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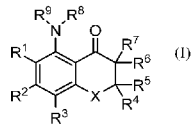

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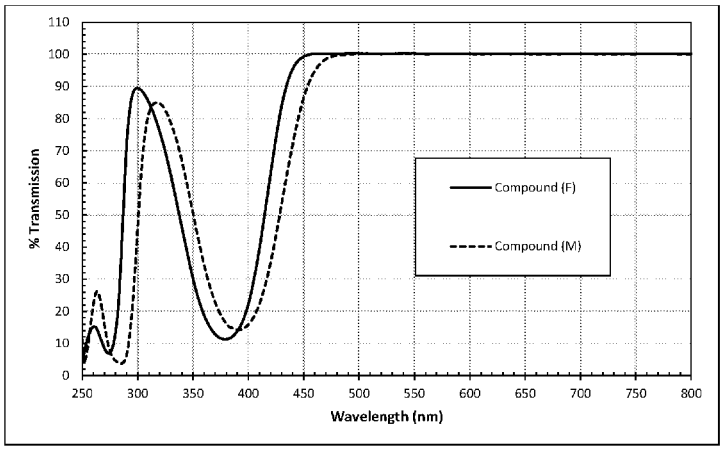

FIG. 1 – UV-VIS Transmission Spectra of 0.2 mM methanol solutions of Compounds (F) and (M)

(57) Abstract: Described are polymerizable high energy light absorbing compounds of formula (I) wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, and X are as described herein. The compounds absorb various wavelengths of ultraviolet and/or high energy visible light and are suitable for incorporation in various products, such as biomedical devices and ophthalmic devices.

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POLYMERIZABLE ABSORBERS OF UV AND HIGH ENERGY VISIBLE LIGHT

Related Applications

This application claims priority to U.S. Patent Application Serial No. 16/548,204, filed on August 22, 2019 and U.S. Provisional Patent Application Serial No. 62/736,496, filed September 26, 2018, which is incorporated herein by reference in its entirety.

Field of the Invention

The invention relates to UV and high energy visible light absorbers. More particularly, the invention relates to compounds with polymerizable functionality that absorb various wavelengths of UV and/or high energy visible light, and yet are visibly transparent when incorporated in an article. Thus, the compounds may be used in polymeric articles, including biomedical devices, such as ophthalmic devices.

Background of the Invention

High energy radiation from the sun, such as UV and high-energy visible light, is known to be responsible for cellular damage. While most of the radiation below 280 nm in wavelength is absorbed by the earth's atmosphere, photons possessing wavelengths ranging between 280 and 400 nm have been associated with several ocular disorders including corneal degenerative changes, and age-related cataract and macular degeneration. (See Statement on Ocular Ultraviolet Radiation Hazards in Sunlight, American Optometric Association, November 10, 1993). The human cornea absorbs some radiation up to 320 nm in wavelength (30% transmission) (Doutch, J.J., Quantock, A.J., Joyce, N.C., Meek, K.M, *Biophys. J.*, 2012, 102, 1258–1264), but is inefficient in protecting the back of the eye from radiation ranging from 320 to 400 nm in wavelength.

Contact lens standards define the upper UV radiation wavelength at 380 nm. The current Class I UV absorbing criteria defined by the American Optometric Association require > 99% of the radiation between 280 and 315 nm (UV B) and > 90% of the 316 to 380 nm (UV A) radiation to be absorbed by the contact lens. While the criteria effectively address absorption of higher energy UV, there is little attention paid to the lower energy UV radiation (> 380 < 400 nm) associated with retinal damage (Ham, W.T, Mueller, H. A., Sliney, D. H. *Nature* 1976; 260(5547):153-5) or to high energy visible radiation.

High energy-visible light may also cause visual discomfort or circadian rhythm disruption. For example, computer and electronic device screens, flat screen televisions, energy efficient lights, and LED lights are known to generate high energy visible light. Prolonged exposure to such sources may cause eye strain. Viewing high energy visible light emitting devices at night is also postulated to disrupt the natural circadian rhythm leading, for example, to inadequate sleep.

Absorption of high energy light before it reaches the eye continues to be a desirable goal in the ophthalmics field. However, the extent to which a particular wavelength range is absorbed is also important. For instance, in the UV A and UV B ranges, it may be desirable to absorb as much radiation as possible. On the other hand, since high energy visible light forms a part of the visible spectrum, complete absorption of such light may negatively affect vision. With high energy visible light, therefore, partial absorption may be more desirable.

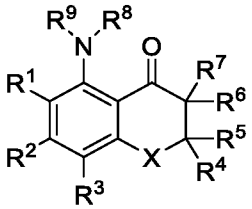
There is a need for materials that provide targeted absorption of undesirable wavelengths of high energy radiation, and that are processable into functional products. Compounds that absorb or attenuate high energy radiation, when used in ophthalmic devices, may help protect the cornea, as well as the interior cells in the ocular environment, from degradation, strain, and/or circadian rhythm disruption.

Summary of the Invention

The invention relates to high energy light absorbing compounds that absorb UV and/or high energy visible (HEV) light while substantially transmitting (e.g., greater than 80% transmission) at wavelengths longer than about 450 nm. The compounds are therefore effective at providing targeted absorption of high energy light, such as UV (UVA and UVB), low energy UV light (385 nm to 400 nm), and/or HEV (e.g., 400 to 450 nm).

The compounds are also polymerizable and are generally compatible with other raw materials, as well as the polymerization and processing conditions, that are used for making ophthalmic devices such as soft contact lenses. The compounds can therefore be readily covalently incorporated into the final product without the need for significant modification of existing manufacturing processes and equipment.

Accordingly, in one aspect the invention provides a compound of formula I:



(I)

wherein R^1 is -Y-P_g;

R^2, R^3, R^4, R^5, R^6, and R^7 are each H;

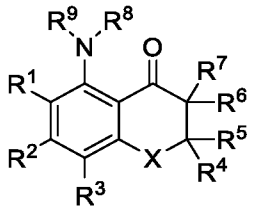
X is CR^4R^5, O, S, or NR^4;

R^8 and R^9 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, or -Y-P_g;

Y is a linking group, wherein Y comprises: C_1-C_8 alkylene, alkyleneoxy, C_1-C_8 oxaalkylene, C_1-C_8 thiaalkylene, C_1-C_8 alkylene-ester-C_1-C_8 alkylene, C_1-C_8 alkylene-amide-C_1-C_8 alkylene, or C_1-C_8 alkylene-amine-C_1-C_8 alkylene; and

P_g is a polymerizable group, wherein P_g comprises: styryl, vinyl carbonate, vinyl ether, vinyl carbamate, N-vinyl lactam, N-vinylamide, (meth)acrylate, or (meth)acrylamide.

In one embodiment, the invention provides a compound of formula I:



(I)

wherein R^1, R^2 and R^3 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, C_1-C_6 alkoxy, aryl, aryloxy, halo, or -Y-P_g; X is CR^4R^5, O, S, or NR^4; R^4, R^5, R^6, R^7, R^8, and R^9 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, or -Y-P_g; Y is a linking group; and P_g is a polymerizable group, wherein at least one of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 is -Y-P_g.

In another aspect, the invention provides an ophthalmic device that is a free radical reaction product of a reactive mixture comprising: one or more monomers suitable for making the ophthalmic device; and a polymerizable high energy light absorbing compound comprising a compound of formula I as described herein.

In a further aspect, the invention provides a method for making an ophthalmic device. The method comprises: (a) providing a reactive mixture containing a compound of formula I as described herein, one or more device forming monomers, and a radical initiator; and (b) polymerizing the reactive mixture to form the ophthalmic device. \

Brief Description of the Figures

FIG. 1 shows UV-VIS Transmission Spectra of 0.2 mM methanol solutions of exemplary Compounds (F) and (M).

FIG. 2 shows UV-VIS Transmission Spectra of Silicone Hydrogel Contact Lenses 4A 4E.

FIG. 3 shows UV-VIS Transmission Spectra of Silicone Hydrogel Contact Lenses 4A and 5A-C.

FIG. 4 shows UV-VIS Transmission Spectra of Conventional Hydrogel Lenses 6A-6E.

Detailed Description of the Invention

It is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways using the teaching herein.

As noted above, in one aspect, the invention provides UV/HEV absorbing compounds. The compounds contain polymerizable functionality. It has been discovered that ophthalmic devices that absorb substantial amounts of UV light as well as some amounts of HEV light can be readily prepared as described herein.

In addition, some known benzotriazole UV absorbing compounds, such as NORBLOC™, exhibit a window, in the range of about 250 to 280 nm, where UV blocking is reduced. Advantageously, compounds of the invention eliminate or significantly reduce this window.

Thus, compounds of the invention may successfully absorb UV (UVA, UVB), and/or HEV, while transmitting in the visible spectrum. The compounds are polymerizable. The compounds therefore are suitable for incorporation in a variety of products, including biomedical devices and ophthalmic devices.

With respect to the terms used in this disclosure, the following definitions are provided.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. The polymer definitions are consistent with those disclosed in the Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008, edited by: Richard G. Jones, Jaroslav Kahovec, Robert Stepto, Edward S. Wilks, Michael Hess, Tatsuki Kitayama, and W. Val Metanomski. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

As used herein, the term "(meth)" designates optional methyl substitution. Thus, a term such as "(meth)acrylates" denotes both methacrylates and acrylates.

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

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

The term "individual" includes humans and vertebrates.

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

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

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

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

The biomedical devices, ophthalmic devices, and lenses of the present invention may be comprised of silicone hydrogels or conventional hydrogels. Silicone hydrogels typically contain

at least one hydrophilic monomer and at least one silicone-containing component that are covalently bound to one another in the cured device.

"Target macromolecule" means the macromolecule being synthesized from the reactive monomer mixture comprising monomers, macromers, prepolymers, cross-linkers, initiators, additives, diluents, and the like.

The term "polymerizable compound" means a compound containing one or more polymerizable groups. The term encompasses, for instance, monomers, macromers, oligomers, prepolymers, cross-linkers, and the like.

"Polymerizable groups" are groups that can undergo chain growth polymerization, such as free radical and/or cationic polymerization, for example a carbon-carbon double bond which can polymerize when subjected to radical polymerization initiation conditions. Non-limiting examples of free radical polymerizable groups include (meth)acrylates, styrenes, vinyl ethers, (meth)acrylamides, *N*-vinyllactams, *N*-vinylamides, O-vinylcarbamates, O-vinylcarbonates, and other vinyl groups. Preferably, the free radical polymerizable groups comprise (meth)acrylate, (meth)acrylamide, N-vinyl lactam, N-vinylamide, and styryl functional groups, and mixtures of any of the foregoing. More preferably, the free radical polymerizable groups comprise (meth)acrylates, (meth)acrylamides, and mixtures thereof. The polymerizable group may be unsubstituted or substituted. For instance, the nitrogen atom in (meth)acrylamide may be bonded to a hydrogen, or the hydrogen may be replaced with alkyl or cycloalkyl (which themselves may be further substituted).

Any type of free radical polymerization may be used including but not limited to bulk, solution, suspension, and emulsion as well as any of the controlled radical polymerization methods such as stable free radical polymerization, nitroxide-mediated living polymerization, atom transfer radical polymerization, reversible addition fragmentation chain transfer polymerization, organotellurium mediated living radical polymerization, and the like.

A "monomer" is a mono-functional molecule which can undergo chain growth polymerization, and in particular, free radical polymerization, thereby creating a repeating unit in the chemical structure of the target macromolecule. Some monomers have di-functional impurities that can act as cross-linking agents. A "hydrophilic monomer" is also a monomer which yields a clear single phase solution when mixed with deionized water at 25°C at a concentration of 5 weight percent. A "hydrophilic component" is a monomer, macromer,

prepolymer, initiator, cross-linker, additive, or polymer which yields a clear single phase solution when mixed with deionized water at 25°C at a concentration of 5 weight percent. A "hydrophobic component" is a monomer, macromer, prepolymer, initiator, cross-linker, additive, or polymer which is slightly soluble or insoluble in deionized water at 25°C.

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

A "macromonomer" or "macromer" is a macromolecule that has one group that can undergo chain growth polymerization, and in particular, free radical polymerization, thereby creating a repeating unit in the chemical structure of the target macromolecule. Typically, the chemical structure of the macromer is different than the chemical structure of the target macromolecule, that is, the repeating unit of the macromer's pendent group is different than the repeating unit of the target macromolecule or its mainchain. The difference between a monomer and a macromer is merely one of chemical structure, molecular weight, and molecular weight distribution of the pendent group. As a result, and as used herein, the patent literature occasionally defines monomers as polymerizable compounds having relatively low molecular weights of about 1,500 Daltons or less, which inherently includes some macromers. In particular, monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight = 500-1500 g/mol) (mPDMS) and mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (molecular weight = 500-1500 g/mol) (OH-mPDMS) may be referred to as monomers or macromers. Furthermore, the patent literature occasionally defines macromers as having one or more polymerizable groups, essentially broadening the common definition of macromer to include prepolymers. As a result and as used herein, di-functional and multi-functional macromers, prepolymers, and crosslinkers may be used interchangeably.

A "silicone-containing component" is a monomer, macromer, prepolymer, cross-linker, initiator, additive, or polymer in the reactive mixture with at least one silicon-oxygen bond, typically in the form of siloxy groups, siloxane groups, carbosiloxane groups, and mixtures thereof.

Examples of silicone-containing components which are useful in this invention may be found in U.S. Patent Nos. 3,808,178, 4,120,570, 4,136,250, 4,153,641, 4,740,533, 5,034,461, 5,070,215, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,760,100, 5,849,811, 5,962,548,

5,965,631, 5,998,498, 6,367,929, 6,822,016, 6,943,203, 6,951,894, 7,052,131, 7,247,692, 7,396,890, 7,461,937, 7,468,398, 7,538,146, 7,553,880, 7,572,841, 7,666,921, 7,691,916, 7,786,185, 7,825,170, 7,915,323, 7,994,356, 8,022,158, 8,163,206, 8,273,802, 8,399,538, 8,415,404, 8,420,711, 8,450,387, 8,487,058, 8,568,626, 8,937,110, 8,937,111, 8,940,812, 8,980,972, 9,056,878, 9,125,808, 9,140,825, 9,156,934, 9,170,349, 9,217,813, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929, and European Patent No. 080539. These patents are hereby incorporated by reference in their entireties.

A "polymer" is a target macromolecule composed of the repeating units of the monomers used during polymerization.

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

A "repeating unit" is the smallest group of atoms in a polymer that corresponds to the polymerization of a specific monomer or macromer.

An "initiator" is a molecule that can decompose into radicals which can subsequently react with a monomer to initiate a free radical polymerization reaction. A thermal initiator decomposes at a certain rate depending on the temperature; typical examples are azo compounds such as 1,1'-azobisisobutyronitrile and 4,4'-aobis(4-cyanovaleric acid), peroxides such as benzoyl peroxide, tert-butyl peroxide, tert-butyl hydroperoxide, tert-butyl peroxybenzoate, dicumyl peroxide, and lauroyl peroxide, peracids such as peracetic acid and potassium persulfate as well as various redox systems. A photo-initiator decomposes by a photochemical process; typical examples are derivatives of benzil, benzoin, acetophenone, benzophenone, camphorquinone, and mixtures thereof as well as various monoacyl and bisacyl phosphine oxides and combinations thereof.

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

A "prepolymer" is a reaction product of monomers which contains remaining polymerizable groups capable of undergoing further reaction to form a polymer.

A "polymeric network" is a cross-linked macromolecule that can swell but cannot dissolve in solvents. "Hydrogels" are polymeric networks that swell in water or aqueous solutions, typically absorbing at least 10 weight percent water. "Silicone hydrogels" are hydrogels that are made from at least one silicone-containing component with at least one hydrophilic component. Hydrophilic components may also include non-reactive polymers.

"Conventional hydrogels" refer to polymeric networks made from components without any siloxy, siloxane or carbosiloxane groups. Conventional hydrogels are prepared from reactive mixtures comprising hydrophilic monomers. Examples include 2-hydroxyethyl methacrylate ("HEMA"), N-vinyl pyrrolidone ("NVP"), N, N-dimethylacrylamide ("DMA") or vinyl acetate. U.S. Patent Nos. 4,436,887, 4,495,313, 4,889,664, 5,006,622, 5,039459, 5,236,969, 5,270,418, 5,298,533, 5,824,719, 6,420,453, 6,423,761, 6,767,979, 7,934,830, 8,138,290, and 8,389,597 disclose the formation of conventional hydrogels. Commercially available conventional hydrogels include, but are not limited to, etafilcon, genfilcon, hilafilcon, lenefilcon, nesofilcon, omafilcon, polymacon, and vifilcon, including all of their variants.

"Silicone hydrogels" refer to polymeric networks made from at least one hydrophilic component and at least one silicone-containing component. Examples of silicone hydrogels include acquafilcon, asmofilcon, balafilcon, comfilcon, delefilcon, enfilcon, fanfilcon, formofilcon, galyfilcon, lotrafilcon, narafilcon, riofilcon, samfilcon, senofilcon, somofilcon, and stenfilcon, including all of their variants, as well as silicone hydrogels as prepared in US Patent Nos. 4,659,782, 4,659,783, 5,244,981, 5,314,960, 5,331,067, 5,371,147, 5,998,498, 6,087,415, 5,760,100, 5,776,999, 5,789,461, 5,849,811, 5,965,631, 6,367,929, 6,822,016, 6,867,245, 6,943,203, 7,247,692, 7,249,848, 7,553,880, 7,666,921, 7,786,185, 7,956,131, 8,022,158, 8,273,802, 8,399,538, 8,470,906, 8,450,387, 8,487,058, 8,507,577, 8,637,621, 8,703,891, 8,937,110, 8,937,111, 8,940,812, 9,056,878, 9,057,821, 9,125,808, 9,140,825, 9156,934, 9,170,349, 9,244,196, 9,244,197, 9,260,544, 9,297,928, 9,297,929 as well as WO 03/22321, WO 2008/061992, and US 2010/0048847. These patents are hereby incorporated by reference in their entireties.

An "interpenetrating polymeric network" comprises two or more networks which are at least partially interlaced on the molecular scale but not covalently bonded to each other and

which cannot be separated without braking chemical bonds. A "semi-interpenetrating polymeric network" comprises one or more networks and one or more polymers characterized by some mixing on the molecular level between at least one network and at least one polymer. A mixture of different polymers is a "polymer blend." A semi-interpenetrating network is technically a polymer blend, but in some cases, the polymers are so entangled that they cannot be readily removed.

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

"Reactive components" are the components in the reactive mixture which become part of the chemical structure of the polymeric network of the resulting hydrogel by covalent bonding, hydrogen bonding, electrostatic interactions, the formation of interpenetrating polymeric networks, or any other means.

The term "silicone hydrogel contact lens" refers to a hydrogel contact lens that is made from at least one silicone-containing compound. Silicone hydrogel contact lenses generally have increased oxygen permeability compared to conventional hydrogels. Silicone hydrogel contact lenses use both their water and polymer content to transmit oxygen to the eye.

The term "multi-functional" refers to a component having two or more polymerizable groups. The term "mono-functional" refers to a component having one polymerizable group.

The terms "halogen" or "halo" indicate fluorine, chlorine, bromine, and iodine.

"Alkyl" refers to an optionally substituted linear or branched alkyl group containing the indicated number of carbon atoms. If no number is indicated, then alkyl (including any optional substituents on alkyl) may contain 1 to 16 carbon atoms. Preferably, the alkyl group contains 1 to 10 carbon atoms, alternatively 1 to 8 carbon atoms, alternatively 1 to 6 carbon atoms, or alternatively 1 to 4 carbon atoms. Examples of alkyl include methyl, ethyl, propyl, isopropyl, butyl, iso-, sec- and tert-butyl, pentyl, hexyl, heptyl, 3-ethylbutyl, and the like. Examples of substituents on alkyl include 1, 2, or 3 groups independently selected from hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, thioalkyl, carbamate, carbonate, halogen, phenyl, benzyl, and combinations thereof. "Alkylene" means a divalent alkyl group, such as -CH_2-, -CH_2CH_2-, -$CH_2CH_2CH_2$-, -$CH_2CH(CH_3)CH_2$-, and -$CH_2CH_2CH_2CH_2$-.

