-mPDMS (n=15)]	0	0	0	0	0.93	0
DMA	28.89	26.89	24.89	22.89	19.89	19.89
HEMA	7	7	7	7	7	7
Blue HEMA	0.02	0.02	0.02	0.02	0.02	0.02
PVP K90	3	5	7	9	12	12
EGDMA	0.75	0.75	0.75	0.75	0.75	0.75
Norbloc	2	2	2	2	2	2
CGI 1870	0.34	0.34	0.34	0.34	0.34	0.34
Diluent	23	23	23	23	23	23
D3O	100	100	100	100	100	100

TABLE 2

Component	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13	Ex 14	Ex 15
OH-mPDMS (n=15)	30	30	30	30	30	30	28	27	27
OH-mPDMS (n=4)	28	28	28	28	25	25	25	24.5	24
[OH-mPDMS (n=15)] : [OH-mPDMS (n=4)]	0.93	0.93	0.93	0.93	0.83	0.83	0.89	0.91	0.89
DMA	16.89	14.89	11.89	9.89	14.89	12.90	11.89	10.89	8.89
HEMA	7	7	7	7	7	7	7	7	7
Blue HEMA	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
PVP K90	15	17	20	22	20	22	25	27.5	30
EGDMA	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Norbloc	2	2	2	2	2	2	2	2	2

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(continued)

Component	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13	Ex 14	Ex 15
CGI 1870	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Diluent	23	23	23	23	23	23	23	23	23
D3O	100	100	100	100	100	100	100	100	100

TABLE 3

Ex	Wt. % PVP	DCA (adv., rec)	WC	% Haze	Mechanicals		Dk	Lipids (ug/lens)
					M (psi)	%ETB		
1	3	89 (9), 26 (5)	39.2 (0.3)	3 (0)	99 (7)	103 (31)	120	11.34 (0.41)
2	5	62 (6), 28 (7)	41.3 (0.4)	5(0)	101 (8)	100 (36)	131	11.47 (0.44)
3	7	63 (6), 30 (4)	41.5 (0.3)	5(1)	104 (7)	93 (29)	134	12.41 (0.87)
4	9	36 (15), 29 (10)	41.4 (0.3)	5(1)	104 (8)	89 (25)	129	11.74 (0.57)
5	12	17 (17), 26 (8)	41 (0)	7 (11)	134(11)	205 (28)	104	NT
6	12	12 (10), NR	42.0 (0.2)	8 (1)	106 (7)	105 (41)	158	12.19 (0.57)
7	15	9 (10), 30 (9)	41.5 (0.6)	10 (1)	132(18)	106 (35)	139	10.89 (0.48)
8	17	36 (10), 16 (12)	42.1 (0.4)	13 (1)	117(7)	131 (48)	118	11.85 (0.84)
9	20	30 (9), 9 (11)	42.9 (0.2)	15 (1)	124(11)	131 (66)	125	10.14 (0.89)
11	20	44 (7), 23 (9)	45.1 (0.3)	10 (1)	102(15)	88 (25)	120	9.88 (0.60)
10	22	33 (12), 9 (10)	41.4 (0.5)	16 (1)	145 (11)	142 (50)	NT	8.75 (0.39)
12	22	21 (13), 3 (7)	44.6 (0.2)	16 (1)	127(15)	91 (23)	146	9.31 (0.09)
13	25	63 (5), 36 (6)	52.9 (0.6)	11 (1)	108 (9)	232 (62)	119	NT
14	27.5	NT	NT	NT	NT	NT	NT	NT
15	30	72 (13)	51 (1)	13 (1)	120 (8)	252 (33)	98	NT

[0192] Examples 1-15 prepared contact lenses from formulations having 3 to 30 wt% PVP and a mixture of two hydroxyl functional silicone components (HO-mPMDS having 4 and 15 repeating units). The lenses having 15-30 wt% PVP displayed haze values of 16% or less, which is far better than the haze values displayed by Comparative Examples 3-5. Examples 7-13 also displayed desirably low advancing contact angles (9°-63°), as well as a desirable balance of other properties, including water content, modulus, Dk and lipid uptake. This is particularly surprising given that these formulations contain less than 15 wt% hydrophilic monomer (DMA).

[0193] Comparing Example 5, which contained SiMAA instead of HO-mPDMS, n=4, with Example 6, it Example 6 displayed a Dk value which was 50% higher than Example 5 (158 barrers v. the 104 barrers), and lower modulus value (106 psi v. 132 psi) while maintaining similar water content, haze and contact angle values.

Examples 16-24

[0194] Each reactive mixture was formed by mixing the reactive components listed in Table 4, filtering through a 3 μm filter using a heated or unheated stainless steel or glass syringe, and then degassed by applying vacuum at ambient temperature for about 10-20 minutes. In a glove box with a nitrogen gas atmosphere and less than 0.1 percent oxygen gas, about 75-100 μL of the reactive mixture were dosed using an Eppendorf pipet at room temperature into the FC made of Zeonor. The BC made of a 55:45 (w/w) blend of Z:PP was then placed onto the FC. The molds were equilibrated for at least twelve hours in the glove box prior to dosing. Eight trays, each containing eight such mold assemblies, were placed on a mirrored metallic plate and quartz plates were placed on top of the trays to maintain proper fit and alignment. The plate was transferred into an adjacent glove box maintained at 60-65°C, and the lenses were cured from the top for 15 minutes using TL03 lights having intensity of 4-5 mW/cm². Reactive monomer mixtures exhibiting high viscosities

at room temperature were dosed into molds in the heated glove box. The light source was about six inches above the trays. A detailed description of the curing process and apparatus can be found in U.S. Patent No. 8,937,110.

[0195] The lenses were manually de-molded with most lenses adhering to the FC and released by suspending about 64-112 lenses in about one liter of 70% IPA for about one hour, followed by washing with 25% IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasted between 10 and 30 minutes. Lens release is typically performed in jars on a laboratory roller. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all of the lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses were transferred into vials and subsequently sterilized by autoclaving at 122°C for 30 minutes. The physical and mechanical properties of the sterile lenses were measured and listed in Table 5.

TABLE 4

Component	Ex 16	Ex 17	Ex 18	Ex 19	Ex 20	Ex 21	Ex 22	Ex 23	Ex 24
OH-mPDMS (n=15)	31	31	31	31	31	31	31	31	31
OH-mPDMS (n=4)	25	25	25	25	25	25	25	25	25
[OH-mPDMS (n=15)]: [OH-mPDMS (n=4)]	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
NVP	10.35	9.35	8.35	6.85	5.35	5.35	2.85	1.85	0
DMA	10.35	9.35	8.35	6.85	5.35	5.35	2.85	1.85	0.7
HEMA	11.33	11.33	11.33	11.33	11.33	11.33	11.33	11.33	11.33
Blue HEMA	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
PVP K90	5	7	9	12	12.5	15	20	22	25
pVMA M_w = 628KDa	0	0	0	0	2.5	0	0	0	0
mPEG 950	3	3	3	3	3	3	3	3	3
MAA	1	1	1	1	1	1	1	1	1
EGDMA	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
TAC	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Norbloc	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
CGI 819	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Diluent	30	30	30	30	30	30	30	30	30
D3O	100	100	100	100	100	100	100	100	100

TABLE 5

Ex	Wt.% PVP	DCA (adv, rec)	WC	% Haze	Mechanicals		Dk	Lysozyme (μ g/lens)	PQ1	Lipids (μ g/lens)
					M (psi)	%ETB				
16	5	95 (7), 32 (4)	44.1 (0.2)	5 (1)	106 (9)	90 (21)	118	370 (15)	2.52 (0.55)	10.01 (0.46)
17	7	78 (8), 26 (6)	45.5 (0.3)	5 (0)	112 (12)	107 (31)	117	382 (11)	1.25 (1.92)	10.29 (0.75)
18	9	64 (6), 29 (4)	45.4 (0.1)	5 (1)	134 (15)	73 (23)	139	317(11)	0.93 (1.46)	10.15 (0.26)
19	12	52 (8), 27 (4)	43.8 (0.4)	8 (0)	137 (16)	69 (27)	134	244 (8)	0.93 (2.21)	10.79 (0.57)

(continued)

Ex	Wt.% PVP	DCA (adv, rec)	WC	% Haze	Mechanicals		Dk	Lysozyme (μ g/lens)	PQ1	Lipids (μ g/ lens)
					M (psi)	%ETB				
20	12.5 PVP + 2.5 pVMA	25 (15), 25 (9)	48.5 (0.1)	14(0)	127 (12)	63 (20)	129	160 (18)		8.99 (0.22)
		15 (18), 10 (15)	46.4 (0.3)	15(2)	134 (18)	44 (20)	136	97 $\pm$ 9	2.49 (1.91)	
21	15	18 (14), 16 (10)	46.3 (0.2)	9 (9)	135 (13)	68 (16)	132	139 (8)	NT	
	15	32 (11), 24 (12)	45.2 (0.5)	8 (1)	140 (8)	49 (15)	136	113 $\pm$ 19		9.36 (0.23)
22	20	32 (7), 22 (8)	45.4 (0.5)	12(0)	148 (12)	165 (34)	130	101 (21)	NT	10.81 (0.51)
23	22	63 (35), 14 (4)	45.7 (0.3)	18 (2)	164 (9)	199 (24)	141	195 (72)	NT	10.39 (0.37)
24	25	45 (6), 25 (11)	47.8 (0.2)	41 (2)	165 (13)	202 (18)	127	550 (36)	NT	9.83 (0.28)

[0196] Formulations of Examples 16 to 24 show that lenses having 15% or more PVP were made displaying acceptable haze and contact angles.

Examples 25-33

[0197] Each reactive mixture is formed by mixing the reactive components listed in Table 6, filtering through a 3 μ m filter using a heated or unheated stainless steel or glass syringe, and then degassing by applying vacuum at ambient temperature for about 10-60 minutes depending on the reactive mixture's viscosity. In a glove box with a nitrogen gas atmosphere and less than 0.1 percent oxygen gas, about 75-100 μ L of the reactive mixture is dosed using an Eppendorf pipet at room temperature into the FC made of Zeonor. The BC made of a 55:45 (w/w) blend of Z:PP is then placed onto the FC; alternatively, FC and BC made from 90:10 (w/w) Z:PP or from only PP may be used. The molds are equilibrated for at least twelve hours in the glove box prior to dosing. Eight trays, each containing eight such mold assemblies, are placed on a mirrored metallic plate and quartz plates are placed on top of the trays to maintain proper fit and alignment. The plate is transferred into an adjacent glove box maintained at 60-65°C, and the lenses are cured from the top for 15 minutes using TLO3 bulbs having intensity of 3-4 mW/cm². Reactive monomer mixtures exhibiting high viscosities at room temperature are dosed into molds in the heated glove box. The light source is about six inches above the trays. A detailed description of the curing process and apparatus can be found in US Patent No. 8,937,110.

[0198] The lenses are manually de-molded with most lenses adhering to the FC and releasing by suspending about 64-112 lenses in about one liter of 70% IPA for about one hour, followed by washing with 70% IPA, two times with DI, and finally two times with borate buffered packaging solution. Each washing step lasts between 10 and 30 minutes. Lens release is typically performed in jars on a laboratory roller. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all of the lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels. The lenses are transferred into vials and subsequently sterilized by autoclaving at 122 °C for 30 minutes. The physical and mechanical properties of the sterile lenses are measured and listed in Table 7.

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[0199] Formulations of Examples 25 to 33 show that lenses having 15% or more pVMA were made displaying acceptable haze and contact angles, although these lenses were not as wettable as similar lenses containing PVP instead of pVMA.

TABLE 6

Component	Ex 25	Ex 26	Ex 27	Ex 28	Ex 29	Ex 30	Ex 31	Ex 32	Ex 33
OH-mPDMS (n=15)	31	31	31	31	31	31	31	31	31
OH-mPDMS (n=4)	25	25	25	25	25	25	25	25	25
[OH-mPDMS (n=15)]: [OH-mPDMS (n=4)]	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
NVP	10.35	9.35	8.35	6.85	5.35	4.35	2.85	1.85	0
DMA	10.35	9.35	8.35	6.85	5.35	4.35	2.85	1.85	0.7
HEMA	11.33	11.33	11.33	11.33	11.33	11.33	11.33	11.33	11.33
Blue HEMA	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
pVMA M _w =570KDa	5	7	9	12	15	17	20	22	25
mPEG 950	3	3	3	3	3	3	3	3	3
MAA	1	1	1	1	1	1	1	1	1
EGDMA	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
TAC	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Norbloc	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
CGI 819	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Diluent	30	30	30	30	30	30	30	30	30
D3O	100	100	100	100	100	100	100	100	100

TABLE 7

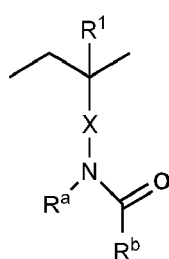
Lens	Wt. % PVMA	DCA (adv, rec)	WC (wt%)	% Haze	Mechanicals		Dk	Lysozyme (μg/lens)	PQ1	Lipids (μg/lens)
					M (psi)	% ETB				
Ex 25	5.0	68(8), 19(17)	48(0)	4(0)	96(8)	174(52)	103	375(7)	0 (0.4)	1.66 (0.09)
Ex 26	7.0	51(13), 18(14)	50(0)	4(0)	91(10)	185(50)	105	434(5)	1.0 (0.4)	1.55 (0.09)
Ex 27	9.0	16(16), 19(7)	49(0)	4(0)	99(6)	190(40)	111	445(28)	1.0 (0.1)	1.62 (0.10)
Ex 28	12.0	16(13), 12(15)	50(0)	7(0)	98(6)	158(39)	107	391(12)	5.8 (0.3)	1.67 (0.09)
Ex 29	15.0	31(14), 27(15)	50(0)	10(0)	112(10)	150(47)	133	214(1)	-1.0 (0.2)	1.52 (0.11)
Ex 30	17.0	82(9), 15(14)	50(0)	13(0)	114(10)	201(36)	126	118(4)	2.9 (0.1)	2.25 (0.46)
Ex. 31	20.0	87(13), 18(19)	49(0)	18(0)	125(10)	150(36)	156	74(43)	1.9 (0.4)	4.30 (1.82)
Ex. 32	22.0	93(19), 10(13)	48(0)	33(2)	150(8)	190(28)	139	85(33)	2.9 (0.70)	2.92 (0.56)

