



(11)

EP 3 181 614 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 2 (W2 B1)
Corrections, see
Description Paragraph(s) 159

(51) International Patent Classification (IPC):
C08G 77/442 ^(2006.01) **C08F 283/12** ^(2006.01)
C08F 290/06 ^(2006.01)

(48) Corrigendum issued on:
05.10.2022 Bulletin 2022/40

(52) Cooperative Patent Classification (CPC):
(C-Sets available)
C08F 283/124; C08F 290/068; C08G 77/442

(45) Date of publication and mention
of the grant of the patent:
30.03.2022 Bulletin 2022/13

(Cont.)

(21) Application number: **16195164.5**

(22) Date of filing: **20.12.2012**

(54) **SILICONE HYDROGELS COMPRISING DESIRABLE WATER CONTENT AND OXYGEN PERMEABILITY**

SILIKONHYDROGELE MIT GEWÜNSCHTEM WASSERGEHALT UND
SAUERSTOFFDURCHLÄSSIGKEIT

HYDROGELS DE SILICIUM COMPRENANT UNE TENEUR EN EAU SOUHAITABLE ET
PRÉSENTANT UNE PERMÉABILITÉ À L'OXYGÈNE

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **23.12.2011 US 201161579683 P**
23.12.2011 US 201161579693 P
19.12.2012 US 201213720277

(43) Date of publication of application:
21.06.2017 Bulletin 2017/25

(60) Divisional application:
21210220.6 / 4 011 940

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
12815933.2 / 2 794 726

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US-A1- 2006 142 525 US-A1- 2010 048 847

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(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets

C08F 283/124, C08F 220/56;

C08F 283/124, C08F 226/10;

C08F 283/124, C08F 226/10, C08F 230/08,

C08F 220/20, C08F 222/102;

C08F 290/068, C08F 220/56;

C08F 290/068, C08F 226/10;

C08F 290/068, C08F 226/10, C08F 220/20,

C08F 222/102

DescriptionField of the Invention

[0001] The present invention relates to silicone hydrogels displaying desirable water content and oxygen permeability.

Background of the Invention

[0002] US 2006/142525 discloses hydrogel copolymers for forming biomedical devices, particularly ophthalmic devices including contact lenses, intraocular lenses and ophthalmic implants. The copolymers are alleged to have a desirable combination of oxygen permeability, tensile modulus, and water content, especially for soft contact lenses.

[0003] Soft contact lenses made from silicone hydrogels offer improved oxygen permeability as compared to soft lenses made from non-silicone materials such as poly(2-hydroxyethyl methacrylate) (HEMA). Initial efforts to make silicone hydrogel contact lenses were hampered by the poor wettability, high modulus, poor clarity, hydrolytic instability or the high cost of raw materials used to make many of these silicone hydrogels. While various solutions have proven somewhat successful for each of these deficiencies, there remains a need for silicone hydrogels that can be made from inexpensive commercially available monomers, and which have excellent wettability (without the need for surface modification), low modulus, good clarity, and hydrolytic stability.

[0004] Silicone hydrogels formulations containing polymeric wetting agents, such as poly(N-vinylpyrrolidone) (PVP) and acyclic polyamides have been disclosed. However, these polymers are quite large and require the use of special compatibilizing components, which need to be custom manufactured. Examples of compatibilizing components include 2-propenoic acid, 2-methyl-,2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (SiGMA).

[0005] An alternative means of forming a wettable silicone hydrogel lens is to incorporate monomeric N-vinylpyrrolidone (NVP) into the monomer mix used to make the silicone hydrogel polymer, typically in amounts of about 25-55% (by weight) of the monomer mix. Such materials have been described in US patents 4,136,250; 4,153,641; 4,260,725 and 6,867,245. The materials described in these references generally incorporate polyfunctional silicone monomers or macromers, that act as crosslinking agents, and thereby increase the modulus of the final polymer. US 4,139,513 discloses that 2-propenoic acid, 2-methyl-,2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (SiGMA) can be used to form lenses from formulations comprising NVP and HEMA. SiGMA is the only source of silicone disclosed. However, because of the relatively low silicone content in those monomers, desirable levels of oxygen permeability in the final polymers are difficult to achieve. There is no disclosure which would suggest how to incorporate silicones which do not comprise compatibilizing functionality into the formulation.

[0006] US 2010/0048847 discloses silicone hydrogels made from a blend of a monomethacryloxyalkyl polydimethylsiloxane methacrylate with about 52% NVP, HEMA and TRIS, and using a blend of ethanol and ethyl acetate as a diluent. The polymers disclosed are (to varying degrees) hazy, but it was disclosed in this application that the haziness could be reduced by the addition of at least about 1.5 % methacrylic acid (MAA).

[0007] Addition of anionic monomers such as MAA can, however, cause hydrolytic instability in silicone hydrogels, as was disclosed in "The role of ionic hydrophilic monomers in silicone hydrogels for contact lens application", Lai, Y., Valint, P., and Friends, G.; 213th ACS National Meeting, San Francisco, April 13-17, 1997. For this reason, it remains desirable to form clear, hydrolytically stable, wettable (without surface treatment) silicone hydrogels with low moduli from a combination of a monomethacryloxyalkyl polydimethylsiloxane methacrylate such as mPDMS, and NVP.

Summary of the Invention

[0008] The invention is defined by the claims.

[0009] The silicone hydrogels of the present invention are useful for making biomedical devices, ophthalmic devices, and particularly contact lenses.

Description of the Figure**[0010]**

Figure 1 is a schematic of a lens assembly.

Figure 2 is a schematic of the cure chamber described herein.

Figure 3 is a schematic of compartment 2 of the cure box show in Figure 2

Figure 4 is a graph of the Dk v. the ratio of ancillary components to reactive mixture (AC/RM) of the data from Examples 3-13.

Detailed Description of the Invention

[0011] The present invention relates to compositions comprising from about 40 to about 60 wt% of at least one slow reacting hydrophilic monomer, at least one at least one mono(meth)acryloxyalkyl polydialkylsiloxane monomer; one hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer, and at least one crosslinking monomer; wherein said at least one hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer and said slow reacting hydrophilic monomer are present in mole percents which form a molar ratio between about 0.15 and 0.4.

[0012] It has been surprisingly found that the formulations of the present invention form hydrogels with a desirable balance of properties. The formulations may be made using a range of diluents, no diluent and in some embodiments may also be cured using light.

[0013] As used herein, "diluent" refers to a diluent for the reactive composition. Diluents do not react to form part of the biomedical devices.

[0014] As used herein, "compatibilizing agent" means a compound, which is capable of solubilizing the selected reactive components. Compatibilizing agents have a number average molecular weight of about less than 5000 Daltons, and in another less than about 3000 Daltons. The compatibilizing agent of the present invention solubilizes via hydrogen bonding, dispersive forces, combinations thereof and the like. Thus, any functionality which interacts in any of these ways with the high molecular weight hydrophilic polymer may be used as a compatibilizing agent. Compatibilizing agents in the present invention may be used in an amount so long as they do not degrade other desirable properties of the resulting ophthalmic device. The amount will depend in part on the amount of high molecular weight hydrophilic polymer used. One class of compatibilizing agents comprises at least one silicone and at least one hydroxyl group. Such components are referred to as "silicone containing compatibilizing component" and have been disclosed in WO03/022321 and WO03/022322.

[0015] As used herein, a "biomedical device" is any article that is designed to be used while either in or on mammalian tissues or fluid, on human tissue or fluids. Examples of these devices include but are not limited to catheters, implants, stents, and ophthalmic devices such as intraocular lenses, punctal plugs and contact lenses. The biomedical devices may be ophthalmic devices, particularly contact lenses, most particularly contact lenses made from silicone hydrogels.

[0016] As used herein, the terms "ophthalmic product" "lens" and "ophthalmic device" refer to devices that reside in or on the eye. These devices can provide optical correction, wound care, drug delivery, diagnostic functionality, cosmetic enhancement or effect, glare reduction, UV blocking or a combination of these properties. Non-limiting examples of ophthalmic devices include lenses, punctal plugs and the like. The term lens (or contact lens) includes but is not limited to soft contact lenses, hard contact lenses, intraocular lenses, overlay lenses, ocular inserts, and optical inserts.

[0017] As used herein "reaction mixture" refers to reactive and non-reactive components (including the diluent) that are mixed together and reacted to form the silicone hydrogels of the present invention. The reactive components are everything in the reaction mixture except the diluent and any additional processing aids which do not become part of the structure of the polymer.

[0018] As used herein "(meth)" refers to an optional methyl substitution. Thus, a term such as "(meth)acrylate" denotes both methacrylic and acrylic radicals.

[0019] All percentages in this specification are weight percentages unless otherwise noted.

[0020] As used herein, the phrase "without a surface treatment" or "not surface treated" means that the exterior surfaces of the devices of the present invention are not separately treated to improve the wettability of the device. Treatments which may be foregone because of the present invention include, plasma treatments, grafting, coating and the like. However, coatings 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.

[0021] As used herein "silicone macromers" and silicone "prepolymers" mean mono- and multi-functional silicone containing compounds having molecular weights of greater than about 2000.

[0022] As used herein "hydroxyl-containing component" is any component containing at least one hydroxyl group.

[0023] As used herein "monovalent reactive groups" are groups that can undergo free radical and/or cationic polymerization. Non-limiting examples of free radical reactive groups include (meth)acrylates, styryls, vinyls, vinyl ethers, C₁₋₆alkyl(meth)acrylates, (meth)acrylamides, C₁₋₆alkyl(meth)acrylamides, N-vinyl lactams, N-vinyl amides, C₂₋₁₂alkenyls, C₂₋₁₂alkenylphenyls, C₂₋₁₂alkenyl naphthyls, C₂₋₆alkenylphenyl C₁₋₆alkyls, O-vinyl carbamates and O-vinyl carbonates. Non-limiting examples of cationic reactive groups include vinyl ethers or epoxide groups and mixtures thereof. Non-limiting examples of the free radical reactive groups include (meth)acrylate, acryloxy, (meth)acrylamide, and mixtures thereof.

[0024] In the present invention the components are selected to react at specific points in the reaction. For example, "fast reacting" components are selected to polymerize primarily at the beginning of the reaction, while the slow reacting hydrophilic monomer is selected to polymerize primarily at the end of the reaction. Fast reacting components include the silicone-containing components, the hydroxyalkyl monomers and some crosslinkers.

In one embodiment, slow reacting components have kinetic half lives which are at least about two times greater than

the fastest silicone containing monomer. Kinetic half lives may be measured as described herein. It should be appreciated that the kinetic half lives are relative to specific formulations.

[0025] Examples of slow reacting groups include (meth)acrylamides, vinyls, allyls and combinations thereof and a least one hydrophilic group. In another embodiment the slow reacting group is selected from N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group. In yet another embodiment the slow reacting group is selected from N-vinyl amides, O-vinyl carbonates, and O-vinyl carbamates.

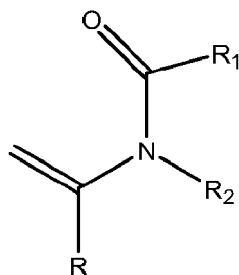
[0026] Examples of fast reacting groups include (meth)acrylates, styryls, methacryamides and mixtures thereof. Generally (meth)acrylates are faster than (meth)acrylamides, and acrylamides are faster than (meth)acrylamides

[0027] Throughout the specification, 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_1 and R_2 , each of which contained three lists of potential groups, 9 combinations are disclosed. The same applies for combinations of properties.

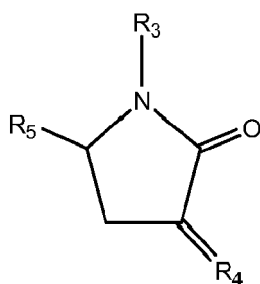
[0028] The present invention relates silicone hydrogels which display a balance of desirable properties, particularly a bulk water content of at least about 50%, at least about 55% and at least about 60%, with oxygen permeabilities of at least about 85 barrers, about least about 90 barrers, at least about 100 barrers, from about 85 to about 150 barrers, and from about 85 to 130 barrers. It is a surprising benefit of the present invention that both the water contents and the oxygen permeabilities can be achieved in the same lens.

[0029] The silicone hydrogels of the present invention may be formed from a combination of three components, at least one slow-reacting hydrophilic monomer, at least one silicone-containing monomer and at least one hydroxyalkyl monomer. Applicants have found that by controlling the amount of the components other than the slow-reacting monomer and silicone containing components to about 11 to about 92 mmol/gm of reactive components, silicone hydrogels having combination of water content and oxygen permeability described herein may be produced. The silicone hydrogels of the present invention are in one embodiment particularly well suited for contact lenses as they transmit levels of oxygen desirable for healthy corneal function and have water contents which approach those of the ocular environment.

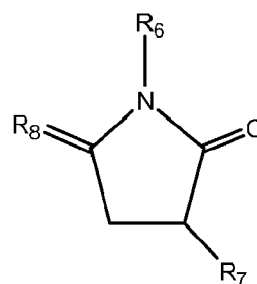
[0030] The first component of the reactive mixture is a slow reacting component selected from N-vinylamide monomers of Formula I, vinyl pyrrolidones of Formula II-IV, n-vinyl piperidone of Formula V:



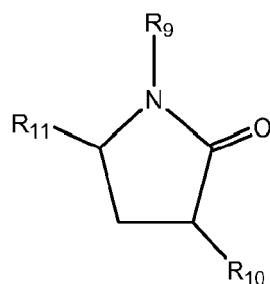
Formula I



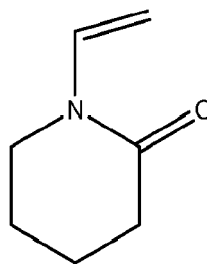
Formula II



Formula III



Formula IV



Formula V

wherein R is H or methyl, preferably R is H;

$R_1, R_2, R_3, R_6, R_7, R_{10}$, and R_{11} are independently selected from H, CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$, $C(CH_3)_2$; R_4 and R_8 are independently selected from CH_2 , $CHCH_3$ and $-C(CH_3)_3$; R_5 is selected from H, methyl, ethyl; and R_9 is selected from $CH=CH_2$, $CCH_3=CH_2$, and $CH=CHCH_3$.

[0031] The total number of carbon atoms in R_1 and R_2 may be 4 or less, R_1 and R_2 maybe methyl.

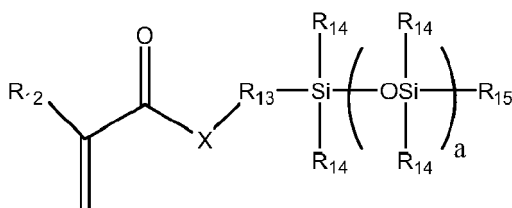
[0032] The slow-reacting hydrophilic monomer may be selected from the N-vinyl amide monomer of Formula I or a vinyl pyrrolidone of Formula II or IV. Suitably R_6 is methyl, R_7 is hydrogen, R_9 is $CH=CH_2$, R_{10} and R_{11} are H.

[0033] The slow-reacting hydrophilic monomer may be selected from ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), N-vinyl lactams, including N-vinyl pyrrolidone (NVP), 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-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-carboxyvinyl- β -alanine (VINAL), N-carboxyvinyl- α -alanine and mixtures thereof.

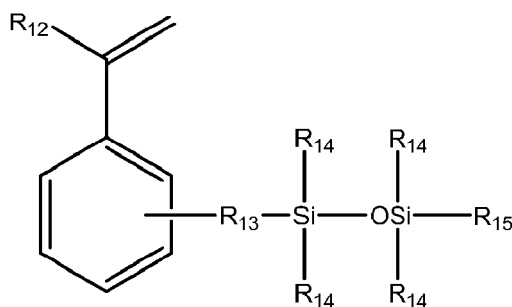
[0034] The slow-reacting hydrophilic monomer may be selected from NVP, VMA and 1-methyl-5-methylene-2-pyrrolidone. The slow-reacting hydrophilic monomer may comprise NVP.

[0035] The slow reacting hydrophilic monomer is present in amounts to provide wettability to the resulting polymer. Wettability may be measured via advancing contact angle, and desirable contact angles are less than about 80° , less than about 70° and in some embodiments less than about 60° . The slow reacting hydrophilic monomer may be present in amounts between about 30 and about 75 wt%, between about 37 and about 75 wt%, between about 30 and about 70 wt%, between about 37 and about 70 wt%, and between about 39 and about 60 wt%, all based upon all reactive components.

[0036] The at least one silicone-containing monomer is monofunctional and comprises (a) a fast reacting group and (b) a polydialkyl siloxane chain. The silicon-containing monomer may comprise a fast reacting group selected from (meth)acrylates, styryls, (meth)acrylamides and mixtures thereof. The at least one silicone-containing monomer may also contain at least one fluorine. The silicone-containing component may be selected from mono (meth)acryloxyalkyl polydialkylsiloxane and mono (meth)acrylamide alkyl polydialkylsiloxane monomer of Formula VII or the styryl polydialkylsiloxane monomer of Formula VIII:



Formula VII



Formula VIII

wherein R_{12} is H or methyl;

X is O or NR_{16} ;

Each R_{14} is independently a phenyl or C_1 to C_4 alkyl which may be substituted with fluorine, hydroxyl or ether, or each R_{14} is independently selected from ethyl and methyl groups, All R_{14} may be methyl;

R_{15} is a C_1 to C_4 alkyl;

R_{13} is a divalent alkyl group, which may further be functionalized with a group selected from the group consisting of ether groups, hydroxyl groups, carbamate groups and combinations thereof, C_1 - C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof, or C_1 or C_3 - C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof;

a is 2 to 50, or 5 to 15.

R_{16} is selected from H, C_{1-4} alkyl, which may be further substituted with one or more hydroxyl groups, or H or methyl.

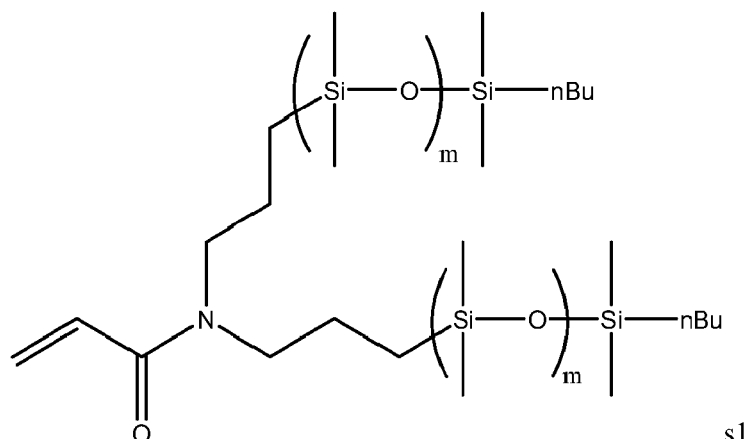
R_{12} and each R_{14} may be methyl.

[0037] At least one R_{14} may be 3,3,3-trifluoropropyl.