"Haloalkyl" refers to an alkyl group as defined above substituted with one or more halogen atoms, where each halogen is independently F, Cl, Br or I. A preferred halogen is F. Preferred haloalkyl groups contain 1-6 carbons, more preferably 1-4 carbons, and still more preferably 1-2 carbons. "Haloalkyl" includes perhaloalkyl groups, such as -CF_3- or -CF_2CF_3-. "Haloalkylene" means a divalent haloalkyl group, such as -CH_2CF_2-.

"Cycloalkyl" refers to an optionally substituted cyclic hydrocarbon containing the indicated number of ring carbon atoms. If no number is indicated, then cycloalkyl may contain 3 to 12 ring carbon atoms. Preferred are C_3-C_8 cycloalkyl groups, C_3-C_8 cycloalkyl, more preferably C_4-C_8 cycloalkyl, and still more preferably C_5-C_6 cycloalkyl. Examples of cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. Examples of substituents on cycloalkyl include 1, 2, or 3 groups independently selected from alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, thioalkyl, amido, carbamate, carbonate, halo, phenyl, benzyl, and combinations thereof. "Cycloalkylene" means a divalent cycloalkyl group, such as 1,2-cyclohexylene, 1,3- cyclohexylene, or 1,4- cyclohexylene.

"Heterocycloalkyl" refers to a cycloalkyl ring or ring system as defined above in which at least one ring carbon has been replaced with a heteroatom selected from nitrogen, oxygen, and sulfur. The heterocycloalkyl ring is optionally fused to or otherwise attached to other heterocycloalkyl rings and/or non-aromatic hydrocarbon rings and/or phenyl rings. Preferred heterocycloalkyl groups have from 5 to 7 members. More preferred heterocycloalkyl groups have 5 or 6 members. Heterocycloalkylene means a divalent heterocycloalkyl group.

"Aryl" refers to an optionally substituted aromatic hydrocarbon ring system containing at least one aromatic ring. The aryl group contains the indicated number of ring carbon atoms. If no number is indicated, then aryl may contain 6 to 14 ring carbon atoms. The aromatic ring may optionally be fused or otherwise attached to other aromatic hydrocarbon rings or non-aromatic hydrocarbon rings. Examples of aryl groups include phenyl, naphthyl, and biphenyl. Preferred examples of aryl groups include phenyl. Examples of substituents on aryl include 1, 2, or 3 groups independently selected from alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, thioalkyl, carbamate, carbonate, halo, phenyl, benzyl, and combinations thereof. "Arylene" means a divalent aryl group, for example 1,2-phenylene, 1,3-phenylene, or 1,4-phenylene.

"Heteroaryl" refers to an aryl ring or ring system, as defined above, in which at least one ring carbon atom has been replaced with a heteroatom selected from nitrogen, oxygen, and sulfur. The heteroaryl ring may be fused or otherwise attached to one or more heteroaryl rings, aromatic or nonaromatic hydrocarbon rings or heterocycloalkyl rings. Examples of heteroaryl groups include pyridyl, furyl, and thienyl. "Heteroarylene" means a divalent heteroaryl group.

"Alkoxy" refers to an alkyl group attached to the parent molecular moiety through an oxygen bridge. Examples of alkoxy groups include, for instance, methoxy, ethoxy, propoxy and isopropoxy. "Thioalkyl" means an alkyl group attached to the parent molecule through a sulfur bridge. Examples of thioalkyl groups include, for instance, methylthio, ethylthio, n-propylthio and iso-propylthio. "Aryloxy" refers to an aryl group attached to a parent molecular moiety through an oxygen bridge. Examples include phenoxy. "Cyclic alkoxy" means a cycloalkyl group attached to the parent moiety through an oxygen bridge.

"Alkylamine" refers to an alkyl group attached to the parent molecular moiety through an -NH bridge. Alkyleneamine means a divalent alkylamine group, such as $-CH_2CH_2NH-$.

"Siloxanyl" refers to a structure having at least one Si-O-Si bond. Thus, for example, siloxanyl group means a group having at least one Si-O-Si group (i.e. a siloxane group), and siloxanyl compound means a compound having at least one Si-O-Si group. "Siloxanyl" encompasses monomeric (e.g., Si-O-Si) as well as oligomeric/polymeric structures (e.g., $-[Si-O]_n-$, where n is 2 or more). Each silicon atom in the siloxanyl group is substituted with independently selected R^A groups (where R^A is as defined in formula A options (b)-(i)) to complete their valence.

"Silyl" refers to a structure of formula R_3Si- and "siloxy" refers to a structure of formula R_3Si-O-, where each R in silyl or siloxy is independently selected from trimethylsiloxy, C_1-C_8 alkyl (preferably C_1-C_3 alkyl, more preferably ethyl or methyl), and C_3-C_8 cycloalkyl.

"Alkyleneoxy" refers to groups of the general formula -(alkylene-O)$_p$- or -(O-alkylene)$_p$-, wherein alkylene is as defined above, and p is from 1 to 200, or from 1 to 100, or from 1 to 50, or from 1 to 25, or from 1 to 20, or from 1 to 10, wherein each alkylene is independently optionally substituted with one or more groups independently selected from hydroxyl, halo (e.g., fluoro), amino, amido, ether, carbonyl, carboxyl, and combinations thereof. If p is greater than 1, then each alkylene may be the same or different and the alkyleneoxy may be in block or random configuration. When alkyleneoxy forms a terminal group in a molecule, the terminal end of the alkyleneoxy may, for instance, be a hydroxy or alkoxy (e.g., HO-[CH_2CH_2O]$_p$- or CH_3O-[CH_2CH_2O]$_p$-). Examples of alkyleneoxy include polyethyleneoxy, polypropyleneoxy, polybutyleneoxy, and poly(ethyleneoxy-co-propyleneoxy).

"Oxaalkylene" refers to an alkylene group as defined above where one or more non-adjacent CH_2 groups have been substituted with an oxygen atom, such as -$CH_2CH_2OCH(CH_3)CH_2$-. "Thiaalkylene" refers to an alkylene group as defined above where one or more non-adjacent CH_2 groups have been substituted with a sulfur atom, such as -$CH_2CH_2SCH(CH_3)CH_2$-.

The term "linking group" refers to a moiety that links a polymerizable group to the parent molecule. The linking group may be any moiety that is compatible with the compound of which it is a part, and that does not undesirably interfere with the polymerization of the compound, is stable under the polymerization conditions as well as the conditions for the processing and storage of the final product. For instance, the linking group may be a bond, or it may comprise one or more alkylene, haloalkylene, amide, amine, alkyleneamine, carbamate, ester (-CO_2-), arylene, heteroarylene, cycloalkylene, heterocycloalkylene, alkyleneoxy, oxaalkylene, thiaalkylene, haloalkyleneoxy (alkyleneoxy substituted with one or more halo groups, e.g., -OCF_2-, -OCF_2CF_2-, -OCF_2CH_2-), siloxanyl, alkylenesiloxanyl, or combinations thereof. The linking group may optionally be substituted with 1 or more substituent groups. Suitable substituent groups may include those independently selected from alkyl, halo (e.g., fluoro), hydroxyl, HO-alkyleneoxy, MeO-alkyleneoxy, siloxanyl, siloxy, siloxy-alkyleneoxy-, siloxy-alkylene-alkyleneoxy- (where more than one alkyleneoxy groups may be present and wherein

each methylene in alkylene and alkyleneoxy is independently optionally substituted with hydroxyl), ether, amine, carbonyl, carbamate, and combinations thereof. The linking group may also be substituted with a further polymerizable group, such as (meth)acrylate (in addition to the polymerizable group to which the linking group is linked).

Preferred linking groups include C_1-C_8 alkylene (preferably C_2-C_6 alkylene) and C_1-C_8 oxaalkylene (preferably C_2-C_6 oxaalkylene), each of which is optionally substituted with 1 or 2 groups independently selected from hydroxyl and siloxy. Preferred linking groups also include carboxylate, amide, C_1-C_8 alkylene-carboxylate-C_1-C_8 alkylene, or C_1-C_8 alkylene-amide-C_1-C_8 alkylene.

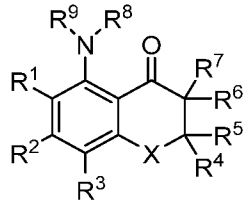
When the linking group is comprised of combinations of moieties as described above (e.g., alkylene and cycloalkylene), the moieties may be present in any order. For instance, if in Formula E below, L is indicated as being -alkylene-cycloalkylene-, then Rg-L may be either Rg-alkylene-cycloalkylene-, or Rg-cycloalkylene-alkylene-. Notwithstanding this, the listing order represents the preferred order in which the moieties appear in the compound starting from the terminal polymerizable group (e.g., Rg or Pg) to which the linking group is attached. For example, if in Formula E, L and L^2 are indicated as both being alkylene-cycloalkylene, then Rg-L is preferably Rg-alkylene-cycloalkylene- and -L^2-Rg is preferably -cycloalkylene-alkylene-Rg.

The terms "high energy radiation absorber," "UV/HEV absorber," or "high energy light absorbing compound" refer to chemical materials that absorb various wavelengths of ultraviolet light, high energy visible light, or both. A material's ability to absorb certain wavelengths of light can be determined by measuring its UV/Vis transmission spectrum. Compounds that exhibit no absorption at a particular wavelength will exhibit substantially 100 percent transmission at that wavelength. Conversely, compounds that completely absorb at a particular wavelength will exhibit substantially 0 % transmission at that wavelength. If the amount of a material's transmission is indicated as a percentage for a particular wavelength range, it is to be understood that the material exhibits the percent transmission at all wavelengths within that range.

Unless otherwise indicated, ratios, percentages, parts, and the like are by weight.

Unless otherwise indicated, numeric ranges, for instance as in "from 2 to 10," are inclusive of the numbers defining the range (e.g., 2 and 10).

As noted above, in one aspect the invention provides UV/HEV absorbing compounds of formula I:



(I)

wherein R^1, R^2 and R^3 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, C_1-C_6 alkoxy, aryl, aryloxy, halo, or -Y-P_g;

X is CR^4R^5, O, S, or NR^4;

R^4, R^5, R^6, R^7, R^8, and R^9 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, or -Y-P_g;

Y is a linking group; and

P_g is a polymerizable group,

wherein at least one of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 is -Y-P_g.

Formula I-1. Compounds of formula I may include compounds of formula I-1, which are compounds of formula I wherein the compound contains one or two independent -Y-P_g groups. Preferably, the compound contains one -Y-P_g group.

I-2. Preferred compounds of formulae I and I-1 include compounds of formula I-1, which are compounds of formula I or I-1 wherein R^1 is -Y-P_g.

I-3. Preferred compounds of formulae I, I-1, and I-2 include compounds of formula I-3, which are compounds of formula I, I-1, or I-2 wherein R^2 and R^3 are independently H or C_1-C_6 alkyl. Preferably, R^2 and R^3 are each H.

I-4. Preferred compounds of formulae I, I-1, I-2, and I-3 include compounds of formula I-4, which are compounds of formula I, I-1, I-2, or I-3 wherein R^4, R^5, R^6, R^7, R^8, and R^9 are independently H or C_1-C_6 alkyl. Preferably, R^4, R^5, R^6, R^7, R^8, and R^9 are each H.

I-5. Preferred compounds of formulae I, I-1, I-2, I-3, and I-4 include compounds of formula I-5, which are compounds of formula I, I-1, I-2, I-3, or I-4 wherein X is CH_2, O, NH, or NCH_3. Preferred compounds include those where X is CH_2. Preferred compounds also include those where X is O.

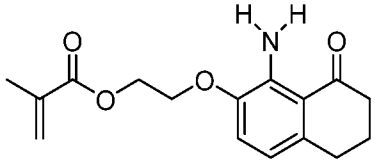
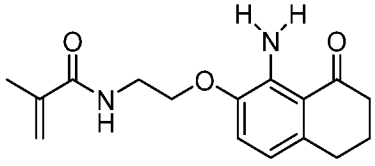
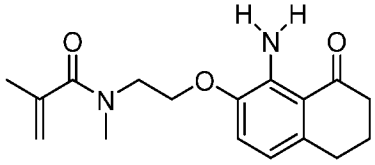
I-6. Preferred compounds of formulae I, I-1, I-2, I-3, I-4, and I-5 include compounds of formula I-6, which are compounds of formula I, I-1, I-2, I-3, I-4, or I-5 wherein P_g (a

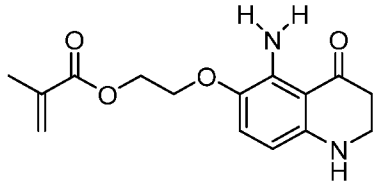
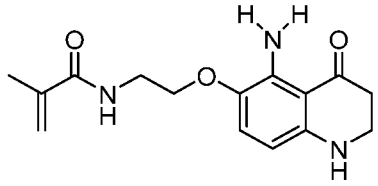
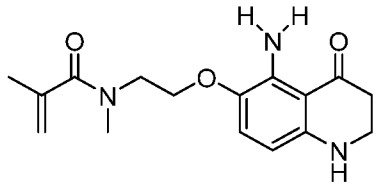
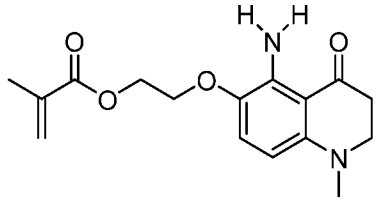
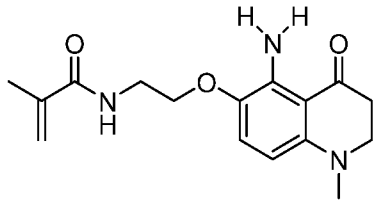
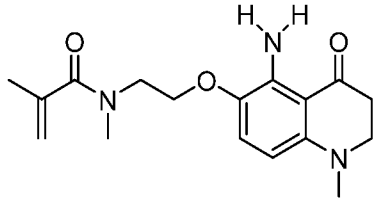
polymerizable group) is styryl, vinyl carbonate, vinyl ether, vinyl carbamate, N-vinyl lactam, N-vinylamide, (meth)acrylate, or (meth)acrylamide. Preferably, P_g is (meth)acrylate or (meth)acrylamide. More preferably, P_g is methacrylate.

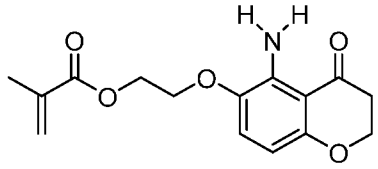
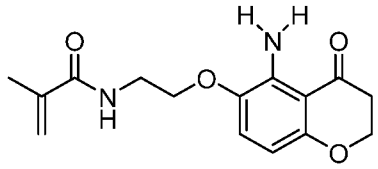
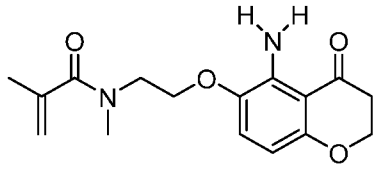
I-7. Preferred compounds of formulae I, I-1, I-2, I-3, I-4, I-5, and I-6 include compounds of formula I-7, which are compounds of formula I, I-1, I-2, I-3, I-4, I-5, or I-6 wherein Y (a linking group) is alkylene, cycloalkylene, heterocycloalkylene, arylene (e.g., phenylene), heteroarylene, oxaalkylene, thialkylene, alkyleneamine, alkylene-amide-alkylene, alkylene-amine-alkylene, or combinations of any of the foregoing groups. Preferred linking groups include C_1-C_8 alkylene (e.g., ethylene or propylene), C_1-C_8 oxaalkylene, C_1-C_8 thialkylene, C_1-C_8 alkyleneamine, C_1-C_8 alkylene-amide-C_1-C_8 alkylene, and C_1-C_8 alkylene-amine-C_1-C_8 alkylene. Particularly preferred are C_1-C_8 oxaalkylene (e.g., $-CH_2CH_2-O-$), C_1-C_8 thialkylene (e.g., $-CH_2CH_2-S-$), and C_1-C_8 alkyleneamine (e.g., $-CH_2CH_2-N(H)-$ or $-CH_2CH_2-N(CH_3)-$).

Specific examples of compounds of formula I include, but are not limited to, the compounds shown in Table 1.

Table 1

 2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl methacrylate (Compound F)
 N-(2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl)methacrylamide
 N-(2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl)-N-methylmethacrylamide

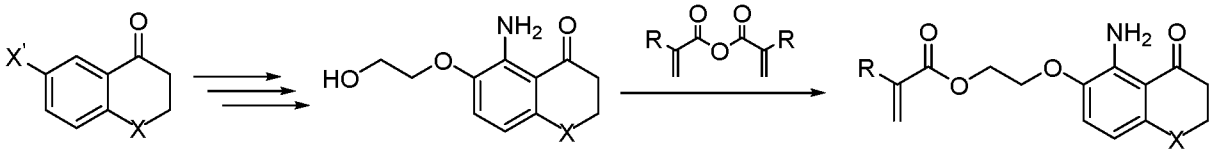
 2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl methacrylate
 N-(2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)methacrylamide
 N-(2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)-N-methylmethacrylamide
 2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl methacrylate
 N-(2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)methacrylamide
 N-(2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)-N-methylmethacrylamide

 2-((5-amino-4-oxochroman-6-yl)oxy)ethyl methacrylate (Compound M)
 N-(2-((5-amino-4-oxochroman-6-yl)oxy)ethyl)methacrylamide
 N-(2-((5-amino-4-oxochroman-6-yl)oxy)ethyl)-N-methylmethacrylamide

Compounds of formula I may be used in combination with other absorbing compounds to provide desirable absorption characteristics. For example, preferred compositions may comprise a compound of formula I and a second compound that is a UV absorbing compound. UV absorbing compounds are known in the art and fall into several classes which include, but are not limited to, benzophenones, benzotriazoles, triazines, substituted acrylonitriles, salicyclic acid derivatives, benzoic acid derivatives, cinnamic acid derivatives, chalcone derivatives, dypnone derivatives, crotonic acid derivatives, or any mixtures thereof. A preferred class of UV absorbing compound is benzotriazoles, such as Norbloc (2-(2′-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole).

A particularly preferred composition comprises 2-(4-acetyl-3-amino-2,6-dimethoxyphenoxy)ethyl methacrylate and 2-(2′-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole.

Compounds of formula I may be prepared as shown in the following reaction Scheme 1 and the associated description, as well as relevant literature procedures that may be used by one of skill in the art. Exemplary reagents and procedures for these reactions appear in the working examples.



Scheme 1

Referring to Scheme 1, a commercially available 7-substituted-3,4-dihydronaphthalen-1(2H)-one, 6-substituted-chroman-4-one, 6-substituted-2,3-dihydroquinolin-4(1H)-one, 1-alkyl-6-substituted-2,3-dihydroquinolin-4(1H)-one, or similar compound, wherein X is typically CH_2, O, S, NH, or NR, the substituent X' is typically Cl, Br, or OCH_3, and R is a proton or methyl group, is converted by a series of reactions including protection and deprotection steps into the corresponding amino 2-hydroxyethoxy derivative, such as 8-amino-7-(2-hydroxyethoxy)-3,4-dihydronaphthalen-1(2H)-one, 5-amino-6-(2-hydroxyethoxy)chroman-4-one, 5-amino-6-(2-hydroxyethoxy)-2,3-dihydroquinolin-4(1H)-one, or 5-amino-6-(2-hydroxyethoxy)-1-alkyl-2,3-dihydroquinolin-4(1H)-one, which is subsequently acetylated with (meth)acrylic anhydride to form the (meth)acrylates of formula I. A different series of reactions including protection and deprotection steps can be used to synthesize the corresponding amino 2-aminoethoxy derivatives that when acetylated with (meth)acrylic anhydride can form the (meth)acrylamides of formula I. As will be recognized by those skilled in the art, the above steps may be readily modified as needed to provide the desired compounds. The compounds of formula I may also be made by other procedures other than shown in Scheme 1.

High energy light absorbing compounds of formula I may be included in reactive mixtures to form various products, including biomedical devices and ophthalmic devices. Generally, the high energy light absorbing compounds can be present in any amount up to the limit of their solubility. For instance, the compounds may be present in an amount in the range of about 0.1 % to about 10 % by weight, or from about 0.5 to about 5% by weight, or from about 0.75% to about 4% by weight. The upper limit is typically determined by the solubility of the compound with other co-monomers and or diluents in the reactive monomer mix.