(continued)

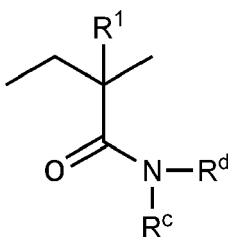
Lens	Wt. % PVMA	DCA (adv, rec)	WC (wt%)	% Haze	Mechanicals		Dk	Lysozyme (μ g/lens)	PQ1	Lipids (μ g/ lens)
					M (psi)	% ETB				
Ex. 33	25.0	91(30), 25(10)	48(0)	72(6)	146(7)	184 (47)	137	474(92)	3.8 (0.3)	1.85 (0.41)

Claims

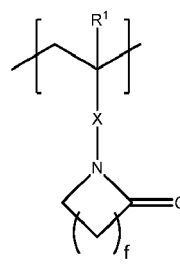
1. A silicone hydrogel formed from a reactive monomer mixture comprising:
 - a. at least one hydroxyalkyl (meth)acrylate monomer;
 - b. at least one first mono-functional hydroxyl-substituted poly(disubstituted siloxane) having 4 to 8 siloxane repeating units;
 - c. at least one second hydroxyl-substituted poly(disubstituted siloxane) selected from the group consisting of mono-functional hydroxyl-substituted poly(disubstituted siloxane) having 10 to 200 or 10-100 siloxane repeating units, multifunctional hydroxyl-substituted poly(disubstituted siloxanes) having 10 to 200 or 10-100 siloxane repeating units, and mixtures thereof;
 - d. at least 15 wt% at least one polyamide, based on the total weight of reactive components in the reactive monomer mixture; and
 - e. optional further constituents.
2. The silicone hydrogel of claim 1, wherein the polyamide is present in the reactive mixture in an amount between 15.1 weight percent and 40 weight percent or between 15.1 and 30 wt%, based on the total weight of all reactive components in the reactive monomer mixture.
3. The silicone hydrogel of claims 1 or 2, wherein the polyamide is selected from the group essentially consisting of cyclic polyamides, acyclic polyamides, and mixtures thereof.
4. The silicone hydrogel of claim 3, wherein the polyamide comprises repeating units selected from Formula I, Formula II and Formula IV



Formula I



Formula II



Formula IV

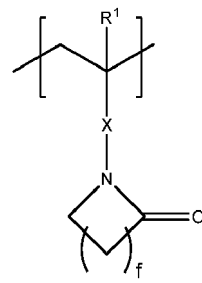
wherein

R^1 is independently a hydrogen atom or methyl;
 X is a direct bond, $-(CO)-$, or $-(CO)-NH-R^e$, wherein R^e is a C_1 to C_3 alkyl group;
 R^a is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups;
 R^b is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups, amino groups having up to two carbon atoms, amide groups having up to four carbon atoms, and alkoxy groups having up to two carbon groups;
 R^c is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups;
 R^d is selected from H, straight or branched, substituted or unsubstituted C_1 to C_4 alkyl groups;
 wherein the number of carbon atoms in R^a and R^b taken together is 8 or less, optionally 6 or less, and wherein

the number of carbon atoms in R^c and R^d taken together is 8 or less.

5. The silicone hydrogel of claim 3, wherein:

- (a) the cyclic polyamide is prepared from at least one of α -lactam, β -lactam, γ -lactam, δ -lactam, and ϵ -lactam; or
 (b) the cyclic polyamide comprises repeating units of Formula IV



wherein

R¹ is independently a hydrogen atom or methyl; f is a number from 1 to 10, or 8 or less, or 6 or less, or 2 to 6, or 3, or 2, and

X is a direct bond, -(CO)-, or -(CO)-NH-R^e-, wherein R^e is a C₁ to C₃ alkyl group.

6. The silicone hydrogel of claim 3, wherein the polyamide is a copolymer; optionally:

(a) wherein the copolymer comprises at least 80 mole percent of the repeating units selected from NVP, VMA, DMA, NVA, and mixtures thereof; or

(b) wherein the copolymer further comprises at least one repeating unit selected from the group consisting of N-vinyl amides, acrylamides, hydroxyalkyl (meth)acrylates, alkyl(meth)acrylates, N-vinylpyrrolidone, N,N-dimethylacrylamide, 2-hydroxyethyl methacrylate, vinyl acetate, acrylonitrile, hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, methyl methacrylate, butyl methacrylate, methacryloxypropyl trimethylsiloxysilane, siloxane substituted acrylates or methacrylates, and mixtures thereof.

7. The silicone hydrogel of claim 1, wherein the polyamide is selected from polyvinylpyrrolidone (PVP), polyvinylmethacrylamide (PVMA), polydimethylacrylamide (PDMA), polyvinylacetamide (PNVA), poly(hydroxyethyl(meth)acrylamide), polyacrylamide, and copolymers and mixtures thereof; optionally

(a) wherein the polyamide is PVP; or

(b) wherein the polyamide is PVMA.

8. The silicone hydrogel of any of the foregoing claims further comprising at least one additional hydrophilic monomer; optionally

(a) wherein the additional hydrophilic monomer is selected from the group consisting of ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), N-vinyl pyrrolidone (NVP), 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-methyl-3-methylene-2-pyrrolidone; 1-ethyl-5-methylene-2-pyrrolidone, N-methyl-3-methylene-2-pyrrolidone, 5-ethyl-3-methylene-2-pyrrolidone, 1-n-propyl-3-methylene-2-pyrrolidone, 1-n-propyl-5-methylene-2-pyrrolidone, 1-isopropyl-3-methylene-2-pyrrolidone, 1-isopropyl-5-methylene-2-pyrrolidone, N-vinyl-N-methyl acetamide (VMA), N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, N-vinyl formamide, N-vinyl acetamide, N-vinyl isopropylamide, allyl alcohol, N-vinyl caprolactam, N-2-hydroxyethyl vinyl carbamate, N-carboxy- β -alanine N-vinyl ester; N-carboxyvinyl- β -alanine (VINAL), N-carboxyvinyl- α -alanine and mixtures thereof; or

(b) wherein the additional hydrophilic monomer is selected from N,N-dimethylacrylamide, N-vinylpyrrolidone, N-vinyl-N-methyl acetamide, N-vinyl acetamide, and 1-methyl-5-methylene-2-pyrrolidone; or

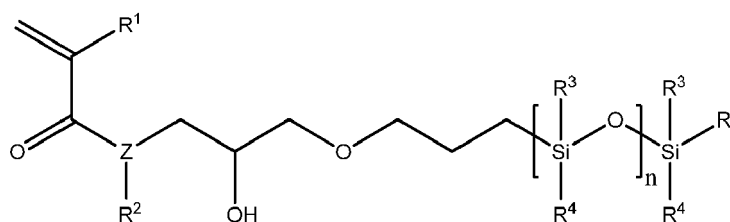
(c) wherein the additional hydrophilic monomer comprises N-vinylpyrrolidone, N,N-dimethylacrylamide, and mixtures thereof.

9. The silicone hydrogel of any of the foregoing claims wherein

(a) said hydroxyalkyl (meth)acrylate monomer is selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 1-hydroxypropyl-2-(meth)acrylate, 2-hydroxy-2-methylpropyl (meth)acrylate, 3-hydroxy-2,2-dimethyl-propyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycerol (meth)acrylate, polyethylene glycol monomethacrylate, and mixtures thereof; or

(b) said hydroxyalkyl (meth)acrylate monomer is selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxypropyl methacrylate, hydroxybutyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, and mixtures thereof or 2-hydroxyethyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, hydroxybutyl methacrylate or glycerol methacrylate and mixtures thereof.

10. The silicone hydrogel of any of the foregoing claims, wherein the first mono-functional hydroxyl-substituted poly(disubstituted siloxane) has the structure shown Formula VI-1



Formula VI-1

wherein

Z is selected from O, N, S or NCH₂CH₂O, when Z is O or S R² is not present;

R¹ is independently H or methyl;

R² is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

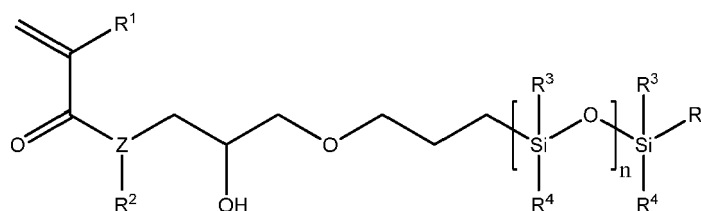
R³ and R⁴ are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amide, ether, and combinations thereof;

R³ and R⁴ may be independently selected from methyl, ethyl or phenyl, or may be methyl;

n is 4-8, and

R⁵ is selected from straight or branched C₁ to C₈ alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, and combinations thereof; or R⁵ is methyl or straight or branched C₄ alkyl, either of which may optionally be substituted with hydroxyl.

11. The silicone hydrogel of claim 1 or 10, wherein the second hydroxyl-substituted poly(dialkylsiloxane) comprises a compound of Formula VI-2



Formula VI-2

wherein Z is selected from O, N, S or NCH₂CH₂O, when Z is O or S R² is not present;

R¹ is independently H or methyl;

R² is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

R^3 and R^4 are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof; R^3 and R^4 may be independently selected from methyl, ethyl or phenyl, or may be methyl;

n is the number of siloxane units and is from 10 to 200; and

R^5 is selected from straight or branched C_1 to C_8 alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, and combinations thereof.

12. The silicone hydrogel of any of the foregoing claims wherein:

(a) the total weight percent of the first mono-functional hydroxyl-substituted poly(dialkylsiloxane) and the second hydroxyl-substituted poly(dimethylsiloxane) is between 40 and 70 wt% or 45 to 70 wt%; and/or

(b) wherein the first mono-functional hydroxyl-substituted poly(disubstituted siloxane) and the second hydroxyl-substituted poly(disubstituted siloxane) are present in the reactive monomer mixture in concentrations that provide a weight ratio, of the first mono-functional hydroxyl-substituted poly(disubstituted siloxane) to the second hydroxyl-substituted poly(disubstituted siloxane) of between 0.1 to 1.3; and/or

(c) wherein the weight ratio of the first mono-functional hydroxyl-substituted poly(dialkylsiloxane) to the second hydroxyl-substituted poly(dimethylsiloxane) is between 0.1 and 1 or 0.4 and 1.

13. The silicone hydrogel of any of the foregoing claims, further comprising at least one additional silicone-containing component selected from the group consisting of non-hydroxyl silicone-containing monomers, macromers, cross-linking agents.

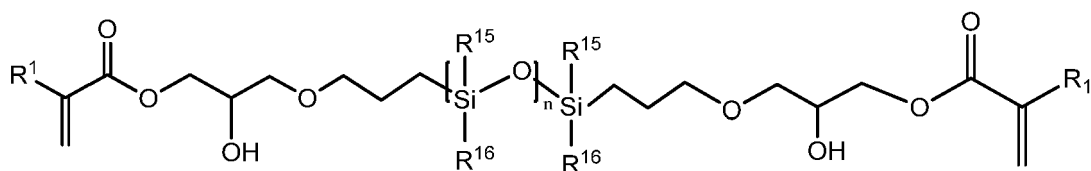
14. The silicone hydrogel of claim 11 wherein $n=4-8$ in the first mono-functional hydroxyl-substituted poly(disubstituted siloxane) and $n=10-20$ in the second hydroxyl-substituted poly(disubstituted siloxane).

15. The silicone hydrogel of claim 2, wherein the average number of siloxane repeating units of the first mono-functional hydroxyl-substituted poly(dialkylsiloxane) is 4 and the average number of siloxane repeating units of the second hydroxyl-substituted poly(dimethylsiloxane) is between 10 and 20.

16. The silicone hydrogel of claim 8, wherein the total weight percent of additional hydrophilic monomer is between 5 and 30 wt.%, or 8 to 25 wt%.

17. The silicone hydrogel of any preceding claim, further comprising at least one cross-linking agent selected from the group consisting of bifunctional crosslinkers, trifunctional crosslinkers, tetrafunctional crosslinkers, multifunctional crosslinkers, and mixtures thereof.

18. The silicone hydrogel of any of claim 11, wherein the second mono-functional hydroxyl-substituted poly(disubstituted siloxane) is selected from the group consisting of hydroxyl-substituted poly(disubstituted siloxane) of Formula VI-2, wherein n is from 10 to 20, a difunctional hydroxyl-substituted poly(disubstituted siloxane) of Formula XI, and mixtures thereof



Formula XI

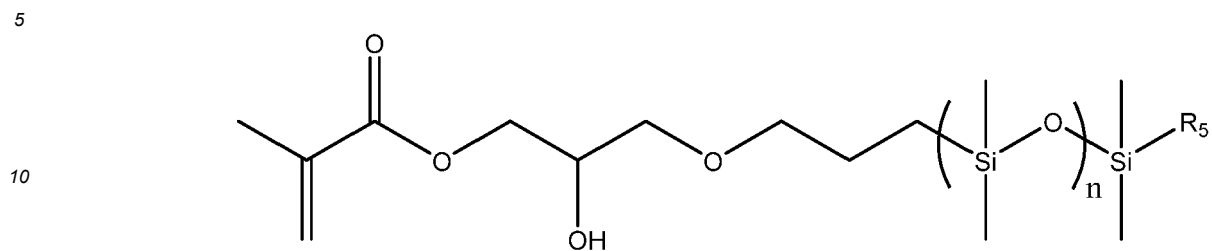
wherein

R_1 is independently a hydrogen atom or methyl group;

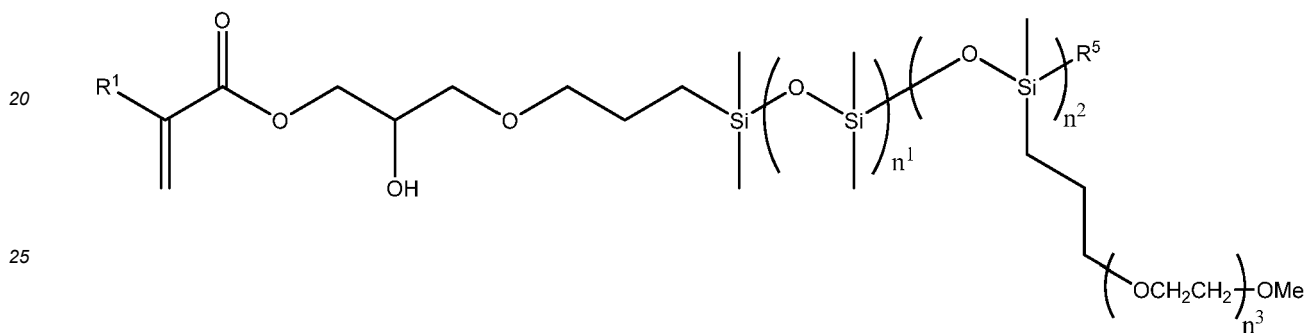
R_{15} and R_{16} are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amido, ether, amino, carboxyl, carbonyl groups and combinations thereof; or are independently methyl or ethyl; and

n is 10 to 200; 10 to 100; 10 to 50; 10 to 20.