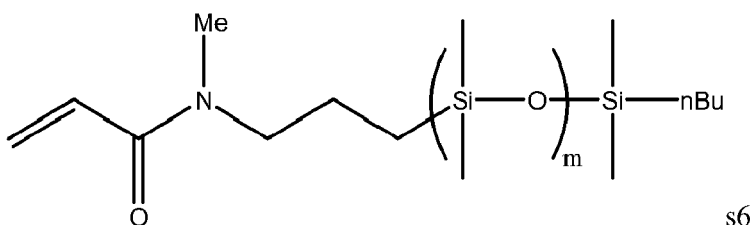
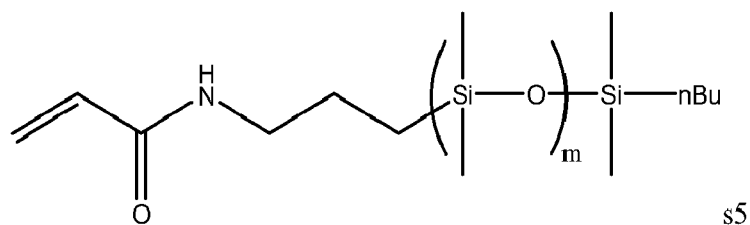
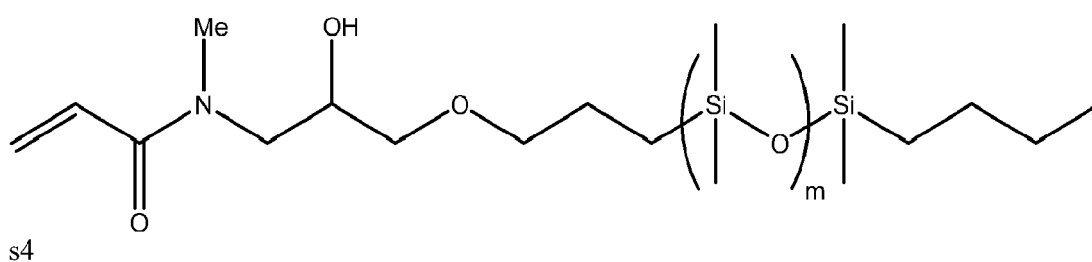
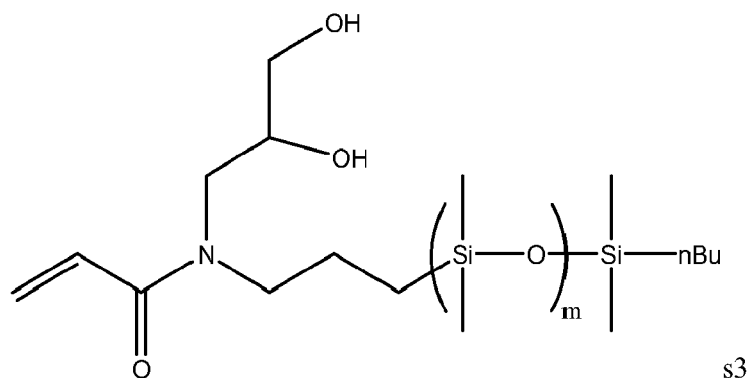
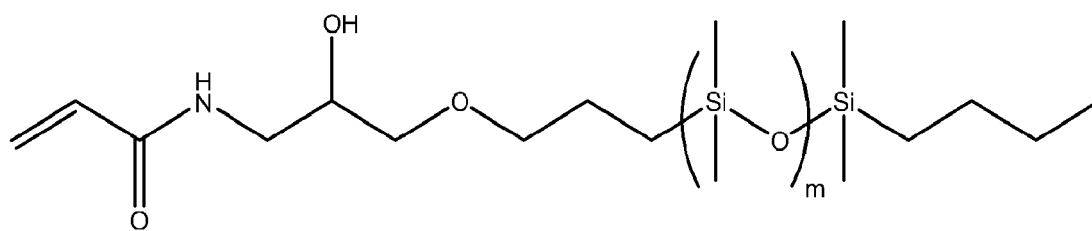
[0038] Examples of suitable silicone-containing monomers include monomethacryloxyalkylpolydimethylsiloxane methacrylates selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, α -(2-hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-decamethylpentasiloxane, and mixtures thereof.

[0039] The silicone-containing component may be selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, α -(2-hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-decamethylpentasiloxane, and mixtures thereof.

[0040] The silicone containing component may be selected from acrylamide silicones of USSN 13/048469, US20110237766, and particularly the silicone monomers expressed in the following general formulae (s1) through (s6).



s1



wherein m is 4-12 or 4-10.

[0041] Additional silicone containing components containing one or more polymerizable groups may also be included. Any additional disclosed silicone components having the herein disclosed reactive groups may be included. Examples

include silicone containing monomers displaying branched siloxane chains such as SiMAA.

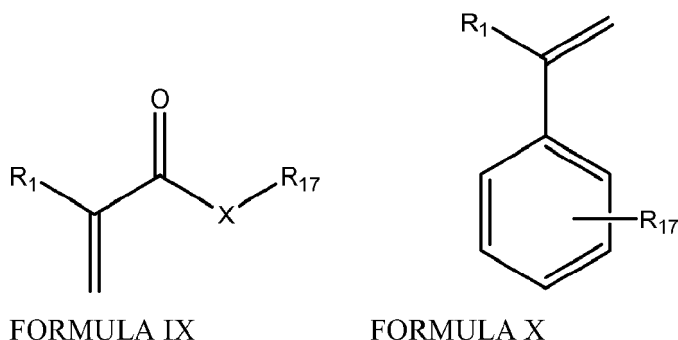
[0042] The at least one silicone-containing component is present in the reactive mixture in an amount sufficient to provide the desired oxygen permeability. It is a benefit of the present invention that oxygen permeabilities greater than about 70 barrer, greater than about 80 barrer, greater than about 90 barrer, or greater than about 100 barrer may be

achieved. Suitable amounts will depend on the length of the siloxane chain included in the silicone-containing monomers, with silicone-containing monomers having longer chains requiring less monomer. Amounts include from about 20 to about 60 weight%, or from about 30 to about 55 weight %.

[0043] The total amount of silicon in the reactive mixture (excluding diluent) may be between about 9 and 14 wt% and between about 9 and 13%. Limiting the amount of silicon, in combination balancing the amount of the slow-reacting hydrophilic monomer and the other reactive components, provides the desirable combination of properties achieved by the present invention. It is a benefit of the present application that silicone hydrogels having the combination oxygen permeabilities and water contents may be formed with only moderate amounts (less than 14 wt%) silicon.

[0044] The reaction mixture may comprise less than about 10 wt% TRIS, less than 5 wt% TRIS or may be substantially free of TRIS. The silicone hydrogels may also be made without silicone containing macromers or prepolymers.

[0045] The reactive mixtures of the present invention further comprise at least one hydroxyalkyl monomer selected from hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer of Formula IX or a styryl compound of Formula X



wherein R_1 is H or methyl,

X is O or NR_{16} , R_{16} is a H, C_1 to C_4 alkyl, which may be further substituted with at least one OH, methyl or 2-hydroxyethyl; and

R_{17} is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; 2-hydroxyethyl, 2,3-dihydroxypropyl, 2-hydroxypropyl.

[0046] Suitably, R_1 is H or methyl, X is oxygen and R is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units. Suitably, R_1 methyl, X is oxygen and R is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 2-20 repeating units. Suitably, R_1 methyl, X is oxygen and R is selected from C_2 - C_4 mono or dihydroxy substituted alkyl. In one embodiment, at least one hydroxyl group is on the terminal end of the R alkyl group.

[0047] Examples of suitable hydroxyalkyl monomer include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (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, 2-hydroxyethyl (meth)acrylamide, polyethyleneglycol monomethacrylate, bis-(2-hydroxyethyl) (meth)acrylamide, 2,3-dihydroxypropyl (meth)acrylamide, and mixtures thereof.

[0048] The hydroxyalkyl monomer may 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.

[0049] The hydroxyalkyl monomer may comprise 2-hydroxyethyl methacrylate, and in another embodiment comprises 3-hydroxy-2,2-dimethyl-propyl methacrylate. The reactive hydroxyalkyl monomer may comprise glycerol methacrylate.

[0050] The hydroxyl containing components may have the same reactive functionality as the silicone-containing monomers.

[0051] The hydroxyalkyl monomers are present in mole percents which form a molar ratio of hydroxyl groups to slow reacting hydrophilic monomer of at least about 0.15 or between about 0.15 and about 0.4. This is calculated by dividing the number of moles of hydroxyl groups in the hydroxyalkyl monomers (including any hydroxyl groups on the slow-reacting hydrophilic monomer and the silicone-containing monomer) by the number of moles of the slow-reacting hydrophilic monomer per a given mass of the monomer mix. In this case, for a reaction mixture comprising HO-mPDMS, HEMA, EGVE and NVP, the hydroxyl groups on each of HO-mPDMS, HEMA and EGVE would be counted. Any hydroxyl groups present in the diluent (if used) are not included in the calculation. The lower amount of hydroxyalkyl monomers may be selected to provide a haze value to the final lens of less than about 50% and in some embodiments less than about 30%.

[0052] Alternatively, the molar ratio of hydroxyl groups in the reaction mixture to silicon (HO:Si) may be between about

0.16 and about 0.4. The molar ratio is calculated by dividing molar concentration of hydroxyl groups in the components of the reactive mixture (other than any hydroxyls which are part of the slow-reacting hydrophilic monomer or diluents) by the molar concentration of silicon. In this case, both the hydroxyalkyl monomers and any hydroxyl-containing silicone components are included in the calculation. Thus, in calculating the HO:Si ratio of the reaction mixture comprising HO-mPDMS, HEMA, EGVE and NVP, only the hydroxyl groups on each of HO-mPDMS, HEMA would be counted in calculating the HO:Si.

[0053] Alternatively, the molar ratio of hydroxyl groups in non-silicone containing components (other than any hydroxyls which are part of the slow-reacting hydrophilic monomer or diluents) to silicon is between about 0.13 and about 0.35, about 0.13 and about 0.3, and about 0.13 and about 0.25. Thus, in calculating the $\text{HO}_{\text{non-Si}}:\text{Si}$ ratio of the reaction mixture comprising HO-mPDMS, HEMA, EGVE, and NVP only the hydroxyl groups on, HEMA would be counted in calculating the $\text{HO}_{\text{non-Si}}:\text{Si}$ ratio.

[0054] It will be appreciated that the minimum 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 or absence of hydrophilic functionality on the silicone containing components. For example, where HEMA is used as the hydroxyalkyl monomer and mPDMS is used in amounts about 38wt% as the sole silicone containing monomer, at least about 8wt% HEMA (0.16 HO:Si) is included to provide the desired haze values. However, when lesser amounts of mPDMS are used (about 20%), as little as about 2 or 3% HEMA provides silicone hydrogel contact lenses having haze values below about 50%.

[0055] The reactive mixture may further comprise additional hydrophilic monomers. Any hydrophilic monomers used to prepare hydrogels may be used. For example monomers containing acrylic groups ($\text{CH}_2=\text{CROX}$, where R is hydrogen or C_{1-6} alkyl and X is O or N) or vinyl groups ($-\text{C}=\text{CH}_2$) may be used. Examples of additional hydrophilic monomers are N,N-dimethylacrylamide, polyethyleneglycol monomethacrylate, methacrylic acid, acrylic acid, combinations thereof and the like. If the additional hydrophilic monomers are not slow reacting monomers as defined herein, their concentrations in the formulations of the present invention may be limited to concentrations which do not provide the lens with a contact angle higher than about 80° . As used herein, "intermediate" half life is one that is between 20% and 70% faster than the slowest reacting silicone component. For example, if the additional hydrophilic monomer has a kinetic half life which is between the half lives of the vinyl containing monomer and the silicone components, (such as N,N-dimethylacrylamide), the amount of the additional hydrophilic monomer is limited to below about 3 wt%. In embodiments where the lens is to be surface modified, higher amounts of additional monomers may be included.

[0056] The total amount of reactive components other than silicone-containing components and slow-reacting hydrophilic components ("ancillary components") is between about 11 and about 92 mmol ancillary components/100 gm reactive mixture and between about 38 and about 76 mmol ancillary components/100 gm reactive mixture. In another embodiment the amount of fast or intermediate curing ancillary reactive components is between about 11 and about 92 mmol ancillary components/100 gm reactive mixture and between about 38 and about 76 mmol ancillary components/gm reactive mixture.

[0057] Ancillary components include non-silicone containing hydroxyalkyl monomer, additional hydrophilic monomers which are not slow reacting as defined herein, and additional components including, crosslinkers, reactive tints, dyes and pigments, and combinations thereof.

[0058] The reaction mixtures of the present invention may further comprise at least one crosslinker. A crosslinker is a monomer with two or more polymerizable double bonds. Suitable crosslinkers include ethylene glycol dimethacrylate ("EGDMA"), trimethylolpropane trimethacrylate ("TMPTMA"), glycerol trimethacrylate, polyethylene glycol dimethacrylate (wherein the polyethylene glycol preferably has a molecular weight up to, e.g., about 5000), and other polyacrylate and polymethacrylate esters, such as the end-capped polyoxyethylene polyols described above containing two or more terminal methacrylate moieties. The crosslinker 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. Where the hydrophilic monomers and/or the silicone containing monomers act as the cross-linking agent, the addition of an additional crosslinking agent to the reaction mixture is optional. Examples of hydrophilic monomers which can act as the crosslinking agent and when present do not require the addition of an additional crosslinking agent to the reaction mixture include polyoxyethylene polyols described above containing two or more terminal methacrylate moieties.

[0059] An example of a silicone containing monomer which can act as a crosslinking agent and, when present, does not require the addition of a crosslinking monomer to the reaction mixture includes α , ω -bismethacryloxypropyl polydimethylsiloxane.

[0060] The reaction mixtures can also contain multiple crosslinkers depending on the reaction rate of the hydrophilic component. With very slow reacting hydrophilic components (e.g. VMA, EGVE, DEGVE) crosslinkers having slow reacting functional groups (e.g. di-vinyl, tri-vinyl, di-allyl, tri-allyl) or a combination of slow reacting functional groups and fast reacting functional groups (e.g. HEMAvc) can be combined with crosslinkers having fast reacting functional groups ((meth)acrylates) to improve the retention of the polymers of the slow-reacting monomers in the final hydrogel.

[0061] The reaction mixture may also comprise at least two crosslinkers, at least one first crosslinker having at least

two fast reacting groups which will react with the silicone components and hydroxyl alkyl (meth)acrylates and at least one second crosslinker having at least two slow reacting groups which react with the slow reacting hydrophilic monomer. This mixture of fast and slow reacting crosslinkers provides the final polymer with improved resilience and recovery, particularly on the surface of the lens. Examples of suitable first crosslinkers include those having only (meth)acrylate functionality, such as EGDMA, TEGDMA and combinations thereof. Examples of suitable second crosslinkers include those having only vinyl functionality, such as triallyl cyanurate (TAC). When mixtures are used, suitable total amounts of all crosslinker in the reactive mixture include between about 0.10% and about 2%, or about 0.1 to about 1 % wt, excluding diluent respectively. The total amount of all crosslinker in the reactive mixtures may be between 0.7 to about 6.0 mmol/100 g of polymerizable components; between about 0.7 to about 4.0 mmoles per 100 g of reactive components. The fast and slow reacting crosslinkers are present in respective amounts of about 0.3 to about 2.0 mmol/100 g of polymerizable components and between about 0.4 to about 2.0 mmoles per 100 g of reactive components.

[0062] The reaction mixture may also comprise at least one UV absorbing compound. When the silicone hydrogel will be used as an ophthalmic device it may be desirable to incorporate a reactive UV absorbing compound in the reaction mixture so that the resulting silicone hydrogel will be UV absorbing. Suitable UV absorbers may be derived from 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyltriazines, oxanilides, cyanoacrylates, salicylates and 4-hydroxybenzoates; which may be further reacted to incorporate reactive polymerizable groups, such as (meth)acrylates. Specific examples of UV absorbers which include polymerizable groups include 2-(2'-hydroxy-5-methacryloyloxyethylphenyl)-2H-benzotriazole (Norbloc), 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, mixtures thereof and the like. When a UV absorber is included, it may be included in amounts between about 0.5 and about 4 wt%, or between about 1 wt% and about 2 wt%.

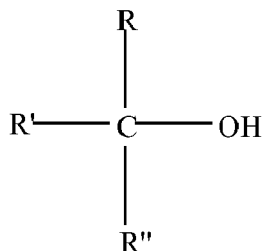
[0063] A polymerization initiator is preferably included in the reaction mixture. The reaction mixtures of the present invention comprise at least one thermal, photoinitiator or a mixture thereof. The use of photoinitiation provides desirable cure times (time to reach essentially complete cure) of less than about 30 minutes, less than about 20 minutes or less than about 15 minutes. Suitable photoinitiator systems include 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-phenylpropan-1-one, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (DMBAPO), 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. Commercially available visible light initiator systems include Irgacure 819, Irgacure 1700, Irgacure 1800, Irgacure 819, Irgacure 1850 (all from Ciba Specialty Chemicals) and Lucirin TPO initiator (available from BASF). Commercially available UV photoinitiators include Darocur 1173 and Darocur 2959 (Ciba Specialty Chemicals). These and other photoinitiators which may be used are disclosed in Volume III, Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition by J.V. Crivello & K. Dietliker; edited by G. Bradley; John Wiley and Sons; New York; 1998. Suitable thermal initiators include lauryl peroxide, benzoyl peroxide, isopropyl percarbonate, azobisisobutyronitrile, and the like. The initiator is used in the reaction mixture in effective amounts to initiate polymerization of the reaction mixture, e.g., from about 0.1 to about 2 parts by weight per 100 parts of reactive monomer.

[0064] The reaction mixture may also comprise at least one diluent or may be "neat". If a diluent is used, the selected diluents should solubilize the components in the reactive mixture. It will be appreciated that the properties of the selected hydrophilic and hydrophobic components may affect the properties of the diluents which will provide the desired compatibilization. For example, if the reaction mixture contains only moderately polar components, diluents having moderate δ_p may be used. If however, the reaction mixture contains strongly polar components, the diluent may need to have a high δ_p . However, as the diluent becomes more hydrophobic, processing steps necessary to replace the diluent with water will require the use of solvents other than water. This may undesirably increase the complexity and cost of the manufacturing process. Thus, it is important to select a diluent which provides the desired compatibility to the components with the necessary level of processing convenience.

[0065] The type and amount of diluent used also effects the properties of the resultant polymer and article. The haze, wettability and modulus of the final article may be improved by selecting relatively hydrophobic diluents and/or decreasing the concentration of diluent used.

[0066] Diluents useful in preparing the devices of this invention include polar diluents such as ethers, esters, amides, alcohols, carboxylic acids and combinations thereof. Amides, carboxylic acids and alcohols are preferred diluents, and secondary and tertiary alcohols are more preferred alcohol diluents.

[0067] Examples of alcohols useful as diluents for this invention include those having the formula



wherein R, R' and R'' are independently selected from H, a linear, branched or cyclic monovalent alkyl having 1 to 10 carbons which may optionally be substituted with one or more groups including halogens, ethers, esters, aryls, amines, amides, alkenes, alkynes, carboxylic acids, alcohols, aldehydes, ketones or the like, or any two or all three of R, R' and R'' can together bond to form one or more cyclic structures, such as alkyl having 1 to 10 carbons which may also be substituted as just described, with the proviso that no more than one of R, R' or R'' is H.

[0068] It is preferred that R, R' and R'' are independently selected from H or unsubstituted linear, branched or cyclic alkyl groups having 1 to 7 carbons. It is more preferred that R, R', and R'' are independently selected from unsubstituted linear, branched or cyclic alkyl groups having 1 to 7 carbons. The preferred diluent may have 4 or more, more preferably 5 or more total carbons, because the higher molecular weight diluents have lower volatility, and lower flammability. When one of the R, R' and R'' is H, the structure forms a secondary alcohol. When none of the R, R' and R'' are H, the structure forms a tertiary alcohol. Tertiary alcohols are more preferred than secondary alcohols. The diluents are preferably inert and easily displaceable by water when the total number of carbons is five or less.

[0069] Examples of useful secondary alcohols include 2-butanol, 2-propanol, menthol, cyclohexanol, cyclopentanol and exonorborneol, 2-pentanol, 3-pentanol, 2-hexanol, 3-hexanol, 3-methyl-2-butanol, 2-heptanol, 2-octanol, 2-nonanol, 2-decanol, 3-octanol, norborneol, and the like.

[0070] Examples of useful tertiary alcohols include tert-butanol, tert-amyl alcohol, 2-methyl-2-pentanol, 2,3-dimethyl-2-butanol, 3-methyl-3-pentanol, 1-methylcyclohexanol, 2-methyl-2-hexanol, 3,7-dimethyl-3-octanol, 1-chloro-2-methyl-2-propanol, 2-methyl-2-heptanol, 2-methyl-2-octanol, 2,2-methyl-2-nonanol, 2-methyl-2-decanol, 3-methyl-3-hexanol, 3-methyl-3-heptanol, 4-methyl-4-heptanol, 3-methyl-3-octanol, 4-methyl-4-octanol, 3-methyl-3-nonanol, 4-methyl-4-nonanol, 3-methyl-3-octanol, 3-ethyl-3-hexanol, 3-methyl-3-heptanol, 4-ethyl-4-heptanol, 4-propyl-4-heptanol, 4-isopropyl-4-heptanol, 2,4-dimethyl-2-pentanol, 1-methylcyclopentanol, 1-ethylcyclopentanol, 1-ethylcyclopentanol, 3-hydroxy-3-methyl-1-butene, 4-hydroxy-4-methyl-1-cyclopentanol, 2-phenyl-2-propanol, 2-methoxy-2-methyl-2-propanol, 2,3,4-trimethyl-3-pentanol, 3,7-dimethyl-3-octanol, 2-phenyl-2-butanol, 2-methyl-1-phenyl-2-propanol and 3-ethyl-3-pentanol, and the like.