Preferably, the high energy light absorbing compounds of the invention are included in ophthalmic devices. A variety of ophthalmic devices may be prepared, including hard contact lenses, soft contact lenses, corneal onlays, corneal inlays, intraocular lenses, or overlay lenses. Preferably, the ophthalmic device is a soft contact lens, which may be made from conventional or silicone hydrogel formulations.

Ophthalmic devices of the invention comprise a free radical reaction product of a reactive mixture containing one or more compounds of formula I, one or more monomers suitable for making the desired ophthalmic device (also referred to herein as device forming monomers or hydrogel forming monomers), and optional components. Thus, the reactive mixture may, for example, include, in addition to compounds of formula I, one or more of: hydrophilic components, hydrophobic components, silicone-containing components, wetting agents such as polyamides, crosslinking agents, and further components such as diluents and initiators.

Hydrophilic Components

Examples of suitable families of hydrophilic monomers include (meth)acrylates, styrenes, vinyl ethers, (meth)acrylamides, N-vinyl lactams, N-vinyl amides, N-vinyl imides, N-vinyl ureas, O-vinyl carbamates, O-vinyl carbonates, other hydrophilic vinyl compounds, and mixtures thereof.

Non-limiting examples of hydrophilic (meth)acrylate and (meth)acrylamide monomers include: acrylamide, N-isopropyl acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-dimethyl acrylamide (DMA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, N-(2-hydroxyethyl) (meth)acrylamide, N,N-bis(2-hydroxyethyl) (meth)acrylamide, N-(2-hydroxypropyl) (meth)acrylamide, N,N-bis(2-hydroxypropyl) (meth)acrylamide, N-(3-hydroxypropyl) (meth)acrylamide, N-(2-hydroxybutyl) (meth)acrylamide, N-(3-hydroxybutyl) (meth)acrylamide, N-(4-hydroxybutyl) (meth)acrylamide, 2-aminoethyl (meth)acrylate, 3-aminopropyl (meth)acrylate, 2-aminopropyl (meth)acrylate, N-2-aminoethyl (meth)acrylamides), N-3-aminopropyl (meth)acrylamide, N-2-aminopropyl (meth)acrylamide, N,N-bis-2-aminoethyl (meth)acrylamides, N,N-bis-3-aminopropyl (meth)acrylamide), N,N-bis-2-aminopropyl (meth)acrylamide, glycerol methacrylate, polyethyleneglycol monomethacrylate, (meth)acrylic acid, vinyl acetate, acrylonitrile, and mixtures thereof.

Hydrophilic monomers may also be ionic, including anionic, cationic, zwitterions, betaines, and mixtures thereof. Non-limiting examples of such charged monomers include (meth)acrylic acid, N-[(ethenyloxy)carbonyl]-β-alanine (VINAL), 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopentanoic acid (ACA2), 3-acrylamido-3-methylbutanoic acid (AMBA), 2-(methacryloyloxy)ethyl trimethylammonium chloride (Q Salt or METAC), 2-acrylamido-2-

methylpropane sulfonic acid (AMPS), 1-propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt (CBT), 1-propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT), 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT), 2-methacryloyloxyethyl phosphorylcholine, 3-(dimethyl(4-vinylbenzyl)ammonio)propane-1-sulfonate (DMVBAPS), 3-((3-acrylamidopropyl)dimethylammonio)propane-1-sulfonate (AMPDAPS), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (MAMPDAPS), 3-((3-(acryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (APDAPS), and methacryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (MAPDAPS).

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

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

Other hydrophilic vinyl compounds include ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), allyl alcohol, and 2-ethyl oxazoline.

The hydrophilic monomers may also be macromers or prepolymers of linear or branched poly(ethylene glycol), poly(propylene glycol), or statistically random or block copolymers of

ethylene oxide and propylene oxide, having polymerizable moieties such as (meth)acrylates, styrenes, vinyl ethers, (meth)acrylamides, N-vinylamides, and the like. The macromers of these polyethers have one polymerizable group; the prepolymers may have two or more polymerizable groups.

The preferred hydrophilic monomers of the present invention are DMA, NVP, HEMA, VMA, NVA, and mixtures thereof. Preferred hydrophilic monomers include mixtures of DMA and HEMA. Other suitable hydrophilic monomers will be apparent to one skilled in the art.

Generally, there are no particular restrictions with respect to the amount of the hydrophilic monomer present in the reactive monomer mixture. The amount of the hydrophilic monomers may be selected based upon the desired characteristics of the resulting hydrogel, including water content, clarity, wettability, protein uptake, and the like. Wettability may be measured by contact angle, and desirable contact angles are less than about 100°, less than about 80°, and less than about 60°. The hydrophilic monomer may be present in an amount in the range of, for instance, about 0.1 to about 100 weight percent, alternatively in the range of about 1 to about 80 weight percent, alternatively about 5 to about 65 weight percent, alternatively in the range of about 40 to about 60 weight percent, or alternatively about 55 to about 60 weight percent, based on the total weight of the reactive components in the reactive monomer mixture.

Silicone-Containing Components

Silicone-containing components suitable for use in the invention comprise one or more polymerizable compounds, where each compound independently comprises at least one polymerizable group, at least one siloxane group, and one or more linking groups connecting the polymerizable group(s) to the siloxane group(s). The silicone-containing components may, for instance, contain from 1 to 220 siloxane repeat units, such as the groups defined below. The silicone-containing component may also contain at least one fluorine atom.

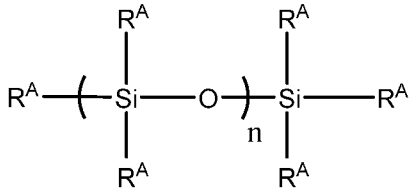
The silicone-containing component may comprise: one or more polymerizable groups as defined above; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units. The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a styryl, a vinyl ether, a (meth)acrylamide, an N-vinyl lactam, an N-vinylamide, an O-vinylcarbamate, an O-vinylcarbonate, a vinyl group, or mixtures of the foregoing; one or more

optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a (meth)acrylamide, an N-vinyl lactam, an N-vinylamide, a styryl, or mixtures of the foregoing; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

The silicone-containing component may comprise: one or more polymerizable groups that are independently a (meth)acrylate, a (meth)acrylamide, or mixtures of the foregoing; one or more optionally repeating siloxane units; and one or more linking groups connecting the polymerizable groups to the siloxane units.

Formula A. The silicone-containing component may comprise one or more polymerizable compounds of Formula A:



Formula A

wherein:

at least one R^A is a group of formula R_g-L- wherein R_g is a polymerizable group and L is a linking group, and the remaining R^A are each independently:

(a) R_g-L-,

(b) C_1-C_{16} alkyl optionally substituted with one or more hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,

(c) C_3-C_{12} cycloalkyl optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,

(d) a C_6-C_{14} aryl group optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, amido, carbamate, carbonate, halo, phenyl, benzyl, or combinations thereof,

(e) halo,

(f) alkoxy, cyclic alkoxy, or aryloxy,

(g) siloxy,

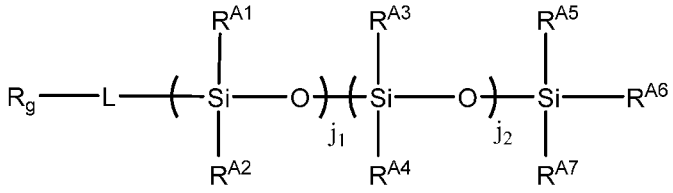
(h) alkyleneoxy-alkyl or alkoxy-alkyleneoxy-alkyl, such as polyethyleneoxyalkyl, polypropyleneoxyalkyl, or poly(ethyleneoxy-co-propyleneoxyalkyl), or

(i) a monovalent siloxane chain comprising from 1 to 100 siloxane repeat units optionally substituted with alkyl, alkoxy, hydroxy, amino, oxa, carboxy, alkyl carboxy, alkoxy, amido, carbamate, halo or combinations thereof; and

n is from 0 to 500 or from 0 to 200, or from 0 to 100, or from 0 to 20, where it is understood that when n is other than 0, n is a distribution having a mode equal to a stated value. When n is 2 or more, the SiO units may carry the same or different R^A substituents and if different R^A substituents are present, the n groups may be in random or block configuration.

In Formula A, three R^A may each comprise a polymerizable group, alternatively two R^A may each comprise a polymerizable group, or alternatively one R^A may comprise a polymerizable group.

Formula B. The silicone-containing component of formula A may be a mono-functional polymerizable compound of formula B:



Formula B

wherein:

Rg is a polymerizable group;

L is a linking group;

j1 and j2 are each independently whole numbers from 0 to 220, provided that the sum of j1 and j2 is from 1 to 220;

R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, and R^{A7} are independently at each occurrence C_1-C_6 alkyl, C_3-C_{12} cycloalkyl, C_1-C_6 alkoxy, C_4-C_{12} cyclic alkoxy, alkoxy-alkyleneoxy-alkyl, aryl (e.g., phenyl), aryl-alkyl (e.g., benzyl), haloalkyl (e.g., partially or fully fluorinated alkyl), siloxy, fluoro, or combinations thereof, wherein each alkyl in the foregoing groups is optionally substituted with

one or more hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl, each cycloalkyl is optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl and each aryl is optionally substituted with one or more alkyl, hydroxy, amino, amido, oxa, carboxy, alkyl carboxy, carbonyl, alkoxy, carbamate, carbonate, halo, phenyl, or benzyl; and

R^{A6} is siloxy, C_1-C_8 alkyl (e.g., C_1-C_4 alkyl, or butyl, or methyl), or aryl (e.g., phenyl), wherein alkyl and aryl may optionally be substituted with one or more fluorine atoms.

Formula B-1. Compounds of formula B may include compounds of formula B-1, which are compounds of formula B wherein j1 is zero and j2 is from 1 to 220, or j2 is from 1 to 100, or j2 is from 1 to 50, or j2 is from 1 to 20, or j2 is from 1 to 5, or j2 is 1.

B-2. Compounds of formula B may include compounds of formula B-2, which are compounds of formula B wherein j1 and j2 are independently from 4 to 100, or from 4 to 20, or from 4 to 10, or from 24 to 100, or from 10 to 100.

B-3. Compounds of formulae B, B-1, and B-2 may include compounds of formula B-3, which are compounds of formula B, B-1, or B-2 wherein R^{A1}, R^{A2}, R^{A3}, and R^{A4} are independently at each occurrence C_1-C_6 alkyl or siloxy. Preferred alkyl are C_1-C_3 alkyl, or more preferably, methyl. Preferred siloxy is trimethylsiloxy.

B-4. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-4, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently alkoxy-alkyleneoxy-alkyl, preferably they are independently a methoxy capped polyethyleneoxyalkyl of formula CH_3O-$[CH_2CH_2O]_p$-$CH_2CH_2CH_2$, wherein p is a whole number from 1 to 50.

B-5. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-5, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently siloxy, such as trimethylsiloxy.

B-6. Compounds of formulae B, B-1, B-2, and B-3 may include compounds of formula B-6, which are compounds of formula B, B-1, B-2, or B-3 wherein R^{A5} and R^{A7} are independently C_1-C_6 alkyl, alternatively C_1-C_4 alkyl, or alternatively, butyl or methyl.

B-7. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, and B-6 may include compounds of formula B-7, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, or B-6

wherein R^{A6} is C_1-C_8 alkyl, preferably C_1-C_6 alkyl, more preferably C_1-C_4 alkyl (for example methyl, ethyl, n-propyl, or n-butyl). More preferably R^{A6} is n-butyl.

B-8. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, and B-7, may include compounds of formula B-8, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, or B-7 wherein Rg comprises styryl, vinyl carbonate, vinyl ether, vinyl carbamate, N-vinyl lactam, N-vinylamide, (meth)acrylate, or (meth)acrylamide. Preferably, Rg comprises (meth)acrylate, (meth)acrylamide, or styryl. More preferably, Rg comprises (meth)acrylate or (meth)acrylamide. When Rg is (meth)acrylamide, the nitrogen group may be substituted with R^{A9}, wherein R^{A9} is H, C_1-C_8 alkyl (preferably C_1-C_4 alkyl, such as n-butyl, n-propyl, methyl or ethyl), or C_3-C_8 cycloalkyl (preferably C_5-C_6 cycloalkyl), wherein alkyl and cycloalkyl are optionally substituted with one or more groups independently selected from hydroxyl, amide, ether, silyl (e.g., trimethylsilyl), siloxy (e.g., trimethylsiloxy), alkyl-siloxanyl (where alkyl is itself optionally substituted with fluoro), aryl-siloxanyl (where aryl is itself optionally substituted with fluoro), and silyl-oxaalkylene- (where the oxaalkylene is itself optionally substituted with hydroxyl).

B-9. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, and B-8 may include compounds of formula B-9, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, or B-8 wherein the linking group comprises alkylene (preferably C_1-C_4 alkylene), cycloalkylene (preferably C_5-C_6 cycloalkylene), alkyleneoxy (preferably ethyleneoxy), haloalkyleneoxy (preferably haloethyleneoxy), amide, oxaalkylene (preferably containing 3 to 6 carbon atoms), siloxanyl, alkylenesiloxanyl, carbamate, alkyleneamine (preferably C_1-C_6 alkyleneamine), or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, siloxy, and carbamate.

B-10. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-10, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-siloxanyl-alkylene-alkyleneoxy-, or alkylene-siloxanyl-alkylene-[alkyleneoxy-alkylene-siloxanyl]$_q$-alkyleneoxy-, where q is from 1 to 50.

B-11. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-11, which are compounds of formula B, B-1, B-2, B-3, B-4, B-

5, B-6, B-7, B-8, or B-9 wherein the linking group is C_1-C_6 alkylene, preferably C_1-C_3 alkylene, more preferably n-propylene.

B-12. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-12, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-carbamate-oxaalkylene. Preferably, the linking group is $CH_2CH_2N(H)$-C(=O)-O-CH_2CH_2-O-$CH_2CH_2CH_2$.

B-13. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-13, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is oxaalkylene. Preferably, the linking group is CH_2CH_2-O-$CH_2CH_2CH_2$.

B-14. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-14, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-[siloxanyl-alkylene]$_q$-, where q is from 1 to 50. An example of such a linking group is: -$(CH_2)_3$-[$Si(CH_3)_2$-O-$Si(CH_3)_2$-$(CH_2)_2$]$_q$-.

B-15. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-15, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkyleneoxy-carbamate-alkylene-cycloalkylene-carbamate-oxaalkylene, wherein cycloalkylene is optionally substituted with or 1, 2, or 3 independently selected alkyl groups (preferably C_1-C_3 alkyl, more preferably methyl). An example of such a linking group is -[OCH_2CH_2]$_q$-OC(=O)-NH-CH_2-[1,3-cyclohexylene]-NHC(=O)O-CH_2CH_2-O-CH_2CH_2-, wherein the cyclohexylene is substituted at the 1 and 5 positions with 3 methyl groups.

B-16. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-16, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein Rg comprises styryl and the linking group is a bond or is alkyleneoxy, wherein each alkylene in alkyleneoxy is independently optionally substituted with hydroxyl. An example of such a linking group is -O-$(CH_2)_3$-. Another example of such a linking group is -O-$CH_2CH(OH)CH_2$-O-$(CH_2)_3$-.

B-17. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-17, which are compounds of formula B, B-1, B-2, B-3, B-4, B-

5, B-6, B-7, B-8, or B-9 wherein Rg comprises styryl and the linking group is alkyleneamine. An example of such a linking group is -NH-$(CH_2)_3$-.

B-18. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-18, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is oxaalkylene optionally substituted with hydroxyl, siloxy, or silyl-alkyleneoxy (where the alkyleneoxy is itself optionally substituted with hydroxyl). An example of such a linking group is -$CH_2CH(G)CH_2$-O-$(CH_2)_3$-, wherein G is hydroxyl. In another example, G is R_3SiO- wherein two R groups are trimethylsiloxy and the third is C_1-C_8 alkyl (preferably C_1-C_3 alkyl, more preferably methyl) or the third is C_3-C_8 cycloalkyl. In a further example, G is R_3Si-$(CH_2)_3$-O-$CH_2CH(OH)CH_2$-O-, wherein two R groups are trimethylsiloxy and the third is C_1-C_8 alkyl (preferably C_1-C_3 alkyl, more preferably methyl) or C_3-C_8 cycloalkyl. In a still further example, G is a polymerizable group, such as (meth)acrylate. Such compounds may function as crosslinkers.

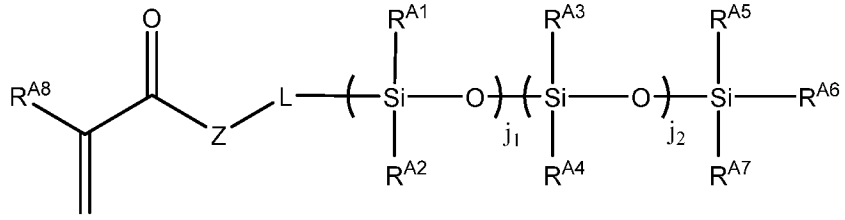
B-19. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-19, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein Rg comprises styryl and the linking group is amine-oxaalkylene optionally substituted with hydroxyl. An example of such a linking group is -NH-$CH_2CH(OH)CH_2$-O-$(CH_2)_3$-.

B-20. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-20, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein Rg comprises styryl and the linking group is alkyleneoxy-carbamate-oxaalkylene. An example of such a linking group is -O-$(CH_2)_2$-N(H)C(=O)O-$(CH_2)_2$-O-$(CH_2)_3$-.

B-21. Compounds of formulae B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, and B-9 may include compounds of formula B-21, which are compounds of formula B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, or B-9 wherein the linking group is alkylene-carbamate-oxaalkylene. An example of such a linking group is -$(CH_2)_2$-N(H)C(=O)O-$(CH_2)_2$-O-$(CH_2)_3$-.

Formula C. Silicone-containing components of formulae A, B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, B-9, B-10, B-11, B-12, B-13, B-14, B-15, B-18, and B-21 may include

compounds of formula C, which are compounds of formula A, B, B-1, B-2, B-3, B-4, B-5, B-6, B-7, B-8, B-9, B-10, B-11, B-12, B-13, B-14, B-15, B-18, or B-21 having the structure:



Formula C

wherein

R^{A8} is hydrogen or methyl;

Z is O, S, or N(R^{A9}); and

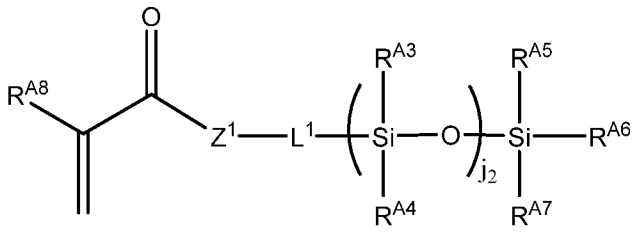
L, j1, j2, R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, R^{A6}, R^{A7}, and R^{A9} are as defined in formula B or its various sub-formulae (e.g., B-1, B-2, etc.).

C-1. Compounds of formula C may include (meth)acrylates of formula C-1, which are compounds of formula C wherein Z is O.

C-2. Compounds of formula C may include (meth)acrylamides of formula C-2, which are compounds of formula C wherein Z is N(R^{A9}), and R^{A9} is H.

C-3. Compounds of formulae C may include (meth)acrylamides of formula C-3, which are compounds of formula C wherein Z is N(R^{A9}), and R^{A9} is C_1-C_8 alkyl that is unsubstituted or is optionally substituted as indicated above. Examples of R^{A9} include CH_3, -$CH_2CH(OH)CH_2(OH)$, -$(CH_2)_3$-siloxanyl, -$(CH_2)_3$-SiR_3, and -$CH_2CH(OH)CH_2$-O-$(CH_2)_3$-SiR_3 where each R in the foregoing groups is independently selected from trimethylsiloxy, C_1-C_8 alkyl (preferably C_1-C_3 alkyl, more preferably methyl), and C_3-C_8 cycloalkyl. Further examples of R^{A9} include: -$(CH_2)_3$-Si(Me)($SiMe_3$)$_2$, and -$(CH_2)_3$-$Si(Me_2)$-[O-$SiMe_2$]$_{1\text{-}10}$-CH_3.