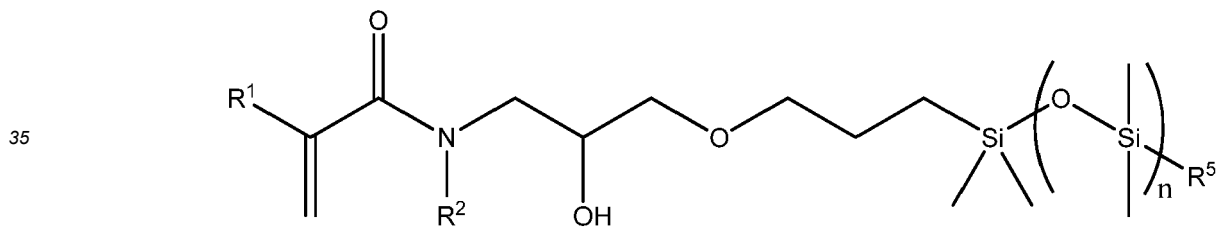
19. The silicone hydrogel of claim 1, wherein the monofunctional hydroxyl substituted, poly(disubstituted siloxane)s are selected from the group consisting of monofunctional hydroxyl substituted, poly(dimethylsiloxane) of Formula VIIa-IXb



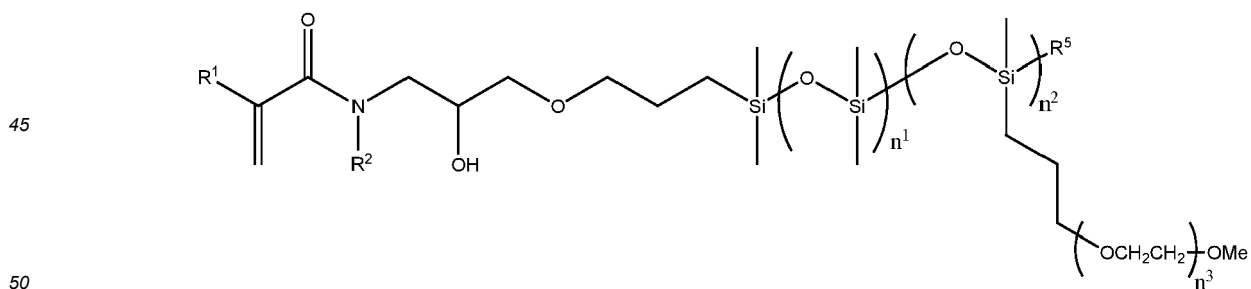
Formula VIIa



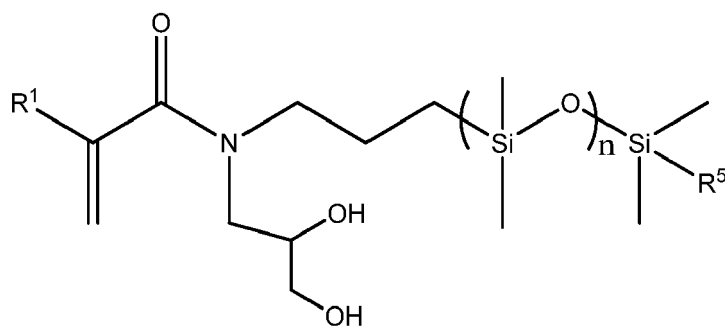
Formula VIIb



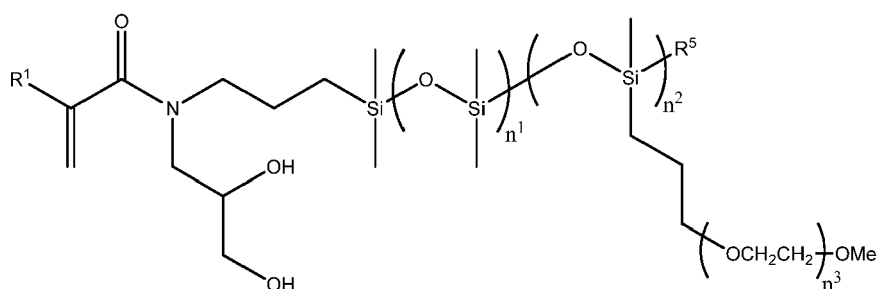
Formula VIIIa



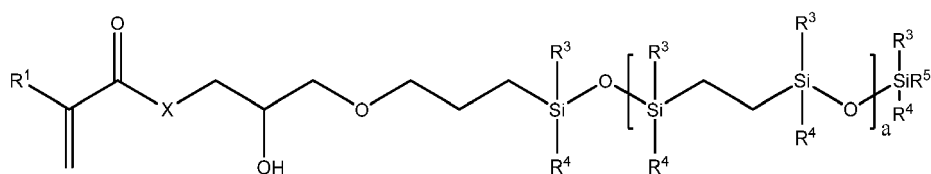
Formula VIIIb



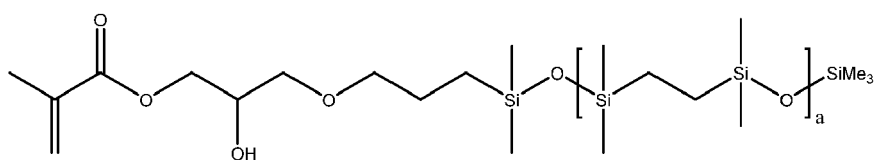
Formula VIIIc



Formula VIIIId



Formula IXa



Formula IXb

wherein R^1 is methyl or H; n is between 4 and 30, 4-8 or 10-20;

R^2 is independently selected from the group consisting of H or a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

n^1 n^2 are independently between 4 to 100; 4 to 50; or 4 to 25;

n^3 is 1-50, 1-20, or 1-10;

R^5 is selected from straight or branched C_1 to C_8 alkyl groups, which may be optionally substituted with one or more hydroxyl, amide, ether, polyhydroxyl groups selected from straight or branched C_1 to C_8 groups having a formula of $C_fH_g(OH)_h$ wherein $f=1-8$ and $g+h=2f+1$ and cyclic C_1 to C_8 groups having a formula of $CrH_g(OH)_h$ wherein $f=1-8$ and $g+h=2f-1$, and combinations thereof; or R^5 may be selected from methyl, butyl or hydroxyl substituted C_2 - C_5 alkyl, including hydroxyl ethyl, hydroxyl propyl, hydroxyl butyl, hydroxyl pentyl and 2,3-dihydroxypropyl;

a is 4-8 for the first hydroxyl-containing silicone component and between 4-100 for the second hydroxyl-containing silicone component.

20. The silicone hydrogel of any of the foregoing claims, wherein the further constituent is selected from a diluent, a UV absorbing compound, a medicinal agent, an antimicrobial compound, a pharmaceutical compound, a nutraceutical compound, a photochromic compound, a reactive tint, a pigment, a copolymerizable dye, a nonpolymerizable dye, a release agent, a copolymer, and combinations thereof; optionally

(a) wherein the UV absorbing compound is selected from the group consisting of reactive 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyltriazines, oxanilides, cyanoacrylates, salicylates, 4-hydroxybenzoates, and mixtures thereof; or

(b) wherein the UV absorbing compound is selected from the group consisting of 2-(2'-hydroxy-5-methacryloxyethylphenyl)-2H-benzotriazole, 5-vinyl and 5-isopropenyl derivatives of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole and 4-acrylates or 4-methacrylates of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole or 2-(2,4-dihydroxyphenyl)-1,3-2H-dibenzotriazole, and mixtures thereof.

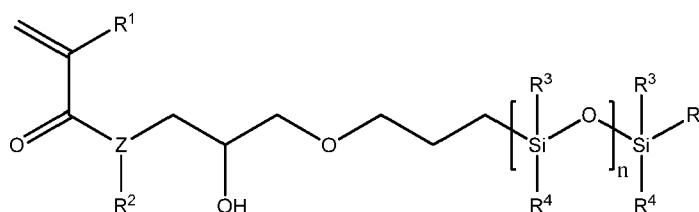
21. The silicone hydrogel of any of the foregoing claims, wherein the silicone hydrogel has an oxygen permeability (Dk) of at least 80 barrers, or 80 to 200 barrers, 90 to 180 barrers, 100 to 160 barrers.

22. The silicone hydrogel of any of foregoing claims, further comprising at least one charged monomer comprises at least one ionic moiety selected from the group consisting of anions, cations, zwitterions, betaines, and mixtures thereof.

23. The silicone hydrogel of claim 1 formed from a reactive monomer mixture comprising:

a. At least one hydroxyalkyl (meth)acrylate;

b. a hydroxyl-containing silicone component that comprises a mixture of a first hydroxyl substituted, linear poly(dialkylsiloxane) of Formula VI,



Formula VI

wherein

Z is selected from O, N, S or NCH₂CH₂O, when Z is O or S R² is not present;

R¹ is independently H or methyl;

R² is H or is a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, and which may be optionally substituted with amide, ether, and combinations thereof;

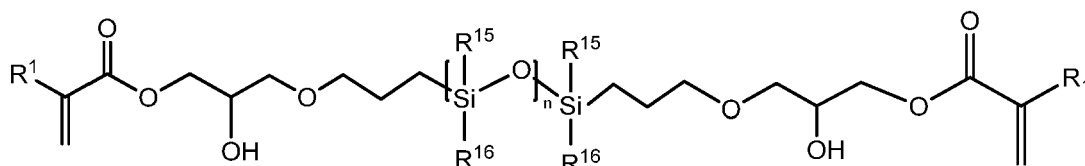
R³ and R⁴ are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amide, ether, and combinations thereof;

R³ and R⁴ may be independently selected from methyl, ethyl or phenyl, or may be methyl;

n is 4-8 for the first monofunctional hydroxyl substituted, poly(disubstituted siloxane), and, a second hydroxyl substituted, linear poly(dialkylsiloxane) selected from the group consisting of

a monofunctional hydroxyl substituted, linear poly(dialkylsiloxane) of Formula I, wherein n is 10 to 20 and R¹³ is selected from straight or branched C₁ to C₈ alkyl groups, optionally substituted with one or more hydroxyl, amide, ether, and combinations thereof; and

a multifunctional hydroxyl substituted, linear poly(dialkylsiloxane) of Formula XI having 10 to 200, or 10 to 100 siloxane repeating units,



Formula XI

Wherein R_1 is independently a hydrogen atom or methyl group;

R_{15} and R_{16} are independently a linear, branched, or cyclic alkyl group containing one to eight carbon atoms, any of which may be further substituted with at least one hydroxy group, amido, ether, amino, carboxyl, carbonyl groups and combinations thereof; or are independently methyl or ethyl; and

n is 10 to 200; 10 to 100; 10 to 50; 10 to 20;

wherein a ratio of the second hydroxyl substituted, linear poly(dialkylsiloxane) to the first hydroxyl substituted, linear poly(dialkylsiloxane) is in a range of 0.1 to 1.3, or 0.4 to 1;

greater than 15 weight percent, based on the total weight of the reactive monomer mixture, of at least one polyamide selected from the group consisting of PVP, PVMA, PDMA, PNVA, polyacrylamide, and copolymers and mixtures thereof; and optionally, methacrylic acid.

24. The silicone hydrogel of claim 23, further comprising at least one additional hydrophilic monomer is selected from the group consisting of *N*-vinyl amides, *N*-vinylimides, *N*-vinyl lactams, hydrophilic (meth)acrylates, (meth)acrylamides, hydrophilic styrenes, vinyl ethers, *O*-vinyl carbonates, *O*-vinyl carbamates, *N*-vinyl ureas, other hydrophilic vinyl compounds and mixtures thereof.

25. The silicone hydrogel of any of claims 1-24, wherein the polyamide has a weight average molecular weight of at least 100,000 Daltons; or greater than 150,000 Daltons; or between 150,000 to 2,000,000 Daltons, or between 300,000 to 1,800,000 Daltons.

26. The silicone hydrogel of any of claims 1-25 wherein the polyamide is added to the reaction mixture such that the hydrogel polymerizes around the polyamide, forming a semi-interpenetrating network.

27. A contact lens comprising the silicone hydrogel of any of claims 1-26.

28. The contact lens of claim 27, wherein:

(a) the lipid uptake is less than 15 $\mu\text{g}/\text{lens}$, or less than 10 $\mu\text{g}/\text{lens}$; and/or

(b) the PQ1 uptake is less than 20%; and/or

(c) the dynamic contact angle is less than 95°, or less than 60°; and/or

(d) the lysozyme uptake is at least 50 $\mu\text{g}/\text{lens}$, at least 100 $\mu\text{g}/\text{lens}$, at least 200 $\mu\text{g}/\text{lens}$, at least 500 $\mu\text{g}/\text{lens}$, at least 700 $\mu\text{g}/\text{lens}$ or at least 800 $\mu\text{g}/\text{lens}$; 50-1500 $\mu\text{g}/\text{lens}$, 100-1500 $\mu\text{g}/\text{lens}$, or 200-1500 $\mu\text{g}/\text{lens}$.