[0071] Examples of useful carboxylic acids include C₂-C₁₆, carboxylic acids, with one or two carboxylic acid groups and optionally a phenyl group. Specific examples include acetic acid, decanoic acid, dodecanoic acid, octanoic acid, benzylic acid, combinations thereof and the like.

[0072] A single alcohol or mixtures of two or more of the above-listed alcohols or two or more alcohols according to the structure above can be used as the diluent to make the polymer of this invention.

[0073] The diluent may be selected from secondary and tertiary alcohols having at least 4 carbons. Suitable examples include tert-butanol, tert-amyl alcohol, 2-butanol, 2-methyl-2-pentanol, 2,3-dimethyl-2-butanol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, 3,7-dimethyl-3-octanol. It has been found secondary and tertiary alcohols having at least 4 carbon atoms, even in relatively low amounts, have a beneficial effect on the modulus of the final polymer. These alcohols, such as t-amyl alcohol, even in amounts as low as 20-20 wt%, can lower the modulus of the resulting polymer by about 20%.

[0074] The diluent may also be selected from hexanol, heptanol, octanol, nonanol, decanol, tert-butyl alcohol, 3-methyl-3-pentanol, isopropanol, t amyl alcohol, ethyl lactate, methyl lactate, i-propyl lactate, 3,7-dimethyl-3-octanol, dimethyl formamide, dimethyl acetamide, dimethyl propionamide, N methyl pyrrolidinone and mixtures thereof. Additional diluents useful for this invention are disclosed in US patent 6,020,445, US20100280146.

[0075] The diluent may be selected from t-amyl alcohol, 3-methyl-3-pentanol, 3,7-dimethyl-3-octanol, decanoic acid, and combinations thereof and the like.

[0076] The diluent may be water soluble at processing conditions and readily washed out of the lens with water in a short period of time. Suitable water soluble diluents include 1-ethoxy-2-propanol, 1-methyl-2-propanol, t-amyl alcohol, tripropylene glycol methyl ether, isopropanol, 1-methyl-2-pyrrolidone, N,N-dimethylpropionamide, ethyl lactate, dipropylene glycol methyl ether, mixtures thereof and the like. The use of a water soluble diluent allows the post molding process to be conducted using water only or aqueous solutions which comprise water as a substantial component.

[0077] The diluents may be used in amounts up to about 40% by weight of the total of all components in the reactive mixture. The diluent(s) may be used in amounts less than about 30%, or between about 5 and about 20% by weight of the total of all components in the reactive mixture.

[0078] The diluent may also comprise additional components to lower the modulus of the resulting polymers and improve the lens curing efficiency and reducing residuals. Components capable of increasing the viscosity of the reactive mixture and/or increasing the degree of hydrogen bonding with the slow-reacting hydrophilic monomer, are desirable. Suitable components include polyamides, polylactams, such as PVP and copolymers thereof, polyols and polyol containing components such as glycerin, boric acid, boric acid glycerol esters, polyalkylene glycols, combinations thereof and the like.

[0079] Suitable polylactams include PVP and copolymers comprising repeating units from NVP and hydrophilic monomers. In one embodiment, the polylactam is selected from, PVP, and the polyamide comprises DMA.

[0080] When polyamides or polylactams are used they have a molecular weight of between about K12-K120 (about 3900 to about 3,000,000 Dalton M_w) or from K30 to K90 (about 42,000 to about 1,300,000 Dalton M_w).

[0081] Suitable polyalkylene glycols include polyethylene glycol and polypropylene glycols having molecular weight up to about 350 also optionally less than about 200 gm/mol.

[0082] When used, the polyols and polyol containing components are used in amounts less than about 5 wt% or from about 0.2 to about 5 wt%. The diluents and codiluents of the present invention also reduce the residuals remaining in the polymer at the end of the photocure. This provides lenses with more consistent properties, including diameter. The residual slow-reacting hydrophilic component present at the end of cure may be less than about 2 wt% of the lens ((wt of residual component/wt of cured polymer) * 100%), less than about 1 wt% and in some cases less than about 0.8 wt%. The reduction in residuals also leads to more consistent lens properties, including lens diameters, which can vary by less than about 0.05 mm.

[0083] The reactive mixture may contain additional components such as, but not limited to, medicinal agents, antimicrobial compounds, reactive tints, pigments, copolymerizable and non-polymerizable dyes, including UV blockers, photochromic compounds, spectral filtering dyes, release agents and combinations thereof.

[0084] The range of slow-reacting hydrophilic monomer in the reaction mixture include from about 37 to about 70wt%, from about 39 to about 60 weight percent. The hydroxyalkyl monomers are present in amounts suitable to provide a molar ratio of hydroxyalkyl monomer to slow-reacting hydrophilic monomer of about 0.15 to about 0.4. Suitable ranges of silicone-containing component(s) are from about 20 to about 60 weight%, or from about 30 to about 55 weight % of the reactive components in the reaction mixture. The reaction mixtures also comprise from about 0.2 to about 3 weight % of a crosslinking monomer, from about 0 to about 3 weight % of a UV absorbing monomer, (all based upon the weight % of all reactive components) and where diluent is desired, about 20 to about 60 weight % (weight % of all components, both reactive and non-reactive) of one or more of the claimed diluents. It should be appreciated that the foregoing ranges may be combined in any permutation.

[0085] In one embodiment the hydroxyalkyl monomer comprises GMMA and the diluent comprises t-amyl alcohol.

[0086] The reaction mixtures of the present invention can be formed by any of the methods known to those skilled in the art, such as shaking or stirring, and used to form polymeric articles or devices by known methods.

[0087] For example, the biomedical devices of the invention may be prepared by mixing reactive components and the diluent(s) with a polymerization initiator and curing by appropriate conditions to form a product 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 cured into the appropriate article.

[0088] Various processes are known for processing the reaction mixture in the production of contact lenses, including spincasting and static casting. Spincasting methods are disclosed in U.S. Pat. Nos. 3,408,429 and 3,660,545, and static casting methods are disclosed in U.S. Pat. Nos. 4,113,224 and 4,197,266. The method for producing contact lenses comprising the polymer of this invention may be 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, i.e., water-swollen polymer, and the reaction mixture is subjected to conditions whereby the monomers polymerize, to thereby produce a polymer/diluent mixture in the shape of the final desired product.

[0089] Referring to Fig. 1, a diagram is illustrated of an ophthalmic lens 100, such as a contact lens, and mold parts 101-102 used to form the ophthalmic lens 100. The mold parts may include a back surface mold part 101 and a front surface mold part 102. As used herein, the term "front surface mold part" refers to the mold part whose concave surface 104 is a lens forming surface used to form the front surface of the ophthalmic lens. Similarly, the term "back surface mold part" refers to the mold part 101 whose convex surface 105 forms a lens forming surface, which will form the back surface of the ophthalmic lens 100. Mold parts 101 and 102 may be of a concavo-convex shape, preferably including planar annular flanges, which surround the circumference of the uppermost edges of the concavo-convex regions of the mold parts 101-102.

[0090] Typically, the mold parts 101-102 are arrayed as a "sandwich". The front surface mold part 102 is on the bottom, with the concave surface 104 of the mold part facing upwards. The back surface mold part 101 can be disposed symmetrically on top of the front surface mold part 102, with the convex surface 105 of the back surface mold part 101 projecting partially into the concave region of the front surface mold part 102. The back surface mold part 101 may be

dimensioned such that the convex surface 105 thereof engages the outer edge of the concave surface 104 of the front mold part 102 throughout its circumference, thereby cooperating to form a sealed mold cavity in which the ophthalmic lens 100 is formed.

[0091] The mold parts 101-102 may be fashioned of thermoplastic and are transparent to polymerization-initiating actinic radiation, by which is meant that at least some, and sometimes all, radiation of an intensity and wavelength effective to initiate polymerization of the reaction mixture in the mold cavity can pass through the mold parts 101-102.

[0092] For example, thermoplastics suitable for making the mold parts can include: polystyrene; polyvinylchloride; polyolefin, such as polyethylene and polypropylene; copolymers or mixtures of styrene with acrylonitrile or butadiene, polyacrylonitrile, polyamides, polyesters, cyclic olefin copolymers such as Topas available from Ticona or Zeonor available from Zeon, copolymers and blends of any of the foregoing, or other known material.

[0093] Following polymerization of the reaction mixture to form a lens 100, the lens surface 103 will typically adhere to the mold part surface 104. The steps of the present invention facilitate release of the surface 103 from the mold part surface. The first mold part 101 can be separated from the second mold part 102 in a demolding process. The lens 100 may have adhered to the second mold part 102 (i.e. the front curve mold part) during the cure process and remain with the second mold part 102 after separation until the lens 100 has been released from the front curve mold part 102. Alternatively, the lens 100 can adhere to the first mold part 101.

[0094] The lens 100 may be released from the mold by any process, including contacting with a solvent or dry release. For example, the lens 100 and the mold part to which it is adhered after demolding may be contacted with an aqueous solution. The aqueous solution can be heated to any temperature below the boiling point of the aqueous solution. Heating can be accomplished with a heat exchange unit to minimize the possibility of explosion, or by any other feasible means or apparatus for heating a liquid.

[0095] As used herein, processing includes the steps of removing the lens from the mold and removing or exchanging the diluent with an aqueous solution. The steps may be done separately, or in a single step or stage. The processing temperature may be any temperatures between about 30°C and the boiling point of the aqueous solutions, for example between about 30°C and about 95°C, or between about 50°C and about 95°C.

[0096] The aqueous solution is primarily water. The aqueous solution may be at least about 70 wt% water, at least about 90 weight % water or at least about 95%. The aqueous solution may also be a contact lens packaging solution such as borate buffered saline solution, sodium borate solutions, sodium bicarbonate solutions and the like. The aqueous solution may also include additives, such as surfactants, preservatives, release aids, antibacterial agents, pharmaceutical and nutraceutical components, lubricants, wetting agents, salts, buffers, mixtures thereof and the like. Specific examples of additives which may be included in the aqueous solution include Tween 80, which is polyoxyethylene sorbitan monooleate, Tyloxapol, octylphenoxy (oxyethylene) ethanol, amphoteric 10), EDTA, sorbic acid, DYMED, chlorhexadine gluconate, hydrogen peroxide, thimerosal, polyquad, polyhexamethylene biguanide, mixtures thereof and the like. Where various zones are used, different additives may be included in different zones. Additives may be added to the hydration solution in amounts varying between 0.01% and 10% by weight, but cumulatively less than about 10% by weight.

[0097] Exposure of the ophthalmic lens 100 to the aqueous solution can be accomplished by any method, such as washing, spraying, soaking, submerging, or any combination of the aforementioned. For example, the lens 100 can be washed with an aqueous solution comprising deionized water in a hydration tower.

[0098] Using a hydration tower, front curve mold parts 102 containing lenses 100 can be placed in pallets or trays and stacked vertically. The aqueous solution can be introduced at the top of the stack of lenses 100 so that the solution will flow downwardly over the lenses 100. The solution can also be introduced at various positions along the tower. The trays can be moved upwardly allowing the lenses 100 to be exposed to increasingly fresher solution.

[0099] Alternatively, the ophthalmic lenses 100 may be soaked or submerged in the aqueous solution.

[0100] The contacting step can last up to about 12 hours, up to about 2 hours or from about 2 minutes to about 2 hours; however, the length of the contacting step depends upon the lens materials, including any additives, the materials that are used for the solutions or solvents, and the temperatures of the solutions. Sufficient treatment times typically shrink the contact lens and release the lens from the mold part. Longer contacting times will provide greater leaching.

[0101] The volume of aqueous solution used may be any amount greater than about 1 ml/lens and in some embodiments greater than about 5 ml/lens.

[0102] After separation or demolding, the lenses on the front curves, which may be part of a frame, are mated with individual concave slotted cups to receive the contact lenses when they release from the front curves. The cups can be part of a tray. Examples can include trays with 32 lenses each, and 20 trays that can be accumulated into a magazine.

[0103] Alternatively, the lenses may be submerged in the aqueous solution. Magazines can be accumulated and then lowered into tanks containing the aqueous solution. The aqueous solution may also include other additives as described above.

[0104] As used herein clarity means substantially free from visible haze. Clear lenses have a haze value of less than about 100%, less than about 50%, less than about 20 %, and less than about 15%.

[0105] The contact lenses of the present invention may further comprise modulus values less than about 150, about

120 and about 100 psi.

[0106] The biomedical devices, and particularly ophthalmic devices and contact lenses have average contact angles (advancing) which are less than about 80°, less than about 70° and less than about 60°. In some embodiments the articles of the present invention have combinations of the above described oxygen permeability, water content and contact angle. All combinations of the above ranges are deemed to be within the present invention.

Hansen Solubility Parameter

[0107] The Hansen solubility parameter, δp may be calculated by using the group contribution method described in Barton, CRC Handbook of Solubility Par., 1st. Ed. 1983, page 85 - 87 and using Tables 13, 14.

Haze Measurement

[0108] Haze is measured by placing a hydrated test lens in borate buffered saline in a clear 20 x 40 x 10 mm 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. fiber optic light with 0.5" diameter light guide set at a power setting of 4-5.4) at an angle 66° normal to the lens cell, and capturing an image of the lens from above, normal to the lens cell with a video camera (DVC 1300C: 19130 RGB camera with Navitar TV Zoom 7000 zoom lens) placed 14 mm above the lens platform. The background scatter is subtracted from the scatter of the lens by subtracting an image of a blank cell using EPIX XCAP V 2.2 software. The subtracted scattered light image is quantitatively analyzed, by integrating over the central 10 mm of the lens, and then comparing to a -1.00 diopter CSI Thin Lens®, which is arbitrarily set at a haze value of 100, with no lens set as a haze value of 0. Five lenses are analyzed and the results are averaged to generate a haze value as a percentage of the standard CSI lens. Lenses have haze levels of less than about 150% (of CSI as set forth above) and in some cases less than about 100%. Alternatively, instead of a -1.00 diopter CSI Thin Lenses®, a series of aqueous dispersions of stock latex spheres (commercially available as 0.49 μ m Polystyrene Latex Spheres - Certified Nanosphere Size Standards from Ted Pella, Inc., Product Number 610-30) can be used as standards. A series of calibration samples were prepared in deionized water. Each solution of varying concentration was placed in a cuvette (2mm path length) and the solution haze was measured using the above method.

Solution	Concentration (wt% x 10 ⁻⁴)	Mean GS
1	10.0	533
2	6.9	439
3	5.0	379
4	4.0	229
5	2.0	172
6	0.7	138
Mean GS = mean gray scale		

A corrective factor was derived by dividing the slope of the plot of Mean GS against the concentration (47.1) by the slope of an experimentally obtained standard curve, and multiplying this ratio times measured scatter values for lenses to obtain GS values.

[0109] "CSI haze value" may be calculated as follows:

$$\text{CSI haze value} = 100 \times (\text{GS} - \text{BS}) / (217 - \text{BS})$$

Where GS is gray scale and BS is background scatter.

Water Content

[0110] The water content of contact lenses was measured as follows: Three sets of three lenses are allowed to sit in packing solution for 24 hours. Each lens is blotted with damp wipes and weighed. The lenses are dried at 60°C for four hours at a pressure of 0.4 inches Hg or less. The dried lenses are weighed. The water content is calculated as follows:

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

[0111] The average and standard deviation of the water content are calculated for the samples and are reported.

Modulus

[0112] Modulus is measured by using the crosshead of a constant rate of movement type tensile testing machine equipped with a load cell that is lowered to the initial gauge height. A suitable testing machine includes an Instron model 1122. A dogbone shaped sample having a 0.522 inch length, 0.276 inch "ear" width and 0.213 inch "neck" width is loaded into the grips and elongated at a constant rate of strain of 2 in/min. until it breaks. The initial gauge length of the sample (L_0) and sample length at break (L_f) are measured. Twelve specimens of each composition are measured and the average is reported. Percent elongation is $= [(L_f - L_0)/L_0] \times 100$. Tensile modulus is measured at the initial linear portion of the stress/strain curve.

Advancing Contact Angle

[0113] All contact angles reported herein are advancing contact angles. The advancing contact angle was measured as follows. Four samples from each set were prepared by cutting out a center strip from the lens approximately 5 mm in width and equilibrated in packing solution. The wetting force between the lens surface and borate buffered saline is measured at 23°C using a Wilhelmy microbalance while the sample is being immersed into or pulled out of the saline. The following equation is used

$$F = 2\gamma p \cos\theta \quad \text{or} \quad \theta = \cos^{-1}(F/2\gamma p)$$

where F is the wetting force, γ is the surface tension of the probe liquid, p is the perimeter of the sample at the meniscus and θ is the contact angle. The advancing contact angle is obtained from the portion of the wetting experiment where the sample is being immersed into the packing solution. Each sample was cycled four times and the results were averaged to obtain the advancing contact angles for the lens.

Oxygen Permeability (Dk)

[0114] The Dk is measured as follows. Lenses are positioned on a polarographic oxygen sensor consisting of a 4 mm diameter gold cathode and a silver ring anode then covered on the upper side with a mesh support. The lens is exposed to an atmosphere of humidified 2.1% O_2 . The oxygen that diffuses through the lens is measured by the sensor. Lenses are either stacked on top of each other to increase the thickness or a thicker lens is used. The L/Dk of 4 samples with significantly different thickness values are measured and plotted against the thickness. The inverse of the regressed slope is the Dk of the sample. The reference values are those measured on commercially available contact lenses using this method. Balafilecon A lenses available from Bausch & Lomb give a measurement of approx. 79 barrer. Etafilecon lenses give a measurement of 20 to 25 barrer. (1 barrer = 10^{-10} (cm³ of gas x cm²)/(cm³ of polymer x sec x cm Hg)).

Lysozyme uptake

[0115] Lysozyme uptake was measured as follows: The lysozyme solution used for the lysozyme uptake testing contained lysozyme from chicken egg white (Sigma, L7651) solubilized 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.

[0116] Three lenses for each example were tested using each protein solution, and three were tested using PBS (phosphate buffered saline) 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 lysozyme solution. Each lens was fully immersed in the solution. 2 ml of the lysozyme solution was placed in a well without a contact lens as a control.

[0117] The plates containing the lenses and the control plates containing only protein solution and the lenses in the PBS, were parafilm to prevent evaporation and dehydration, 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 three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper

towel to remove excess PBS solution 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 needs to be within the albumin standards range as described by the manufacturer (0.05 microgram to 30 micrograms). Samples known to uptake a level of lysozyme lower than 100 μ g per lens were diluted 5 times. Samples known to uptake levels of lysozyme higher than 500 μ g per lens (such as etafilcon A lenses) are diluted 20 times.

[0118] 1 ml aliquot of PBS was used for all samples other than etafilcon. 20ml were used for etafilcon A lens. Each control lens was identically processed, except that the well plates contained PBS instead of lysozyme solution.

[0119] Lysozyme uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in lysozyme solution.

[0120] Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

[0121] Lipocalin uptake was measured using the following solution and method. The lipocalin solution contained B Lactoglobulin (Lipocalin) from bovine milk (Sigma, L3908) solubilized at a concentration of 2 mg/ml in phosphate saline buffer (Sigma, D8662) supplemented by sodium bicarbonate at 1.37g/l and D-Glucose at 0.1 g/l.

[0122] Three lenses for each example were tested using the lipocalin 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 lipocalin solution. Each lens was fully immersed in the solution. Control lenses were prepared using PBS as soak solution instead of lipocalin. The plates containing the lenses immersed in lipocalin solution as well as plates containing control lenses immersed in PBS, were parafilmed to prevent evaporation and dehydration, 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 three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper towel to remove excess PBS solution and transferred into sterile 24 well plates each well containing 1 ml of PBS solution.

[0123] Lipocalin uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in lipocalin solution. Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

[0124] Mucin uptake was measured using the following solution and method. The Mucin solution contained Mucins from bovine submaxillary glands (Sigma, M3895-type 1-S) solubilized at a concentration of 2 mg/ml in phosphate saline buffer (Sigma, D8662) supplemented by sodium bicarbonate at 1.37g/l and D-Glucose at 0.1 g/l.

[0125] Three lenses for each example were tested using Mucin 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 Mucin solution. Each lens was fully immersed in the solution. Control lenses were prepared using PBS as soak solution instead of lipocalin.