Formula D. Compounds of formula C may include compounds of formula D:



Formula D

wherein

R^{A8} is hydrogen or methyl;

Z^1 is O or $N(R^{A9})$;

L^1 is alkylene containing 1 to 8 carbon atoms, or oxaalkylene containing 3 to 10 carbon atoms, wherein L^1 is optionally substituted with hydroxyl; and

j2, R^{A3}, R^{A4}, R^{A5}, R^{A6}, R^{A7}, and R^{A9} are as defined above in formula B or its various sub-formulae (e.g., B-1, B-2, etc.).

D-1. Compounds of formula D may include compounds of formula D-1, which are compounds of formula D wherein L^1 is C_2-C_5 alkylene optionally substituted with hydroxyl. Preferably L^1 is n-propylene optionally substituted with hydroxyl.

D-2. Compounds of formula D may include compounds of formula D-2, which are compounds of formula D wherein L^1 is oxaalkylene containing 4 to 8 carbon atoms optionally substituted with hydroxyl. Preferably L^1 is oxaalkylene containing five or six carbon atoms optionally substituted with hydroxyl. Examples include $-(CH_2)_2-O-(CH_2)_3-$, and $-CH_2CH(OH)CH_2-O-(CH_2)_3-$.

D-3. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-3, which are compounds of formula D, D-1, or D-2 wherein Z^1 is O.

D-4. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-4, which are compounds of formula D, D-1, or D-2 wherein Z^1 is $N(R^{A9})$, and R^{A9} is H.

D-5. Compounds of formulae D, D-1, and D-2 may include compounds of formula D-5, which are compounds of formula D, D-1, or D-2 wherein Z^1 is $N(R^{A9})$, and R^{A9} is C_1-C_4 alkyl optionally substituted with 1 or 2 substituents selected from hydroxyl, siloxy, and C_1-C_6 alkyl-siloxanyl-.

D-6. Compounds of formulae D, D-1, D-2, D-3, D-4, and D-5 may include compounds of formula D-6, which are compounds of formula D, D-1, D-2, D-3, D-4, or D-5 wherein j2 is 1.

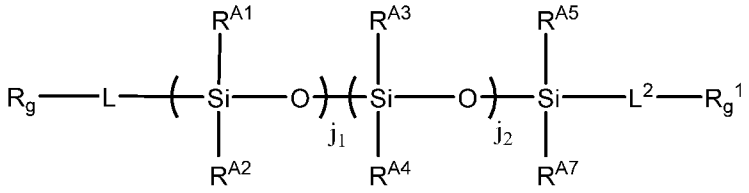
D-7. Compounds of formulae D, D-1, D-2, D-3, D-4, and D-5 may include compounds of formula D-7, which are compounds of formula D, D-1, D-2, D-3, D-4, or D-5 wherein j2 is from 2 to 220, or from 2 to 100, or from 10 to 100, or from 24 to 100, or from 4 to 20, or from 4 to 10.

D-8. Compounds of formulae D, D-1, D-2, D-3, D-4, D-5, D-6, and D-7 may include compounds of formula D-8, which are compounds of formula D, D-1, D-2, D-3, D-4, D-5, D-6,

or D-7 wherein R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently C_1-C_6 alkyl or siloxy. Preferably R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently selected from methyl, ethyl, n-propyl, n-butyl, and trimethylsiloxy. More preferably, R^{A3}, R^{A4}, R^{A5}, R^{A6}, and R^{A7} are independently selected from methyl, n-butyl, and trimethylsiloxy.

D-9. Compounds of formulae D, D-1, D-2, D-3, D-4, D-5, D-6, and D-7 may include compounds of formula D-9, which are compounds of formula D, D-1, D-2, D-3, D-4, D-5, D-6, or D-7 wherein R^{A3} and R^{A4} are independently C_1-C_6 alkyl (e.g., methyl or ethyl) or siloxy (e.g., trimethylsiloxy), and R^{A5}, R^{A6}, and R^{A7} are independently C_1-C_6 alkyl (e.g., methyl, ethyl, n-propyl, or n-butyl).

Formula E. The silicone-containing component for use in the invention may comprise a multi-functional silicone-containing component. Thus, for example, the silicone-containing component of formula A may comprise a bifunctional material of formula E:



Formula E

wherein

Rg, L, j1, j2, R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5}, and R^{A7} are as defined above for formula B or its various sub-formulae (e.g., B-1, B-2, etc.);

L^2 is a linking group; and

Rg^1 is a polymerizable group.

E-1. Compounds of formula E may include compounds of formula E-1, which are compounds of formula E wherein Rg and Rg^1 are each a vinyl carbonate of structure CH_2=CH-O-C(=O)-O- or structure CH_2=C(CH_3)-O-C(=O)-O-.

E-2. Compounds of formula E may include compounds of formula E-2, which are compounds of formula E wherein Rg and Rg^1 are each (meth)acrylate.

E-3. Compounds of formula E may include compounds of formula E-3, which are compounds of formula E wherein Rg and Rg^1 are each (meth)acrylamide, wherein the nitrogen group may be substituted with R^{A9} (wherein R^{A9} is as defined above).

E-4. Suitable compounds of formulae E, E-1, E-2, and E-3 include compounds of formula E-4, which are compounds of formula E, E-1, E-2, or E-3 wherein j1 is zero and j2 is from 1 to 220, or j2 is from 1 to 100, or j2 is from 1 to 50, or j2 is from 1 to 20.

E-5. Suitable compounds of formulae E, E-1, E-2, and E-3 include compounds of formula E-5, which are compounds of formula E, E-1, E-2, or E-3, wherein j1 and j2 are independently from 4 to 100.

E-6. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, and E-5 include compounds of formula E-6, which are compounds of formula E, E-1, E-2, E-3, E-4, or E-5 wherein R^{A1}, R^{A2}, R^{A3}, R^{A4}, and R^{A5} are independently at each occurrence C_1-C_6 alkyl, preferably they are independently C_1-C_3 alkyl, or preferably, each is methyl.

E-7. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, and E-6 include compounds of formula E-7, which are compounds of formula E, E-1, E-2, E-3, E-4, E-5, or E-6 wherein R^{A7} is alkoxy-alkyleneoxy-alkyl, preferably it is a methoxy capped polyethyleneoxyalkyl of formula CH_3O-$[CH_2CH_2O]_p$-$CH_2CH_2CH_2$, wherein p is a whole number from 1 to 50, or from 1 to 30, or from 1 to 10, or from 6 to 10.

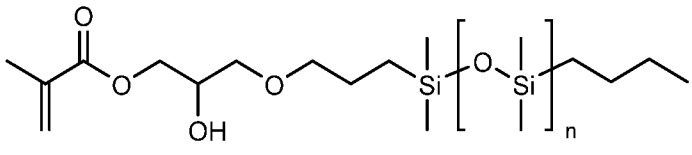
E-8. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, E-6, and E-7 include compounds of formula E-8, which are compounds of formula E, E-1, E-2, E-3, E-4, E-5, E-6, or E-7 wherein L comprises alkylene, carbamate, siloxanyl, cycloalkylene, amide, haloalkyleneoxy, oxaalkylene, or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, and carbamate.

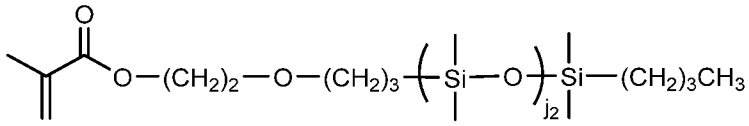
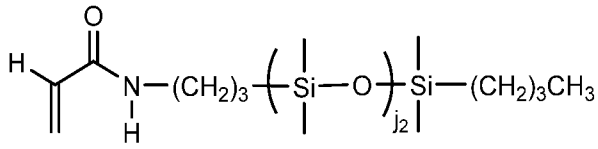
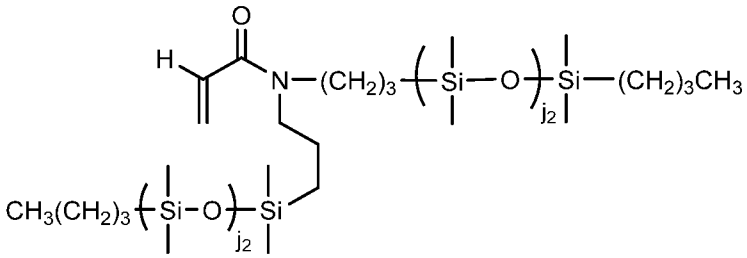
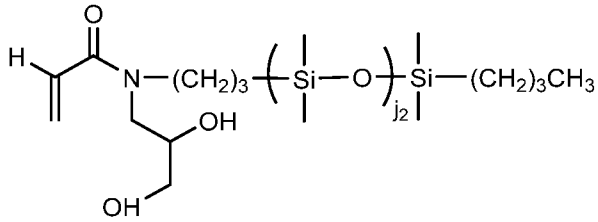
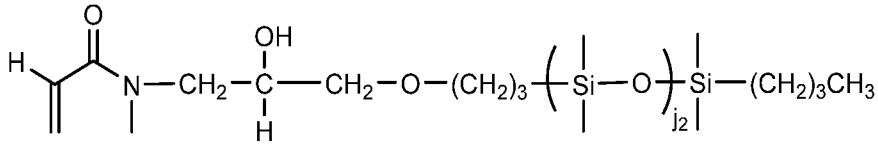
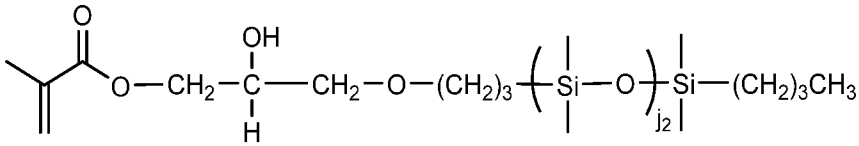
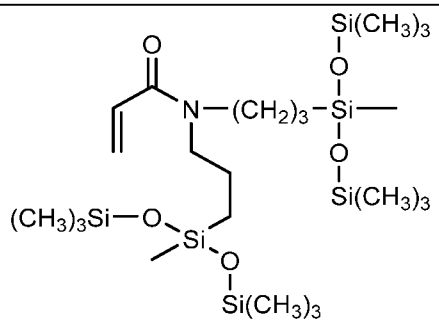
E-9. Suitable compounds of formulae E, E-1, E-2, E-3, E-4, E-5, E-6, E-7, and E-8 include compounds of formula E-9, which are compounds of formula E, E-1, E-2, E-3, E-4, E-5, E-6, E-7, or E-8 wherein L^2 comprises alkylene, carbamate, siloxanyl, cycloalkylene, amide, haloalkyleneoxy, oxaalkylene, or combinations of two or more thereof, wherein the linking group is optionally substituted with one or more substituents independently selected from alkyl, hydroxyl, ether, amine, carbonyl, and carbamate.

Examples of silicone-containing components suitable for use in the invention include, but are not limited to, compounds listed in Table 2. Where the compounds in Table 2 contain polysiloxane groups, the number of SiO repeat units in such compounds, unless otherwise

indicated, is preferably from 3 to 100, more preferably from 3 to 40, or still more preferably from 3 to 20.

Table 2

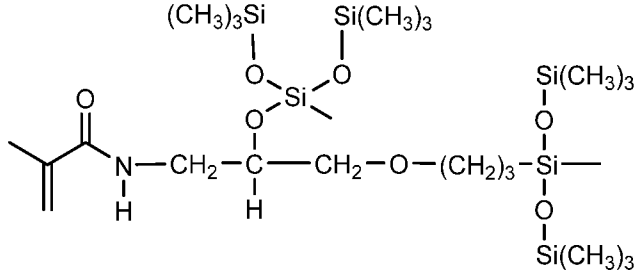
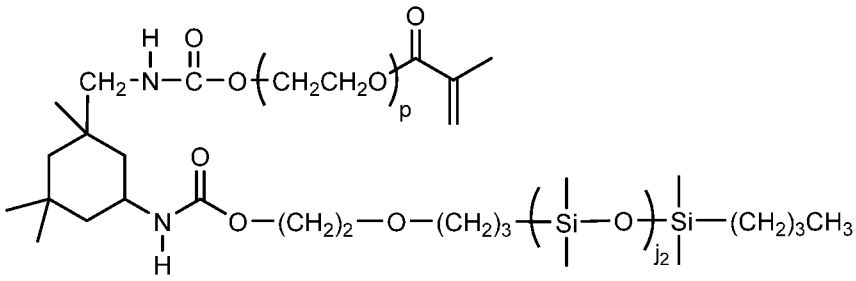
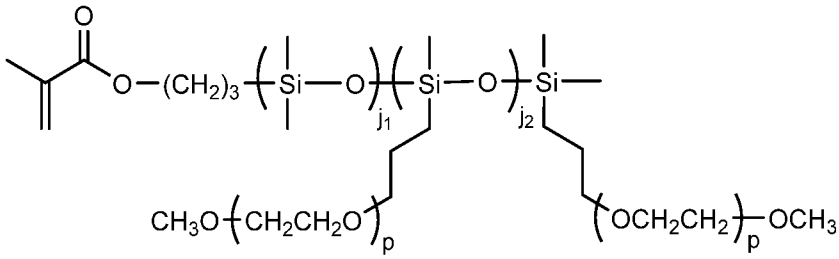
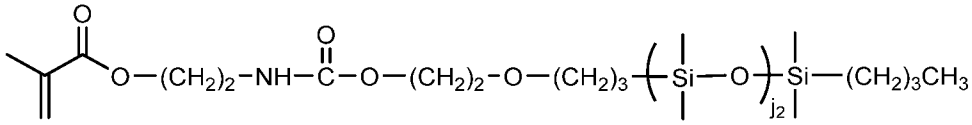
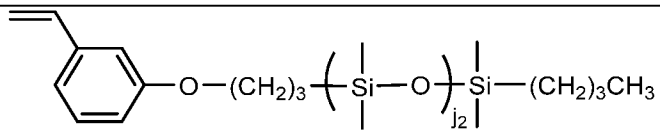
1	mono-methacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxanes (mPDMS) (preferably containing from 3 to 15 SiO repeating units)
2	mono-acryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane
3	mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane
4	mono(meth)acryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane
5	mono(meth)acryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane
6	mono(meth)acrylamidoalkylpolydialkylsiloxanes
7	mono(meth)acryloxyalkyl terminated mono-alkyl polydiarylsiloxanes
8	3-methacryloxypropyltris(trimethylsiloxy)silane (TRIS)
9	3-methacryloxypropylbis(trimethylsiloxy)methylsilane
10	3-methacryloxypropylpentamethyl disiloxane
11	mono(meth)acrylamidoalkylpolydialkylsiloxanes
12	mono(meth)acrylamidoalkyl polydimethylsiloxanes
13	N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide
14	N-[3-tris(trimethylsiloxy)silyl]-propyl acrylamide (TRIS-Am)
15	2-hydroxy-3-[3-methyl-3,3-di(trimethylsiloxy)silylpropoxy]-propyl methacrylate (SiMAA)
16	2-hydroxy-3-methacryloxypropyloxypropyl-tris(trimethylsiloxy)silane
17	 mono-(2-hydroxy-3-methacryloxypropyloxy)-propyl terminated mono-n-butyl terminated polydimethylsiloxanes (OH-mPDMS) (containing from 4 to 30, or from 4 to 20, or from 4 to 15 SiO repeat units)

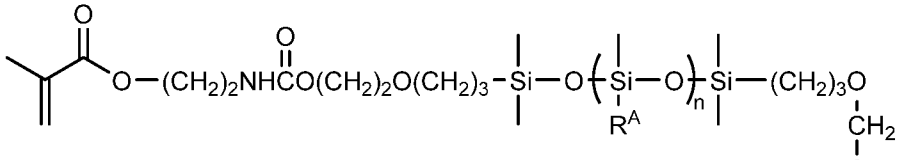
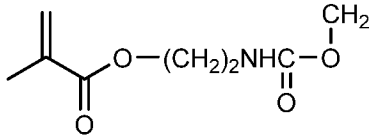
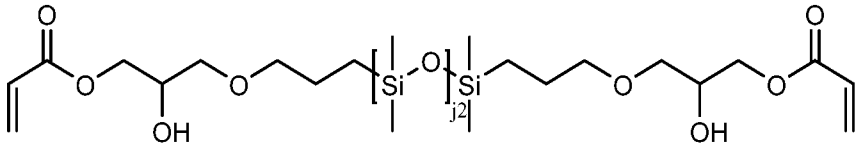
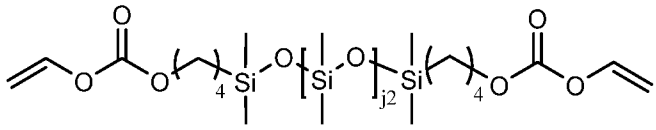
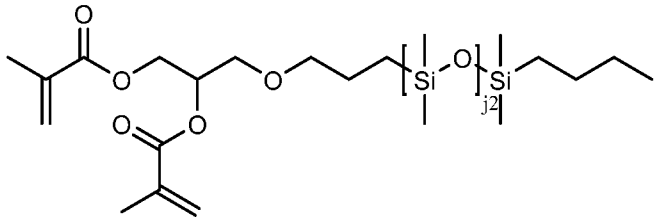
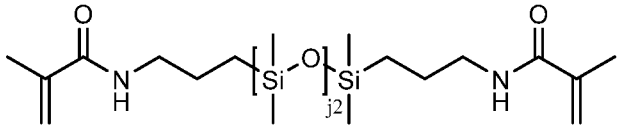
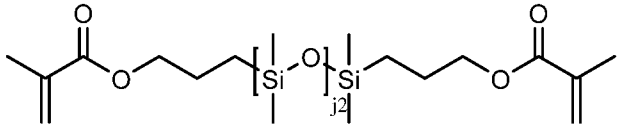
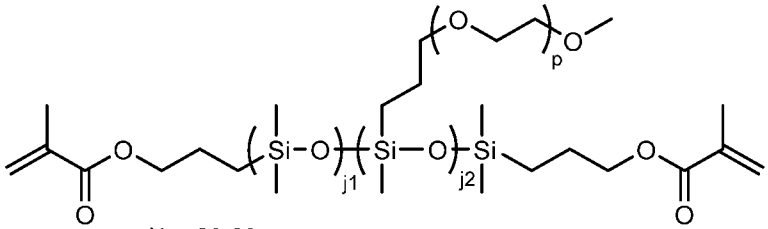
18	
19	
20	
21	
22	
23	
24	

Additional non-limiting examples of suitable silicone-containing components are listed in Table 3. Unless otherwise indicated, j2 where applicable is preferably from 1 to 100, more

preferably from 3 to 40, or still more preferably from 3 to 15. In compounds containing j1 and j2, the sum of j1 and j2 is preferably from 2 to 100, more preferably from 3 to 40, or still more preferably from 3 to 15.

Table 3

25	
26	 p is 1 to 10
27	 p is 5-10
28	
29	
30	1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyl-disiloxane
31	3-(vinyloxycarbonylthio) propyl-[tris (trimethylsiloxy)silane]
32	3-[tris(trimethylsiloxy)silyl] propyl allyl carbamate

33	3-[tris(trimethylsiloxy)silyl] propyl vinyl carbamate
34	tris(trimethylsiloxy)silylstyrene (Styryl-TRIS)
35	  R^A = CH_3 (*a*) or $CH_2CH_2CF_3$ (*b*) or CH_2-$(CH_2)_2$-$[OCH_2CH_2]_{1\text{-}10}$-$OCH_3$ (*c*); *a* + *b* + *c* = n
36	
37	
38	
39	
40	
41	 j1 = 80-90 j2 = 5-6 p = 7-8

Mixtures of silicone-containing components may be used. By way of example, suitable mixtures may include, but are not limited to: a mixture of mono-(2-hydroxy-3-methacryloxypropyloxy)-propyl terminated mono-n-butyl terminated polydimethylsiloxane (OH-mPDMS) having different molecular weights, such as a mixture of OH-mPDMS containing 4 and 15 SiO repeat units; a mixture of OH-mPDMS with different molecular weights (e.g., containing 4 and 15 repeat SiO repeat units) together with a silicone based crosslinker, such as bis-3-acryloxy-2-hydroxypropyloxypropyl polydimethylsiloxane (ac-PDMS); a mixture of 2-hydroxy-3-[3-methyl-3,3-di(trimethylsiloxy)silylpropoxy]-propyl methacrylate (SiMAA) and mono-methacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (mPDMS), such as mPDMS 1000.