29. A method of making the silicone hydrogel of any of claims 1-26, the method comprising:

preparing the reactive monomer mixture, and

subjecting the reactive monomer mixture to polymerization conditions to form the silicone hydrogel;

optionally wherein polymerization of the reaction mixture is initiated using heat or visible or ultraviolet light.

Patentansprüche

1. Silikonhydrogel, gebildet aus einer reaktiven Monomerenmischung, umfassend:

a. mindestens ein Hydroxyalkyl(meth)acrylat-Monomer;

b. mindestens ein erstes monofunktionelles hydroxylsubstituiertes Polysiloxan mit disubstituiertem Siloxan mit

4 bis 8 Siloxan-Wiederholungseinheiten;

c. mindestens ein zweites hydroxylsubstituiertes Polysiloxan mit disubstituiertem Siloxan ausgewählt aus der Gruppe bestehend aus monofunktionellem hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan mit 10 bis 200 oder 10-100 Siloxan-Wiederholungseinheiten, multifunktionellen hydroxylsubstituierten Polysiloxanen mit disubstituiertem Siloxan mit 10 bis 200 oder 10-100 Siloxan-Wiederholungseinheiten und Mischungen davon;

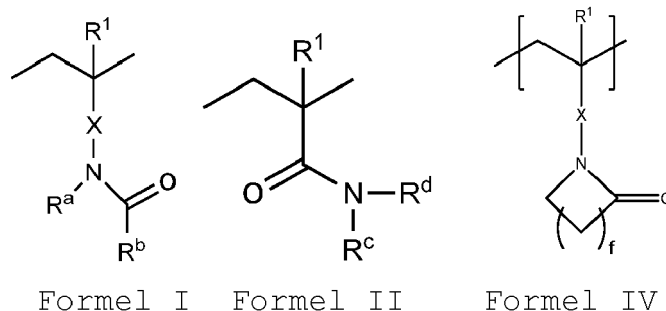
d. mindestens 15 Gew.-% eines Polyamids, bezogen auf das Gesamtgewicht von reaktiven Komponenten in der reaktiven Monomerenmischung; und

e. gegebenenfalls weitere Bestandteile.

2. Silikonhydrogel nach Anspruch 1, wobei das Polyamid in der reaktiven Mischung in einer Menge zwischen 15,1 Gewichtsprozent und 40 Gewichtsprozent oder zwischen 15,1 und 30 Gew.-%, bezogen auf das Gesamtgewicht aller reaktiven Komponenten in der reaktiven Mischung, vorliegt.

3. Silikonhydrogel nach Anspruch 1 oder 2, wobei das Polyamid aus der Gruppe ausgewählt ist, die im Wesentlichen aus cyclischen Polyamiden, acyclischen Polyamiden und Mischungen davon besteht.

4. Silikonhydrogel nach Anspruch 3, wobei das Polyamid Wiederholungseinheiten umfasst, die aus Formel I, Formel II und Formel IV ausgewählt sind:



wobei

R^1 unabhängig für ein Wasserstoffatom oder Methyl steht;

X für eine direkte Bindung, $-(CO)-$ oder $-(CO)-NH-R^e$ steht, wobei R^e für eine C_1 - bis C_3 -Alkylgruppe steht;

R^a aus H und geraden oder verzweigten, substituierten oder unsubstituierten C_1 - bis C_4 -Alkylgruppen ausgewählt ist;

R^b aus H, geraden oder verzweigten, substituierten oder unsubstituierten C_1 - bis C_4 -Alkylgruppen, Aminogruppen mit bis zu zwei Kohlenstoffatomen, Amidgruppen mit bis zu vier Kohlenstoffatomen und Alkoxygruppen mit bis zu zwei Kohlenstoffgruppen ausgewählt ist;

R^c aus H und geraden oder verzweigten, substituierten oder unsubstituierten C_1 - bis C_4 -Alkylgruppen ausgewählt ist;

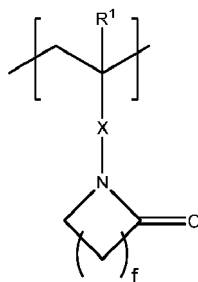
R^d aus H und geraden oder verzweigten, substituierten oder unsubstituierten C_1 - bis C_4 -Alkylgruppen ausgewählt ist;

wobei die Zahl der Kohlenstoffatome in R^a und R^b zusammengekommen 8 oder weniger, gegebenenfalls 6 oder weniger, beträgt und wobei die Zahl der Kohlenstoffatome in R^c und R^d zusammengekommen 8 oder weniger beträgt.

5. Silikonhydrogel nach Anspruch 3, wobei:

(a) das cyclische Polyamid aus mindestens einem von α -Lactam, β -Lactam, γ -Lactam, δ -Lactam und ϵ -Lactam hergestellt wird oder

(b) das cyclische Polyamid Wiederholungseinheiten der Formel IV



umfasst, wobei

R^1 unabhängig für ein Wasserstoffatom oder Methyl steht; f für eine Zahl von 1 bis 10 oder 8 oder weniger oder 6 oder weniger oder 2 bis 6 oder 3 oder 2 steht und
 X für eine direkte Bindung, $-(CO)-$ oder $-(CO)-NH-R^e-$ steht, wobei R^e für eine C_1- bis C_3- Alkylgruppe steht.

6. Silikonhydrogel nach Anspruch 3, wobei es sich bei dem Polyamid um ein Copolymer handelt, gegebenenfalls:

- (a) wobei das Copolymer mindestens 80 Molprozent der Wiederholungseinheiten umfasst, die aus NVP, VMA, DMA, NVA und Mischungen davon ausgewählt sind; oder
 (b) wobei das Copolymer ferner mindestens eine Wiederholungseinheit umfasst, die aus der Gruppe bestehend aus N-Vinylamiden, Acrylamiden, Hydroxyalkyl(meth)acrylaten, Alkyl(meth)acrylaten, N-Vinylpyrrolidon, N,N-Dimethylacrylamid, 2-Hydroxyethylmethacrylat, Vinylacetat, Acrylnitril, Hydroxypropylmethacrylat, 2-Hydroxyethylacrylat, Methylmethacrylat, Butylmethacrylat, Methacryloxypropyltrimethylsiloxysilan, siloxansubstituierten Acrylaten oder Methacrylaten und Mischungen davon ausgewählt ist.

7. Silikonhydrogel nach Anspruch 1, wobei das Polyamid aus Polyvinylpyrrolidon (PVP), Polyvinylmethylacetamid (PVMA), Polydimethylacrylamid (PDMA), Polyvinylacetamid (PNVA), Poly(hydroxyethyl(meth)-acrylamid), Polyacrylamid und Copolymeren und Mischungen davon ausgewählt ist; gegebenenfalls

- (a) wobei es sich bei dem Polyamid um PVP handelt oder
 (b) wobei es sich bei dem Polyamid um PVMA handelt.

8. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend mindestens ein zusätzliches hydrophiles Monomer; gegebenenfalls

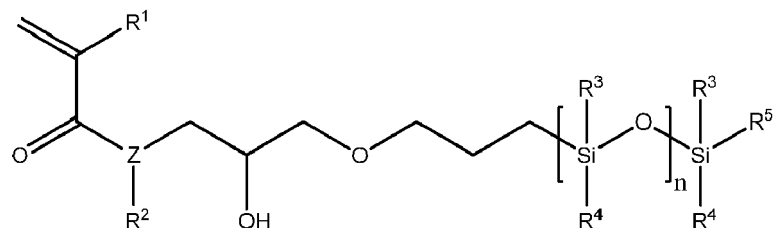
- (a) wobei das zusätzliche hydrophile Monomer aus der Gruppe bestehend aus Ethylenglykolvinyether (EGVE), Di(ethylenglykol)vinyether (DEGVE), N-Vinylpyrrolidon (NVP), 1-Methyl-3-methylen-2-pyrrolidon, 1-Methyl-5-methylen-2-pyrrolidon, 5-Methyl-3-methylen-2-pyrrolidon; 1-Ethyl-5-methylen-2-pyrrolidon, N-Methyl-3-methylen-2-pyrrolidon, 5-Ethyl-3-methylen-2-pyrrolidon, 1-n-Propyl-3-methylen-2-pyrrolidon, 1-n-Propyl-5-methylen-2-pyrrolidon, 1-Isopropyl-3-methylen-2-pyrrolidon, 1-Isopropyl-5-methylen-2-pyrrolidon, N-Vinyl-N-methylacetamid (VMA), N-Vinyl-N-ethylacetamid, N-Vinyl-N-ethylformamid, N-Vinylformamid, N-Vinylacetamid, N-Vinylisopropylamid, Allylalkohol, N-Vinylcaprolactam, N-2-Hydroxyethylvinyl-carbamat, N-Carboxy- β -alanin-N-viny-lester; N-Carboxyvinyl- β -alanin (VINAL), N-Carboxyvinyl- α -alanin und Mischungen davon ausgewählt ist oder
 (b) wobei das zusätzliche hydrophile Monomer aus N,N-Dimethylacrylamid, N-Vinylpyrrolidon, N-Vinyl-N-methylacetamid, N-Vinylacetamid und 1-Methyl-5-methylen-2-pyrrolidon ausgewählt ist oder
 (c) wobei das zusätzliche hydrophile Monomer N-Vinylpyrrolidon, N,N-Dimethylacrylamid und Mischungen davon umfasst.

9. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei

- (a) das Hydroxyalkyl(meth)acrylat-Monomer aus der Gruppe bestehend aus 2-Hydroxyethyl(meth)acrylat, 3-Hydroxypropyl(meth)acrylat, 2-Hydroxypropyl-(meth)acrylat, 2,3-Dihydroxypropyl(meth)acrylat, 2-Hydroxybutyl(meth)acrylat, 3-Hydroxybutyl(meth)-acrylat, 1-Hydroxypropyl-2-(meth)acrylat, 2-Hydroxy-2-methylpropyl(meth)acrylat, 3-Hydroxy-2,2-dimethylpropyl(meth)acrylat, 4-Hydroxybutyl-(meth)acrylat, Glycerin(meth)acrylat, Polyethylenglykolmonomethacrylat und Mischungen davon ausgewählt ist oder
 (b) das Hydroxyalkyl(meth)acrylat-Monomer aus der Gruppe bestehend aus 2-Hydroxyethylmethacrylat, Gly-

cerinmethacrylat, 2-Hydroxypropylmethacrylat, Hydroxybutylmethacrylat, 3-Hydroxy-2,2-dimethyl-propylmethacrylat und Mischungen davon oder 2-Hydroxyethylmethacrylat, 3-Hydroxy-2,2-dimethyl-propylmethacrylat, Hydroxybutylmethacrylat oder Glycerinmethacrylat und Mischungen davon ausgewählt ist.

10. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei das erste monofunktionelle hydroxylsubstituierte Polysiloxan mit disubstituiertem Siloxan die in Formel VI-1 gezeigte Struktur aufweist:

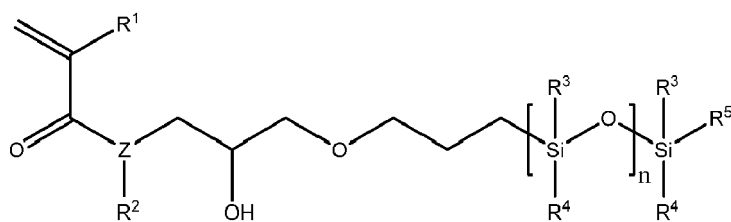


Formel VI-1

wobei

Z aus O, N, S oder NCH₂CH₂O ausgewählt ist und dann, wenn Z für O oder S steht, R² nicht vorhanden ist;
 R¹ unabhängig für H oder Methyl steht;
 R² für H oder eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe substituiert sein kann und die gegebenenfalls durch Amid, Ether und Kombinationen davon substituiert sein kann, steht;
 R³ und R⁴ unabhängig für eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe, Amid, Ether und Kombinationen davon substituiert sein kann, steht; R³ und R⁴ unabhängig aus Methyl, Ethyl oder Phenyl ausgewählt sein können oder für Methyl stehen können;
 n für 4-8 steht und
 R⁵ aus geraden oder verzweigten C₁- bis C₈-Alkylgruppen, die gegebenenfalls durch ein oder mehrere Hydroxyl, Amid, Ether und Kombinationen davon substituiert sein können, ausgewählt ist oder R⁵ für Methyl oder gerades oder verzweigtes C₄-Alkyl, das jeweils gegebenenfalls durch Hydroxyl substituiert sein kann, steht.

11. Silikonhydrogel nach Anspruch 1 oder 10, wobei das zweite hydroxylsubstituierte Poly(dialkylsiloxan) eine Verbindung der Formel VI-2 umfasst:



Formel VI-2

wobei

Z aus O, N, S oder NCH₂CH₂O ausgewählt ist und dann, wenn Z für O oder S steht, R² nicht vorhanden ist;
 R¹ unabhängig für H oder Methyl steht;
 R² für H oder eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe substituiert sein kann und die gegebenenfalls durch Amid, Ether und Kombinationen davon substituiert sein kann, steht;
 R³ und R⁴ unabhängig für eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe substituiert sein kann und die gegebenenfalls durch Amid, Ether und Kombinationen davon substituiert sein kann, steht; R³ und R⁴ unabhängig aus Methyl, Ethyl oder Phenyl ausgewählt sein können oder für Methyl stehen können;

n für die Zahl der Siloxaneinheiten steht und für 10 bis 200 steht und

R⁵ aus geraden oder verzweigten C₁- bis C₈-Alkylgruppen, die gegebenenfalls durch ein oder mehrere Hydroxyl-, Amid-, Ether und Kombinationen davon substituiert sein können, ausgewählt ist.

12. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei:

(a) der gesamte Gewichtsprozentanteil des ersten monofunktionellen hydroxylsubstituierten Poly-(dialkylsiloxan)s und des zweiten hydroxylsubstituierten Poly(dimethylsiloxan)s zwischen 40 und 70 Gew.-% liegt oder 45 bis 70 Gew.-% beträgt und/oder

(b) wobei das erste monofunktionelle hydroxylsubstituierte Polysiloxan mit disubstituiertem Siloxan und das zweite hydroxylsubstituierte Polysiloxan mit disubstituiertem Siloxan in der reaktiven Monomerenmischung in Konzentrationen vorliegen, die ein Gewichtsverhältnis von erstem monofunktionellem hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan zu zweitem hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan zwischen 0,1 und 1,3 liefern; und/oder

(c) wobei das Gewichtsverhältnis von erstem monofunktionellem hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan zu zweitem hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan zwischen 0,1 und 1 oder 0,4 und 1 liegt.

13. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend mindestens eine zusätzliche silikonhaltige Komponente, die aus der Gruppe bestehend aus hydroxylgruppenfreien silikonhaltigen Monomeren, Makromeren und Vernetzungsmitteln ausgewählt ist.

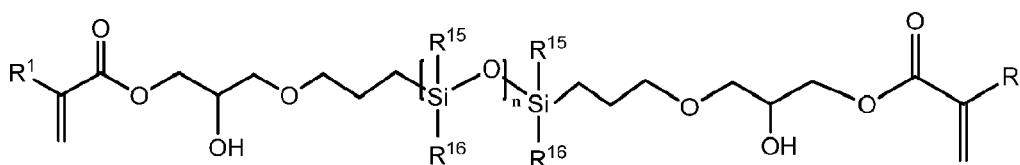
14. Silikonhydrogel nach Anspruch 11, wobei in dem ersten monofunktionellen hydroxylsubstituierten Polysiloxan mit disubstituiertem Siloxan n = 4-8 ist und in dem zweiten hydroxylsubstituierten Polysiloxan mit disubstituiertem Siloxan n = 10-20 ist.

15. Silikonhydrogel nach Anspruch 2, wobei die durchschnittliche Zahl von Siloxan-Wiederholungseinheiten des ersten monofunktionellen hydroxylsubstituierten Poly(dialkylsiloxan)s 4 beträgt und die durchschnittliche Zahl von Siloxan-Wiederholungseinheiten des zweiten hydroxylsubstituierten Poly(dimethylsiloxan)s zwischen 10 und 20 liegt.

16. Silikonhydrogel nach Anspruch 8, wobei der Gesamtgewichtsanteil von zusätzlichem hydrophilem Monomer zwischen 5 und 30 Gew.-% liegt oder 8 bis 25 Gew.-% beträgt.

17. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend mindestens ein Vernetzungsmittel, das aus der Gruppe bestehend aus bifunktionellen Vernetzern, trifunktionellen Vernetzern, tetrafunktionellen Vernetzern, multifunktionellen Vernetzern Mischungen davon ausgewählt ist.

18. Silikonhydrogel nach Anspruch 11, wobei das zweite monofunktionelle hydroxylsubstituierte Polysiloxan mit disubstituiertem Siloxan aus der Gruppe bestehend aus hydroxylsubstituiertem Polysiloxan mit disubstituiertem Siloxan der Formel VI-2, wobei n für 10 bis 20 steht, einem difunktionellen hydroxylsubstituierten Polysiloxan mit disubstituiertem Siloxan der Formel XI und Mischungen davon ausgewählt ist:



Formel XI

wobei

R¹ unabhängig für ein Wasserstoffatom oder eine Methylgruppe steht;

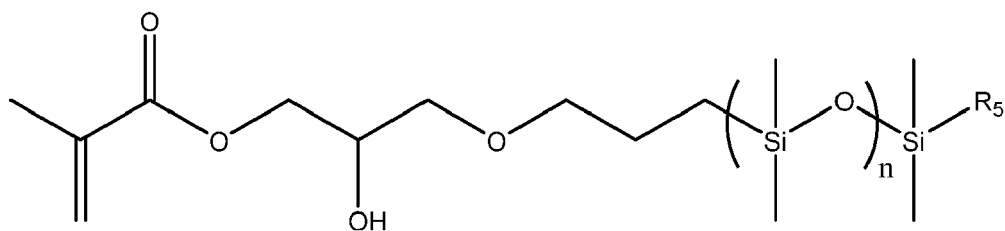
R¹⁵ und R¹⁶ unabhängig für eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe, Amido-, Ether-, Amino-, Carboxyl-, Carbo- nylgruppen und Kombinationen davon substituiert sein kann, stehen oder unabhängig für Methyl oder Ethyl stehen und

n für 10 bis 200; 10 bis 100; 10 bis 50; 10 bis 20 steht.

19. Silikonhydrogel nach Anspruch 1, wobei die monofunktionellen hydroxylsubstituierten Polysiloxane mit disubstituiertem Siloxan aus der Gruppe bestehend aus monofunktionellen hydroxylsubstituierten Polysiloxanen mit disubstituiertem Siloxan der Formel VIIa-IXb ausgewählt sind:

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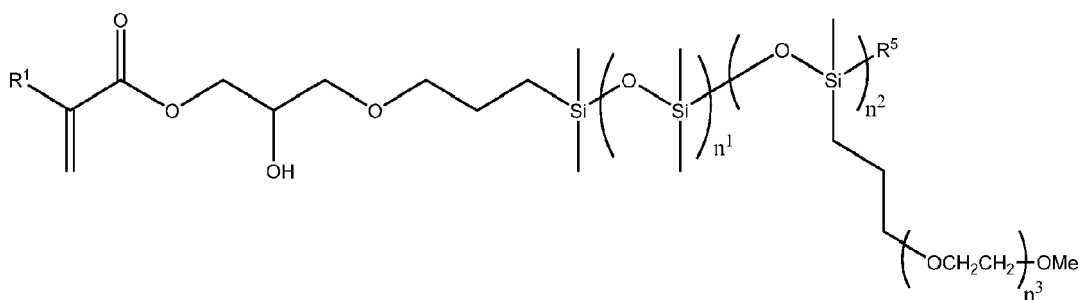
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Formel VIIa

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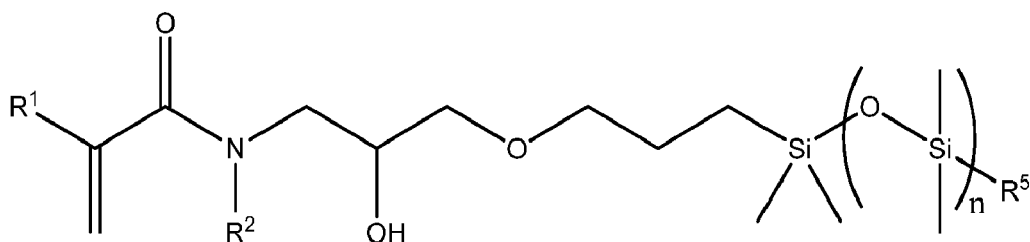


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Formel VIIb

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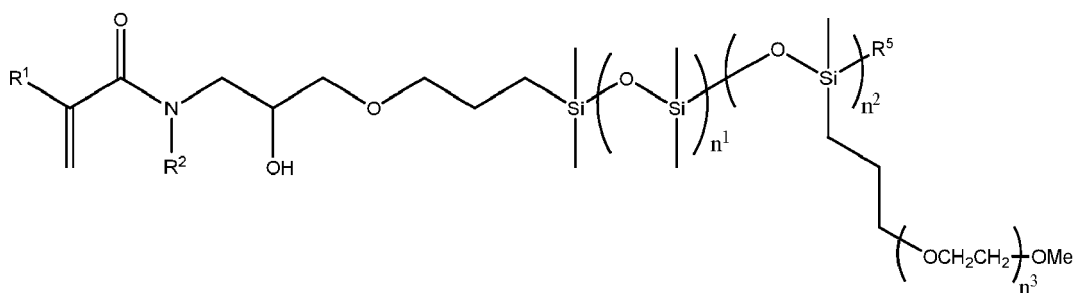
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Formel VIIIa

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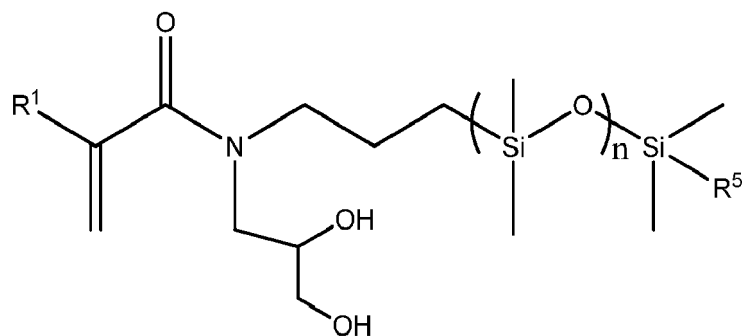
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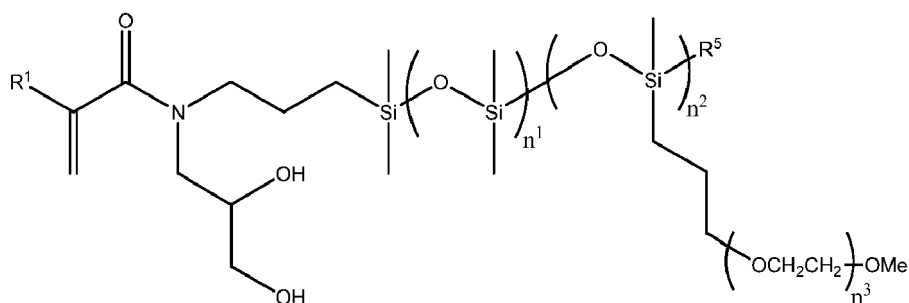
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Formel VIIIb

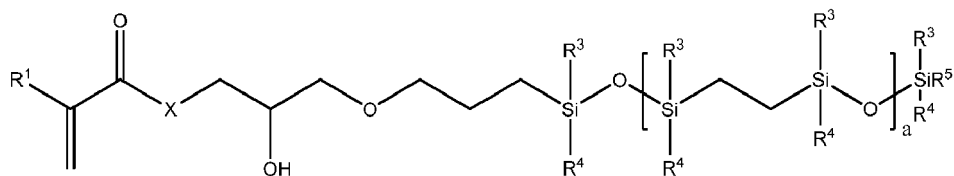
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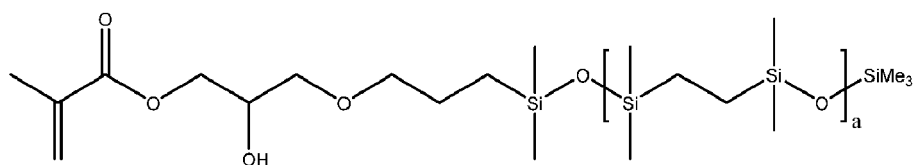
Formel VIIIc



Formel VIIIId



Formel IXa



Formel IXb

wobei R¹ für Methyl oder H steht; n zwischen 4 und 30, 4-8 oder 10-20 liegt;

R² unabhängig aus der Gruppe bestehend aus H oder einer linearen, verzweigten oder cyclischen Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe substituiert sein kann und die gegebenenfalls durch Amid, Ether und Kombinationen davon substituiert sein kann, ausgewählt ist;

n¹ und n² unabhängig zwischen 4 bis 100; 4 bis 50 oder 4 bis 25 liegen;

n³ für 1-50, 1-20 oder 1-10 steht;

R⁵ aus geraden oder verzweigten C₁- bis C₈-Alkylgruppen, die gegebenenfalls durch eine oder mehrere Hydroxyl-, Amid-, Ether-, Polyhydroxylgruppen substituiert sein können, die aus geraden oder verzweigten C₁- bis C₈-Alkylgruppen mit der Formel CₓHᵧ(OH)ₙ, wobei f = 1-8 und g + h = 2f + 1, und cyclischen C₁- bis C₈-Alkylgruppen mit der Formel CₓHᵧ(OH)ₙ, wobei f = 1-8 und g + h = 2f - 1, ausgewählt sind, und Kombinationen davon ausgewählt ist oder R⁵ aus Methyl, Butyl oder hydroxylsubstituiertem C₂-C₅-Alkyl einschließlich Hydroxylethyl, Hydroxylpropyl, Hydroxylbutyl, Hydroxylpentyl und 2,3-Dihydroxypropyl ausgewählt sein kann;

a für die erste hydroxylgruppenhaltige Silikonkomponente für 4-8 steht und für die zweite hydroxylgruppenhaltige Silikonkomponente zwischen 4-100 liegt.

20. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei der weitere Bestandteil aus einem Verdünnungsmittel, einer UV-absorbierenden Verbindung, einem medizinischen Mittel, einer antimikrobiellen Verbindung, einer pharmazeutischen Verbindung, einer nutraceutical Verbindung, einer photochromen Verbindung, einem reaktiven Tönungsmittel, einem Pigment, einem copolymerisierbaren Farbstoff, einem nichtpolymerisierbaren Farbstoff, einem Trennmittel, einem Copolymer und Kombinationen davon ausgewählt ist; gegebenenfalls

(a) wobei die UV-absorbierende Verbindung aus der Gruppe bestehend aus reaktiven 2-(2'-Hydroxyphenyl)benzotriazolen, 2-Hydroxybenzophenonen, 2-Hydroxyphenyltriazinen, Oxaniliden, Cyanoacrylaten, Salicylaten, 4-Hydroxybenzoaten und Mischungen davon ausgewählt ist oder

(b) wobei die UV-absorbierende Verbindung aus der Gruppe bestehend aus 2-(2'-Hydroxy-5-methacrylyl-oxyethylphenyl)-2H-benzotriazol, 5-Vinyl- und 5-Isopropenylderivaten von 2-(2,4-Dihydroxyphenyl)-2H-benzotriazol und 4-Acrylaten oder 4-Methacrylaten von 2-(2,4-Dihydroxyphenyl)-2H-benzotriazol oder 2-(2,4-Dihydroxyphenyl)-1,3-2H-dibenzotriazol und Mischungen davon ausgewählt ist.