[0126] The plates containing the lenses immersed in Mucin as well as plates containing control lenses immersed in PBS were parafilmed to prevent evaporation and dehydration, 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 three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper towel to remove excess PBS solution and transferred into sterile 24 well plates each well containing 1 ml of PBS solution.

[0127] Mucin uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in Mucin solution. Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

Kinetics

[0128] The kinetic half lives for components may be determined as follows. The components for each kinetics example were weighed into a 20 mL amber borosilicate glass scintillation vial (Wheaton 320 brand; Catalogue # 80076-576, or equivalent). Vials were capped (using PTFE lined green cap, Qorpak; Supplier # 5205/100, Catalogue # 16161-213) and rolled on jar roller until all solids were dissolved and a homogeneous mixtures were obtained.

Degas

[0129] Reactive monomer mixes were degassed under vacuum, under yellow light for 7 - 10 minutes, and back-filling with nitrogen after breaking vacuum. Vials were quickly capped and placed in compartment 1 of a two compartment nitrogen cure box, via the gated aperture, 7, as shown in Figure 2. The conditions in compartment 1 were room temperature and <0.5% oxygen (using continuous nitrogen purge).

Nitrogen Cure Box - Compartment 2

[0130] The oxygen level in both compartments was maintained by continuous/constant nitrogen purge. The temperature in Compartment 2 was maintained by a heater (COY, Laboratory Products Inc.). The nitrogen cure box was allowed to equilibrate for a minimum of 4 hours prior to performing each kinetics study. The degassed reactive mixture (in tightly capped amber vial) was placed in compartment 1 during the equilibration period.

Light Source and Intensity Setting

[0131] As depicted in Figure 3, 2 fluorescent light fixtures (Lithonia Lighting Fluorescent Luminaire (Gas Tube Luminaire), 60 cm x 10.5 cm) each equipped with 2 fluorescent lamps (Philips TLK 40W/03, 58 cm) were arranged in parallel. The cure intensity was attenuated by adjusting the height of the shelf (shown in Figures 2 and 3) relative to the light source. The intensity at a given shelf height was measured by placing the sensor of a calibrated radiometer/photometer on the mirrored surface, consistent with the position of the sample, as shown in Figure 3. The sensor was placed directly under the space between the 2nd and 3rd lamps in the 4 lamps arrangement.

[0132] Using a calibrated analytical balance (4 decimal places) the weight of a clear borosilicate glass scintillation vial (Wheaton 986541) with cap (white cap with polyethylene insert) was determined. The vial with cap was transferred to Compartment 1 of the Nitrogen Cure Box. The cap was unscrewed and using a calibrated 10 - 100 μ L Eppendorf Pipet, 100 μ L of the Reactive Monomer Mixture was transferred into the vial. The vial was tightly capped, quickly moved into Compartment 2, via door 6, and placed on the mirrored surface 4, as shown in Figure 2. The sample was placed directly under the space between the 2nd and 3rd lamps in the 4 lamps arrangement. The light source 3, was turned on and the sample was exposed for a specified time period. Although the light source was set at 4 - 5 mW/cm², the actual intensity reaching the sample is 0.7 - 1.3 mW/cm², due the cap on the sample glass vials. After exposure, the light source 3, was turned off and the vial (with cap) was re-weighed to determine the sample weight by difference. Using a calibrated 500 - 5000 μ L Eppendorf Pipet, 10 mL HPLC grade methanol was added to the vial.

[0133] Aliquots (100 μ L) of the Reactive Monomer Mixture were pipetted into separate borosilicate glass scintillation vials and the above procedure described above was performed to generate samples at the following minimum time points (minutes): 0, 0.25, 0.50, 0.75, 1, 2, 4, 6, 8, 10.

Cured polymers were extracted in methanol overnight by gently shaking at room temperature.

[0134] Extracts were analyzed for residual components by High Performance Liquid Chromatography with UV detection (HPLC/UV) using the following procedures.

[0135] Quantitation of the mPDMS in the extracts was performed against external calibration standards (about 6 - 11, using the response of the n=6 oligomer), typically covering the range of 1 μ g/mL - 800 μ g/mL. If the concentrations of mPDMS in the extracts were outside the calibration range, the extracts were diluted with methanol to render concentrations within the calibration range for more accurate quantitation.

Chromatographic Conditions**[0136]**

Column: Agilent Zorbax Eclipse XDB18, 4.6 x 50 mm x 1.8 μ m

Column Temperature: 30 °C

UV Detector: 217 nm

Injection Volume: 20 μ L

Mobile Phase**[0137]**

Eluent A: De-ionized

Eluent B: Acetonitrile

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Eluent C: Isopropanol

Flow Rate: 1 mL/min

5		Time (mins)	%A	%B	%C
		0.0	50	48	2
		0.5	50	48	2
10		2.0	0	60	40
		5.0	0	60	40
		5.1	0	30	70
		8.0	0	30	70
15		8.1	50	48	2
		10.0	50	48	2

20 **[0138]** Quantitation of the components in the extracts other than mPDMS was performed against external calibration standards (about 6 - 11) for each component, typically covering the range of 1 µg/mL - 800 µg/mL. If the concentrations of components in the extracts were outside the calibration range, the extracts were appropriately diluted with methanol to render concentrations within the calibration range for more accurate quantitation.

25 Chromatographic Conditions

[0139]

Column: Agilent Zorbax Eclipse Plus 18, 4.6 x 75 mm x 1.8 µm

Column Temperature: 30 °C

30 UV Detector: 217 nm

Injection Volume: 5 µL

Mobile Phase

35 **[0140]**

Eluent A: De-ionized water with 0.05% H₃PO₄

Eluent B: Acetonitrile with 0.05% H₃PO₄

Eluent C: Methanol

40 Flow Rate: 1 mL/min

45		Time (mins)	%A	%B	%C
		0	95	5	0
		5	95	5	0
		15	0	100	0
		23	0	100	0
50		24	0	30	70
		28	0	30	70
		29	95	5	0
55		35	95	5	0

Calculations**[0141]**

1. At each time point the following values are determined:

The concentration ($\mu\text{g/mL}$) of each component in the sample extract.

The concentration of each component in the sample extract, expressed as a percent of the sample weight as follows:

$$\% \text{ Component} = [(\mu\text{g/mL} * \text{Volume of Extract} * \text{Dilution Factor} * 10^{-6} \text{ g}/\mu\text{g}) / (\text{g Sample Weight})] * 100$$

The percent unreacted component present, expressed as a percent relative to T_0 (where T_0 represented 100 % unreacted component)

$$\% \text{ at } T_x = (\% \text{ Measured at } T_x / \% \text{ Measured at } T_0) * 100$$

2. Using the % Component calculated above, the concentration of each component in $\mu\text{moles/g}$, is calculated as follows:

$$\mu\text{moles/g} = (\% \text{ Component} * 10^3) / (\text{Molecular Weight of Component})$$

3. Using the concentration of each component determined in $\mu\text{moles/g}$ in step 2, the concentration at Time_x was expressed as

$$\text{Log } [A_x]/[A_0],$$

where $[A_x]$ is the concentration of component A at x minutes and

$[A_0]$ is the concentration of component A at 0 minutes (T_0)

[0142] The expression $\text{Log } [A_x]/[A_0]$ was determined for each time point.

[0143] First order kinetics were assumed for determining both the polymerization kinetics rate and half life for each component. The following equations were used for calculating polymerization rate

$$\text{Log}[A]/[A_0] = -kt/2.303$$

and half life

$$\ln[A_0]/[0.5A_0] = kt_{1/2} \text{ or } t_{1/2} = 0.693/k$$

[0144] For each component, a plot of $\text{Log } [A_x]/[A_0]$ versus time (minutes) was generated. Typically, the data points (x, y) that best correspond to linear growth (shorter cure times) were plotted and the data were fitted to a linear equation.

[0145] Using the slope, the kinetic rate constant (k) of each component was evaluated from the following equation:

$$k (\text{minute}^{-1}) = \text{Slope} * -2.303$$

[0146] The half-life (minutes) of each component was evaluated from the following equation:

$$t_{1/2} = 0.693/k$$

[0147] The evaluated half-life for each component was compared to the data generated for the percent of each component relative to T_0 , at each time point. Typically for each component, the time taken to attain 50% consumption was close to the half-life based on 1st order kinetics. In cases where the two were significantly different (typically about 30% for half-life of less than about 1 minute, 25% for half-life less than about 2.5 minutes but greater than 1 minute and 20% for half-life greater than 2.5 minutes), the data points (x, y) were re-evaluated to generate kinetic rate constants (k) which would provide half-lives (based on 1st order considerations) more consistent (within 20%) with the measured values.

[0148] The Examples below further describe this invention, but do not limit the invention. They are meant only to suggest a method of practicing the invention. Those knowledgeable in the field of contact lenses as well as other specialties may find other methods of practicing the invention. However, those methods are deemed to be within the scope of this invention.

[0149] Some of the other materials that are employed in the Examples are identified as follows:

EXAMPLES

[0150] The following abbreviations are used in the examples below:

FC Front mold curves

BC Back mold curves

SiMAA (3-methacryloxy-2-hydroxypropoxy)propyl-bis(trimethylsiloxy)methylsilane (Also known as SiGMA)

DMA N,N-dimethylacrylamide

HEMA 2-hydroxyethyl methacrylate

HEAA hydroxyethylacrylamide

HBMA 2-hydroxybutyl methacrylate, prepared as in Synthetic Example 1

HPMA 2-hydroxypropyl methacrylate (ACROS)

DMHEMA dimethylhydroxyethylmethacrylate, prepared as in Synthetic Example 2

mPDMS 800-1000 MW (M_n) monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane
OH-mPDMS α -(2-hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-decamethylpentasiloxane, (MW 612g/mol),
prepared as in Example 8 of US20100249356 A1

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

D3O 3,7-dimethyl-3-octanol

IPA isopropyl alcohol

TAC triallylcyanurate

TEGDMA tetraethyleneglycol dimethacrylate

TRIS 3-methacryloxypropyltris(trimethylsiloxy)silane

acPDMS bis-3-methacryloxy-2-hydroxypropyloxypropyl polydimethylsiloxane (MW about 1000 g/mole)

CGI 819 bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide

EtOAc ethyl acetate

DA dodecanoic acid

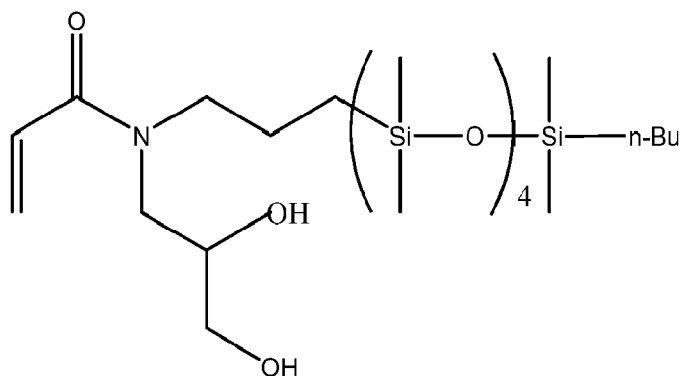
Macromer A Described in Example 25 of US 6,943,203

GMMA 2,3-dihydroxypropyl methacrylate

TAA t-amyl alcohol

ETOH ethanol

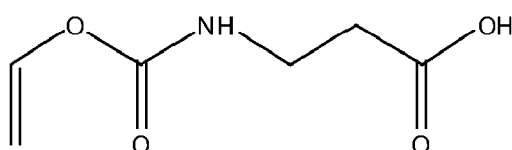
SA-2 N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, as shown in Formula XI



NVP N-vinylpyrrolidone

PVP poly(N-vinylpyrrolidone)

VINAL an ionic amide containing vinyl ether having the structure



and prepared in Synthetic Preparation 1.

BAE (Boric Acid Ester) was formed as follows:

[0151] 1.24 parts of a 5% (wt) solution of ethylenediaminetetraacetic acid, 299 parts (wt) glycerol and 100 parts (wt) boric acid were added to a reaction flask. The mixture was heated with stirring to 90°C. Vacuum was applied to reduce the pressure to less than 6 torr as the mixture was stirred for 155 minutes, with removal of water vapor. The pressure was reduced to less than 2 torr and the reaction was continued for 2 hours, or longer as needed until the % water of the mixture was reduced to less than 0.2% using a Karl Fischer test.

BAGE (Boric Acid Glycerol Ester) was formed as follows:

[0152] To BAE prepared as described above was added 624 parts (wt) glycerol with stirring for 60 minutes at 35-40°C.

Comparative Example

[0153] A reaction mixture formed by mixing the components listed in Table 1 with a diluent (50% ethanol/50% ethyl acetate) in mixtures of 80% reactive components/20% diluents. The reaction mixture was degassed by applying vacuum at ambient temperature for about 17(±3) minutes. The reaction mixture was then dosed into thermoplastic contact lens molds (front curves made from Zeonor, and back curves from polypropylene), and cured for about 20 minutes at 45°C, under a nitrogen atmosphere, using Philips TL 20W/03T fluorescent bulbs and 4-5 mW/cm². The resulting lenses were released from the front curve molds using deionized water at ambient temperature transferred into vials containing borate buffered saline for at least 24 hours and then autoclaved at 122°C for 30 minutes. The resulting lenses were hazy, but felt lubricious when rubbed between the thumb and forefinger.

[0154] The percent haze was measured and the results are listed in Table 1.

Examples 1 and 2

[0155] The Comparative Example was repeated, except that the HEMA was increased and NVP was decreased as shown in Table 1, below. The lenses were released from the front curve mold using mechanical force and extracted in di-ionized water at ambient temperature and pressure. Both lenses felt lubricious when rubbed between the thumb and index finger. The percent haze was measured for both lenses and is shown in Table 1, below.

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Table 1

Ex. #	Ex. 1	Ex. 2	CE1
Component	Wt%	Wt%	Wt%
mPDMS 1000	20	20	20
TRIS	20	20	20
NVP	47	39.25	52
HEMA	10.75	18.5	5.75
CGI 819	2	2	2
TEGDMA	0.25	0.25	0.25
% Haze	22	15	259

[0156] The lenses of the Comparative Example 1 were very hazy, displaying a haze value of 259%, while the lenses of Examples 1 and 2 had dramatically improved haze values of 22% and 15% respectively. The lenses of the Comparative Example were so hazy that they could not be used as contact lenses.

Examples 3-13

[0157] A series of lens formulations were formed from the following components:

38.5 wt% mPDMS
58.25 wt% NVP and HEMA, combined (individual amounts shown in Table 2).
2% Norbloc
1 wt % TEGDMA
0.25 CGI 819

[0158] The reactive components were mixed with a diluents (50% TAA/50% DA) in a ratio of 80 wt% reactive components:20 wt% diluent. The reaction mixtures were cast and cured into lenses following the process described in Examples 1 and 2. Lenses were released in 50/50 IPA/water, extracted in 70/30 IPA/water and subsequently equilibrated in de-ionized water. Lenses were transferred into vials containing borate buffered saline for at least 24 hours and then autoclaved at 122°C for 30 minutes. Lens properties were measured and are reported in Table 2, below.

Table 2

Ex#	[HEMA] wt%	[NVP] wt%	HEMA: NVP ¹	%H ₂ O	% Haze	DCA	Mechanicals		Dk	AC: RC
							Mod. (psi)	Elong. (%)		
3	5.75	52.50	0.0935	61.8 (0.1)	479 (8)	62(4)	53.2 (2.5)	162.6 (34.8)	102.1	54
4	6.75	51.50	0.112	61.4 (0.2)	464 (20)	54 (6)	57.9 (3.6)	187.3 (51.1)	98.3	62
5	7.75	50.50	0.131	58.9 (0.1)	233 (59)	58 (5)	61.6 (5.2)	189.8 (50.4)	102.1	69
6	8.75	49.50	0.152	58.2 (0.2)	17(17)	60(5)	67.0 (3.9)	157.4 (43.8)	100.3	77
7	9.75	48.50	0.172	60.0 (0.3)	5(1)	59.5(5)	70.6 (4)	159.2 (47.5)	96.3	85
8	10.75	47.50	0.193	59.1 (0.0)	8 (0)	60 (7)	79.9 (1.9)	196.2 (24.6)	89.1	92

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(continued)

Ex#	[HEMA] wt%	[NVP] wt%	HEMA: NVP ¹	%H ₂ O	% Haze	DCA	Mechanicals		Dk	AC: RC
							Mod. (psi)	Elong. (%)		
9	15.75	42.50	0.316	55.7 (0.0)	11 (1)	70 (7)	97.5 (4.2)	192.8 (39.2)	83.5	131
10	18.75	39.50	0.405	51.7 (0.1)	16 (2)	* NW	102.5 (4.0)	180.6 (38.6)	77.3	154
11	21.75	36.50	0.509	49.7 (0.1)	44 (2)	* NW	115.9 (3.1)	206.3 (53.8)	62.3	177
12	25.75	32.50	0.677	46.5 (0.3)	112 (4)	* NW	119.6 (6.9)	199.5 (46.6)	63.2	208
13	29.00	29.25	0.839	40.7 (0.2)	186 (3)	* NW	138.8 (6.7)	190.7 (32.4)	59.7	233
1 molar ratio AC:RC= mmol ancillary components/100 gm reactive mixture * NW = Not Wetttable										

[0159] As can be seen from Examples 3-5, lenses made from reaction mixtures containing less than about 8 wt% HEMA displayed very high haze values (> about 200%) which are unsuitable for a contact lens, while lenses having between 10 and 22 wt% HEMA displayed exceptionally good haze values (9-44%). It should also be noted that lenses formed from reaction mixtures having less than about 40 wt% NVP displayed poor wettabilities, and actually repelled water. Examples 3 through 13 also show that as the amount of HEMA is increased, the Dk of the lenses decrease by as much as 40% (comparing Example 6 to Example 13), even though the amount of the silicone-containing component, and the % silicon (12.089) in the reactive mixture remained the same.

[0160] The data from Table 2 is plotted in Figure 2, and shows that as the ratio of ancillary components to reactive mixture decreases, the oxygen permeability of the silicone hydrogel increases.

Examples 14-16

[0161] A reaction mixture was formed by mixing the components listed in Table 3 with 20 wt% of a 50:50 mixture of TAA and decanoic acid and degassed by applying vacuum at ambient temperature for about 17(±3) minutes. The reaction mixture (75 μL) was then dosed at room temperature and <0.1% O₂, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N₂ box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold and the lenses were moved into Compartment 2 and cured for 20 minutes, at an intensity of 4 - 5 mW/cm², <0.1% O₂, and 62 - 65°C.

[0162] Lenses were released in 50/50 IPA/water, extracted in 70/30 IPA/water and subsequently equilibrated in de-ionized water. Lenses were transferred into vials containing borate buffered saline for at least 24 hours and then autoclaved at 122°C for 30 minutes. Lens properties were measured and are reported in Table 4, below.

Table 3

Component	14	15	16	17
mPDMS 1000	20.50	20.50	20.50	20.50
NVP	65.50	70.50	72.50	0
DMA	0	0	0	72.5
HEMA	10.75	5.75	3.25	3.25
TEGDMA	1.00	1.00	1.50	1.50
Norblock	2.00	2.00	2.00	2.00
CGI 819	0.25	0.25	0.25	0.25

Table 4

Ex.#	% H ₂ O	% Haze	DCA	Mechanicals		Dk	AC:RM
				Mod. (psi)	Elong. (%)		
14	70.5 (0.2)	4 (1)	55 (6)	51.0 (6.3)	208.7 (37.5)	48.9	92
15	78.1 (0.1)	6 (0)	50 (6)	30.8 (2.6)	224.9 (29.6)	58.1	54
16	77.9 (0.3)	30 (1)	51 (7)	29.7 (2.2)	172.0 (36.0)	61.0	36
CE2	68.4 (0.3)	1 (0)	99 (4)	138.6 (3.5)	118.6 (32.3)	37.8	769

[0163] The DMA in Comparative Example 2 is an intermediate reacting monomer. As can be seen from the AC:RM ratio replacing the NVP with DMA substantially decreases the Dk of the resulting lenses compared to those of Comparative Example 2.