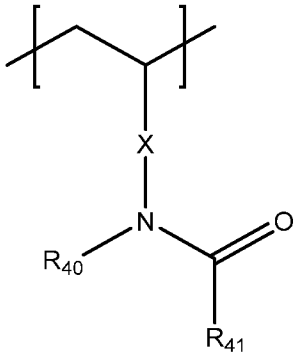
Silicone-containing components for use in the invention may have an average molecular weight of from about 400 to about 4000 daltons.

The silicone containing component(s) may be present in amounts up to about 95 weight %, or from about 10 to about 80 weight %, or from about 20 to about 70 weight %, based upon all reactive components of the reactive mixture (excluding diluents).

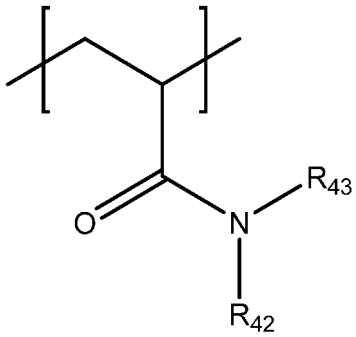
Polyamides

The reactive mixture may include at least one polyamide. As used herein, the term "polyamide" refers to polymers and copolymers comprising repeating units containing amide groups. The polyamide may comprise cyclic amide groups, acyclic amide groups and combinations thereof and may be any polyamide known to those of skill in the art. Acyclic polyamides comprise pendant acyclic amide groups and are capable of association with hydroxyl groups. Cyclic polyamides comprise cyclic amide groups and are capable of association with hydroxyl groups.

Examples of suitable acyclic polyamides include polymers and copolymers comprising repeating units of Formulae G1 and G2:



Formula G1

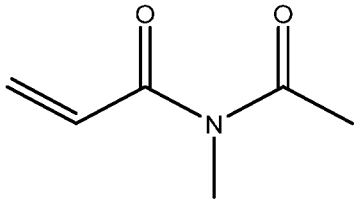


Formula G2

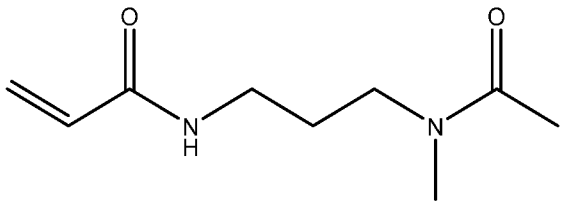
wherein X is a direct bond, -(CO)-, or –(CONHR44)-, wherein R44 is a C1 to C3 alkyl group; R40 is selected from H, straight or branched, substituted or unsubstituted C1 to C4 alkyl groups; R41 is selected from H, straight or branched, substituted or unsubstituted C1 to C4 alkyl groups, amino groups having up to two carbon atoms, amide groups having up to four carbon atoms, and alkoxy groups having up to two carbon groups; R42 is selected from H, straight or branched, substituted or unsubstituted C1 to C4 alkyl groups; or methyl, ethoxy, hydroxyethyl, and hydroxymethyl; R43 is selected from H, straight or branched, substituted or unsubstituted C1 to C4 alkyl groups; or methyl, ethoxy, hydroxyethyl, and hydroxymethyl; wherein the number of carbon atoms in R40 and R41 taken together is 8 or less, including 7, 6, 5, 4, 3, or less; and wherein the number of carbon atoms in R42 and R43 taken together is 8 or less, including 7, 6, 5, 4, 3, or less. The number of carbon atoms in R40 and R41 taken together may be 6 or less or 4 or less. The number of carbon atoms in R42 and R43 taken together may be 6 or less. As used herein substituted alkyl groups include alkyl groups substituted with an amine, amide, ether, hydroxyl, carbonyl or carboxy groups or combinations thereof.

R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. X may be a direct bond, and R_{40} and R_{41} may be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups. R_{42} and R_{43} can be independently selected from H, substituted or unsubstituted C_1 to C_2 alkyl groups, methyl, ethoxy, hydroxyethyl, and hydroxymethyl.

The acyclic polyamides of the present invention may comprise a majority of the repeating units of Formula LV or Formula LVI, or the acyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G or Formula G1, including at least 70 mole percent, and at least 80 mole percent. Specific examples of repeating units of Formula G and Formula G1 include repeating units derived from N-vinyl-N-methylacetamide, N-vinylacetamide, N-vinyl-N-methylpropionamide, N-vinyl-N-methyl-2-methylpropionamide, N-vinyl-2-methyl-propionamide, N-vinyl-N,N'-dimethylurea, N, N-dimethylacrylamide, methacrylamide, and acyclic amides of Formulae G2 and G3:

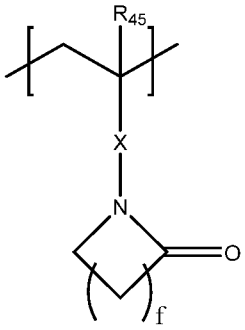


Formula G2



Formula G3

Examples of suitable cyclic amides that can be used to form the cyclic polyamides of include α-lactam, β-lactam, γ-lactam, δ-lactam, and ε-lactam. Examples of suitable cyclic polyamides include polymers and copolymers comprising repeating units of Formula G4:



Formula G4

wherein R_{45} is a hydrogen atom or methyl group; wherein f is a number from 1 to 10; wherein X is a direct bond, -(CO)-, or –(CONHR_{46})-, wherein R_{46} is a C_1 to C_3 alkyl group. In Formula LIX, f may be 8 or less, including 7, 6, 5, 4, 3, 2, or 1. In Formula G4, f may be 6 or less, including 5, 4, 3, 2, or 1. In Formula G4, f may be from 2 to 8, including 2, 3, 4, 5, 6, 7, or 8. In Formula LIX, f may be 2 or 3. When X is a direct bond, f may be 2. In such instances, the cyclic polyamide may be polyvinylpyrrolidone (PVP).

The cyclic polyamides of the present invention may comprise 50 mole percent or more of the repeating unit of Formula G4, or the cyclic polyamides can comprise at least 50 mole percent of the repeating unit of Formula G4, including at least 70 mole percent, and at least 80 mole percent.

The polyamides may also be copolymers comprising repeating units of both cyclic and acyclic amides. Additional repeating units may be formed from monomers selected from hydroxyalkyl(meth)acrylates, alkyl(meth)acrylates, other hydrophilic monomers and siloxane substituted (meth)acrylates. Any of the monomers listed as suitable hydrophilic monomers may be used as co-monomers to form the additional repeating units. Specific examples of additional monomers which may be used to form polyamides include 2-hydroxyethyl (meth)acrylate, vinyl acetate, acrylonitrile, hydroxypropyl (meth)acrylate, methyl (meth)acrylate and hydroxybutyl (meth)acrylate, dihydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, and the like and mixtures thereof. Ionic monomers may also be included. Examples of ionic monomers include (meth)acrylic acid, N-[(ethenyloxy)carbonyl]-β-alanine (VINAL, CAS #148969-96-4), 3-acrylamidopropanoic acid (ACA1), 5-acrylamidopentanoic acid (ACA2), 3-acrylamido-3-methylbutanoic acid (AMBA), 2-(methacryloyloxy)ethyl trimethylammonium chloride (Q Salt or METAC), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 1-propanaminium, N-(2-carboxyethyl)-N,N-dimethyl-3-[(1-oxo-2-propen-1-yl)amino]-, inner salt

(CBT, carboxybetaine; CAS 79704-35-1), 1-propanaminium, N,N-dimethyl-N-[3-[(1-oxo-2-propen-1-yl)amino]propyl]-3-sulfo-, inner salt (SBT, sulfobetaine, CAS 80293-60-3), 3,5-Dioxa-8-aza-4-phosphaundec-10-en-1-aminium, 4-hydroxy-N,N,N-trimethyl-9-oxo-, inner salt, 4-oxide (9CI) (PBT, phosphobetaine, CAS 163674-35-9, 2-methacryloyloxyethyl phosphorylcholine, 3-(dimethyl(4-vinylbenzyl)ammonio)propane-1-sulfonate (DMVBAPS), 3-((3-acrylamidopropyl)dimethylammonio)propane-1-sulfonate (AMPDAPS), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (MAMPDAPS), 3-((3-(acryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (APDAPS), methacryloyloxy)propyl)dimethylammonio)propane-1-sulfonate (MAPDAPS).

The reactive monomer mixture may comprise both an acyclic polyamide and a cyclic polyamide or copolymers thereof. The acyclic polyamide can be any of those acyclic polyamides described herein or copolymers thereof, and the cyclic polyamide can be any of those cyclic polyamides described herein or copolymers thereof. The polyamide may be selected from the group polyvinylpyrrolidone (PVP), polyvinylmethyacetamide (PVMA), polydimethylacrylamide (PDMA), polyvinylacetamide (PNVA), poly(hydroxyethyl(meth)acrylamide), polyacrylamide, and copolymers and mixtures thereof. The polyamide may be a mixture of PVP (e.g., PVP K90) and PVMA (e.g., having a Mw of about 570 KDa).

The total amount of all polyamides in the reactive mixture may be in the range of between 1 weight percent and about 35 weight percent, including in the range of about 1 weight percent to about 15 weight percent, and in the range of about 5 weight percent to about 15 weight percent, in all cases, based on the total weight of the reactive components of the reactive monomer mixture.

Without intending to be bound by theory, when used with a silicone hydrogel, the polyamide functions as an internal wetting agent. The polyamides of the present invention may be non-polymerizable, and in this case, are incorporated into the silicone hydrogels as semi-interpenetrating networks. The polyamides are entrapped or physically retained within the silicone hydrogels. Alternatively, the polyamides of the present invention may be polymerizable, for example as polyamide macromers or prepolymers, and in this case, are covalently incorporated into the silicone hydrogels. Mixtures of polymerizable and non-polymerizable polyamides may also be used.

When the polyamides are incorporated into the reactive monomer mixture they may have a weight average molecular weight of at least 100,000 daltons; greater than about 150,000; between about 150,000 to about 2,000,000 daltons; between about 300,000 to about 1,800,000 daltons. Higher molecular weight polyamides may be used if they are compatible with the reactive monomer mixture.

Cross-linking Agents

It is generally desirable to add one or more cross-linking agents, also referred to as cross-linking monomers, multi-functional macromers, and prepolymers, to the reactive mixture. The cross-linking agents may be selected from bifunctional crosslinkers, trifunctional crosslinkers, tetrafunctional crosslinkers, and mixtures thereof, including silicone-containing and non-silicone containing cross-linking agents. Non-silicone-containing cross-linking agents include ethylene glycol dimethacrylate (EGDMA), tetraethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC), glycerol trimethacrylate, methacryloxyethyl vinylcarbonate (HEMAVc), allylmethacrylate, methylene bisacrylamide (MBA), and polyethylene glycol dimethacrylate wherein the polyethylene glycol has a molecular weight up to about 5000 Daltons. The cross-linking agents are used in the usual amounts, e.g., from about 0.000415 to about 0.0156 mole per 100 grams of reactive Formulas in the reactive mixture. Alternatively, if the hydrophilic monomers and/or the silicone-containing components are multifunctional by molecular design or because of impurities, the addition of a cross-linking agent to the reactive mixture is optional. Examples of hydrophilic monomers and macromers which can act as the cross-linking agents and when present do not require the addition of an additional cross-linking agent to the reactive mixture include (meth)acrylate and (meth)acrylamide endcapped polyethers. Other cross-linking agents will be known to one skilled in the art and may be used to make the silicone hydrogel of the present invention.

It may be desirable to select crosslinking agents with similar reactivity to one or more of the other reactive components in the formulation. In some cases, it may be desirable to select a mixture of crosslinking agents with different reactivity in order to control some physical, mechanical or biological property of the resulting silicone hydrogel. The structure and morphology of the silicone hydrogel may also be influenced by the diluent(s) and cure conditions used.

Multifunctional silicone-containing components, including macromers, cross-linking agents, and prepolymers, may also be included to further increase the modulus and retain tensile strength. The silicone containing cross-linking agents may be used alone or in combination with other cross-linking agents. An example of a silicone containing component which can act as a cross-linking agent and, when present, does not require the addition of a crosslinking monomer to the reactive mixture includes α, ω-bismethacryloxypropyl polydimethylsiloxane. Another example is bis-3-acryloxy-2-hydroxypropyloxypropyl polydimethylsiloxane (ac-PDMS).

Cross-linking agents that have rigid chemical structures and polymerizable groups that undergo free radical polymerization may also be used. Non-limiting examples of suitable rigid structures include cross-linking agents comprising phenyl and benzyl ring, such are 1,4-phenylene diacrylate, 1,4-phenylene dimethacrylate, 2,2-bis(4-methacryloxyphenyl)-propane, 2,2-bis[4-(2-acryloxyethoxy)phenyl]propane, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]propane, and 4-vinylbenzyl methacrylate, and combinations thereof. Rigid crosslinking agents may be included in amounts between about 0.5 and about 15, or 2-10, 3-7 based upon the total weight of all of the reactive components. The physical and mechanical properties of the silicone hydrogels of the present invention may be optimized for a particular use by adjusting the components in the reactive mixture.

Non-limiting examples of silicone cross-linking agents also include the multi-functional silicone-containing components described above, such as compounds of Formula E (and its sub-formulae) and the multi-functional compounds shown in Table 3.

Further Constituents

The reactive mixture may contain additional components such as, but not limited to, diluents, initiators, UV absorbers, visible light absorbers, photochromic compounds, pharmaceuticals, nutraceuticals, antimicrobial substances, tints, pigments, copolymerizable dyes, nonpolymerizable dyes, release agents, and combinations thereof.

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

Generally, the reactive components are mixed in a diluent to form a reactive mixture. Suitable diluents are known in the art. For silicone hydrogels, suitable diluents are disclosed in WO 03/022321 and US 6020445, the disclosure of which is incorporated herein by reference. Classes of suitable diluents for silicone hydrogel reactive mixtures include alcohols having 2 to 20 carbons, amides having 10 to 20 carbon atoms derived from primary amines, and carboxylic acids having 8 to 20 carbon atoms. Primary and tertiary alcohols may be used. Preferred classes include alcohols having 5 to 20 carbons and carboxylic acids having 10 to 20 carbon atoms. Specific diluents which may be used include 1-ethoxy-2-propanol, diisopropylaminoethanol, isopropanol, 3,7-dimethyl-3-octanol, 1-decanol, 1-dodecanol, 1-octanol, 1-pentanol, 2-pentanol, 1-hexanol, 2-hexanol, 2-octanol, 3-methyl-3-pentanol, tert-amyl alcohol, tert-butanol, 2-butanol, 1-butanol, 2-methyl-2-pentanol, 2-propanol, 1-propanol, ethanol, 2-ethyl-1-butanol, (3-acetoxy-2-hydroxypropyloxy)-propylbis(trimethylsiloxy) methylsilane, 1-tert-butoxy-2-propanol, 3,3-dimethyl-2-butanol, tert-butoxyethanol, 2-octyl-1-dodecanol, decanoic acid, octanoic acid, dodecanoic acid, 2-(diisopropylamino)ethanol mixtures thereof and the like. Examples of amide diluents include N,N-dimethyl propionamide and dimethyl acetamide.

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

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

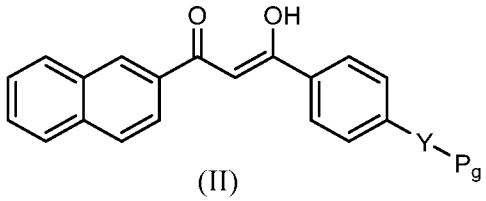
If a diluent is present, generally there are no particular restrictions with respect to the amount of diluent present. When diluent is used, the diluent may be present in an amount in the range of about 2 to about 70 weight percent, including in the range of about 5 to about 50 weight percent, and in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

A polymerization initiator may be used in the reactive mixture. The polymerization initiator may include, for instance, at least one of lauroyl peroxide, benzoyl peroxide, iso- propyl

percarbonate, azobisisobutyronitrile, and the like, that generate free radicals at moderately elevated temperatures, and photoinitiator systems such as aromatic alpha-hydroxy ketones, alkoxyoxybenzoins, acetophenones, acylphosphine oxides, bisacylphosphine oxides, and a tertiary amine plus a diketone, mixtures thereof and the like. Illustrative examples of photoinitiators are 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, bis(2,6-dimethoxybenzoyl)-2,4-4-trimethylpentyl phosphine oxide (DMBAPO), bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide (Irgacure 819), 2,4,6-trimethylbenzyldiphenyl phosphine oxide and 2,4,6-trimethylbenzoyl diphenylphosphine oxide, benzoin methyl ester and a combination of cam- phorquinone and ethyl 4-(N,N-dimethylamino)benzoate.

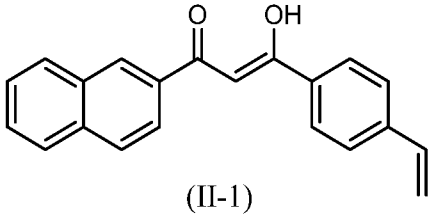
Commercially available (from IGM Resins B.V., The Netherlands) visible light initiator systems include Irgacure® 819, Irgacure® 1700, Irgacure® 1800, Irgacure® 819, Irgacure® 1850 and Lucrin® TPO initiator. Commercially available (from IGM Resins B.V.) UV photoinitiators include Darocur® 1173 and Darocur® 2959. These and other photoinitiators which may be used are disclosed in Volume III, Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition by J. V. Crivello & K. Dietliker; edited by G. Bradley; John Wiley and Sons; New York; 1998. The initiator is used in the reactive mixture in effective amounts to initiate photopolymerization of the reactive mixture, e.g., from about 0.1 to about 2 parts by weight per 100 parts of reactive monomer mixture. Polymerization of the reactive mixture can be initiated using the appropriate choice of heat or visible or ultraviolet light or other means depending on the polymerization initiator used. Alternatively, initiation can be conducted using e-beam without a photoinitiator. However, when a photoinitiator is used, the preferred initiators are bisacylphosphine oxides, such as bis(2,4,6-tri-methylbenzoyl)-phenyl phosphine oxide (Irgacure® 819) or a combination of 1-hydroxycyclohexyl phenyl ketone and bis(2,6-dimethoxybenzoyl)-2,4-4-trimethylpentyl phosphine oxide (DMBAPO).

While the compounds of formula I are the preferred high energy light absorbing compounds for use in the invention, other high energy light absorbing compounds are described in the examples and may be used alone or in combination with the compounds of formula I. These include, for instance, compounds of formula II, II-1, compound III, or combinations thereof:



(II)

wherein Y is a linking group and P_g is a polymerizable group. Preferably Y is a bond. Preferably, Pg is vinyl. Preferred compounds of formula II include compounds of formula II-1:



(II-1)

Compound III: 1-(2-amino-3-methoxyphenyl)-2-methylprop-2-en-1-one.

The reactive mixture for making the ophthalmic devices of the invention may comprise, in addition to one or more high energy light absorbing compounds, any of the other polymerizable compounds and optional components described above.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I and a hydrophilic component.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I and a hydrophilic component selected from DMA, NVP, HEMA, VMA, NVA, methacrylic acid, and mixtures thereof. Preferred are mixtures of HEMA and methacrylic acid.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I, a hydrophilic component, and a silicone-containing component.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I, a hydrophilic component, and a silicone-containing component comprising a compound of formula D (or its sub-formulae, such as D-1, D-2, etc.).

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I, a hydrophilic component selected from DMA, NVP, HEMA, VMA, NVA, and mixtures thereof; a silicone-containing component comprising a compound of formula D (or its sub-formulae, such as D-1, D-2, etc.); and an internal wetting agent.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I, a hydrophilic component selected from DMA, HEMA and mixtures thereof; a silicone-containing component selected from 2-hydroxy-3-[3-methyl-3,3-di(trimethylsiloxy)silylpropoxy]-propyl methacrylate (SiMAA), mono-methacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane (mPDMS), mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated mono-n-butyl terminated polydimethylsiloxane (OH-mPDMS), and mixtures thereof; and a wetting agent (preferably PVP or PVMA). For the hydrophilic component, mixtures of DMA and HEMA are preferred. For the silicone containing component, mixtures of SiMAA and mPDMS are preferred.