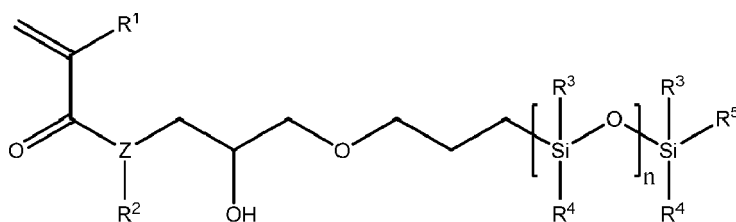
21. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei das Silikonhydrogel eine Sauerstoffdurchlässigkeit (Dk) von mindestens 80 Barrer oder 80 bis 200 Barrer, 90 bis 180 Barrer, 100 bis 160 Barrer aufweist.

22. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend mindestens ein geladenes Monomer mit mindestens einer ionischen Gruppierung, die aus der Gruppe bestehend aus Anionen, Kationen, Zwitterionen, Betainen und Mischungen davon ausgewählt ist.

23. Silikonhydrogel nach Anspruch 1, gebildet aus einer reaktiven Monomerenmischung, umfassend:

a. mindestens ein Hydroxyalkyl(meth)acrylat;

b. eine hydroxylgruppenhaltige Silikonkomponente, die eine Mischung eines ersten hydroxylsubstituierten, linearen Poly(dialkylsiloxan)s der Formel VI,



Formel VI

wobei

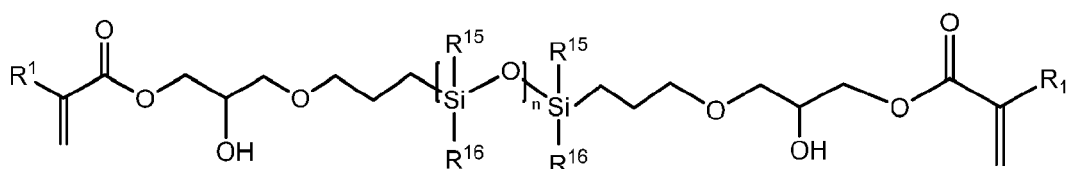
Z aus O, N, S oder $\text{NCH}_2\text{CH}_2\text{O}$ ausgewählt ist und dann, wenn Z für O oder S steht, R^2 nicht vorhanden ist; R^1 unabhängig für H oder Methyl steht;

R^2 für H oder eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe substituiert sein kann und die gegebenenfalls durch Amid, Ether und Kombinationen davon substituiert sein kann, steht;

R^3 und R^4 unabhängig für eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe, Amid, Ether und Kombinationen davon substituiert sein kann, steht; R^3 und R^4 unabhängig aus Methyl, Ethyl oder Phenyl ausgewählt sein können oder für Methyl stehen können;

n für das erste monofunktionelle hydroxylsubstituierte Polysiloxan mit disubstituiertem Siloxan für 4-8 steht, und eines zweiten hydroxylsubstituierten, linearen Poly(dialkylsiloxan)s, ausgewählt aus der Gruppe bestehend aus einem monofunktionellen hydroxylsubstituierten, linearen Poly(dialkylsiloxan) der Formel I, wobei n für 10 bis 20 steht und R^{13} aus geraden oder verzweigten C_1 - bis C_8 -Alkylgruppen, die gegebenenfalls durch ein oder mehrere Hydroxyl, Amid, Ether und Kombinationen davon substituiert sind, ausgewählt ist; und

einem multifunktionellen hydroxylsubstituierten, linearen Poly(dialkylsiloxan) der Formel XI mit 10 bis 200 oder 10 bis 100 Siloxan-Wiederholungseinheiten,



Formel XI

wobei R¹ unabhängig für ein Wasserstoffatom oder eine Methylgruppe steht;

R¹⁵ und R¹⁶ jeweils für eine lineare, verzweigte oder cyclische Alkylgruppe mit eins bis acht Kohlenstoffatomen, die jeweils weiter durch mindestens eine Hydroxygruppe, Amido-, Ether-, Amino-, Carboxyl-, Carbonylgruppen und Kombinationen davon substituiert sein kann, stehen oder unabhängig für Methyl oder Ethyl stehen und n für 10 bis 200; 10 bis 100; 10 bis 50; 10 bis 20 steht;

umfasst;

wobei das Verhältnis von zweitem hydroxylsubstituiertem, linearem Poly(dialkylsiloxan) zu erstem hydroxylsubstituiertem, linearem Poly-(dialkylsiloxan) in einem Bereich von 0,1 bis 1,3 oder 0,4 bis 1 liegt;

mehr als 15 Gew.-%, bezogen auf das Gesamtgewicht der reaktiven Monomerenmischung, mindestens eines Polyamids, das aus der Gruppe bestehend aus PVP, PVMA, PDMA, PNVA, Polyacrylamid und Copolymeren und Mischungen davon ausgewählt ist;

und

gegebenenfalls Methacrylsäure.

24. Silikonhydrogel nach Anspruch 23, ferner umfassend ein zusätzliches hydrophiles Monomer, das aus der Gruppe bestehend aus *N*-Vinylamiden, *N*-Vinylimiden, *N*-Vinylactamen, hydrophilen (Meth)acrylaten, (Meth)acrylamiden, hydrophilen Styrolen, Vinylethern, *O*-Vinylcarbonaten, *O*-Vinylcarbamaten, *N*-Vinylharnstoffen, anderen hydrophilen Vinylverbindungen und Mischungen davon ausgewählt ist.

25. Silikonhydrogel nach einem der Ansprüche 1-24, wobei das Polyamid ein gewichtsmittleres Molekulargewicht von mindestens 100.000 Dalton oder mehr als 150.000 Dalton oder zwischen 150.000 bis 2.000.000 Dalton oder zwischen 300.000 bis 1.800.000 Dalton aufweist.

26. Silikonhydrogel nach einem der Ansprüche 1-25, wobei das Polyamid derart zu der Reaktionsmischung gegeben wird, dass das Hydrogel unter Ausbildung eines semiinterpenetrierenden Netzwerks um das Polymer herum polymerisiert.

27. Kontaktlinse, umfassend das Silikonhydrogel nach einem der Ansprüche 1-26.

28. Kontaktlinse nach Anspruch 27, wobei:

(a) die Lipidaufnahme weniger als 15 µg/Linse oder weniger als 10 µg/Linse beträgt und/oder

(b) die PQ1-Aufnahme weniger als 20 % beträgt und/oder

(c) der dynamische Kontaktwinkel weniger als 95° oder weniger als 60° beträgt und/oder

(d) die Lysozymaufnahme mindestens 50 µg/Linse, mindestens 100 µg/Linse, mindestens 200 µg/Linse, mindestens 500 µg/Linse, mindestens 700 µg/Linse oder mindestens 800 µg/Linse; 50-1500 µg/Linse, 100-1500 µg/Linse oder 200-1500 µg/Linse beträgt.

29. Verfahren zur Herstellung des Silikonhydrogels nach einem der Ansprüche 1-26, bei dem man:

die reaktive Monomerenmischung herstellt und

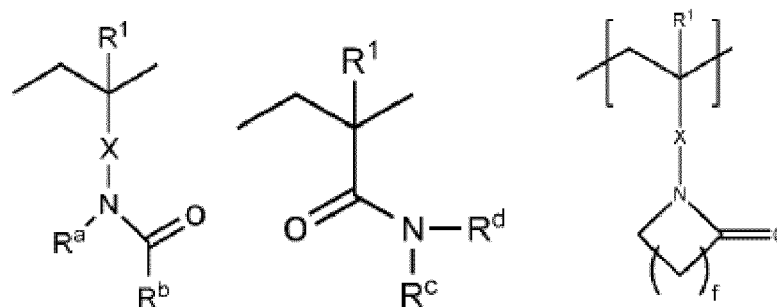
die reaktive Monomerenmischung Polymerisationsbedingungen unterwirft, um das Silikonhydrogel zu bilden; gegebenenfalls wobei die Polymerisation der Reaktionsmischung unter Verwendung von Wärme oder sichtbarem oder ultraviolettem Licht initiiert wird.

Revendications

1. Hydrogel de silicone formé à partir d'un mélange de monomères réactifs comprenant :

- a. au moins un monomère de (méth)acrylate d'hydroxyalkyle ;
 b. au moins un premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel ayant 4 à 8 motifs répétitifs de siloxane ;
 c. au moins un deuxième poly(siloxane disubstitué) substitué par hydroxyle choisi dans le groupe constitué par un poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel ayant 10 à 200 ou 10 à 100 motifs répétitifs de siloxane, des poly(siloxanes disubstitués) substitués par hydroxyle multifonctionnels ayant 10 à 200 ou 10 à 100 motifs répétitifs de siloxane, et des mélanges correspondants ;
 d. au moins 15 % en poids d'au moins un polyamide, sur la base du poids total de composants réactifs dans le mélange de monomères réactifs ; et
 e. des constituants supplémentaires éventuels.

2. Hydrogel de silicone selon la revendication 1, le polyamide étant présent dans le mélange réactif en une quantité comprise entre 15,1 pour cent en poids et 40 pour cent en poids ou entre 15,1 et 30 % en poids, sur la base du poids total de tous les composants réactifs dans le mélange de monomères réactifs.
3. Hydrogel de silicone selon la revendication 1 ou 2, le polyamide étant choisi dans le groupe essentiellement constitué par des polyamides cycliques, des polyamides acycliques et des mélanges correspondants.
4. Hydrogel de silicone selon la revendication 3, le polyamide comprenant des motifs répétitifs choisis parmi la formule I, la formule II et la formule IV

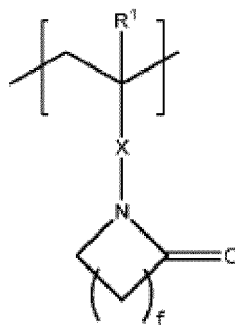


formule I formule II formule IV,

- R^1 étant indépendamment un atome d'hydrogène ou méthyle ;
 X étant une liaison directe, $-(CO)-$, ou $-(CO)-NH-R^e$, R^e étant un groupe alkyle en C_1 à C_3 ;
 R^a étant choisi parmi H, des groupes alkyle en C_1 à C_4 linéaires ou ramifiés, substitués ou non substitués ;
 R^b étant choisi parmi H, des groupes alkyle en C_1 à C_4 linéaires ou ramifiés, substitués ou non substitués, des groupes amino ayant jusqu'à deux atomes de carbone, des groupes amide ayant jusqu'à quatre atomes de carbone et des groupes alcoxy ayant jusqu'à deux atomes de carbone ;
 R^c étant choisi parmi H, des groupes alkyle en C_1 à C_4 linéaires ou ramifiés, substitués ou non substitués ;
 R^d étant choisi parmi H, des groupes alkyle en C_1 à C_4 linéaires ou ramifiés, substitués ou non substitués ;
 le nombre d'atomes de carbone dans R^a et R^b pris ensemble étant de 8 ou moins, éventuellement 6 ou moins, et le nombre d'atomes de carbone dans R^c et R^d pris ensemble étant de 8 ou moins.

5. Hydrogel de silicone selon la revendication 3,

- (a) le polyamide cyclique étant préparé à partir d'au moins un élément parmi un α -lactame, un β -lactame, un γ -lactame, un δ -lactame, et un ϵ -lactame ; ou
 (b) le polyamide cyclique comprenant des motifs répétitifs de formule IV



R^1 étant indépendamment un atome d'hydrogène ou méthyle ; f étant un nombre de 1 à 10, ou 8 ou moins, ou 6 ou moins, ou 2 à 6, ou 3, ou 2, et X étant une liaison directe, $-(CO)-$, ou $-(CO)-NH-R^e$, R^e étant un groupe alkyle en C_1 à C_3 .

6. Hydrogel de silicone selon la revendication 3, le polyamide étant un copolymère ; éventuellement :

(a) le copolymère comprenant au moins 80 pour cent en moles des motifs répétitifs choisis parmi NVP, VMA, DMA, NVA, et des mélanges correspondants ; ou

(b) le copolymère comprenant en outre au moins un motif répétitif choisi dans le groupe constitué par des N-vinylamides, des acrylamides, des (méth)acrylates d'hydroxyalkyle, des (méth)acrylates d'alkyle, la N-vinylpyrrolidone, le N,N-diméthylacrylamide, le méthacrylate de 2-hydroxyéthyle, l'acétate de vinyle, l'acrylonitrile, le méthacrylate d'hydroxypropyle, l'acrylate de 2-hydroxyéthyle, le méthacrylate de méthyle, le méthacrylate de butyle, le méthacryloxypropyl-tris(triméthyl)siloxysilane, des acrylates ou méthacrylates substitués par siloxane, et des mélanges correspondants.

7. Hydrogel de silicone selon la revendication 1, le polyamide étant choisi parmi une polyvinylpyrrolidone (PVP), un polyvinylméthylacétamide (PVMA), un polydiméthylacrylamide (PDMA), un polyvinylacétamide (PNVA), un poly(hydroxyéthyl(méth)acrylamide), un polyacrylamide, et des copolymères et des mélanges correspondants ; éventuellement

(a) le polyamide étant une PVP ; ou

(b) le polyamide étant un PVMA.

8. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre au moins un monomère hydrophile supplémentaire ; éventuellement

(a) le monomère hydrophile supplémentaire étant choisi dans le groupe constitué par éther de vinyle d'éthylène glycol (EGVE), éther de vinyle de diéthylèneglycol (DEGVE), N-vinylpyrrolidone (NVP), 1-méthyl-3-méthylène-2-pyrrolidone, 1-méthyl-5-méthylène-2-pyrrolidone, 5-méthyl-3-méthylène-2-pyrrolidone, 1-éthyl-5-méthylène-2-pyrrolidone, N-méthyl-3-méthylène-2-pyrrolidone, 5-éthyl-3-méthylène-2-pyrrolidone, 1-n-propyl-3-méthylène-2-pyrrolidone, 1-n-propyl-5-méthylène-2-pyrrolidone, 1-isopropyl-3-méthylène-2-pyrrolidone, 1-isopropyl-5-méthylène-2-pyrrolidone, N-vinyl-N-méthylacétamide (VMA), N-vinyl-N-éthylacétamide, N-vinyl-N-éthylformamide, N-vinylformamide, N-vinylacétamide, N-vinylisopropylamide, alcool allylique, N-vinylcaprolactame, N-2-hydroxyéthyl-vinyl-carbamate, ester de N-vinyle de N-carboxy- β -alanine, N-carboxyvinyl- β -alanine (VINAL), N-carboxyvinyl- α -alanine et des mélanges correspondants ; ou

(b) le monomère hydrophile supplémentaire étant choisi parmi N,N-diméthylacrylamide, N-vinylpyrrolidone, N-vinyl-N-méthylacétamide, N-vinylacétamide et 1-méthyl-5-méthylène-2-pyrrolidone ; ou

(c) le monomère hydrophile supplémentaire comprenant N-vinylpyrrolidone, N,N-diméthylacrylamide, et des mélanges correspondants.

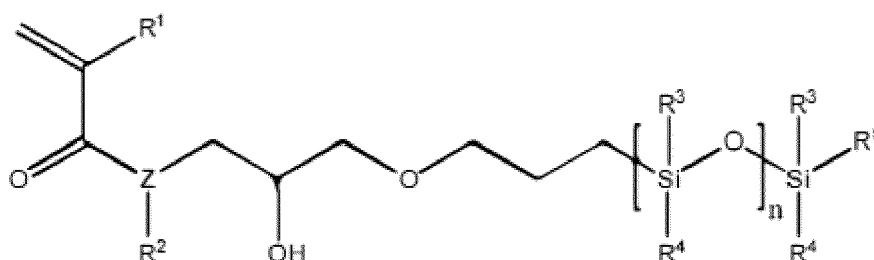
9. Hydrogel de silicone selon l'une quelconque des revendications précédentes,

(a) ledit monomère de (méth)acrylate d'hydroxyalkyle étant choisi dans le groupe constitué par (méth)acrylate de 2-hydroxyéthyle, (méth)acrylate de 3-hydroxypropyle, (méth)acrylate de 2-hydroxypropyle, (méth)acrylate de 2,3-dihydroxypropyle, (méth)acrylate de 2-hydroxybutyle, (méth)acrylate de 3-hydroxybutyle, 2-(méth)acrylate de 1-hydroxypropyle, (méth)acrylate de 2-hydroxy-2-méthyl-propyle, (méth)acrylate de 3-hydroxy-2,2-dimé-

thyl-propyle, (méth)acrylate de 4-hydroxybutyle, (méth)acrylate de glycérol, monométhacrylate de polyéthylène glycol, et des mélanges correspondants ; ou

(b) ledit monomère de (méth)acrylate d'hydroxyalkyle étant choisi dans le groupe constitué par méthacrylate de 2-hydroxyéthyle, méthacrylate de glycérol, méthacrylate de 2-hydroxypropyle, méthacrylate d'hydroxybutyle, méthacrylate de 3-hydroxy-2,2-diméthyl-propyle, et des mélanges correspondants ou méthacrylate de 2-hydroxyéthyle, méthacrylate de 3-hydroxy-2,2-diméthyl-propyle, méthacrylate d'hydroxybutyle ou méthacrylate de glycérol et des mélanges correspondants.

10. Hydrogel de silicone selon l'une quelconque des revendications précédentes, le premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel ayant la structure présentée dans la formule VI-1



formule VI-1

Z étant choisi parmi O, N, S ou $\text{NCH}_2\text{CH}_2\text{O}$, lorsque Z est O ou S R^2 n'est pas présent ;

R^1 étant indépendamment H ou méthyle ;

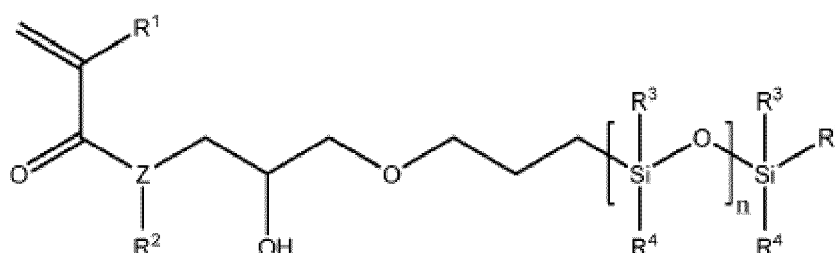
R^2 étant H ou un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, et qui peut éventuellement être substitué par amide, éther et des combinaisons correspondantes ;

R^3 et R^4 étant indépendamment un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, amide, éther, et des combinaisons correspondantes ; R^3 et R^4 pouvant être indépendamment choisis parmi méthyle, éthyle ou phényle, ou pouvant être méthyle ;

n étant 4 à 8, et

R^5 étant choisi parmi des groupes alkyle en C_1 à C_8 linéaires ou ramifiés, qui peuvent éventuellement être substitués par un ou plusieurs hydroxyles, amides, éthers, et des combinaisons correspondantes ; ou R^5 étant méthyle ou alkyle en C_4 linéaire ou ramifié, l'un ou l'autre parmi lesquels pouvant éventuellement être substitué par hydroxyle.

11. Hydrogel de silicone selon la revendication 1 ou 10, le deuxième poly(dialkylsiloxane) substitué par hydroxyle comprenant un composé de formule VI-2



formule VI-2

Z étant choisi parmi O, N, S ou $\text{NCH}_2\text{CH}_2\text{O}$, lorsque Z est O ou S R^2 n'est pas présent ;

R^1 étant indépendamment H ou méthyle ;

R^2 étant H ou un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, et qui peut éventuellement être substitué par amide, éther et des combinaisons correspondantes ;

R^3 et R^4 étant indépendamment un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, et qui peut éventuellement être substitué par amide, éther, et des combinaisons correspondantes ; R^3 et R^4 pouvant être indépendamment choisis parmi méthyle, éthyle ou phényle, ou pouvant être méthyle ;
 η étant le nombre de motifs siloxane et étant de 10 à 200 ; et
 R^5 étant choisi parmi des groupes alkyle en C_1 à C_8 linéaires ou ramifiés, qui peuvent éventuellement être substitués par un ou plusieurs hydroxyles, amides, éthers, et des combinaisons correspondantes.

12. Hydrogel de silicone selon l'une quelconque des revendications précédentes,

(a) le pourcentage en poids total du premier poly(dialkylsiloxane) substitué par hydroxyle monofonctionnel et le deuxième poly(diméthylsiloxane) substitué par hydroxyle étant compris entre 40 et 70 % en poids ou de 45 à 70 % en poids ; et/ou

(b) le premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel et le deuxième poly(siloxane disubstitué) substitué par hydroxyle étant présents dans le mélange de monomères réactifs en des concentrations qui fournissent un rapport en poids, du premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel sur le deuxième poly(siloxane disubstitué) substitué par hydroxyle compris entre 0,1 et 1,3 ; et/ou

(c) le rapport en poids du premier poly(dialkylsiloxane) substitué par hydroxyle monofonctionnel sur le deuxième poly(diméthylsiloxane) substitué par hydroxyle étant compris entre 0,1 et 1 ou entre 0,4 et 1.

13. Hydrogel de silicone selon l'une quelconque des revendications précédentes, comprenant en outre au moins un composant supplémentaire contenant une silicone choisi dans le groupe constitué par des monomères, des macromères et des agents de réticulation contenant une silicone non hydroxylés.

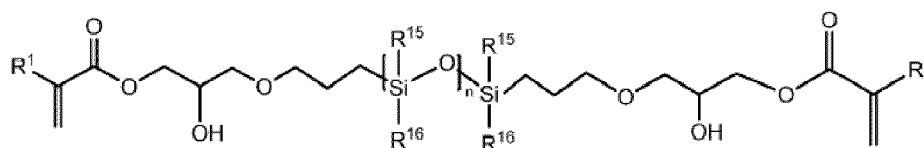
14. Hydrogel de silicone selon la revendication 11, $n = 4$ à 8 dans le premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel et $n = 10$ à 20 dans le deuxième poly(siloxane disubstitué) substitué par hydroxyle.

15. Hydrogel de silicone selon la revendication 2, le nombre moyen de motifs répétitifs de siloxane du premier poly(dialkylsiloxane) substitué par hydroxyle monofonctionnel étant de 4 et le nombre moyen de motifs répétitifs de siloxane du deuxième poly(diméthylsiloxane) substitué par hydroxyle étant compris entre 10 et 20.

16. Hydrogel de silicone selon la revendication 8, le pourcentage en poids total de monomère hydrophile supplémentaire étant compris entre 5 et 30 % en poids, ou de 8 à 25 % en poids.

17. Hydrogel de silicone selon une quelconque revendication précédente, comprenant en outre au moins un agent de réticulation choisi dans le groupe constitué par des agents de réticulation bifonctionnels, des agents de réticulation trifonctionnels, des agents de réticulation tétrafonctionnels, des agents de réticulation multifonctionnels et des mélanges correspondants.

18. Hydrogel de silicone selon la revendication 11, le deuxième poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel étant choisi dans le groupe constitué par un poly(siloxane disubstitué) substitué par hydroxyle de formule VI-2, n étant de 10 à 20, un poly(siloxane disubstitué) substitué par hydroxyle difonctionnel de formule XI, et des mélanges correspondants



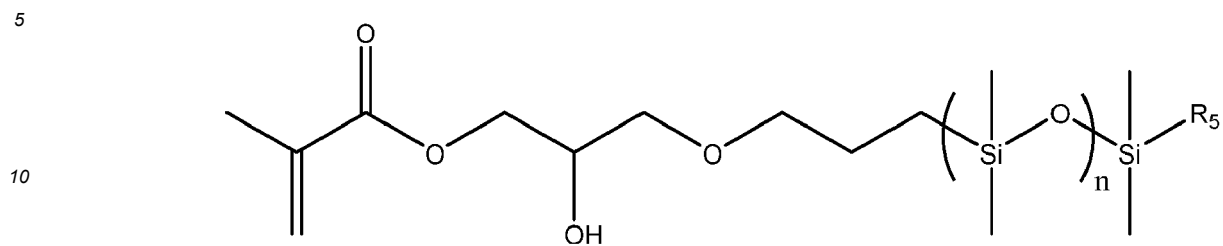
formule XI

R_1 étant indépendamment un atome d'hydrogène ou un groupe méthyle ;

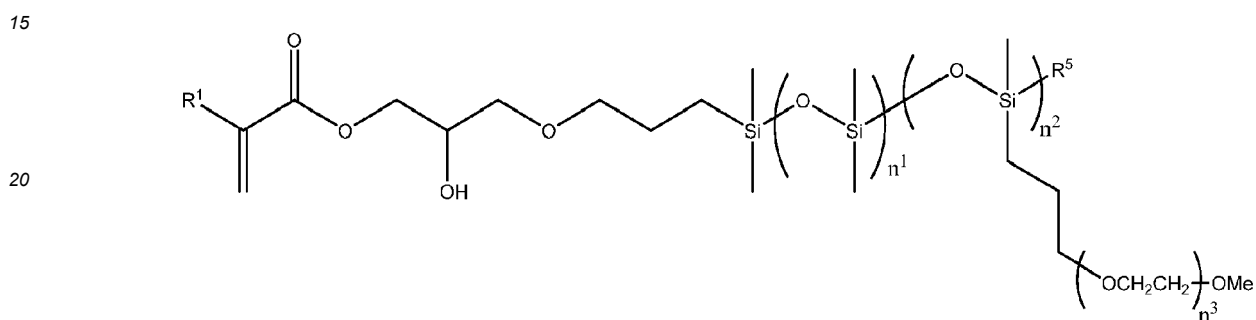
R_{15} et R_{16} étant indépendamment un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, des groupes amido, éther, amino, carboxyle, carbonyle et des combinaisons correspondantes ; ou étant indépendamment méthyle ou éthyle ; et

n étant 10 à 200 ; 10 à 100 ; 10 à 50 ; 10 à 20.