Examples 17-22

[0164] Example 8 was repeated, except that the amount of hydroxylalkyl (meth)acrylate and NVP were varied to provide molar ratios of the hydroxylalkyl (meth)acrylate:NVP of about 0.2. GMA has two hydroxyl groups. Accordingly, formulations having two different concentrations of GMA were prepared, Example 21 (13.23 wt% GMA, 0.408 ratio, counting both hydroxyls) and Example 22 (6.62 wt % GMA, 0.204, counting two hydroxyls).

[0165] Examples 20 and 21 produces hazy reaction mixtures which were not cured into lenses. Examples 17-19 and 22 produced clear reaction mixtures which were cast into lenses following the procedure described in Example 8. Lens properties were measured. The formulations and lens properties are shown in Table 5, below.

[0166] Comparing Examples 21 and 22, it can be seen that when the molar amount of GMA was adjusted to account for both hydroxyls, clear lenses were formed. It is believed that Example 20, which included HEAA as the hydroxylalkyl (meth)acrylate, did not provide wettable lenses because the HEAA contains two polar groups, the amide and hydroxyl groups, making the HEAA more polar than the other hydroxylalkyl (meth)acrylates used in Examples 18-19 and 21-22. It is believed that the increased polarity of HEAA caused compatibility issues with the mPDMS. However, HEAA has the potential to work with more polar silicones, such as SiMAA, OH-mPDMS, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide. Thus, a variety of hydroxylalkyl (meth)acrylate compounds can be used to form the hydrogels of the present invention.

Table 5

Example	17	18	19	20	21	22
Component	HPMA	HBMA	DMHEMA	HEAA	GMA	GMA
NVP (wt%)	47.5	45.18	45.18	48.75	45.01	51.63
HOMA Cpd (wt%)	10.75	13.07	13.07	9.50	13.23	6.62
HOMA:NVP (molar)	0.174	0.203	0.203	0.188	0.408	0.204
% H ₂ O	58.9 (0.1)	54.5	60.4	NT*	NT	62.6
% Haze	16(0)	8	15	NT*	NT*	12
DCA	63 (5)	46	70	NT*	NT*	49
MOD (psi)	73.4 (1.4)	120.5	68.7	NT*	NT*	70.4
Elong (%)	230.1 (1.8)	179.3	206.5	NT*	NT*	203.5
Dk	93.4	93.4	90	NT*	NT*	85.3
AC:RM	84	92	92	92	92	51
NT* = Not Tested						

Examples 23-24 & Comparative Examples 3-6

[0167] Each reaction mixture was formed by mixing the components listed in Table 6 and degassed by applying vacuum at ambient temperature for about 17(\pm 3) minutes. The reaction mixture (75 μ L) was then dosed at room temperature and <0.1% O₂, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N₂ box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold and the lenses were moved into Compartment 2 and cured for 20 minutes, an intensity of 4 - 5 mW/cm², <0.1% O₂, and 62 - 65 °C.

[0168] The molds were mechanically separated demolded (lenses remained in FC). The lenses were dry released by pressing on the back of the front curve. Lenses were extracted in DI water and equilibrated in borate buffered packing solution in lens vials and sterilized at 122°C for 30 minutes.

[0169] The properties of the lenses were measured and are shown in Table 7, below.

Table 6

Component	Ex. 23	24	CE3	CE4	CE5	CE6
mPDMS 1000	16.50	16.50	16.50	16.50	16.50	16.50
OH-mPDMS, n=4	27.50	27.50	27.50	27.50	27.50	27.50
NVP	46.65	44.15	41.65	39.15	35.15	23.35
HEMA	6.75	6.75	6.75	6.75	6.75	6.75
DMA	0.00	2.50	5.00	7.50	11.50	23.30
EGDMA	0.35	0.35	0.35	0.35	0.35	0.35
Norbloc	1.75	1.75	1.75	1.75	1.75	1.75
CGI 819	0.50	0.50	0.50	0.50	0.50	0.50
Diluent	10.00	10.00	10.00	10.00	10.00	10.00
TAA	100.00	100.00	100.00	100.00	100.00	100.00

Table 7

Ex#	% H ₂ O	% H az e	DC A	Mechanicals		Dk	AC RM
				Mod. (psi)	Elong . (%)		
Ex 23	61 (0)	6 (1)	48 (6)	75 (10)	145 (57)	92	59
Ex 24	63 (0)	7 (1)	79 (9)	57 (6)	171 (36)	89	84
CE3	63 (0)	9 (1)	107 (3)	52 (4)	164 (53)	89	110
CE4	63 (0)	9 (1)	110 (4)	46(6)	162 (45)	89	135
CE5	60 (0)	6 (1)	119 (15)	53 (6)	184 (56)	85	175
CE6	56 (0)	4 (0)	114 (13)	66(6)	195 (44)	72	294

[0170] DMA is a hydrophilic component with intermediate reaction kinetics. It can be seen from the data in Table 7, that amounts of DMA as small as 2.5 wt% (Example 24), dramatically decrease the modulus, but increase the contact angle of the resulting contact lenses.

Example 25 and Comparative Examples 5-8

[0171] Each reaction mixture was formed by mixing the components listed in Table 8 and degassed by applying vacuum at ambient temperature for about 17(\pm 3) minutes. The reaction mixture (75 μ L) was then dosed at room temperature and <0.1% O₂, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N₂ box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold and the lenses were moved into Compartment 2 and cured for 20 minutes, an intensity of 4 - 5 mW/cm²,

<0.1% O₂, and 62 - 65 °C.

[0172] The molds were mechanically separated demolded (lenses remained in FC). The lenses were dry released by pressing on the back of the front curve. Lenses were extracted in DI water and equilibrated in borate buffered packing solution in lens vials and sterilized at 122°C for 30 minutes.

Table 8

Component	Ex. 25	CE5	CE6	CE7
SA2	50.00	50.00	50.00	50.00
VMA	40.65	30.50	20.35	10.15
HEMA	6.75	6.75	6.75	6.75
DMA	0.00	10.15	20.30	30.50
EGDMA	0.35	0.35	0.35	0.35
Norbloc	1.75	1.75	1.75	1.75
CGI 819	0.50	0.50	0.50	0.50
Diluent	10.00	10.00	10.00	10.00
TAA	100.00	100.00	100.00	100.00

Table 9

Ex#	Lens	% H ₂ O	% Haze	DCA	Mechanicals Mod. (psi)	Elong. (%)	Dk	AC: RM
25	2766-140A	58 (1)	36(2)	62 (9)	299 (32)	320 (62)	93	59
CE5	2766-140B	65 (1)	10 (1)	117 (14)	42(6)	337 (75)	75	162
CE6	2766-140C	58 (0)	10 (1)	120 (7)	44 (4)	375 (66)	55	264
CE7	2766-140D	48 (0)	19 (2)	123 (12)	95 (9)	399 (95)	37	367

[0173] Addition of 10.15 wt% of DMA in the formulation of Comparative Examples 5 dramatically reduced the Dk from 93 to 75, and increased the contact angle from 62 to 177. However, the addition of DMA also lowered the modulus of the resulting lenses dramatically. Amounts of DMA less than about 5 wt% would have a lower AC:RM ratio, and would produce lenses having a better overall balance of properties.

Examples 26 and 27

[0174] Reaction mixtures were formed from the components listed in Table 10. Lenses were made using the procedure described in Example 25. The properties of the lenses were measured and are reported in Table 11.

[0175] The contact lenses were clinically evaluated in a non-randomized, unmasked, bilateral, single day dispensing study with a lens wear time of 12 (+/-2) hours. The lenses were worn by 10 subjects. Front surface deposition was observed after 60 minutes of contact lens wear and at the follow-up post dispensing visit. Deposits were rated using the following scale:

Grade 0	None	No deposition.
Grade 1	Slight	Deposition, which occupies 1-5% of the lens surface area.
Grade 2	Mild	Deposition, which occupies 6-15% of the lens surface area.
Grade 3	Moderate	Deposition, which occupies 16-25% of the lens surface area.
Grade 4	Severe	Deposition, which occupies 26% of the lens surface area.

Strehl ratios (4th order).were measured on a Mach-Zehnder interferometer, using a 5mm aperture across the optic zone. The values are shown in Table 11, below.

EP 3 181 614 B9

Table 10

Component	Ex. 26	Ex. 27
mPDMS 1000	16.50	17.45
OH-mPDMS, n=4	27.50	29.90
NVP	46.65	43.98
HEMA	6.73	6.00
Blue HEMA	0.02	0.02
EGDMA	0.45	0.00
TEGDMA	0.00	0.20
TAC	0.00	0.20
Norbloc	1.75	1.75
CGI 819	0.50	0.50
Diluent	0.00	5.00
TAA	100.00	100.00

Table 11

EX.#	26	27
% H ₂ O	53 (0)	54 (0)
% Haze	NT	NT
DCA	34 (9)	50 (9)
Mod. (psi)	154 (10)	106 (8)
Elong. (%)	171 (24)	296 (34)
Dk	96	NT
SR	0.9718 (0.0176)	0.9836 (0.0044)
SR =Strehl Ratio (4th order)		

Table 12

Front Surface Deposition	Post Fit - 60 Mins n (%)		Follow Up n (%)	
	Ex. 26	Ex. 27	Ex 26	Ex. 27
Grade 0	17 (85%)	13 (93%)	5 (25%)	1 (7%)
Grade 1	3 (15%)	1 (7%)	7 (35%)	13 (93%)
Grade 2	0	0	8 (40%)	0
Grade 3	0	0	0	0
Grade 4	0	0	0	0
Total Eyes	20	14	20	14

Synthetic Example 1: Preparation of VINAL

[0176] 4.82 g vinyl chloroformate was added to a mixture of 8.19 g β-alanine (Aldrich) in 74 ml acetonitrile. The resulting mixture was refluxed for 2 hours, then cooled to room temperature and allowed to sit for 2 hours. It was filtered and solvent was removed under reduced pressure. The crude product was dissolved in 30 ml distilled water and washed

three times with ethyl acetate. The combined ethyl acetate washes were washed with 50 ml deionized water. Solvent was evaporated from the combined ethyl acetate washes to yield 4.5 g product as a fluffy yellowish solid. ¹H NMR: 7.1 ppm (dd, 1H), 5.4 ppm (br s, OH), 4.7 ppm (dd, 1H), 4.4 ppm (dd, 1H), 3.5 ppm (q, 2H), 2.6 ppm (t, 2H).

5 Synthetic Example 2 Preparation of 2-hydroxybutyl methacrylate (HBMA)

[0177] A blend of 72 grams 1,2-epoxybutane (Aldrich), 0.85 g 4-methoxyphenol (Aldrich), and 6.5 g potassium hydroxide was stirred in a 500 ml round bottomed flask equipped with an addition funnel and thermocouple thermometer. 172 g methacrylic acid was added via the addition funnel, and the blend was slowly to 75°C, and stirred overnight under an air, then increased to 88°C for 4 hours. The mixture was cooled, and 700 ml of 2.0 N NaOH was added to the mixture in a separatory funnel. The upper layer was washed with borate buffered saline three times. Ethyl ether (200 ml) was added to the combined saline washes to extract any product. The combined organic layers were dried over NaSO₄. The NaSO₄ was filtered out and the product was distilled (90-98°C/~4 mm Hg). 17.5 g product was collected, to which was added 4 mg 4-methoxyphenol. ¹H NMR: 6.1 ppm (1H, m), 5.5 (1H, m), 4.8 (0.25H m), 4.2 (0.64 H, dd, 8.1 and 11.7 Hz), 4.0 (0.64 Hz, dd, 6.9 and 11.4 Hz), 3.6-3.8 1.26H, m), 2.3 (OH, br s), 1.9 (3 H, m), 1.4-1.7 (2 H, m), 0.9 (3H, m); consistent with a blend of 2-hydroxy-1-propylmethacrylate and 1-hydroxy-2-propylmethacrylate.

Synthetic Example 3 Preparation of dimethylhydroxyethylmethacrylate

[0178] The same procedure as for HBMA was used, but substituting 1,2-epoxy-2-methylpropane for the 1,2-epoxypropane. The product was isolated by distillation at 47-48°/0.4-0.6 mm Hg.. ¹H NMR: 6.1 ppm (1H, s), 5.5 (1H, m), 4.0 (2H, s), 2.1 (OH, br s), 1.9 (3 H, s), 1.2 (6 H, m); consistent 2-hydroxy-2-methyl propylmethacrylate (dimethylhydroxyethylmethacrylate).

25 **Claims**

1. A silicone hydrogel comprising a water content of at least 50% and an oxygen permeability of at least 80 barrers wherein said silicone hydrogel is formed from a reaction mixture comprising
30 30 to 75 wt% of at least one slow-reacting hydrophilic monomer having a slow-reacting hydrophilic monomer kinetic half life;

at least one silicone-containing component having a silicone-containing component kinetic half life, which may be optionally substituted with at least one hydroxyl containing group;

35 at least one hydroxyl-containing component selected from said silicone-containing components substituted with at least one hydroxyl group, at least one hydroxyalkyl monomer, and mixtures thereof,

wherein the ratio of said slow-reacting hydrophilic component half life to said silicone-containing component half life is at least 2, said reaction mixture comprising between 9 and 14 wt% silicon and less than 15 wt% TRIS and wherein all reactive components other than said slow-reacting hydrophilic monomer and said silicone containing components are ancillary components in the reaction mixture and are present in an amount between
40 11 and 92 mmol/100g reactive components.

2. The silicone hydrogel of claim 1, wherein the reaction mixture comprises:

- 45 i) 37 to 75 wt%; or
- ii) 37 to 70 wt%; or
- iii) 39 to 60 wt%

of the at least one slow-reacting hydrophilic monomer having a slow-reacting hydrophilic monomer kinetic half life.

- 50 3. The silicone hydrogel of any preceding claim wherein said silicone containing components comprise less than 10 wt% TRIS.

4. The silicone hydrogel of claim 1 or claim 2 wherein said silicone containing components are free of TRIS.

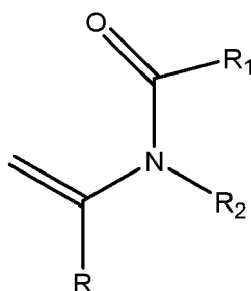
- 55 5. The silicone hydrogel of any preceding claim wherein all ancillary components are present in said reaction mixture in a concentration of less than 12 wt% based upon reactive components.

6. The silicone hydrogel of any preceding claim wherein said water content is:

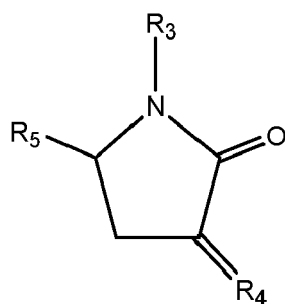
- i) at least 55%; or
- ii) at least 60%.

7. The silicone hydrogel of any preceding claim wherein said ancillary components comprise between 38 and 76 mmol/100g reactive components.

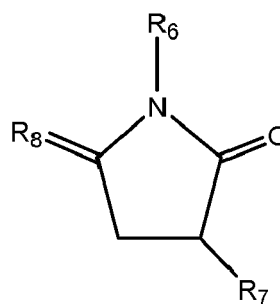
8. The silicone hydrogel of any preceding claim wherein said at least one slow reacting monomer selected from the group consisting of N-vinylamide monomer of Formula I, vinyl pyrrolidone of Formula II-IV, N-vinyl piperidone of Formula V:



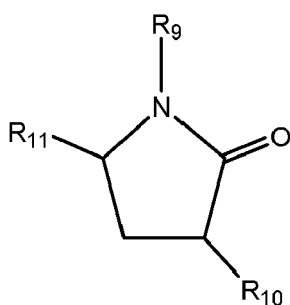
Formula I



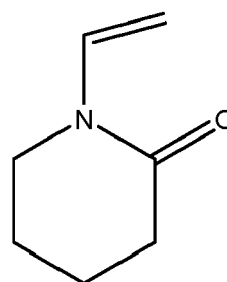
Formula II



Formula III



Formula IV



Formula V

wherein R is H or methyl;

R₁, R₂, R₃, R₆, R₇, R₁₀, and R₁₁ are independently selected from the group consisting of H, CH₃, CH₂CH₃, CH₂CH₂CH₃, C(CH₃)₂;

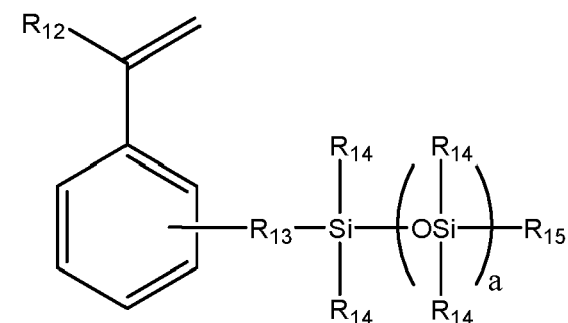
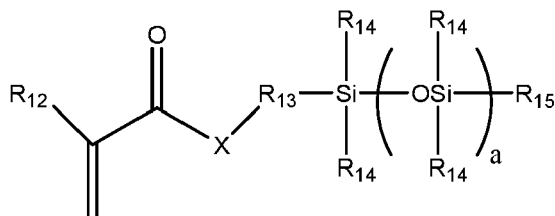
R₄ and R₈ are independently selected from the group consisting of CH₂, CHCH₃ and C(CH₃);

R₅ is selected from H, methyl, ethyl; and

R₉ is selected from CH=CH₂, CCH₃=CH₂, and CH=CHCH₃;

wherein said silicone-containing component is selected from the group consisting of at least one mono (meth)acryloxyalkyl polydialkylsiloxane monomer of Formula VII or the styryl polydialkylsiloxane monomer of Formula VIII:

Formula VII



Formula VIII

wherein R_{12} is H or methyl;

X is O or NR_{16} ;

Each R_{14} is independently a C_1 to C_4 alkyl which may be fluorine substituted, or phenyl;

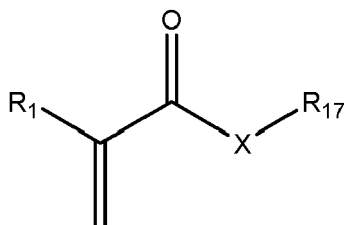
R_{15} is a C_1 to C_4 alkyl;

R_{13} is a divalent alkyl group, which may further be functionalized with a group selected from the group consisting of ether groups, hydroxyl groups, carbamate groups and combinations thereof;

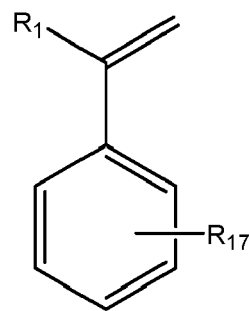
a is 3 to 50;

R_{16} is selected from H, C_1 -4, which may be further substituted with one or more hydroxyl groups; and

said hydroxyalkyl monomer is selected from the group consisting of at least one hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer of Formula IX or a styryl compound of Formula X



FORMULA IX



FORMULA X

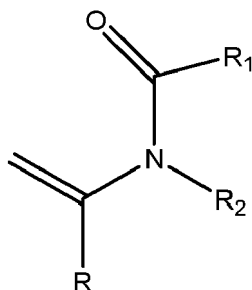
wherein R_1 is H or methyl,

X is O or NR_{16} , R_{16} is a H, C_1 to C_4 alkyl, which may be further substituted with at least one OH;

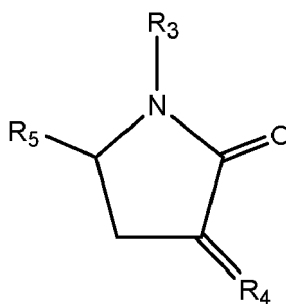
R_{17} is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10

repeating units; wherein said at least one hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer and said slow reacting monomer are present in mole percents which form a molar ratio between 0.15 and 0.4, preferably

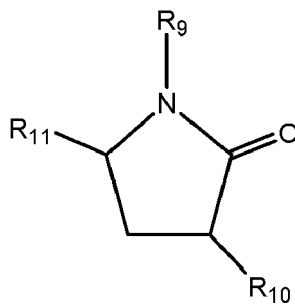
wherein said at least one slow reacting hydrophilic monomer is selected from the group consisting of N-vinylamide monomer of Formula I, vinyl pyrrolidone of Formula II or IV:



Formula I



Formula II



Formula IV

wherein R is H or methyl;

R₁, R₂, R₃, R₁₀, and R₁₁ are independently selected from the group consisting of H, CH₃, CH₂CH₃, CH₂CH₂CH₃, C(CH₃)₂;

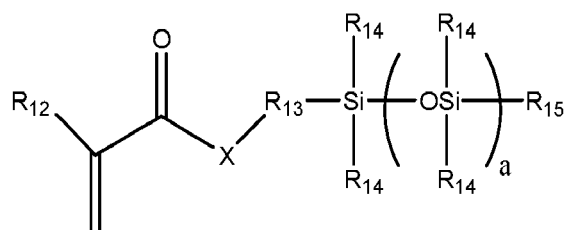
R₄ is selected from the group consisting of CH₂, CHCH₃ and C(CH₃)₂;

R₅ is selected from H, methyl, ethyl; and

R₉ is selected from CH=CH₂, CCH₃=CH₂, and CH=CHCH₃;

(b) said at least one silicone-containing component is selected from the group consisting of at least one mono (meth)acryloxyalkyl polydialkylsiloxane monomer of Formula VII:

Formula VII



wherein R_{12} is H or methyl;

X is O or NR_{16} ;

Each R_{14} is independently a C_1 to C_4 alkyl which may be fluorine substituted, or phenyl;

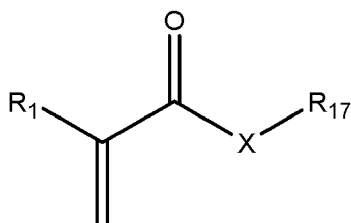
R_{15} is a C_1 to C_4 alkyl;

R_{13} is a divalent alkyl group, which may further be functionalized with a group selected from the group consisting of ether groups, hydroxyl groups, carbamate groups and combinations thereof;

a is 3 to 50;

R_{16} is selected from H, C_{1-4} , which may be further substituted with one or more hydroxyl groups;

(c) at least one hydroxyalkyl monomer is selected from the group consisting of hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer of Formula IX



FORMULA IX

wherein R_1 is H or methyl,

X is O or NR_{16} , R_{16} is a H, C_1 to C_4 alkyl, which may be further substituted with at least one OH;

R_{17} is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; wherein said at least one hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer and said slow reacting monomer are present in mole percents which form a molar ratio between 0.15 and 0.4.