Preferred reactive mixtures may comprise: a high energy light absorbing compound of formula I, a hydrophilic component comprising a mixture of DMA and HEMA; a silicone-containing component comprising a mixture of OH-mPDMS having from 2 to 20 repeat units (preferably a mixture of 4 and 15 repeat units). Preferably, the reactive mixture further comprises a silicone-containing crosslinker, such as ac-PDMS. Also preferably, the reactive mixture contains a wetting agent (preferably DMA, PVP, PVMA or mixtures thereof).

The foregoing reactive mixtures may contain optional ingredients such as, but not limited to, one or more initiators, internal wetting agents, crosslinkers, other UV or HEV absorbers, and diluents.

Curing of Hydrogels and Manufacture of Lens

The reactive mixtures may be formed by any of the methods known in the art, such as shaking or stirring, and used to form polymeric articles or devices by known methods. The reactive components are mixed together either with or without a diluent to form the reactive mixture.

For example, ophthalmic devices may be prepared by mixing reactive components, and, optionally, 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 reactive mixture may be placed in a mold and subsequently cured into the appropriate article.

A method of making a molded ophthalmic device, such as a silicone hydrogel contact lens, may comprise: preparing a reactive monomer mixture; transferring the reactive monomer mixture onto a first mold; placing a second mold on top the first mold filled with the reactive

monomer mixture; and curing the reactive monomer mixture by free radical copolymerization to form the silicone hydrogel in the shape of a contact lens.

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

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

Aqueous solutions are solutions which comprise water. The aqueous solutions of the present invention may comprise at least about 20 weight percent water, or at least about 50 weight percent water, or at least about 70 weight percent water, or at least about 95 weight percent water. Aqueous solutions may also include additional water soluble Formulas such as inorganic salts or release agents, wetting agents, slip agents, pharmaceutical and nutraceutical Formulas, combinations thereof and the like. Release agents are compounds or mixtures of compounds which, when combined with water, decrease the time required to release a contact lens from a mold, as compared to the time required to release such a lens using an aqueous solution that does not comprise the release agent. The aqueous solutions may not require special handling, such as purification, recycling or special disposal procedures.

Extraction may be accomplished, for example, via immersion of the lens in an aqueous solution or exposing the lens to a flow of an aqueous solution. Extraction may also include, for example, one or more of: heating the aqueous solution; stirring the aqueous solution; increasing the level of release aid in the aqueous solution to a level sufficient to cause release of the lens; mechanical or ultrasonic agitation of the lens; and incorporating at least one leaching or extraction aid in the aqueous solution to a level sufficient to facilitate adequate removal of

unreacted components from the lens. The foregoing may be conducted in batch or continuous processes, with or without the addition of heat, agitation or both.

Application of physical agitation may be desired to facilitate leach and release. For example, the lens mold part to which a lens is adhered can be vibrated or caused to move back and forth within an aqueous solution. Other methods may include ultrasonic waves through the aqueous solution.

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

As indicated above, preferred ophthalmic devices are contact lenses, more preferably soft hydrogel contact lenses. The transmission wavelengths and percentages described herein may be measured on various thicknesses of lenses using, for instance, the methodologies described in the Examples. By way of example, a preferred center thickness for measuring transmission spectra in a soft contact lens may be from 80 to 100 microns, or from 90 to 100 microns or from 90 to 95 microns. Typically, the measurement may be made at the center of the lens using, for instance, a 4 nm instrument slit width. Various concentrations of the one or more polymerizable high energy light absorbing compounds may be used to achieve the transmission characteristics described above. For instance, the concentration may be in the range of at least 1 percent, or at least 2 percent; and up to 10 percent, or up to 5 percent, based on the weight percentages of all components in the reactive mixture, excluding diluent. A typical concentration may be in the range of 3 to 5 percent.

Silicone hydrogel ophthalmic devices (e.g., contact lenses) according to the invention preferably exhibit the following properties. All values are prefaced by "about," and the devices may have any combination of the listed properties. The properties may be determined by methods known to those skilled in the art, for instance as described in United States pre-grant publication US20180037690, which is incorporated herein by reference.

$[H_2O]$ %: at least 20 %, or at least 25 % and/or up to 80 % or up to 70 %

Haze: 30 % or less, or 10 % or less

Kruss DCA (°): 100° or less, or 50° or less

Tensile Modulus (psi): 120 or less, or 80 to 120

Dk (barrers): at least 80, or at least 100, or at least 150, or at least 200

Elongation to Break: at least 100

For ionic silicon hydrogels, the following properties may also be preferred (in addition to those recited above):

Lysozyme uptake (μg/lens): at least 100, or at least 150, or at least 500, or at least 700

Polyquaternium 1 (PQ1) uptake (%): 15 or less, or 10 or less, or 5 or less

Some embodiments of the invention will now be described in detail in the following Examples.

EXAMPLES

Test Methods

Ultraviolet-visible spectra of organic compounds in solution were measured on a Perkin Elmer Lambda 45 or an Agilent Cary 6000i UV/VIS scanning spectrometer. The instrument was thermally equilibrated for at least thirty minutes prior to use. For the Perkin Elmer instrument, the scan range was 200-800 nm; the scan speed was 960 nm per minute; the slit width was 4 nm; the mode was set on transmission or absorbance; and baseline correction was selected. For the Cary instrument, the scan range was 200-800 nm; the scan speed was 600 nm/min; the slit width was 2 nm; the mode was transmission or absorbance; and baseline correction was selected. A baseline correction was performed before samples were analyzed using the autozero function.

Ultraviolet-visible spectra of contact lenses formed in part from the claimed compositions were measured on a Perkin Elmer Lambda 45 UV/VIS or an Agilent Cary 6000i UV/VIS scanning spectrometer using packing solution. The instrument was thermally equilibrated for at least thirty minutes prior to use. For the Perkin Elmer instrument, the scan range was 200-800 nm; the scan speed was 960 nm per minute; the slit width was 4 nm; the mode was set on transmission; and baseline correction was selected. Baseline correction was performed using cuvettes containing plastic two-piece lens holders and the same solvents. These two-piece contact lens holders were designed to hold the sample in the quartz cuvette in the location through which the incident light beam traverses. The reference cuvette also contained a two-piece holder. To ensure that the thickness of the samples is constant, all lenses were made using identical molds. The center thickness of the contact lens was measured using an electronic thickness gauge. Reported center thickness and percent transmission spectra are obtained by averaging three individual lens data.

It is important to ensure that the outside surfaces of the cuvette are completely clean and dry and that no air bubbles are present in the cuvette. Repeatability of the measurement is

improved when the reference cuvette and its lens holder remain constant and when all samples use the same sample cuvette and its lens holder, making sure that both cuvettes are properly inserted into the instrument.

Examples

The following abbreviations will be used throughout the Examples and Figures and have the following meanings:

$AlCl_3$: aluminum chloride

NBS: N-bromosuccinimide

$FeCl_3$: iron (III) chloride

DIAD: diisopropyl azodicarboxylate

PPh_3: triphenylphosphine

Cs_2CO_3: cesium carbonate

XantPhos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

$Pd_2(dba)_3$:

HCl: hydrochloric acid

DMAP: dimethylaminopyridine

$Pd(dppf)_2Cl_2$:

KOAc: potassium acetate

AcOH: acetic acid

H_2O_2: hydrogen peroxide

KNO_3: potassium nitrate

THF: tetrahydrofuran

Pd/C: palladium on carbon

H_2: hydrogen gas

L: liter(s)

mL: milliliter(s)

Equiv. or eq.: equivalent(s)

LCMS: Liquid chromatography-mass spectroscopy

kg: kilogram(s)

g: gram(s)

mol: mole(s)

mmol: millimole(s)

TLC: thin layer chromatography

1H NMR: proton nuclear magnetic resonance spectroscopy

UV-VIS: ultraviolet-visible spectroscopy

psi: pounds per square inch

HNO_3: nitric acid

TsOH: p-toluenesulfonic acid

HCl: hydrochloric acid

Et_3N: triethylamine

CH_2Cl_2 or DCM: dichloromethane

$SnCl_2$: tin (II) chloride or stannous chloride

EtOH: ethanol

Na_2CO_3: sodium carbonate

EtOAc: ethyl acetate

BHT: 2,6-bis(1,1-dimethylethyl)-4-methylphenol

$CDCl_3$: deutro-chloroform

Cs_2CO_3: cesium or caesium carbonate

$NaHCO_3$: sodium bicarbonate

Na_2SO_4: sodium sulfate

K_2CO_3: potassium carbonate

DMSO: dimethyl sulfoxide

3-chloropropiophenone (Sigma-Aldrich)

1-(3-hydroxy-4-nitrophenyl)-ethan-1-one (Combi-Blocks)

1-(4-hydroxy-3-nitrophenyl)-ethan-1-one (Combi-Blocks)

Da: dalton or g/mole

kDa: kilodalton or an atomic mass unit equal to 1,000 daltons

DMA: N, N-dimethylacrylamide (Jarchem)

HEMA: 2-hydroxyethyl methacrylate (Bimax)

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

PDMA: polydimethylacrylamide

PVMA: polyvinylmethyacetamide

EGDMA: ethylene glycol dimethacrylate (Esstech)

TEGDMA: tetraethylene glycol dimethacrylate (Esstech)

TMPTMA: trimethylolpropane trimethacrylate (Esstech)

Tegomer V-Si 2250: diacryloxypolydimethylsiloxane (Evonik)

Irgacure 1700: mixture of 25% bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentylphosphineoxide and 75 % 2-hydroxy-2-methyl-1-phenyl-propan-1-one (BASF)

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

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

mPDMS: mono-n-butyl terminated monomethacryloxypropyl terminated polydimethylsiloxane (M_n = 800-1000 daltons) (Gelest)

HO-mPDMS: mono-n-butyl terminated mono-(2-hydroxy-3-methacryloxypropyl)-propyl ether terminated polydimethylsiloxane (M_n = 400-1500 daltons) (Ortec or DSM-Polymer Technology Group)

SiMAA: 2-propenoic acid, 2-methyl-2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (Toray) or 3-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propoxy)-2-hydroxypropyl methacrylate

Norbloc®: 2-(2′-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole (Janssen)

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

RB247: 1,4-Bis[2-methacryloxyethylamino]-9,10-anthraquinone

Bisomer IMT Blue or C.I. Reactive Blue 69: 2-anthracenesulfonic acid, 1-amino-4-[[4-[(2-bromo-1-oxo-2-propen-1-yl)amino]-2-sulfophenyl]amino]-9,10-dihydro-9,10-dioxo-, sodium salt (1:2) or 2-anthracenesulfonic acid, 1-amino-4-[[4-[(2-bromo-1-oxo-2-propenyl)amino]-2-sulfophenyl]amino]-9,10-dihydro-9,10-dioxo-, disodium salt (9CI) (Geo Specialty Chemicals) or disodium N-[4-[(4-amino-9,10-dioxo-3-sulfoanthracen-1-yl)amino]-3-sulfonatophenyl]-2-bromoprop-2-enimidate (CAS#70209-99-3)

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

DIW: deionized water

MeOH: methanol

IPA: isopropyl alcohol

BC: back or base curve plastic mold made from PP, TT, Z or blends thereof

FC: front curve plastic mold from PP, TT, Z or blends thereof

PP: polypropylene which is the homopolymer of propylene

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

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

TL03 lights: Phillips TLK 40W/03 bulbs

LED: light emitting diode

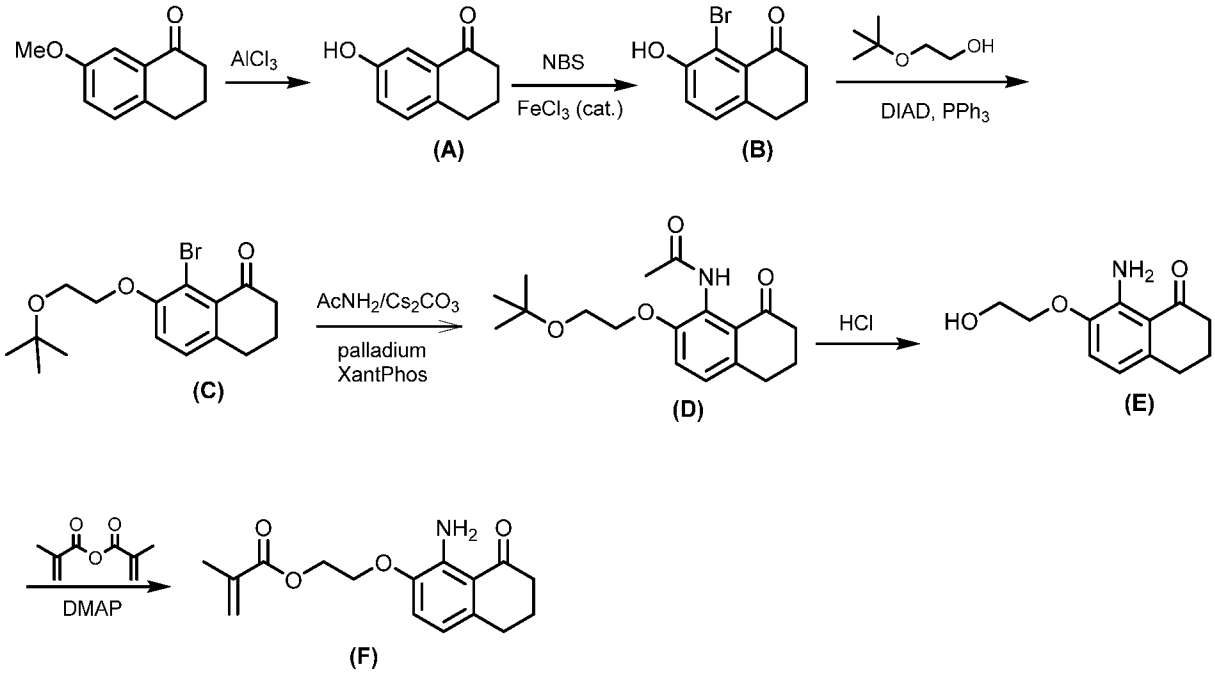
RMM: reactive monomer mixture(s)

NaH: sodium hydride

BAGE: Boric Acid Glycerol Ester (molar ratio of boric acid to glycerol was 1:2) 299.3 grams (mol) of glycerol and 99.8 grams (mol) of boric acid were dissolved in 1247.4 grams of a 5% (w/w) aqueous EDTA solution in a suitable reactor and then heated with stirring to 90-94°C under mild vacuum (2-6 torr) for 4-5 hours and allowed to cool down to room temperature.

Borate Buffered Packing Solution: 18.52 grams (300 mmol) of boric acid, 3.7 grams (9.7 mmol) of sodium borate decahydrate, and 28 grams (197 mmol) of sodium sulfate were dissolved in enough deionized water to fill a 2 liter volumetric flask.

Example 1 – Synthesis of Compound (F) as shown in Scheme 2



Scheme 2

7-Hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (A)

A suspension of 7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (334.0 grams, 1.90 moles, 1.0 equiv.) and anhydrous aluminum chloride (782 grams, 5.86 moles, 3.1 equiv.) in anhydrous toluene (8 L) was heated at 85°C for 30 minutes, at which point LCMS indicated the reaction was complete. The black reaction mixture was cooled to 0°C and poured into ice/water mixture (8.7 L) and stirred 5 minutes. The product was extracted with ethyl acetate (3 x 7 L). The combined organic layers were washed with water (2 x 1.7 L) and saturated brine (1.7 L). The organic layer was concentrated under reduced pressure. The residue was triturated with toluene (2.5 L) overnight. The solids were filtered, rinsed with toluene (0.9 L) and heptanes (0.9 L) to give compound (A) (301 g, 97% yield, >95% purity) as a beige solid. Prior to conversion into compound (B), compound (A) was purified as follows: compound (A) (195.4 grams) was purified over silica gel (200 grams), eluting with ethyl acetate (16 L). The solid was dried under vacuum at 40°C overnight to give compound (A) (192 grams, 94% yield, >95% purity).

8-Bromo-7-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (B)

Ferric chloride (1.9 grams, 11.8 mmol, 0.01 equiv.) was added to a stirred suspension of compound (A) (191 grams, 1.18 moles, 1.0 equiv.) and *N*-bromosuccinimide (209.5 grams, 1.18 moles, 1.0 equiv.) in anhydrous acetonitrile (1.9 L), resulting in a mild exotherm (10°C increase in temperature). After stirring for 16 hours, water (7 L) was added, and the reaction mixture was stirred for one hour. The resulting solid was filtered and washed with water (2 x 2.3 L). The solid was dissolved in ethyl acetate (3.4 L) and washed with water (1 L). The organic solvent was concentrated under reduced pressure, and the residue was purified over silica gel (3 kg), eluting with a gradient of 0 to 10% ethyl acetate in dichloromethane. The solid was dried under vacuum at 40°C overnight to give compound (B) (147 grams, 52% yield, >97% purity) as a light-yellow solid.

8-Bromo-7-(2-(tert-butoxy)ethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (C)

A solution of diisopropyl azodicarboxylate (697 grams, 3.45 moles, 3.5 equiv, DIAD) in anhydrous THF (3.4 L) was added over 30 minutes to a solution of triphenyl-phosphine (900 grams, 3.44 moles, 3.5 equiv.) in THF (6.6 L) at 0°C. After stirring for 45 minutes, a white

precipitate was observed. A solution of compound (B) (238 grams, 0.98 moles, 1.00 equiv.), ethylene glycol mono-*tert*-butyl ether (147 grams, 1.24 moles, 1.25 equiv.) in THF (1.7 L) was added over 30 minutes. The cooling bath was removed, and the reaction mixture was stirred at room temperature overnight, at which point LCMS indicated 30% of compound (B) remained. The tetrahydrofuran was removed under reduced pressure. The residue was dissolved in toluene (18 L) and was washed sequentially with 2N sodium hydroxide (2 x 9 L) and saturated brine (2 x 4.4 L). The combined aqueous washes were extracted with ethyl acetate (9 L). The combined organic layers were concentrated under reduced pressure. The residue was purified by five passes through a Biotage 150 cartridge, eluting with a gradient of 0 to 20% ethyl acetate in heptanes to give compound (C) (421 grams, 55% yield, 44% purity by ^{1}H-NMR). Note: The compound at this point contains both reduced DIAD and DIAD, neither of which effect the next reaction and are readily removed by chromatography in the next step.

N-(2-(2-(*tert*-Butoxy)ethoxy)-8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)acet-amide (D)

A suspension of compound (C) (193 grams, 567 mmol, 1.0 equiv.), acetamide (67 grams, 1.13 mol, 2.0 equiv) and cesium carbonate (555 grams, 1.7 mol, 3 equiv.) in 1,4-dioxane (15 L) was sparged with nitrogen for 15 minutes. XantPhos (16.4 grams, 28 mmol, 0.05 equiv.) and $Pd_2(dba)_3$ (10.2 grams, 11.2 mmol, 0.02 equiv.) were added. The reaction mixture was sparged with nitrogen for an additional 5 minutes. After refluxing for 1.5 hours, the reaction was cooled to 30°C and concentrated under reduced pressure to a volume of ~1.5 L. Ethyl acetate (48 L) was added, and the resulting mixture was washed with saturated brine (7.4 L). The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified over silica gel (1.5 kg) eluting with a gradient of 0 to 80% ethyl acetate in heptanes to yield compound (D) (75.5 grams, 42% yield) as a pale yellow solid.