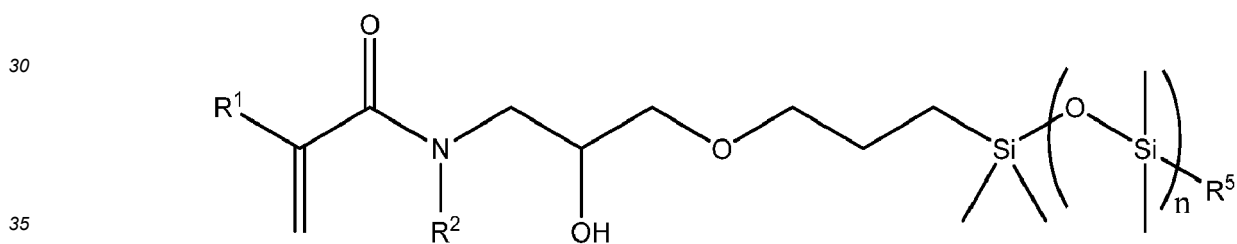
19. Hydrogel de silicone selon la revendication 1, les poly(siloxanes disubstitués) substitués par hydroxyle monofonctionnels étant choisis dans le groupe constitué par un poly(diméthylsiloxane) substitué par hydroxyle monofonctionnel de formule VIIa à IXb



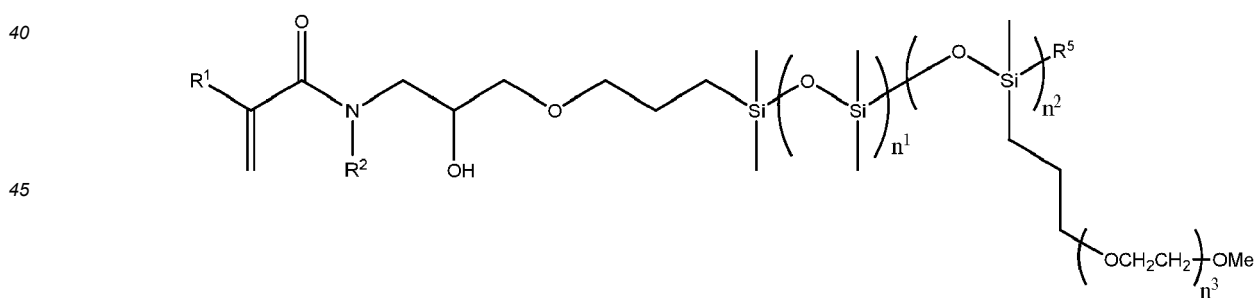
Formule VIIa



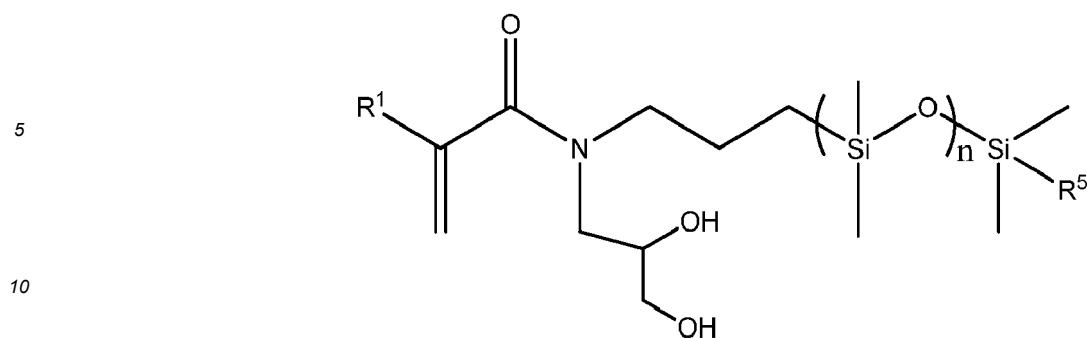
Formule VIIb



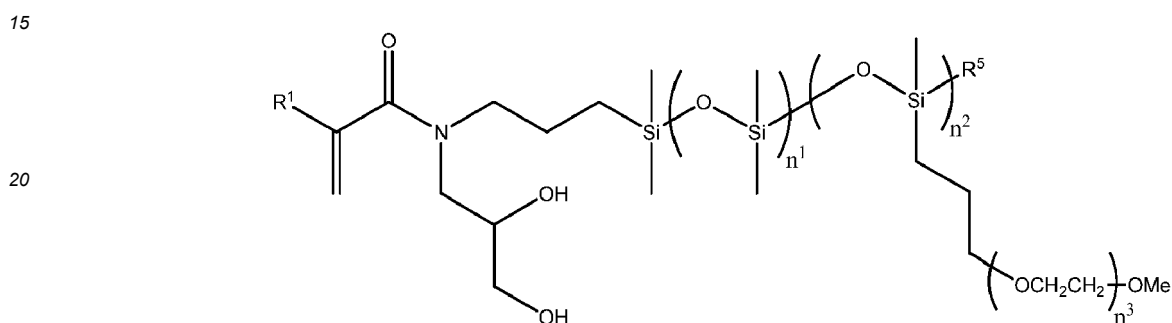
Formule VIIIa



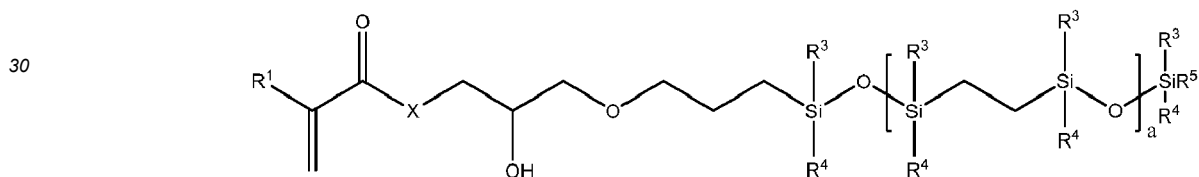
Formule VIIIb



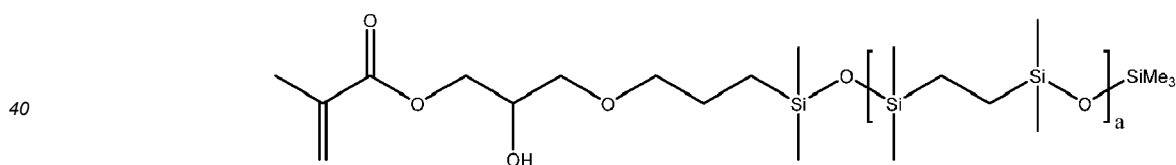
Formule VIIIc



Formule VIIIId



Formule IXa



Formule IXb

45 R^1 étant méthyle ou H ; n étant compris entre 4 et 30, 4 à 8 ou 10 à 20 ;

R^2 étant indépendamment choisi dans le groupe constitué par H ou un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, et qui peut éventuellement être substitué par amide, éther et des combinaisons correspondantes ;

50 n^1 n^2 étant indépendamment compris entre 4 et 100 ; 4 et 50 ; ou 4 et 25 ;

n^3 étant 1 à 50, 1 à 20, ou 1 à 10 ;

R^5 étant choisi parmi des groupes alkyle en C_1 à C_8 linéaires ou ramifiés, qui peuvent éventuellement être substitués par un ou plusieurs groupes hydroxyle, amide, éther, polyhydroxyle choisis parmi des groupes en C_1 à C_8 linéaires ou ramifiés ayant une formule $C_fH_g(OH)_h$ dans laquelle $f = 1$ à 8 et $g + h = 2f + 1$ et des groupes en C_1 à C_8 cycliques ayant une formule $C_fH_g(OH)_h$ dans laquelle $f = 1$ à 8 et $g + h = 2f - 1$, et des combinaisons correspondantes ; ou

55 R^5 pouvant être choisi parmi alkyle en C_2 - C_5 substitué par méthyle, butyle ou hydroxyle, y compris hydroxyléthyle, hydroxylpropyle, hydroxylbutyle, hydroxylpentyle et 2,3-dihydroxypropyle ;

a étant de 4 à 8 pour le premier composant de silicone contenant hydroxyle et entre 4 à 100 pour le deuxième composant de silicone contenant hydroxyle.

20. Hydrogel de silicone selon l'une quelconque des revendications précédentes, le constituant supplémentaire étant choisi parmi un diluant, un composé absorbant des UV, un agent médicinal, un composé antimicrobien, un composé pharmaceutique, un composé nutraceutique, un composé photochromique, une teinture réactive, un pigment, un colorant copolymérisable, un colorant non polymérisable, un agent de libération, un copolymère, et des combinaisons correspondantes ; éventuellement

(a) le composé absorbant des UV étant choisi dans le groupe constitué par des 2-(2'-hydroxyphényl)benzotriazoles, des 2-hydroxybenzophénones, des 2-hydroxyphényltriazines, des oxanilides, des cyanoacrylates, des salicylates, des 4-hydroxybenzoates, et des mélanges correspondants ; ou

(b) le composé absorbant des UV étant choisi dans le groupe constitué par le 2-(2'-hydroxy-5-méthacryloyloxyéthylphényl)-2H-benzotriazole, des dérivés 5-vinyle et 5-isopropényle de 2-(2,4-dihydroxyphényl)-2H-benzotriazole et des 4-acrylates ou 4-méthacrylates de 2-(2,4-dihydroxyphényl)-2H-benzotriazole ou de 2-(2,4-dihydroxyphényl)-1,3-2H-dibenzotriazole, et des mélanges correspondants.

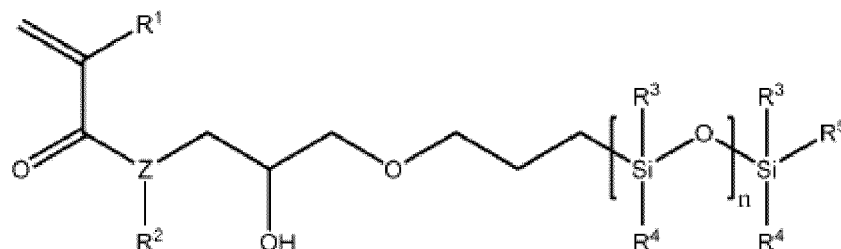
21. Hydrogel de silicone selon l'une quelconque des revendications précédentes, l'hydrogel de silicone ayant une perméabilité à l'oxygène (Dk) d'au moins 80 barrers, ou de 80 à 200 barrers, 90 à 180 barrers, 100 à 160 barrers.

22. Hydrogel de silicone selon l'une quelconque des revendications précédentes, comprenant en outre au moins un monomère chargé comprenant au moins un groupement ionique choisi dans le groupe constitué par des anions, des cations, des zwitterions, des bétaïnes, et des mélanges correspondants.

23. Hydrogel de silicone selon la revendication 1 formé à partir d'un mélange de monomères réactifs comprenant :

a. au moins un (méth)acrylate d'hydroxyalkyle ;

b. un composant de silicone contenant hydroxyle qui comprend un mélange d'un premier poly(dialkylsiloxane) linéaire, substitué par hydroxyle de formule VI,



formule VI

Z étant choisi parmi O, N, S ou NCH₂CH₂O, lorsque Z est O ou S R² n'est pas présent ;

R¹ étant indépendamment H ou méthyle ;

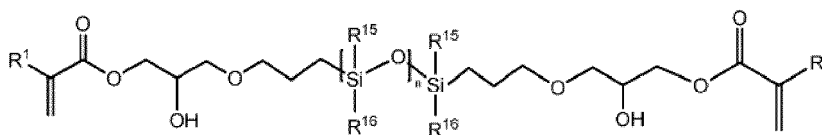
R² étant H ou un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, et qui peut éventuellement être substitué par amide, éther et des combinaisons correspondantes ;

R³ et R⁴ étant indépendamment un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, amide, éther, et des combinaisons correspondantes ; R³ et R⁴ pouvant être indépendamment choisis parmi méthyle, éthyle ou phényle, ou pouvant être méthyle ;

n étant 4 à 8 pour le premier poly(siloxane disubstitué) substitué par hydroxyle monofonctionnel, et, un deuxième poly(dialkylsiloxane) linéaire substitué par hydroxyle choisi dans le groupe constitué par

un poly(dialkylsiloxane) linéaire substitué par hydroxyle monofonctionnel de formule I, n étant 10 à 20 et R¹³ étant choisi parmi des groupes alkyle en C₁ à C₈ linéaires ou ramifiés, éventuellement substitués par un ou plusieurs hydroxyles, amides, éthers, et des combinaisons correspondantes ; et

un poly(dialkylsiloxane) linéaire substitué par hydroxyle multifonctionnel de formule XI ayant 10 à 200, ou 10 à 100 motifs répétitifs de siloxane,



formule XI

R_1 étant indépendamment un atome d'hydrogène ou un groupe méthyle ;

R_{15} et R_{16} étant indépendamment un groupe alkyle linéaire, ramifié ou cyclique contenant un à huit atomes de carbone, l'un quelconque parmi lesquels pouvant être en outre substitué par au moins un groupe hydroxy, des groupes amido, éther, amino, carboxyle, carbonyle et des combinaisons correspondantes ; ou étant indépendamment méthyle ou éthyle ; et

n étant 10 à 200 ; 10 à 100 ; 10 à 50 ; 10 à 20 ;

un rapport du deuxième poly(dialkylsiloxane) linéaire substitué par hydroxyle sur le premier poly(dialkylsiloxane) linéaire substitué par hydroxyle étant dans une plage de 0,1 à 1,3 ou de 0,4 à 1 ;

plus de 15 pour cent en poids, sur la base du poids total du mélange de monomères réactifs, d'au moins un polyamide choisi dans le groupe constitué par PVP, PVMA, PDMA, PNVA, un polyacrylamide, et des copolymères et des mélanges correspondants ; et éventuellement, de l'acide méthacrylique.

24. Hydrogel de silicone selon la revendication 23, comprenant en outre au moins un monomère hydrophile supplémentaire qui est choisi dans le groupe constitué par des *N*-vinylamides, des *N*-vinylimides, des *N*-vinylactames, des (méth)acrylates hydrophiles, des (méth)acrylamides, des styrènes hydrophiles, des éthers de vinyle, des *O*-vinylcarbonates, des *O*-vinylcarbammates, des *N*-vinylurées, d'autres composés vinyliques hydrophiles et des mélanges correspondants.

25. Hydrogel de silicone selon l'une quelconque des revendications 1 à 24, le polyamide ayant un poids moléculaire moyen en poids d'au moins 100 000 Daltons ; ou supérieur à 150 000 Daltons ; ou compris entre 150 000 et 2 000 000 Daltons, ou compris entre 300 000 et 1 800 000 Daltons.

26. Hydrogel de silicone selon l'une quelconque des revendications 1 à 25, le polyamide étant ajouté au mélange réactionnel de sorte que l'hydrogel polymérise autour du polyamide, formant un réseau semi-interpénétrant.

27. Lentille de contact comprenant l'hydrogel de silicone selon l'une quelconque des revendications 1 à 26.

28. Lentille de contact selon la revendication 27,

(a) l'absorption de lipides étant inférieure à 15 pg/lentille, ou inférieure à 10 pg/lentille ; et/ou

(b) l'absorption de PQ1 étant inférieure à 20 % ; et/ou

(c) l'angle de contact dynamique étant inférieur à 95°, ou inférieur à 60° ; et/ou

(d) l'absorption de lysozymes étant d'au moins 50 pg/lentille, d'au moins 100 pg/lentille, d'au moins 200 pg/lentille, d'au moins 500 pg/lentille, d'au moins 700 pg/lentille ou d'au moins 800 pg/lentille ; 50 à 1 500 pg/lentille, 100 à 1 500 pg/lentille, ou 200 à 1 500 pg/lentille.

29. Procédé de fabrication de l'hydrogel de silicone selon l'une quelconque des revendications 1 à 26, le procédé comprenant :

la préparation du mélange de monomères réactifs, et

la soumission du mélange de monomères réactifs à des conditions de polymérisation pour former l'hydrogel de silicone ;

éventuellement, la polymérisation du mélange réactionnel étant initiée en utilisant de la chaleur ou de la lumière visible ou ultraviolette.

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