9. The silicone hydrogel of claim 8 wherein:

- i) each R_3 is independently selected from ethyl and methyl groups; or
- ii) all R_3 are methyl.

10. The silicone hydrogel of claim 8 or claim 9 wherein R_{16} is H or methyl.

11. The silicone hydrogel of any of claims 8 to 10 wherein R_{12} and each R_{14} are methyl.

12. The silicone hydrogel of any of claims 8 to 11 wherein the slow-reacting hydrophilic monomer is selected from:

- i) the vinyl pyrrolidone of Formula II or IV or the N-vinyl amide monomer of Formula I, having a total number of carbon atoms in R_1 and R_2 of 4 or less; or
- ii) a vinyl pyrrolidone of Formula III or IV and R_6 is methyl, R_7 is hydrogen, R_9 is $CH=CH_2$, R_{10} and R_{11} are H.

13. The silicone hydrogel of any of claims 8-11 wherein the slow-reacting hydrophilic monomer is selected from 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 (VINYL), N-carboxyvinyl- α -alanine and mixtures thereof, preferably

wherein the slow-reacting hydrophilic monomer is selected from the group consisting of N-vinylpyrrolidone, N-vinylacetamide, 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-methyl-3-methylene-2-pyrrolidone, and mixtures thereof, more preferably

wherein the slow-reacting hydrophilic monomer is selected from the group consisting of NVP, VMA and 1-methyl-5-methylene-2-pyrrolidone, most preferably

wherein the slow-reacting hydrophilic monomer comprises NVP.

14. The silicone hydrogel of any of claims 8 to 13 wherein at least one R_{14} is 3,3,3-trifluoropropyl.

15. The silicone hydrogel of any of claims 8 to 14 wherein R_{13} is selected from C_1 - C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof, preferably wherein R_{13} is selected from C_1 or C_{3-6} alkylene groups which may be substituted with ether, hydroxyl and combinations thereof.

16. The silicone hydrogel of any of claims 8 to 15 wherein:

- i) a is 5 to 15; or
- ii) a is 7 to 30.

17. The silicone hydrogel of any of claims 8 or 9 or 12 to 15 wherein said monomethacryloxyalkylpolydimethylsiloxane methacrylate is selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide; α -(2-hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-octamethylpentasiloxane and mixtures thereof, preferably

wherein said monomethacryloxyalkylpolydimethylsiloxane methacrylate is selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide.

18. The silicone hydrogel of any of claims 8 to 17 wherein:

- i) R_1 is H or methyl, X is oxygen and R is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; or
- ii) R_1 is methyl, X is oxygen and R is selected from C_2 - C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 2-20 repeating units.

19. The silicone hydrogel of any of claims 8 to 18 wherein R is 2-hydroxyethyl, 2,3-dihydroxypropyl, 2-hydroxypropyl.

20. The silicone hydrogel of any of claims 8 to 19 wherein R_4 is methyl or 2-hydroxy ethyl.

21. The silicone hydrogel of any of claims 1 to 17 wherein said hydroxyalkyl monomer is selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (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, 2-hydroxyethyl (meth)acrylamide, polyethyleneglycol monomethacrylate, bis-(2-hydroxyethyl) (meth)acrylamide, 2,3-dihydroxypropyl (meth)acrylamide, and mixtures thereof, preferably

wherein said hydroxyalkyl 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, more preferably

wherein said hydroxyalkyl monomer comprises 2-hydroxyethyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, glycerol methacrylate and mixtures comprising them.

22. The silicone hydrogel of any preceding claim wherein said reaction mixture further comprises at least one slow reacting crosslinker and at least one fast reacting crosslinker, optionally wherein said at least one slow reacting crosslinker and at least one fast reacting crosslinker are each present in said reaction mixture in amounts between:

- i) 0.05 to 0.3 wt%; or
- ii) 0.1 to 0.2 wt%.

23. The silicone hydrogel of claim 1 wherein said at least one silicone-containing component and said at least one hydroxyl-containing component have the same reactive functionality.

24. The silicone hydrogel of any preceding claim, wherein:

- i) said at least one hydroxyalkyl monomer is present in mole percents which form a molar ratio of hydroxyl groups to slow reacting hydrophilic monomer of between 0.15 and 0.4; or
- ii) wherein the molar ratio of hydroxyl groups in the reaction mixture to silicon (HO:Si) is between 0.16 and 0.4.

25. The silicone hydrogel of any preceding claim, wherein said slow-reacting hydrophilic monomer comprises a slow-reacting group selected from N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group.

26. The silicone hydrogel of any preceding claim, wherein the reaction mixture is substantially free of TRIS.

27. The silicone hydrogel of any preceding claim, wherein the silicone hydrogel is made without silicone containing macromers or prepolymers, wherein "silicone macromers" and silicone "prepolymers" mean mono- and multi-functional silicone containing compounds having molecular weights of greater than 2000.

28. The silicone hydrogel of any preceding claim, said reaction mixture comprising between 9 and 13 wt% silicon.

29. A process for forming the silicone hydrogel of any preceding claim, wherein the process uses photoinitiation and the reaction mixture comprises a photoinitiator, wherein the cure time is less than 30 minutes.

Patentansprüche

1. Silikonhydrogel, das einen Wassergehalt von mindestens 50 % und eine Sauerstoffpermeabilität von mindestens 80 Barrer aufweist, wobei das Silikonhydrogel ausgehend von einer Reaktionsmischung gebildet wird, die Folgendes umfasst

30 bis 75 Gew.-% mindestens eines langsam reagierenden hydrophilen Monomers, welches eine Halbwertszeitkinetik eines langsam reagierenden hydrophilen Monomers aufweist;
mindestens einen silikonhaltigen Bestandteil, welcher eine Halbwertszeitkinetik eines silikonhaltigen Bestandteils aufweist, wobei er möglicherweise mit mindestens einer hydroxylhaltigen Gruppe substituiert sein kann;
mindestens einen hydroxylhaltigen Bestandteil, der aus den silikonhaltigen Bestandteilen, welche mit mindestens einer Hydroxylgruppe substituiert sind, mindestens einem Hydroxyalkylmonomer und Mischungen davon ausgewählt ist,
wobei das Verhältnis der Halbwertszeit des langsam reagierenden hydrophilen Bestandteils zur Halbwertszeit des silikonhaltigen Bestandteils mindestens 2 beträgt, wobei die Reaktionsmischung zwischen 9 und 14 Gew.-% an Silicium und weniger als 15 Gew.-% an TRIS umfasst und wobei sämtliche reaktionsfähige Bestandteile außer dem langsam reagierenden hydrophilen Monomer und den silikonhaltigen Bestandteilen in der Reaktionsmischung als Hilfsbestandteile dienen und in einer Menge zwischen 11 und 92 mmol / 100 g an reaktionsfähigen Bestandteilen vorliegen.

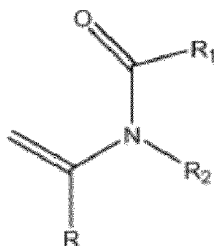
2. Silikonhydrogel nach Anspruch 1, wobei die Reaktionsmischung Folgendes umfasst:

- i) 37 bis 75 Gew.-%; oder

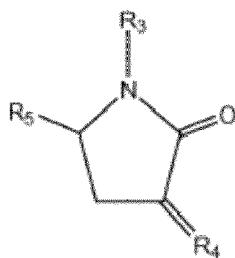
- ii) 37 bis 70 Gew.-%; oder
- iii) 39 bis 60 Gew.-%

des mindestens einen langsam reagierenden hydrophilen Monomers, welches eine Halbwertszeitskinetik eines langsam reagierenden hydrophilen Monomers aufweist.

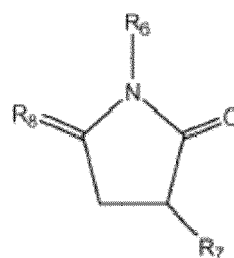
3. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die silikonhaltigen Bestandteile weniger als 10 Gew.-% an TRIS umfassen.
4. Silikonhydrogel nach Anspruch 1 oder Anspruch 2, wobei die silikonhaltigen Bestandteile frei von TRIS sind.
5. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die Hilfsbestandteile in der Reaktionsmischung in einer Konzentration von weniger als 12 Gew.-% vorliegen, bezogen auf die reaktionsfähigen Bestandteile.
6. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei der Wassergehalt folgendermaßen ist:
 - i) mindestens 55 %; oder
 - ii) mindestens 60 %.
7. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die Hilfsbestandteile in einer Menge zwischen 38 und 76 mmol/100 g an reaktionsfähigen Bestandteilen vorliegen.
8. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei das mindestens eine langsam reagierende Monomer aus der Gruppe ausgewählt ist, die aus einem N-Vinylamidmonomer der Formel I, einem Vinylpyrrolidon der Formel II bis IV, einem N-Vinylpiperidon der Formel V besteht:



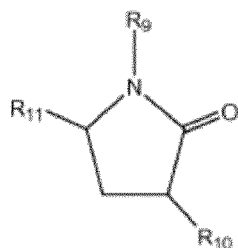
Formel I



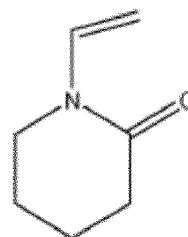
Formel II



Formel III



Formel IV



Formel V

wobei R gleich H oder Methyl ist;

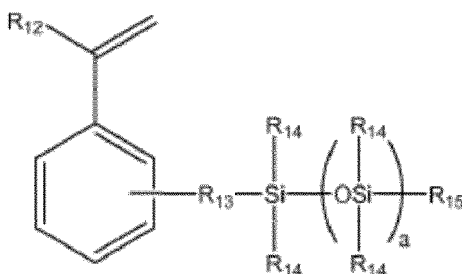
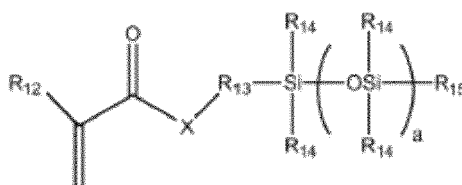
R_1 , R_2 , R_3 , R_6 , R_7 , R_{10} , und R_{11} unabhängig voneinander aus der Gruppe ausgewählt sind, die aus H, CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$, $C(CH_3)_2$ besteht;

R_4 und R_8 unabhängig voneinander aus der Gruppe ausgewählt sind, die aus CH_2 , $CHCH_3$ und $C(CH_3)$ besteht; R_5 aus H, Methyl, Ethyl ausgewählt ist; und

R_9 aus $CH=CH_2$, $C(CH_3)=CH_2$ und $CH=CHCH_3$ ausgewählt ist;

wobei der silikonhaltige Bestandteil aus der Gruppe ausgewählt ist, die aus mindestens einem Mono(meth)acryloxyalkylpolydialkylsiloxan-Monomer der Formel VII oder dem Styrylpolydialkylsiloxan-Monomer der Formel VIII besteht:

Formel VII



Formel VIII

wobei R_{12} gleich H oder Methyl ist;

X für O oder NR_{16} steht;

jedes R_{14} auf unabhängige Weise für ein C_1 - bis C_4 -Alkyl, welches mit Fluor substituiert sein kann, oder Phenyl steht;

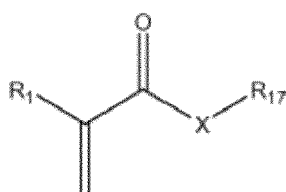
R_{15} für ein C_1 - bis C_4 -Alkyl steht;

R_{13} für eine zweibindige Alkylgruppe steht, die weiterhin mit einer funktionellen Gruppen versehen sein kann, die aus der Gruppe ausgewählt ist, welche aus Ethergruppen, Hydroxylgruppen, Carbamatgruppen und deren Kombinationen besteht;

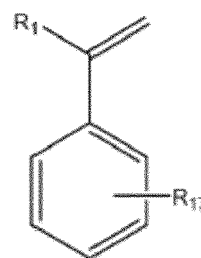
a gleich 3 bis 50 ist;

R_{16} aus H, C1-4, welches weiterhin mit einer oder mehreren Hydroxylgruppen substituiert sein kann, ausgewählt ist; und

wobei das Hydroxyalkylmonomer aus der Gruppe ausgewählt ist, die aus mindestens einem Hydroxyalkyl(meth)acrylat- oder (Meth)acrylamidmonomer der Formel IX oder einer Styrylverbindung der Formel X besteht



FORMEL IX



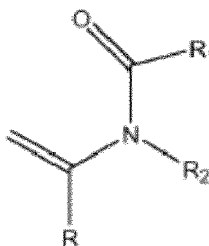
FORMEL X

wobei R_1 gleich H oder Methyl ist;

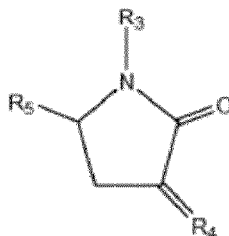
X für O oder NR_{16} steht, R_{16} für ein H, C_1 - bis C_4 -Alkyl, welches weiterhin mit mindestens einem OH substituiert sein kann, steht;

R_{17} aus mono- oder dihydroxysubstituiertem C_2 - C_4 -Alkyl und Polyethylenglykol mit 1 bis 10 Wiederholeinheiten ausgewählt ist; wobei das mindestens eine Hydroxyalkyl(meth)acrylat- oder (Meth)acrylamidmonomer und das langsam reagierende Monomer in Molprozentanteilen vorliegen, welche ein Molverhältnis zwischen 0,15 und 0,4 ergeben

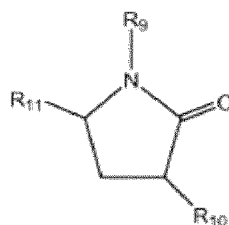
wobei das mindestens eine langsam reagierende hydrophile Monomer vorzugsweise aus der Gruppe ausgewählt ist, die aus einem N-Vinylamidmonomer der Formel I, einem Vinylpyrrolidon der Formel II oder IV besteht:



Formel I



Formel II



Formel IV

wobei R gleich H oder Methyl ist;

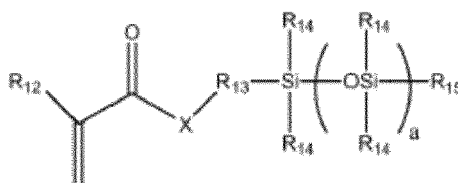
R_1 , R_2 , R_3 , R_{10} , und R_{11} unabhängig voneinander aus der Gruppe ausgewählt sind, die aus H, CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$, $C(CH_3)_2$ besteht;

R_4 aus der Gruppe ausgewählt ist, die aus CH_2 , $CHCH_3$ und $C(CH_3)_2$ besteht;

R₅ aus H, Methyl, Ethyl ausgewählt ist; und

R₉ aus CH=CH₂, CCH₃=CH₂ und CH=CHCH₃ ausgewählt ist;

(b) wobei der mindestens eine silikonhaltige Bestandteil aus der Gruppe ausgewählt ist, die aus mindestens einem Mono(meth)acryloxyalkylpolydialkylsiloxan-Monomer der Formel VII besteht:



Formel VII

wobei R₁₂ gleich H oder Methyl ist;

X für O oder NR₁₆ steht;

jedes R₁₄ auf unabhängige Weise für ein C₁- bis C₄-Alkyl, welches mit Fluor substituiert sein kann, oder Phenyl steht;

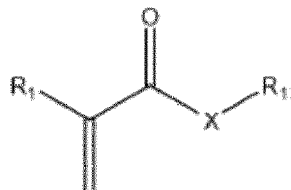
R₁₅ für ein C₁- bis C₄-Alkyl steht;

R₁₃ für eine zweibindige Alkylgruppe steht, die weiterhin mit einer funktionellen Gruppen versehen sein kann, die aus der Gruppe ausgewählt ist, welche aus Ethergruppen, Hydroxylgruppen, Carbatgruppen und deren Kombinationen besteht;

a gleich 3 bis 50 ist;

R₁₆ aus H, C₁₋₄, welches weiterhin mit einer oder mehreren Hydroxylgruppen substituiert sein kann; ausgewählt ist;

(c) wobei mindestens ein Hydroxyalkylmonomer aus der Gruppe ausgewählt ist, die aus einem Hydroxyalkyl(meth)acrylat- oder (Meth)acrylamidmonomer der Formel IX besteht:



FORMEL IX

wobei R₁ gleich H oder Methyl ist;

X für O oder NR₁₆ steht, R₁₆ für ein H, C₁- bis C₄-Alkyl, welches weiterhin mit mindestens einem OH substituiert sein kann, steht;

R₁₇ aus mono- oder dihydroxysubstituiertem C₂-C₄-Alkyl und Polyethylenglykol mit 1 bis 10 Wiederholeinheiten ausgewählt ist; wobei das mindestens eine Hydroxyalkyl(meth)acrylat- oder (Meth)acrylamidmonomer und das langsam reagierende Monomer in Molprozentanteilen vorliegen, welche ein Molverhältnis zwischen 0,15 und 0,4 ergeben.

9. Silikonhydrogel nach Anspruch 8, wobei:

i) jedes R₃ auf unabhängige Weise aus Ethyl- und Methylgruppen ausgewählt ist; oder

ii) sämtliche R₃ gleich Methyl sind.

10. Silikonhydrogel nach Anspruch 8 oder Anspruch 9, wobei R₁₆ gleich H oder Methyl ist.

11. Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 10, wobei R₁₂ und jedes der R₁₄ gleich Methyl sind.

12. Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 11, wobei das langsam reagierende hydrophile Monomer aus den folgenden ausgewählt ist:

i) dem Vinylpyrrolidon der Formel II oder IV oder dem N-Vinylamidmonomer der Formel I, wobei dieses in R₁

und R_2 eine Gesamtzahl an Kohlenstoffatomen von höchstens 4 aufweist; oder

ii) einem Vinylpyrrolidon der Formel III oder IV, wobei R_6 gleich Methyl ist, R_7 gleich Wasserstoff ist, R_9 gleich $\text{CH}=\text{CH}_2$ ist, R_{10} und R_{11} gleich H sind.