8-Amino-7-(2-hydroxyethoxy)-3,4-dihydronaphthalen-1(2*H*)-one (E)

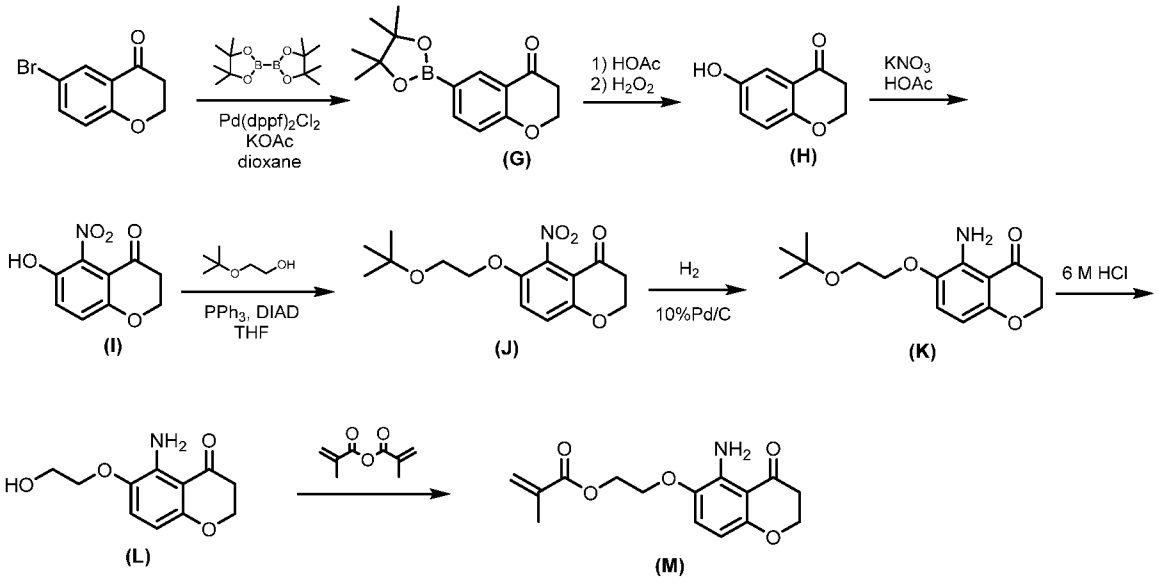
Compound (D) (25 grams, 0.078 mol, 1.0 equiv.) in aqueous HCl (3 M, 750 mL) was heated to 80°C for 3.5 hours at which point LCMS indicate complete deprotection. The reaction was cooled to room temperature, and solid sodium carbonate was added in portions until a pH of 10 was obtained. Dichloromethane (250 mL) was added, and the mixture was stirred for ~ 10 minutes. Two reactions of the same scale were combined in a separatory funnel, and additional dichloromethane (250 mL) was added. The layers were separated, and the aqueous layer was

back extracted with dichloromethane (250 mL). The combined organic layers were concentrated under reduced pressure to give crude compound (E) (43.8 grams, >85% purity by LCMS) as brown oil which was used subsequently.

2-((1-Amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl methacrylate (F)

Crude compound (E) (43.8 grams, ~85% purity, ~0.133 mol, 1.0 equiv) and DMAP (5 grams, 0.041 mol, 0.3 equiv.) in dichloromethane (800 mL) were stirred under nitrogen for 10 minutes. A solution of methacrylic anhydride (21.5 grams, 0.144 mol, 1.08 equiv.) and dichloromethane (125 mL) was added over a period of 30 minutes. An exotherm of ~4°C was observed over the course of the addition. After stirring at room temperature over a weekend, saturated sodium bicarbonate (400 mL) was added, and the layers were separated. The aqueous layer was back extracted with dichloromethane (200 mL). The combined organic layers were washed with saturated brine (250 mL) and concentrated under reduced pressure. The residue was purified over silica gel (450 grams), eluting with a gradient of 0 to 15% ethyl acetate in heptanes. The product was dried under vacuum at 40°C for 24 hours to give compound (F) (25.0 grams, 55% yield from compound (D)) as a yellow solid (MP = 90.7°C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (3H, s, CH_3), 2.02 (2H, m, cyclic-H), 2.61 (2H, t, J = 6.0 Hz, cyclic-H), 2.83 (2H, t, J = 6.0 Hz, cyclic-H), 4.22 (2H, t, J = 5.0 Hz, CH_2), 4.53 (2H, t, J = 5.0 Hz, CH_2), 5.60 (1H, m, vinylic), 6.14 (1H, m, vinylic), 6.37 (1H, d, J = 7.5 Hz, Ar-H), 6.79 (1H, d, J = 7.5 Hz, Ar-H). The UV-VIS spectrum of compound (F) in a 0.2 mM methanol solution is shown in FIG. 1.

Example 2 – Synthesis of Compound (M) as shown in Scheme 3



Scheme 3

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)chroman-4-one (G)

A mixture 6-bromo chroman-4-one (100.85 grams, 444.156 mmol, 1 equiv.), potassium acetate (130.77 grams, 1332.467 mmol, 3 equiv.) and bis(pinacolato)diboron (135.35 grams, 532.985 mmol, 1.2 equiv.) in 1,4-dioxane was sparged with nitrogen for 30 minutes. [1,1'-Bis-(diphenylphosphino)ferrocene]dichloropalladium(II) complex (18.14 grams, 22.208 mmol, 0.05 equiv.) in dichloromethane was added, and the mixture was heated at 95°C overnight. After cooling to room temperature, the mixture was filtered through Celite, and the filter cake was washed with ethyl acetate (2 x 500 mL). The filtrate was washed with water (500 mL) and saturated brine (500 mL). The combined aqueous layers were back-extracted with ethyl acetate (2 x 300 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified on a Biotage-75 column, eluting with a gradient of 0 to 50% ethyl acetate in heptanes, to give compound (G) (151.82 grams, theoretical yield 121.75 grams) as a light-brown oil, which contained some bis(pinacolato)-diboron. This material was used in the preparation of (H).

6-Hydroxychroman-4-one (H)

Acetic acid (150 mL) was added to a solution of compound (G) (151.8 grams, ~444.15 mmol, 1 equiv.) in THF (750 mL) and water (225 mL) at room temperature. After stirring at

room temperature for 1 hour, 30% hydrogen peroxide in water (150 mL) was added in portions to the mixture, and the resulting mixture was stirred at room temperature overnight. After cooling in an ice-bath, a 20% aqueous sodium sulfite (800 mL) was added dropwise (peroxide testing paper was negative). The mixture was extracted with ethyl acetate (3 x 800 mL), and the combined organic layers were washed with saturated brine (800 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified twice on a flash Biotage-75 column, eluting each time with a gradient of 0 to 50% ethyl acetate in heptanes to give compound (H) (59.7 grams, 82% yield for 2 steps) as a light-yellow solid.

6-Hydroxy-5-nitrochroman-4-one (I)

A solution of compound (H) (10 grams, 60.916 mmol, 1 equiv.) in diethyl ether (1000 mL) was added in portions to a mixture of sodium nitrate (5.177 grams, 60.916 mmol, 1 equiv.) and lanthanum(III) nitrate hexahydrate (2.637 grams, 6.092 mmol, 0.1 equiv.) in 6M HCl (200 mL). The mixture was stirred at room temperature for 41 hours at which time the mixture became a reddish solution, and TLC showed that the starting material was consumed. The mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 200 mL). The combined organic layers were washed with water (500 mL), saturated brine (500 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified on an AnaLogix automated column system (220 grams silica gel column), eluting with a gradient of 0 to 60% ethyl acetate in heptanes to give compound (I) (2.4 grams, 19% yield, 85% purity with a 15% bis-nitro by-product) as a yellow solid. The reaction should be monitored and stopped when the reaction is deemed complete by TLC, and then immediately worked-up to isolate the desired product; otherwise the bis-nitro by-product may become the major product.

6-(2-(*tert*-Butoxy)ethoxy)-5-nitrochroman-4-one (J)

Triphenylphosphine (18.81 grams, 71.715 mmol, 1.5 equiv.) and diisopropyl azodicarboxylate (DIAD, 14.12 mL, 71.715 mmol, 1.5 equiv) were added sequentially to a solution of compound (I) (10 grams, 47.81 mmol, 1 equiv.) and ethyleneglycol mono-*t*-butyl ether (6.28 mL, 47.81 mmol, 1 equiv.) in anhydrous THF (500 mL) at room temperature. After stirring at room temperature overnight, the mixture was concentrated under reduced pressure. The residue was purified twice on an AnaLogix automated column system (330 grams silica gel

column), eluting each time with a gradient of 0 to 100% ethyl acetate in heptanes to give compound (J) (16.3 grams, theoretical yield 14.79 grams) as a yellow solid, which contained some reduced DIAD. This material was used in the preparation of compound (K).

5-Amino-6-(2-(*tert*-butoxy)ethoxy)chroman-4-one (K)

A mixture of compound (J) (15.5 grams) which contained some reduced DIAD and 10% palladium on carbon (1.55 grams) in ethanol (1100 mL) was hydrogenated at 20 psi at room temperature for 6 hours. LCMS indicated that a mixture of compound (K) (80%) and an over-reduced by-product (20%) was formed.

Another batch of compound (J) (4 grams) was hydrogenated at 15 psi. LCMS indicated that a mixture of compound (K) (95%) and an over-reduced by-product (5%) was formed. The two batches were combined for work-up. The mixture was filtered through Celite, and the filter cake was washed with ethanol (200 mL). The filtrate was concentrated under reduced pressure. The residue was purified on an AnaLogix automated column system (330 grams silica gel column), eluting with a gradient of 0 to 40% ethyl acetate in heptanes to give compound (K) (7.8 grams, 13% yield for 3 steps) as a yellow oil.

5-Amino-6-(2-hydroxyethoxy)chroman-4-one (L)

A mixture of compound (K) (7.8 grams, 27.923 mmol, 1 equiv.) in 6M HCl (100 mL) was stirred at room temperature for 3 hours at which point LCMS indicated that the reaction was complete. The mixture was cooled in an ice-bath, and solid sodium carbonate was carefully added in portions until the pH was 10. The mixture was diluted with ethyl acetate (400 mL) and water (200 mL). The layers were separated, and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic layers were washed with saturated brine (200 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure to give compound (L) (5.77 grams, 90% yield) as a yellow solid, which was used in the preparation of (M).

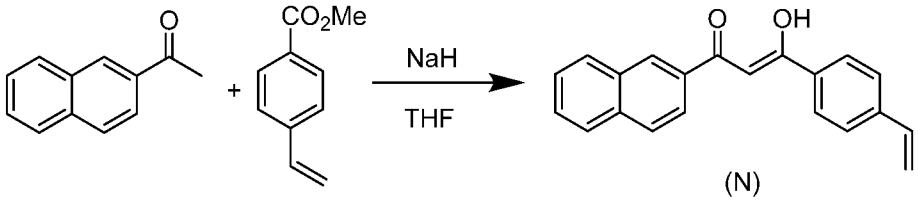
2-((5-Amino-4-oxochroman-6-yl)oxy)ethyl methacrylate (M)

Methacrylic anhydride (4.15 mL, 27.841 mmol, 1.1 equiv.) was added dropwise to a solution of compound (L) (5.65 grams, 25.31 mmol, 1 equiv.) and DMAP (0.93 grams, 7.593 mmol, 0.3 equiv.) in anhydrous dichloromethane (300 mL) at room temperature. After stirring at room temperature overnight, the mixture was washed with saturated sodium bicarbonate (100

mL) and saturated brine solution (100 mL). The combined aqueous layers were back-extracted with dichloromethane (2 x 100 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified on an AnaLogix automated column system (120 grams silica gel column), eluting with a gradient of 0 to 30% ethyl acetate in heptanes to give compound (M) (6.0 grams, 80% yield) as a sticky yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (3H, s, CH_3), 2.70 (2H, t, J = 5.5 Hz, CH_2), 4.22 (2H, t, J = 5.5 Hz, CH_2), 4.41 (2H, t, J = 6.1 Hz, CH_2), 4.53 (2H, t, J = 6.1 Hz, CH_2), 5.60 (1H, m, vinylic), 6.11 (1H, d, J = 8.2 Hz, Ar-H), 6.15 (1H, m, vinylic), 6.85 (1H, d, J = 8.2 Hz, Ar-H). The UV-VIS spectrum of compound (M) in a 0.2 mM methanol solution is shown in FIG. 1.

Example 3

Synthesis of (Z)-3-hydroxy-1-(naphthalen-2-yl)-3-(4-vinylphenyl)prop-2-en-1-one (N) as shown in Scheme 4



Scheme 4

To a 250 mL round bottomed flask containing a magnetic stirring bar, methyl 4-vinylbenzoate (2 grams, 12.3 mmol) and NaH (4.9 grams, 10 eq. 60% sodium hydride in oil suspension) were added. A pressure equalizing addition funnel containing 50 mL of dried THF (molecular sieves) was attached, and the reaction system purged with dry nitrogen gas for 20 minutes. Thereafter, the THF was added slowly with vigorous stirring. 2-Acetonaphthone (3.5 grams, 12.3 mmol) and a small amount of hydroquinone were dissolved in 10 mL dried THF and added dropwise to the reaction mixture. The contents of the reaction vessel were stirred for 12 hours. Then, the reaction flask was placed in an ice bath, and aqueous hydrochloric acid was added slowly to react with excess NaH. The volatile components were removed by rotary evaporation, and the residual dissolved/suspended in DCM. After filtration, the organic layer was extracted with dichloromethane in a separatory funnel, washed with dilute hydrochloric acid and brine, and then dried over $MgSO_4$. After filtration, the solvent was removed by rotary

evaporation. The residual was dissolved in ethyl acetate. The unreacted acetonaphthone was removed by precipitation into excess hexanes. The crude product was isolated by filtration and rotary evaporation which was then further purified using a silica column with ethyl acetate/hexane (1:5) as eluent, yielding (Z)-3-hydroxy-1-(naphthalen-2-yl)-3-(4-vinylphenyl)prop-2-en-1-one (N). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (1H, d, J = 11.0 Hz, vinylic), 5.91 (1H, d, J = 17.5 Hz, vinylic), 6.79 (1H, dd, J = 11.0 Hz, J = 17.5 Hz, vinylic), 6.99 (1H, s, enol H-C=C-O-), 7.52-8.03 (10H, m, Ar-H), 8.54 (1H, s, Ar-H); note: the exchangeable enolic proton was not observed.

Example 4

Reactive monomer mixtures (RMM 1-4) were prepared, composed of 77 weight percent of the formulations listed in Table 4, and 23 weight percent of the diluent D3O. All components except the PVP were mixed in a jar under a nitrogen atmosphere at ambient temperature for about 90 minutes, after which the PVP was added and mixed for about 240 minutes at ambient temperature. Thereafter, the jar was capped and placed on a roller for about 1000-6000 minutes at room temperature until a homogeneous solution was obtained, typically around 1500 to 1600 minutes. Ambient and room temperatures are typically between 25-30°C. The reactive monomer mixtures were then filtered through a 3 μm filter using a stainless-steel syringe under pressure. All reactive monomer mixtures were degassed at ambient temperature by applying vacuum (40 torr) for 45 minutes prior to making contact lenses.

TABLE 4

Component	RMM 1 (wt. %)	RMM 2 (wt. %)	RMM 3 (wt. %)	RMM 4 (wt. %)	RMM 5 (wt. %)	RMM 6 (wt. %)	RMM 7 (wt. %)	RMM 8 (wt. %)
mPDMS 1000	31.4	31.75	31.13	30.53	30.66	31.08	30.80	30.87
SiMAA	28.35	28.66	28.1	27.57	27.49	28.07	27.82	27.78
DMA	24.31	24.58	24.1	23.63	23.69	24.06	23.84	23.88
HEMA	6.08	6.15	6	5.91	6.00	5.93	5.92	5.97
TEGDMA	1.5	1.5	1.47	1.5	1.5	1.5	1.5	1.5
PVP K90	7	7	6.9	7	6.8	7	7.01	6.9
Irgacure 1870	0.34	0.34	0.3	0.34	0.34	0.34	0.34	0.34
Norbloc®	1	0	0	1.5	1.5	0	0.75	0.75
Bisomer IMT Blue	0	0	0	0.02	0.02	0.02	0.02	0.02
Compound (F)	0	0	2	2	0	0	1	0
Compound (M)	0	0	0	0	2	0	0	1
Compound (N)	0	0	0	0	0	2	1	1
Σ Components	100	100	100	100	100	100	100	100

In a glove box with a nitrogen gas atmosphere and less than about 0.2 percent oxygen gas, about 75-100 µL of the RMM 1 and RMM 2 were dosed separately using an Eppendorf pipet at room temperature into the FC made of 90:10 Z:TT blend. The BC made of 90:10 Z:TT blend was then placed onto the FC. The molds were equilibrated for a minimum of twelve hours in the glove box prior to dosing. Trays containing eight mold assemblies each were transferred into an adjacent glove box maintained at 63°C, and a quartz plate was used to cover and secure

the mold assemblies in the trays. Lenses were cured from the top and the bottom for 10 minutes using 435 nm LED lights having an intensity of about 2.1 mW/cm^2 at the tray's location.

The lenses were manually de-molded with most lenses adhering to the FC and released by suspending the lenses in about one liter of 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA and then three times with DI water. Each washing step lasted about 30 minutes. The lenses were equilibrated in borate buffered packaging solution overnight and then stored in fresh borate buffered packaging solution thereafter. Lenses (4A) made from RMM 1 had an average center thickness of 87 microns. Lenses (4B) made from RMM 2 had an average center thickness of 87 microns.

Lenses (4C) were prepared from RMM 3 using the same curing conditions and hydration steps as used to make the previous lenses (4A and 4B) except that the curing time was 15 minutes. The average center thickness of these lenses (4C) was 86 microns.

Lenses (4D) were prepared on a pilot line using RMM 4 and similar curing and hydration conditions as used to make the previous lenses (4A and 4B) except for the oxygen gas concentration was less than 3% and the irradiation conditions were 1.5 mW/cm^2 for about 5 minutes and then 2.5 mW/cm^2 for about 10 minutes. The average center thickness of these lenses (4C) was 80 microns.

Lenses (4E) were prepared from RMM 5 using the same curing conditions and hydration steps as used to make the previous lenses (4A and 4B) except that the curing conditions were 1.5 mW/cm^2 for about 5 minutes and then 2.5 mW/cm^2 for about 10 minutes at 65°C. The average center thickness of these lenses (4E) was about 85 microns.

The UV-VIS transmission spectra of lenses (4A), (4B), (4C), (4D) and (4E) are shown in FIG. 2, demonstrating that silicone hydrogel contact lenses with about 2 weight percent of compound (F) or compound (M) and about 1.5 weight percent Norbloc® exhibit complete absorption between about 250 nm and about 400 nm while absorbing some blue light between about 400 nm and about 450 nm. Compound (M) absorbed further into the visible region than compound (F).

Example 5

Reactive monomer mixtures (RMM 6, RMM 7, and RMM 8) were prepared, composed of 77 weight percent of the formulations listed in Table 4, and 23 weight percent of the diluent D3O. All components except the PVP were mixed in a jar under a nitrogen atmosphere at

ambient temperature for about 90 minutes, after which the PVP was added and mixed for about 240 minutes at ambient temperature. Thereafter, the jar was capped and placed on a roller for about 1000-6000 minutes at room temperature until a homogeneous solution was obtained, typically around 1500 to 1600 minutes. Ambient and room temperatures are typically between 25-30°C. The reactive monomer mixtures were then filtered through a 3 μm filter using a stainless-steel syringe under pressure. All reactive monomer mixtures were degassed at ambient temperature by applying vacuum (40 torr) for 45 minutes prior to making contact lenses.

In a glove box with a nitrogen gas atmosphere and less than about 0.2 percent oxygen gas, about 75-100 μL of the RMM 6, RMM 7, and RMM 8 were dosed separately using an Eppendorf pipet at room temperature into the FC made of 90:10 Z:TT blend. The BC made of 90:10 Z:TT blend was then placed onto the FC. The molds were equilibrated for a minimum of twelve hours in the glove box prior to dosing. Trays containing eight mold assemblies each were transferred into an adjacent glove box maintained at 65°C, and a quartz plate was used to cover and secure the mold assemblies in the trays. Lenses were cured from the top and the bottom using 1.0 mW/cm^2 for about 5 minutes and then 2.5 mW/cm^2 for about 10 minutes using 435 nm LED lights.