5 **13.** Silikonhydrogel nach den Ansprüchen 8-11, wobei das langsam reagierende hydrophile Monomer aus Ethylenglykolvinylether (EGVE), Di(ethylenglykol)-vinylether (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-Hydroxyethylvinylcarbammat, N-Carboxy- β -alanin-N-vinylester; N-Carboxyvinyl- β -alanin (VINAL), N-Carboxyvinyl- α -alanin und deren Mischungen ausgewählt ist,

15 wobei das langsam reagierende hydrophile Monomer vorzugsweise aus der Gruppe ausgewählt ist, die aus N-Vinylpyrrolidon, N-Vinylacetamid, 1-Methyl-3-methylen-2-pyrrolidon, 1-Methyl-5-methylen-2-pyrrolidon, 5-Methyl-3-methylen-2-pyrrolidon und deren Mischungen besteht

wobei das langsam reagierende hydrophile Monomer insbesondere aus der Gruppe ausgewählt ist, die aus NVP, VMA und 1-Methyl-5-methylen-2-pyrrolidon besteht,

wobei das langsam reagierende hydrophile Monomer mit dem größten Vorzug NVP umfasst.

20 **14.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 13, wobei mindestens ein R_{14} gleich 3,3,3-Trifluorpropyl ist.

25 **15.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 14, wobei R_{13} aus C_1 - C_6 -Alkylengruppen ausgewählt ist, die mit Ether, Hydroxyl und deren Kombinationen substituiert sein können, wobei R_{13} vorzugsweise aus C_1 - oder C_{3-6} -Alkylengruppen ausgewählt ist, die mit Ether, Hydroxyl und deren Kombinationen substituiert sein können.

30 **16.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 15, wobei:

i) a gleich 5 bis 15 ist; oder

ii) a gleich 7 bis 30 ist.

35 **17.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 oder 9 oder 12 bis 15, wobei das Monomethacryloxyalkylpolydimethylsiloxanmethacrylat aus der Gruppe ausgewählt ist, die aus Polydimethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-butyl, Polydimethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-methyl, Polydiethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-butyl, Polydiethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-methyl, N-(2,3-Dihydroxypropan)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilan)-acrylamid; α -(2-Hydroxy-1-methacryloxypropyloxypropyl)- ω -butyl-octamethylpentasiloxan und deren Mischungen besteht,

40 wobei das Monomethacryloxyalkylpolydimethylsiloxanmethacrylat vorzugsweise aus der Gruppe ausgewählt ist, die aus Polydimethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-butyl, Polydimethylsiloxan mit endständigem Monomethacryloxypropyl und endständigem Mono-n-methyl, N-(2,3-Dihydroxypropan)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilan)-acrylamid besteht.

45 **18.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 17, wobei:

i) R_1 gleich H oder Methyl ist, X gleich Sauerstoff ist und R aus mono- oder dihydroxysubstituiertem C_2 - C_4 -Alkyl und Polyethylenglykol mit 1 bis 10 Wiederholeinheiten ausgewählt ist; oder

50 ii) R_1 gleich Methyl ist, X gleich Sauerstoff ist und R aus mono- oder dihydroxysubstituiertem C_2 - C_4 -Alkyl und Polyethylenglykol mit 2 bis 20 Wiederholeinheiten ausgewählt ist.

19. Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 18, wobei R gleich 2-Hydroxyethyl, 2,3-Dihydroxypropyl, 2-Hydroxypropyl ist.

55 **20.** Silikonhydrogel nach einem beliebigen der Ansprüche 8 bis 19, wobei R_4 gleich Methyl oder 2-Hydroxyethyl ist.

21. Silikonhydrogel nach einem beliebigen der Ansprüche 1 bis 17, wobei das Hydroxyalkylmonomer aus der Gruppe

ausgewählt ist, die aus 2-Hydroxyethyl(meth)acrylat, 3-Hydroxypropyl(meth)acrylat, 2-Hydroxypropyl(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, 2-Hydroxyethyl(meth)acrylamid, Polyethylenglykolmonomethacrylat, bis-(2-Hydroxyethyl)(meth)acrylamid, 2,3-Dihydroxypropyl(meth)acrylamid und deren Mischungen besteht,

wobei das Hydroxyalkylmonomer vorzugsweise aus der Gruppe ausgewählt ist, die aus 2-Hydroxyethylmethacrylat, Glycerinmethacrylat, 2-Hydroxypropylmethacrylat, Hydroxybutylmethacrylat, 3-Hydroxy-2,2-dimethylpropylmethacrylat und deren Mischungen besteht,

wobei das Hydroxyalkylmonomer insbesondere 2-Hydroxyethylmethacrylat, 3-Hydroxy-2,2-dimethylpropylmethacrylat, Glycerinmethacrylat und Mischungen, in welchen diese enthalten sind, umfasst.

22. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die Reaktionsmischung weiterhin mindestens ein langsam reagierendes Quervernetzungsmittel und mindestens ein schnell reagierendes Quervernetzungsmittel umfasst, wobei das mindestens eine langsam reagierende Quervernetzungsmittel und das mindestens eine schnell reagierende Quervernetzungsmittel jeweils in den folgenden Mengen in der Reaktionsmischung vorliegen:

i) zwischen 0,05 und 0,3 Gew.-%; oder

ii) zwischen 0,1 und 0,2 Gew.-%.

23. Silikonhydrogel nach Anspruch 1, wobei der mindestens eine silikonhaltige Bestandteil und der mindestens eine hydroxylhaltige Bestandteil dieselben reaktionsfähigen funktionellen Gruppen haben.

24. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei:

i) das mindestens eine Hydroxyalkylmonomer in Molprozentanteilen vorliegt, welche ein Molverhältnis Hydroxylgruppen zu langsam reagierendem hydrophilem Monomer zwischen 0,15 und 0,4 ergeben; oder

ii) wobei das Molverhältnis von Hydroxylgruppen in der Reaktionsmischung zu Silicium (HO:Si) zwischen 0,16 und 0,4 liegt.

25. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei das langsam reagierende hydrophile Monomer eine langsam reagierende Gruppe umfasst, die aus N-Vinylamiden, O-Vinylcarbamaten, O-Vinylcarboxylaten, N-Vinylcarbamaten, O-Vinylethern, O-2-Propenyl ausgewählt ist, wobei die Vinyl- oder Alkylgruppen weiterhin mit einer Methylgruppe substituiert sein können.

26. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die Reaktionsmischung weitgehend frei von TRIS ist.

27. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei das Silikonhydrogel ohne silikonhaltige Makromere oder Präpolymere hergestellt wird, wobei unter "Silikon-Makromeren" und Silikon-"Prepolymeren" mono- und multifunktionelle silikonhaltige Verbindungen mit Molekulargewichten von mehr als 2000 zu verstehen sind.

28. Silikonhydrogel nach einem beliebigen der vorhergehenden Ansprüche, wobei die Reaktionsmischung zwischen 9 und 13 Gew.-% an Silicium umfasst.

29. Verfahren zum Bilden des Silikonhydrogels nach einem der vorhergehenden Ansprüche, bei dem Photoinitiation verwendet wird und die Reaktionsmischung einen Photoinitiator umfasst, wobei die Härtingszeit weniger als 30 Minuten beträgt.

Revendications

1. Hydrogel de silicone comprenant une teneur en eau d'au moins 50 % et une perméabilité à l'oxygène d'au moins 80 barrers, ledit hydrogel de silicone étant formé à partir d'un mélange réactionnel comprenant 30 à 75 % en poids d'au moins un monomère hydrophile réagissant lentement ayant une demi-vie cinétique de monomère hydrophile réagissant lentement ;

au moins un composant contenant une silicone ayant une demi-vie cinétique de composant contenant une silicone, qui peut être éventuellement substitué par au moins un groupe contenant hydroxyle ;
 au moins un composant contenant hydroxyle choisi parmi lesdits composants contenant une silicone substitués
 par au moins un groupe hydroxyle, au moins un monomère de type hydroxyalkyle et des mélanges de ceux-ci,
 dans lequel le rapport de ladite demi-vie du composant hydrophile réagissant lentement sur ladite demi-vie du
 composant contenant une silicone est d'au moins 2, ledit mélange réactionnel comprenant entre 9 et 14 % en
 poids de silicone et moins de 15 % en poids de TRIS et dans lequel tous les composants réactifs autres que
 ledit monomère hydrophile réagissant lentement et lesdits composants contenant une silicone sont des com-
 posants auxiliaires dans le mélange réactionnel et sont présents en une quantité comprise entre 11 et 92
 mmole/100 g de composants réactifs.

2. Hydrogel de silicone selon la revendication 1, dans lequel le mélange réactionnel comprend :

- i) 37 à 75 % en poids ; ou
- ii) 37 à 70 % en poids ; ou
- iii) 39 à 60 % en poids

de l'au moins un monomère hydrophile réagissant lentement ayant une demi-vie cinétique de monomère hydrophile réagissant lentement.

3. Hydrogel de silicone selon une quelconque revendication précédente, dans lequel lesdits composants contenant une silicone comprennent moins de 10 % en poids de TRIS.

4. Hydrogel de silicone selon la revendication 1 ou la revendication 2, dans lequel lesdits composants contenant une silicone sont exempts de TRIS.

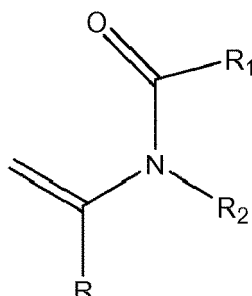
5. Hydrogel de silicone selon une quelconque revendication précédente dans lequel lesdits composants auxiliaires sont présents dans ledit mélange réactionnel en une concentration inférieure à 12 % en poids sur la base des composants réactifs.

6. Hydrogel de silicone selon une quelconque revendication précédente dans lequel ladite teneur en eau est :

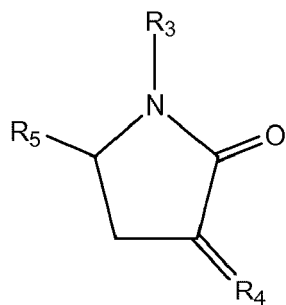
- i) d'au moins 55 % ; ou
- ii) d'au moins 60 %.

7. Hydrogel de silicone selon une quelconque revendication précédente dans lequel lesdits composants comprennent entre 38 et 76 mmole/100 g de composant réactifs.

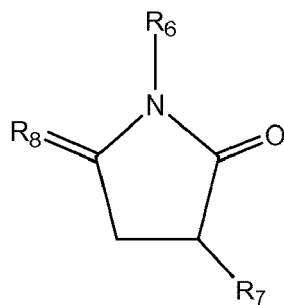
8. Hydrogel de silicone selon une quelconque revendication précédente dans lequel ledit au moins un monomère réagissant lentement est choisi dans le groupe constitué par un monomère de type N-vinylamide de formule I, une vinylpyrrolidone de formule II-IV, une N-vinylpipéridone de formule V :



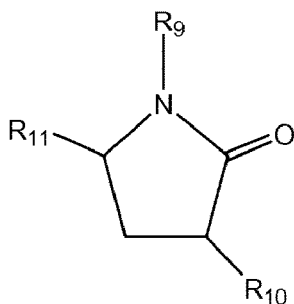
Formule I



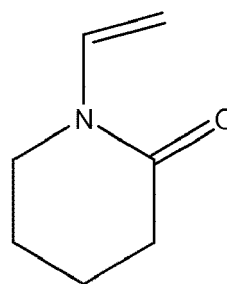
Formule II



Formule III



Formule IV



Formule V

dans lesquelles

R est H ou méthyle ;

R₁, R₂, R₃, R₆, R₇, R₁₀ et R₁₁ sont indépendamment choisis dans le groupe constitué par H, CH₃, CH₂CH₃, CH₂CH₂CH₃, C(CH₃)₂ ;

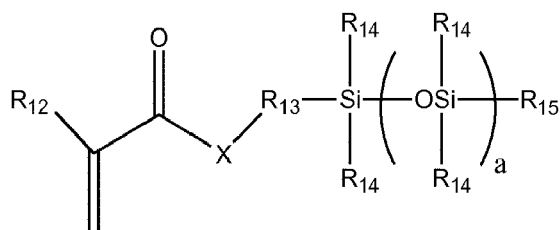
R₄ et R₈ sont indépendamment choisis dans le groupe constitué par CH₂, CHCH₃ et C(CH₃) ;

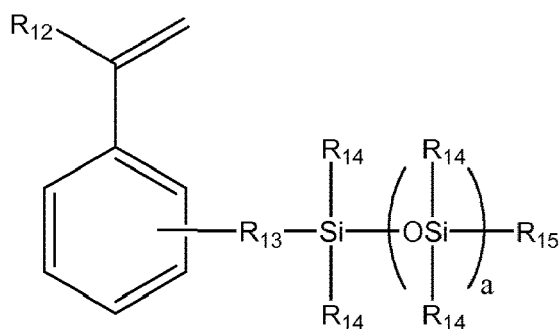
R₅ est choisi parmi H, méthyle, éthyle ; et

R₉ est choisi parmi CH=CH₂, C(CH₃)=CH₂ et CH=CHCH₃ ;

dans lequel ledit composant contenant une silicone est choisi dans le groupe constitué par au moins un monomère de type mono(méth)acryloxyalkyl-polydialkylsiloxane de formule VII ou le monomère de type styryl-polydialkylsiloxane de formule VIII :

Formule VII





Formule VIII

dans lesquelles

R_{12} est H ou méthyle ;

X est O ou NR_{16} ;

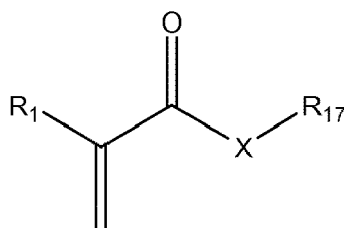
chaque R_{14} est indépendamment un alkyle en C_1 à C_4 qui peut être substitué par fluor, ou phényle ;

R_{15} est un alkyle en C_1 à C_4 ;

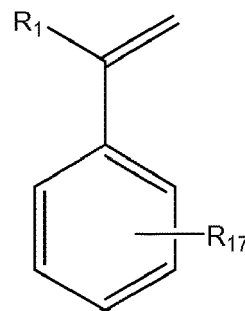
R_{13} est un groupe alkyle divalent, qui peut être en outre fonctionnalisé par un groupe choisi dans le groupe constitué par des groupes éther, des groupes hydroxyle, des groupes carbamate et des combinaisons de ceux-ci ;

a est 3 à 50 ;

R_{16} est choisi parmi H, C_1 -4, qui peut être en outre substitué par un ou plusieurs groupes hydroxyle ; et ledit monomère de type hydroxyalkyle est choisi dans le groupe constitué par au moins un monomère de type (méth)acrylate d'hydroxyalkyle ou hydroxyalkyl(méth)acrylamide de formule IX ou un composé de type styryle de formule X



FORMULE IX



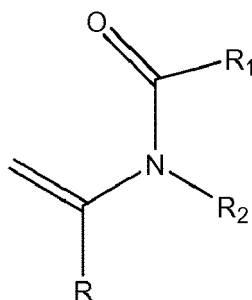
FORMULE X

dans lesquelles

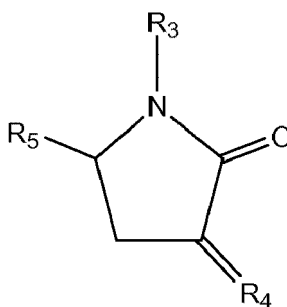
R_1 est H ou méthyle,

X est O ou NR_{16} , R_{16} est un H, alkyle en C_1 à C_4 , qui peut être en outre substitué par au moins un OH ;

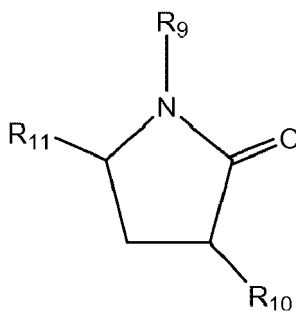
R_{17} est choisi parmi alkyle en C_2 - C_4 substitué par monohydroxy ou dihydroxy, et un polyéthylèneglycol ayant 1 à 10 motifs répétitifs ; dans lequel ledit au moins un monomère de type (méth)acrylate d'hydroxyalkyle ou hydroxyalkyl(méth)acrylamide et ledit monomère réagissant lentement sont présents en des pourcentages en mole qui forment un rapport molaire compris entre 0,15 et 0,4, préférablement dans lequel ledit au moins un monomère réagissant lentement est choisi dans le groupe constitué par un monomère de type N-vinylamide de formule I, une vinylpyrrolidone de formule II ou IV :



Formule I



Formule II



Formule IV

dans lesquelles

R est H ou méthyle ;

R₁, R₂, R₃, R₁₀ et R₁₁ sont indépendamment choisis dans le groupe constitué par H, CH₃, CH₂CH₃, CH₂CH₂CH₃, C(CH₃)₂ ;

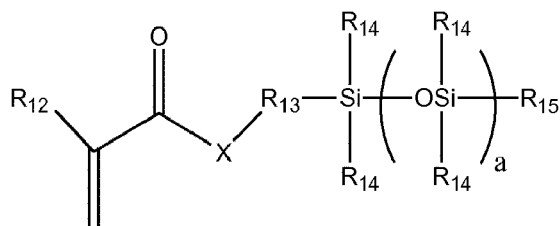
R₄ est choisi dans le groupe constitué par CH₂, CHCH₃ et C(CH₃) ;

R₅ est choisi parmi H, méthyle, éthyle ; et

R₉ est choisi parmi CH=CH₂, CCH₃=CH₂ et CH=CHCH₃ ;

(b) ledit au moins un composant contenant une silicone est choisi dans le groupe constitué par au moins un monomère de type mono(méth)acryloxyalkylpolydialkylsiloxane de formule VII :

Formule VII



dans laquelle

R_{12} est H ou méthyle ;

X est O ou NR_{16} ;

chaque R_{14} est indépendamment un alkyle en C_1 à C_4 qui peut être substitué par fluor, ou un groupe phényle ;

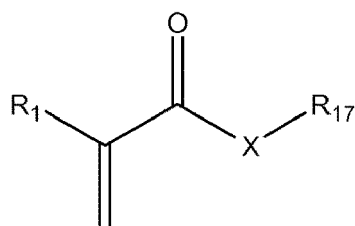
R_{15} est un alkyle en C_1 à C_4 ;

R_{13} est un groupe divalent, qui peut être en outre fonctionnalisé par un groupe choisi dans le groupe constitué par des groupes éther, des groupes hydroxyle, des groupes carbamate et des combinaisons de ceux-ci ;

a est 3 à 50 ;

R_{16} est choisi parmi H, C_{1-4} , qui peut être en outre substitué par un ou plusieurs groupes hydroxyle ;

(c) au moins un monomère de type hydroxyalkyle est choisi dans le groupe constitué par un monomère de type (méth)acrylate d'hydroxyalkyle ou hydroxyalkyl(méth)acrylamide de formule IX



FORMULE IX

dans laquelle

R_1 est H ou méthyle,

X est O ou NR_{16} , R_{16} est un H, alkyle en C_1 à C_4 , qui peut être en outre substitué par au moins un OH ;

R_{17} est choisi parmi alkyle en C_2 - C_4 substitué par monohydroxy ou dihydroxy et un polyéthylèneglycol ayant 1 à 10 motifs répétitifs ; dans lequel ledit au moins un monomère de type (méth)acrylate d'hydroxyalkyle ou hydroxyalkyl(méth)acrylamide et ledit monomère réagissant lentement sont présents en des pourcentages en mole qui forment un rapport molaire compris entre 0,15 et 0,4.

9. Hydrogel de silicone selon la revendication 8 dans lequel :

i) chaque R_3 est indépendamment choisi parmi des groupes éthyle et méthyle ; ou

ii) tous les R_3 sont méthyle.

10. Hydrogel de silicone selon la revendication 8 ou la revendication 9, dans lequel R_{16} est H ou méthyle.

11. Hydrogel de silicone selon l'une quelconque des revendications 8 à 10 dans lequel R_{12} et chaque R_{14} sont méthyle.

12. Hydrogel de silicone selon l'une quelconque des revendications 8 à 11 dans lequel le monomère hydrophile réagissant lentement est choisi parmi :

i) la vinylpyrrolidone de formule II ou IV ou le monomère de type N-vinylamide de formule I, ayant un nombre total d'atomes de carbone dans R_1 et R_2 inférieur ou égal à 4 ; ou

ii) une vinylpyrrolidone de formule III ou IV et R_6 est méthyle, R_7 est hydrogène, R_9 est $CH=CH_2$, R_{10} et R_{11} sont H.

13. Hydrogel de silicone selon les revendications 8 à 11 dans lequel le monomère hydrophile réagissant lentement est choisi parmi l'éther de vinyle d'éthylène glycol (EGVE), l'éther de vinyle de diéthylèneglycol (DEGVE), la N-vinylpyrrolidone (NVP), la 1-méthyl-3-méthylène-2-pyrrolidone, la 1-méthyl-5-méthylène-2-pyrrolidone, la 5-méthyl-3-méthylène-2-pyrrolidone ; la 1-éthyl-5-méthylène-2-pyrrolidone, la N-méthyl-3-méthylène-2-pyrrolidone, la 5-éthyl-3-méthylène-2-pyrrolidone, la 1-n-propyl-3-méthylène-2-pyrrolidone, la 1-n-propyl-5-méthylène-2-pyrrolidone, la 1-isopropyl-3-méthylène-2-pyrrolidone, la 1-isopropyl-5-méthylène-2-pyrrolidone, le N-vinyl-N-méthylacétamide

(VMA), le N-vinyl-N-éthylacétamide, le N-vinyl-N-éthylformamide, le N-vinylformamide, le N-vinylacétamide, le N-vinylisopropylamide, l'alcool allylique, le N-vinylcaprolactame, le N-2-hydroxyéthylcarbamate de vinyle, l'ester N-vinyle de la N-carboxy- β -alanine ; la N-carboxyvinyl- β -alanine (VINAL), la N-carboxyvinyl- α -alanine et des mélanges de ceux-ci, préférablement

dans lequel le monomère hydrophile réagissant lentement est choisi dans le groupe constitué par la N-vinylpyrrolidone, le N-vinylacétamide, la 1-méthyl-3-méthylène-2-pyrrolidone, la 1-méthyl-5-méthylène-2-pyrrolidone, la 5-méthyl-3-méthylène-2-pyrrolidone et des mélanges de ceux-ci, plus préférablement dans lequel le monomère hydrophile réagissant lentement est choisi dans le groupe constitué par la NVP, le VMA et la 1-méthyl-5-méthylène-2-pyrrolidone, le plus préférablement dans lequel le monomère hydrophile réagissant lentement comprend de la NVP.

14. Hydrogel de silicone selon l'une quelconque des revendications 8 à 13 dans lequel au moins un R_{14} est 3,3,3-trifluoropropyle.

15. Hydrogel de silicone selon l'une quelconque des revendications 8 à 14 dans lequel R_{13} est choisi parmi des groupes alkylène en C_1 - C_6 qui peuvent être substitués par éther, hydroxyle et des combinaisons de ceux-ci, préférablement dans lequel R_{13} est choisi parmi des groupes alkylène en C_1 ou C_{3-6} qui peuvent être substitués par éther, hydroxyle et des combinaisons de ceux-ci.

16. Hydrogel de silicone selon l'une quelconque des revendications 8 à 15 dans lequel :

- i) a est 5 à 15 ; ou
- ii) a est 7 à 30.

17. Hydrogel de silicone selon l'une quelconque des revendications 8 ou 9 ou 12 à 15 dans lequel ledit méthacrylate de monométhacryloxyalkylpolydiméthylsiloxane est choisi dans le groupe constitué par un polydiméthylsiloxane terminé par mono-n-butyle terminé par monométhacryloxypropyle, un polydiméthylsiloxane terminé par mono-n-méthyle terminé par monométhacryloxypropyle, un polydiéthylsiloxane terminé par mono-n-butyle terminé par monométhacryloxypropyle, un polydiéthylsiloxane terminé par mono-n-méthyle et terminé par monométhacryloxypropyle, le N-(2,3-dihydroxypropane)-N'-(propyltétra(diméthylsiloxyl)diméthylbutylsilane)-acrylamide ; l' α -(2-hydroxy-1-méthacryloxypropyloxypropyl)- ω -butyloctaméthylpentasiloxane et des mélanges de ceux-ci, préférablement dans lequel ledit méthacrylate de monométhacryloxyalkylpolydiméthylsiloxane est choisi dans le groupe constitué par un polydiméthylsiloxane terminé par mono-n-butyle terminé par monométhacryloxypropyle, le polydiméthylsiloxane terminé par mono-n-méthyle terminé par monométhacryloxypropyle, un N-(2,3-dihydroxypropane)-N'-(propyltétra(diméthylsiloxyl)diméthylbutylsilane)-acrylamide.

18. Hydrogel de silicone selon l'une quelconque des revendications 8 à 17 dans lequel :

- i) R_1 est H ou méthyle, X est oxygène et R est choisi parmi alkyle en C_2 - C_4 substitué par monohydroxy ou dihydroxy, et un polyéthylèneglycol ayant 1 à 10 motifs répétitifs ; ou
- ii) R_1 est méthyle, X est oxygène et R est choisi parmi alkyle en C_2 - C_4 substitué par monohydroxy ou dihydroxy, et un polyéthylèneglycol ayant 2 à 20 motifs répétitifs.

19. Hydrogel de silicone selon l'une quelconque des revendications 8 à 18 dans lequel R est 2-hydroxyéthyle, 2,3-dihydroxypropyle, 2-hydroxypropyle.

20. Hydrogel de silicone selon l'une quelconque des revendications 8 à 19 dans lequel R_4 est méthyle ou 2-hydroxyéthyle.

21. Hydrogel de silicone selon l'une quelconque des revendications 1 à 17 dans lequel ledit monomère de type hydroxyalkyle est choisi dans le groupe constitué par le (méth)acrylate de 2-hydroxyéthyle, le (méth)acrylate de 3-hydroxypropyle, le (méth)acrylate de 2-hydroxypropyle, le 2-(méth)acrylate de 1-hydroxypropyle, le (méth)acrylate de 2-hydroxy-2-méthylpropyle, le (méth)acrylate de 3-hydroxy-2,2-diméthylpropyle, le (méth)acrylate de 4-hydroxybutyle, le (méth)acrylate de glycérol, le 2-hydroxyéthyl(méth)acrylamide, un monométhacrylate de polyéthylèneglycol, le bis(2-hydroxyéthyl)(méth)acrylamide, le 2,3-dihydroxypropyl(méth)acrylamide et des mélanges de ceux-ci, préférablement

dans lequel ledit monomère de type hydroxyalkyle est choisi dans le groupe constitué par le méthacrylate de

2-hydroxyéthyle, le méthacrylate de glycérol, le méthacrylate de 2-hydroxypropyle, le méthacrylate d'hydroxybutyle, le méthacrylate de 3-hydroxy-2,2-diméthylpropyle et des mélanges de ceux-ci, plus préférablement dans lequel ledit monomère de type hydroxyalkyle comprend le méthacrylate de 2-hydroxyéthyle, le méthacrylate de 3-hydroxy-2,2-diméthylpropyle, le méthacrylate de glycérol et des mélanges les comprenant.

22. Hydrogel de silicone selon une quelconque revendication précédente dans lequel ledit mélange réactionnel comprend en outre au moins un agent de réticulation réagissant lentement et au moins un agent de réticulation réagissant rapidement, éventuellement dans lequel lesdits au moins un agent de réticulation réagissant lentement et au moins un agent de réticulation réagissant rapidement sont chacun présents dans ledit mélange réactionnel en des quantités comprises entre :

- i) 0,05 et 0,3 % en poids ; ou
- ii) 0,1 et 0,2 % en poids.

23. Hydrogel de silicone selon la revendication 1 dans lequel ledit au moins un composant contenant une silicone et ledit au moins un composant contenant un hydroxyle ont la même fonctionnalité réactive.

24. Hydrogel de silicone selon une quelconque revendication précédente, dans lequel :

- i) ledit au moins un monomère de type hydroxyalkyle est présent en des pourcentages en mole qui forment un rapport molaire de groupes hydroxyle sur monomère hydrophile réagissant lentement compris entre 0,15 et 0,4 ; ou
- ii) dans lequel le rapport molaire de groupes hydroxyle dans le mélange réactionnel sur le silicium (HO : Si) est compris entre 0,16 et 0,4.

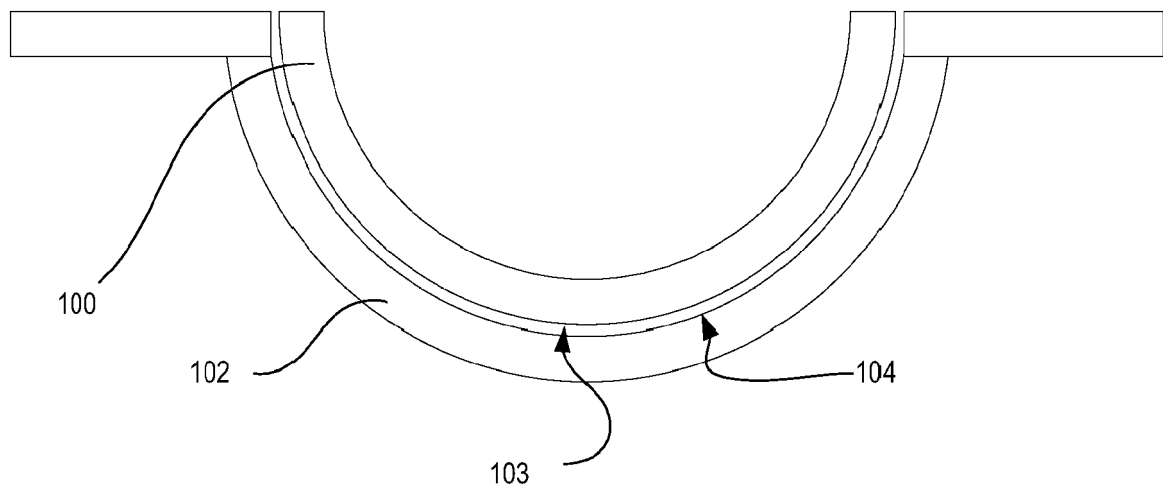
25. Hydrogel de silicone selon une quelconque revendication précédente, dans lequel ledit monomère hydrophile réagissant lentement comprend un groupe réagissant lentement choisi parmi des N-vinylamides, des O-vinylcarbammates, des O-vinylcarbonates, des N-vinylcarbammates, des O-vinyléthers, O-2-propényle, dans lesquels les groupes vinyle ou allyle peuvent être en outre substitués par un groupe méthyle.

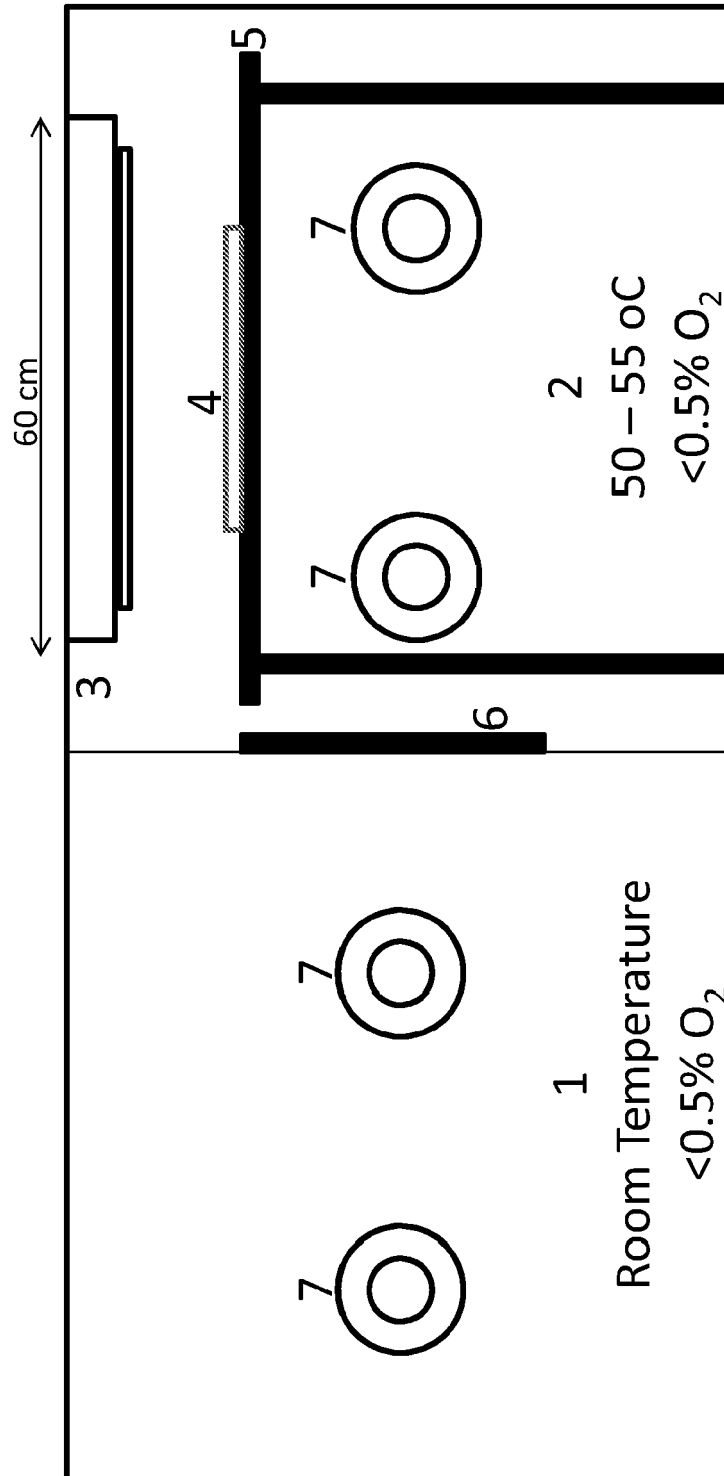
26. Hydrogel de silicone selon une quelconque revendication précédente, dans lequel le mélange réactionnel est sensiblement exempt de TRIS.

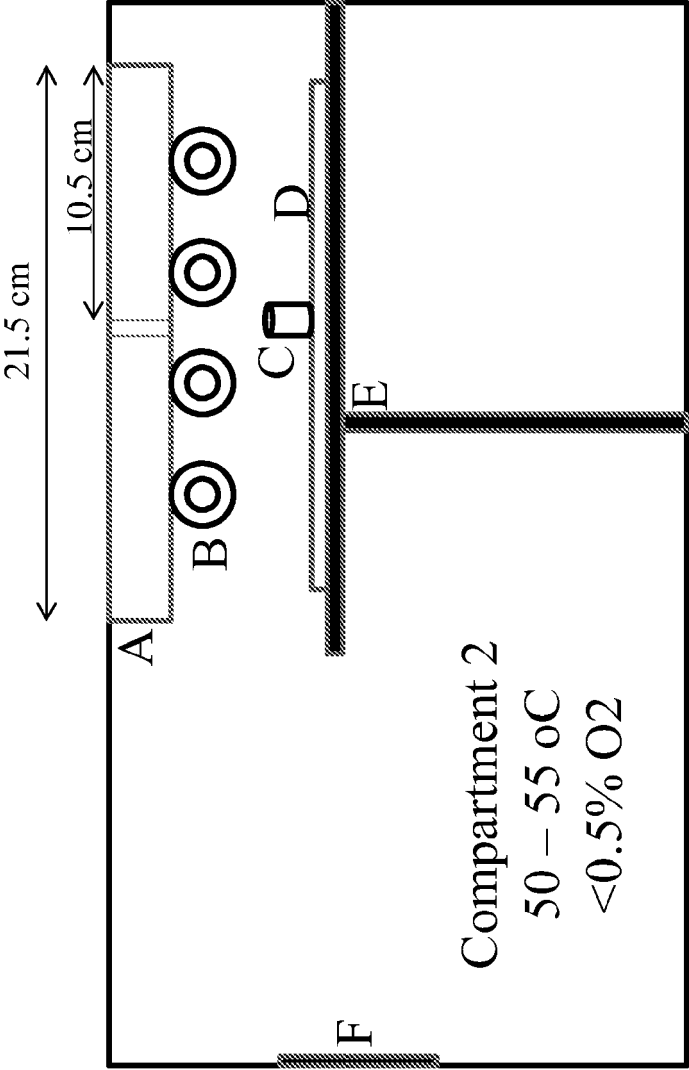
27. Hydrogel de silicone selon une quelconque revendication précédente, dans lequel l'hydrogel de silicone est préparé sans macromères ou prépolymères contenant une silicone, les termes « macromères de silicone » et « prépolymères » de silicone signifiant des composés contenant une silicone monofonctionnelle et multifonctionnelle possédant des poids moléculaires supérieurs à 2 000.

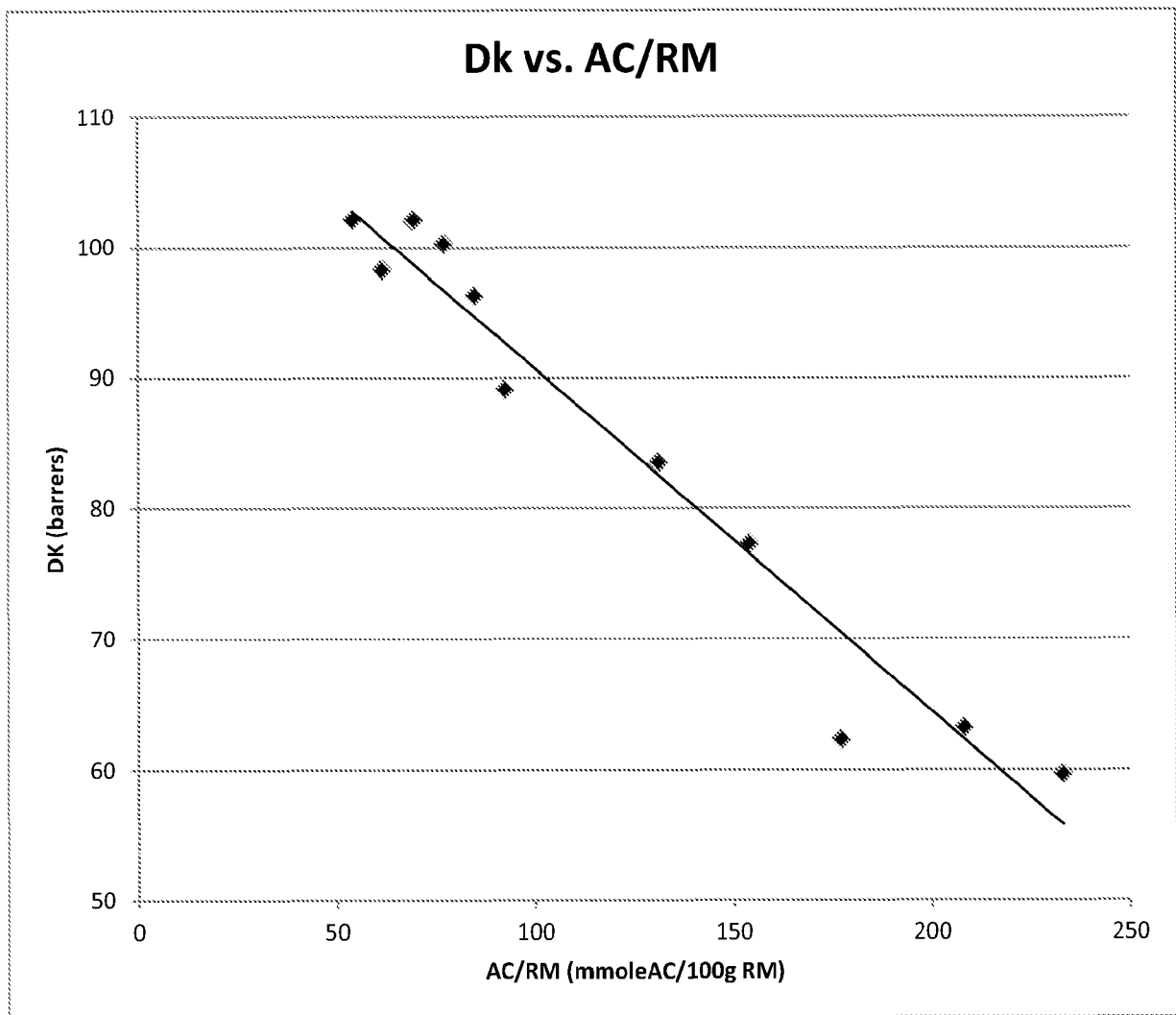
28. Hydrogel de silicone selon une quelconque revendication précédente, ledit mélange réactionnel comprenant entre 9 et 13 % en poids de silicium.

29. Procédé pour la formation de l'hydrogel de silicone selon une quelconque revendication précédente, le procédé utilisant une photoinitiation et le mélange réactionnel comprenant un photoinitiateur, le temps de durcissement étant inférieur à 30 minutes.









REFERENCES CITED IN THE DESCRIPTION

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