The lenses were manually de-molded with most lenses adhering to the FC and released by suspending the lenses in about one liter of 70 percent IPA for about one or two hours, followed by washing two times with 70 percent IPA and then three times with DI water. Each washing step lasted about 30 minutes. The lenses were equilibrated in borate buffered packaging solution overnight and then stored in fresh borate buffered packaging solution thereafter. Lenses (5A) were made from RMM 6. Lenses (5B) were made from RMM 7. Lenses (5C) were made from RMM 8. The average center thickness of these lenses (5A-5C) was about 85 microns.

The UV-VIS transmission spectra of lenses (4A), (5A), (5B), and (5C) are shown in FIG. 3, demonstrating that silicone hydrogel contact lenses with 2 weight percent of compound (N) and no Norbloc® or with about 1 weight percent of compound (N), about 1 weight percent of either compound (F) or compound (M), and 0.75 weight percent Norbloc® exhibit complete absorption between about 250 nm and about 400 nm while absorbing some HEV light between about 400 nm and about 450 nm.

Example 6

Reactive monomer mixtures (RMM 9 and RMM 10) were prepared, composed of 52 weight percent of the formulation listed in Table 5, and 48 weight percent of the diluent BAGE. The components were mixed in a jar under a nitrogen atmosphere at ambient temperature. Thereafter, the jar was capped and placed on a roller for about 1400 minutes at ambient temperature until the reactive monomer mixture was homogeneous. The reactive monomer mixture was then filtered through a 3 μm filter using a stainless-steel syringe under pressure.

TABLE 5

Component	**RMM 9 Weight %**	**RMM 10 Weight %**
HEMA	94.91	95.81
MAA	1.94	1.95
EGDMA	0.77	0.79
TMPTMA	0.09	0.09
Blue HEMA	0.01	0.01
Irgacure 1700	1.33	1.34
Norbloc®	0.95	0
Σ Components	100	100

The reactive monomer mixtures RMM 9 and RMM 10 were degassed at ambient temperature by applying vacuum (40 torr) for 45 minutes. Then, in a glove box with a nitrogen gas atmosphere and less than about 0.2 percent oxygen gas, about 75 μL of the reactive mixtures RMM 9 and RMM 10 were separately dosed using an Eppendorf pipet at room temperature into the FC made of 90:10 Z:TT blend. The BC made of 90:10 Z:TT blend was then placed onto the FC. The molds were equilibrated for a minimum of twelve hours in the glove box prior to dosing. Trays containing eight mold assemblies each were transferred into an adjacent glove box maintained at 65°C, and a quartz plate was used to cover and secure the mold assemblies in the trays. Lenses were cured from the top and the bottom for 8 minutes using 435 nm LED lights having an intensity of about 2.1 mW/cm^2 at the tray's location. The lenses were manually de-molded with most lenses adhering to the FC and released by suspending the lenses in 30 percent IPA for about 30-60 minutes, followed by soaking in DIW for 30 minutes and then in PS for 30

minutes. The lenses were still somewhat tacky, so the lenses were soaked again in DIW and individually placed in vials containing PS. Lenses (6A) were made from RRM 9 and had an average center thickness of 86 microns. Lenses (6B) were made from RRM 10 and had an average center thickness of 83 microns. A person of ordinary skill recognizes that the exact lens release process can be varied depending on the lens formulation and mold materials, regarding the concentrations of the aqueous isopropanol solutions, the number of washings with each solvent, and the duration of each step. The purpose of the lens release process is to release all lenses without defects and transition from diluent swollen networks to the packaging solution swollen hydrogels.

45.9 Milligrams of compound (F) was dissolved in 4.4423 grams of RMM 9 to yield a reactive monomer mixture containing about 2 weight percent of compound (F). Lenses (6C) were then prepared using the same curing conditions and hydration steps as used to make the previous lenses (6A and 6B) except that the curing time was 15 minutes. The average center thickness of these lenses (6C) was 87 microns.

45.6 Milligrams of compound (F) was dissolved in 4.4146 grams of RMM 10 to yield a reactive monomer mixture containing about 2 weight percent of compound (F). Lenses (6D) were then prepared using the same curing conditions and hydration steps as used to make the previous lenses (6A and 6B) except that the curing time was 15 minutes. The average center thickness of these lenses (6D) was 84 microns.

56.5 Milligrams of compound (M) was dissolved in 5.1395 grams of RMM 9 to yield a reactive monomer mixture containing about 2 weight percent of compound (M). There were some visible undissolved particles of compound (M) that were filtered off prior to making lenses. As a result, the concentration of compound (M) may be less than 2 weight percent in this formulation. Lenses (6E) were then prepared using the same curing conditions and hydration steps as used to make the previous lenses (6A and 6B) except that the curing time was 15 minutes. The average center thickness of these lenses (6C) was 91 microns.

The UV-VIS transmission spectra of lenses (6A), (6B), (6C), (6D), and (6E) are shown in FIG. 4, demonstrating that conventional hydrogel contact lenses (6C) and (6E) with about 2 weight percent of compound (F) or compound (M) and about 1 weight percent Norbloc® exhibit nearly complete absorption between about 250 nm and about 400 nm while absorbing some blue light between about 400 nm and about 450 nm. Compound (M) absorbed further into the visible

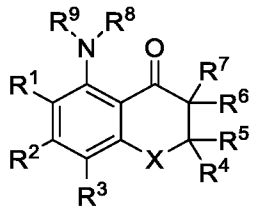
region than compound (F). Increasing the concentration of compound (F) or compound (M) in the formulation may provide complete absorption between about 250 nm and about 400 nm while absorbing some blue light between about 400 nm and about 450 nm.

The reference to any prior art in this specification is not and should not be taken as an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge.

In the present specification and claims, the term 'comprising' and its derivatives including 'comprises' and 'comprise' is used to indicate the presence of the stated integers but does not preclude the presence of other unspecified integers.

Claims:

1. A compound of formula I:



(I)

wherein R^1 is -Y-P_g;

R^2, R^3, R^4, R^5, R^6, and R^7 are each H;

X is CR^4R^5, O, S, or NR^4;

R^8 and R^9 are independently H, C_1-C_6 alkyl, C_5-C_8 cycloalkyl, or -Y-P_g;

Y is a linking group, wherein Y comprises: C_1-C_8 alkylene, alkyleneoxy, C_1-C_8 oxaalkylene, C_1-C_8 thiaalkylene, C_1-C_8 alkylene-ester-C_1-C_8 alkylene, C_1-C_8 alkylene-amide-C_1-C_8 alkylene, or C_1-C_8 alkylene-amine-C_1-C_8 alkylene; and

P_g is a polymerizable group, wherein P_g comprises: styryl, vinyl carbonate, vinyl ether, vinyl carbamate, N-vinyl lactam, N-vinylamide, (meth)acrylate, or (meth)acrylamide.

2. The compound of claim 1 wherein X is CH_2, O, or NH.

3. A compound of claim 1 that is:

2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl methacrylate;

N-(2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl)methacrylamide;

N-(2-((1-amino-8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)oxy)ethyl)-N-methylmethacrylamide;

2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl methacrylate;

N-(2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)methacrylamide;

N-(2-((5-amino-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)-N-methylmethacrylamide;

2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl methacrylate;

N-(2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)methacrylamide;

N-(2-((5-amino-1-methyl-4-oxo-1,2,3,4-tetrahydroquinolin-6-yl)oxy)ethyl)-N-methylmethacrylamide;
2-((5-amino-4-oxochroman-6-yl)oxy)ethyl methacrylate;
N-(2-((5-amino-4-oxochroman-6-yl)oxy)ethyl)methacrylamide; or
N-(2-((5-amino-4-oxochroman-6-yl)oxy)ethyl)-N-methylmethacrylamide.

4. An ophthalmic device that is a free radical reaction product of a reactive mixture comprising: one or more monomers suitable for making the ophthalmic device; and a polymerizable high energy light absorbing compound comprising a compound of any one of claims 1 to 3.

5. The ophthalmic device of claim 4 further comprising a second polymerizable high energy light absorbing compound.

6. The ophthalmic device of claim 5 wherein the second polymerizable high energy light absorbing compound is a UV absorbing compound.

7. The ophthalmic device of claim 6 wherein the UV absorbing compound comprises a compound of formula I, a benzophenone, a benzotriazole, a triazine, a substituted acrylonitrile, a salicylic acid derivative, a benzoic acid derivative, a cinnamic acid derivative, a chalcone derivative, a dypnone derivative, a crotonic acid derivative, or mixtures thereof.

8. The ophthalmic device of claim 5 wherein the second polymerizable high energy light absorbing compound is 2-(2′-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole, (Z)-3-hydroxy-1-(naphthalen-2-yl)-3-(4-vinylphenyl)prop-2-en-1-one, 1-(2-amino-3-methoxyphenyl)-2-methylprop-2-en-1-one, or combinations thereof.

9. The ophthalmic device of any one of claims 4 to 8 wherein the monomer suitable for making the ophthalmic device comprises a hydrophilic component, a silicone-containing component, or mixtures thereof.

10. The ophthalmic device of any one of claims 4 to 9 that is a contact lens, a corneal onlay, a corneal inlay, an intraocular lens, or an overlay lens.

11. The ophthalmic device of any one of claims 4 to 10 that is a hydrogel contact lens.

12. A method for making an ophthalmic device, the method comprising:

(a) providing a reactive mixture containing a compound according to any one of claims 1 to 3, one or more device forming monomers, and a radical initiator; and

(b) polymerizing the reactive mixture to form the ophthalmic device.

13. A silicone hydrogel contact lens that is a reaction product of a reactive mixture comprising: the polymerizable high energy light absorbing compound of any one of claims 1 to 3; and one or more monomers suitable for making an ophthalmic device.

14. The silicone hydrogel contact lens of claim 13 wherein the contact lens has a contact angle of about 70° or less, a water content of at least 25 percent, and an oxygen permeability of at least 80 barrers.

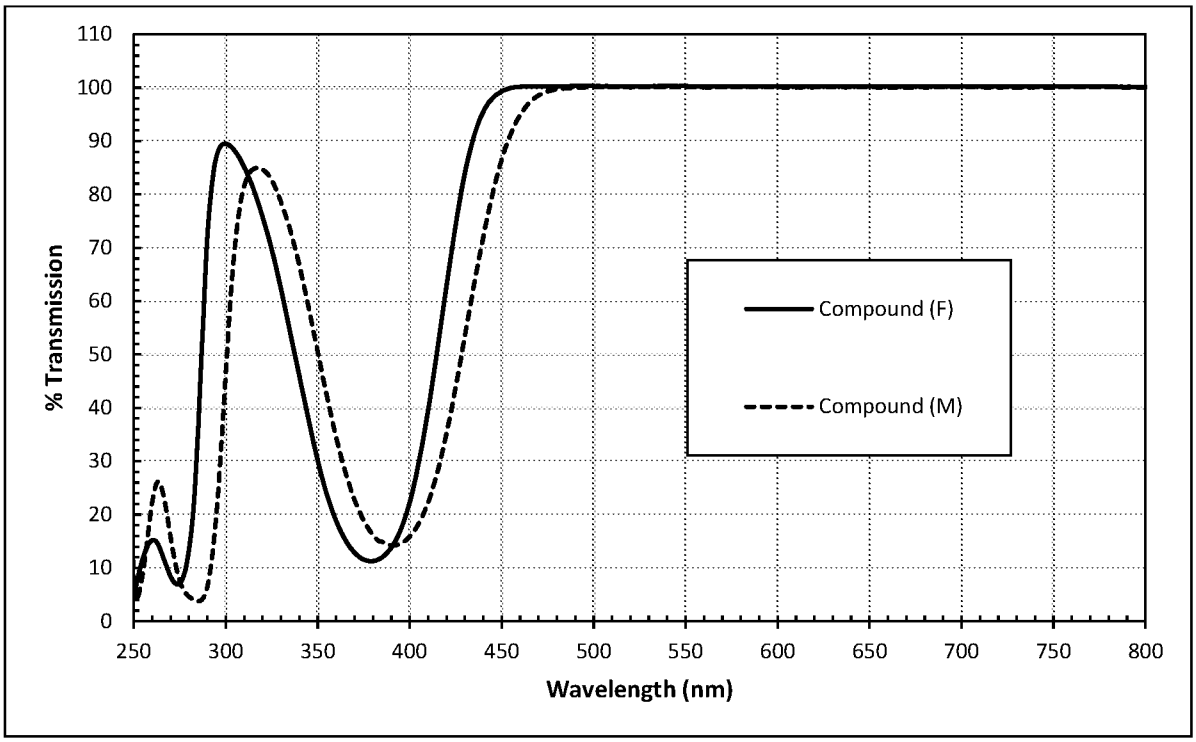


FIG. 1 – UV-VIS Transmission Spectra of 0.2 mM methanol solutions of Compounds (F) and (M)

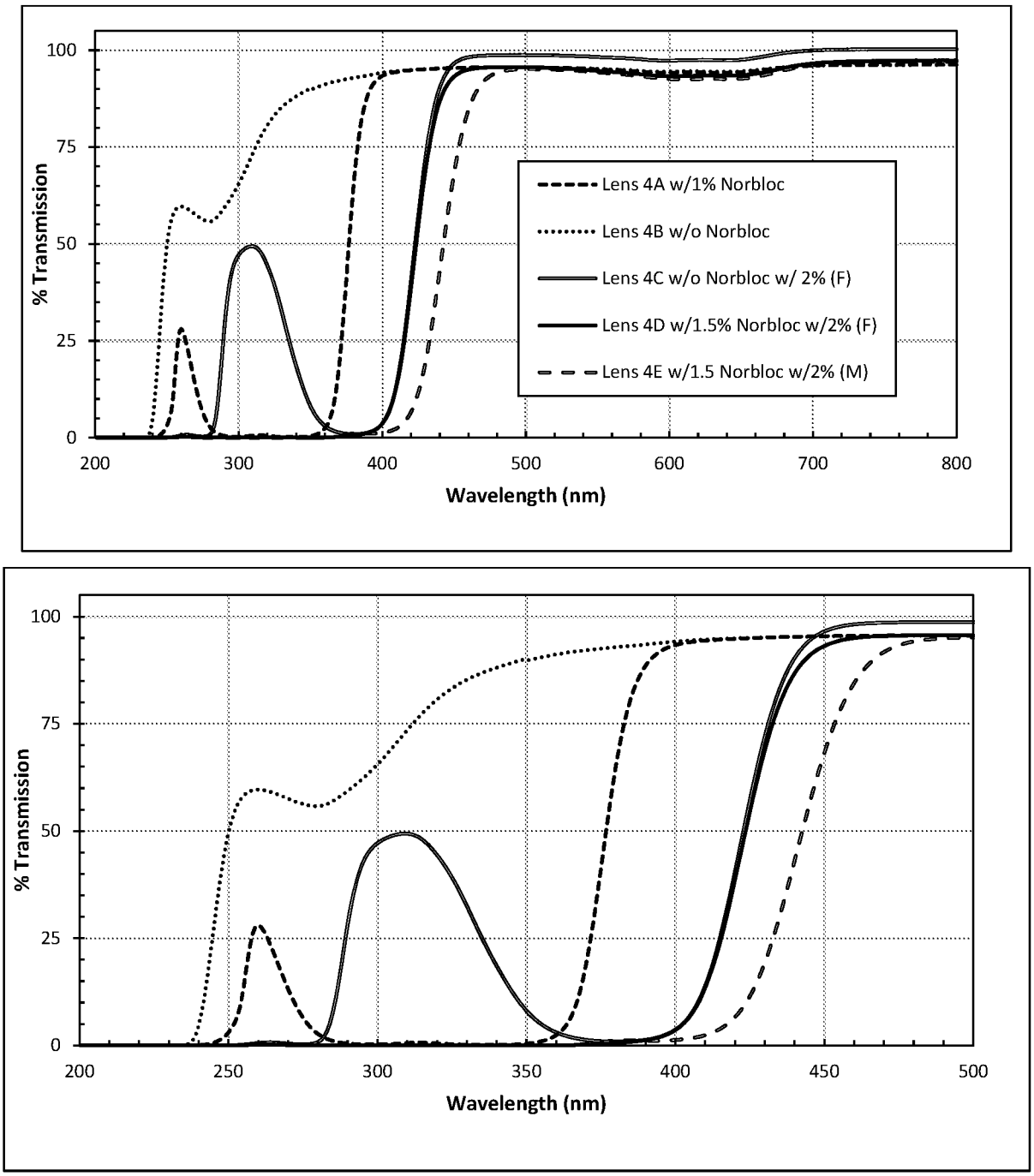


FIG. 2 – UV-VIS Transmission Spectra of Silicone Hydrogel Contact Lenses 4A-4E

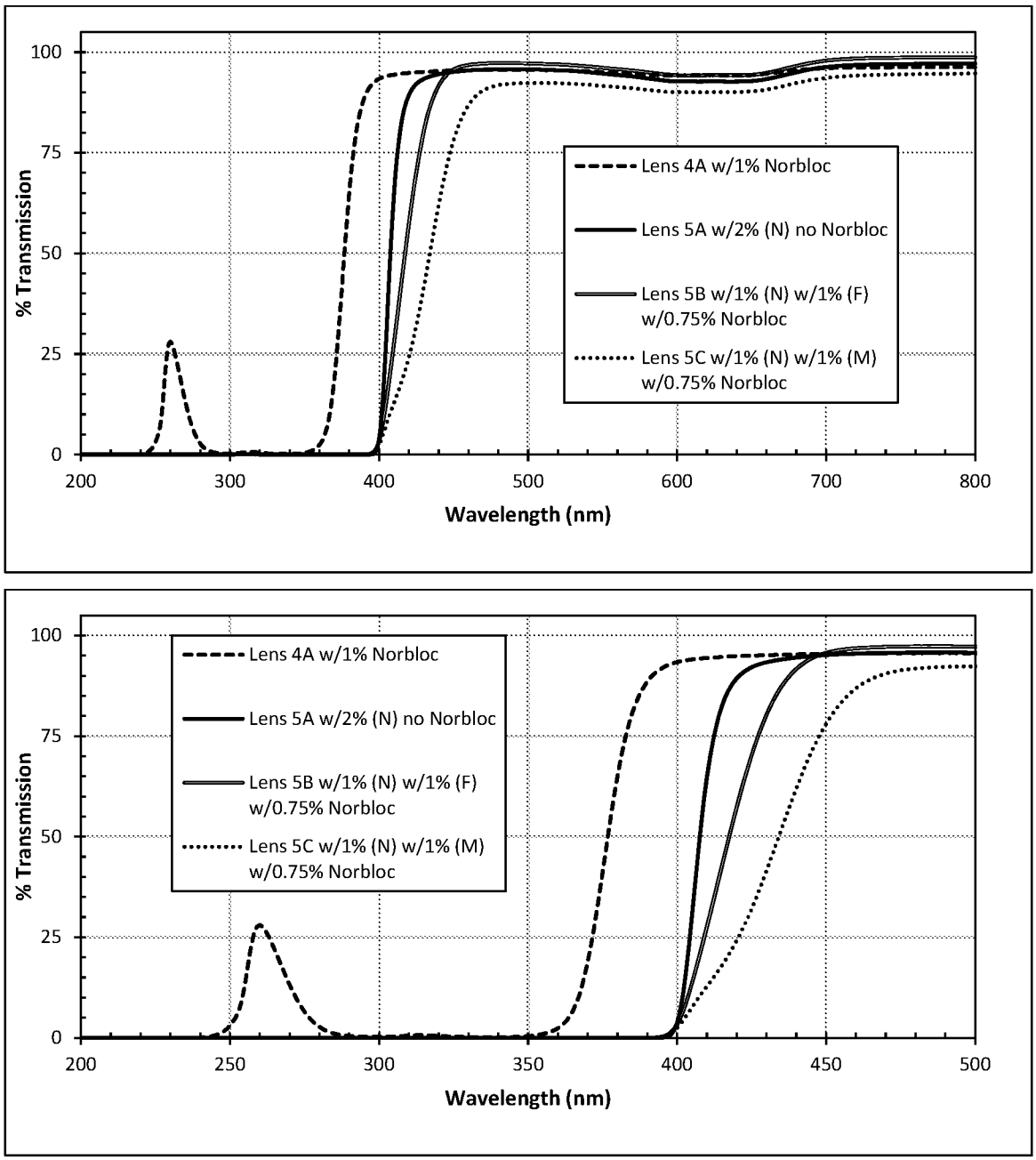
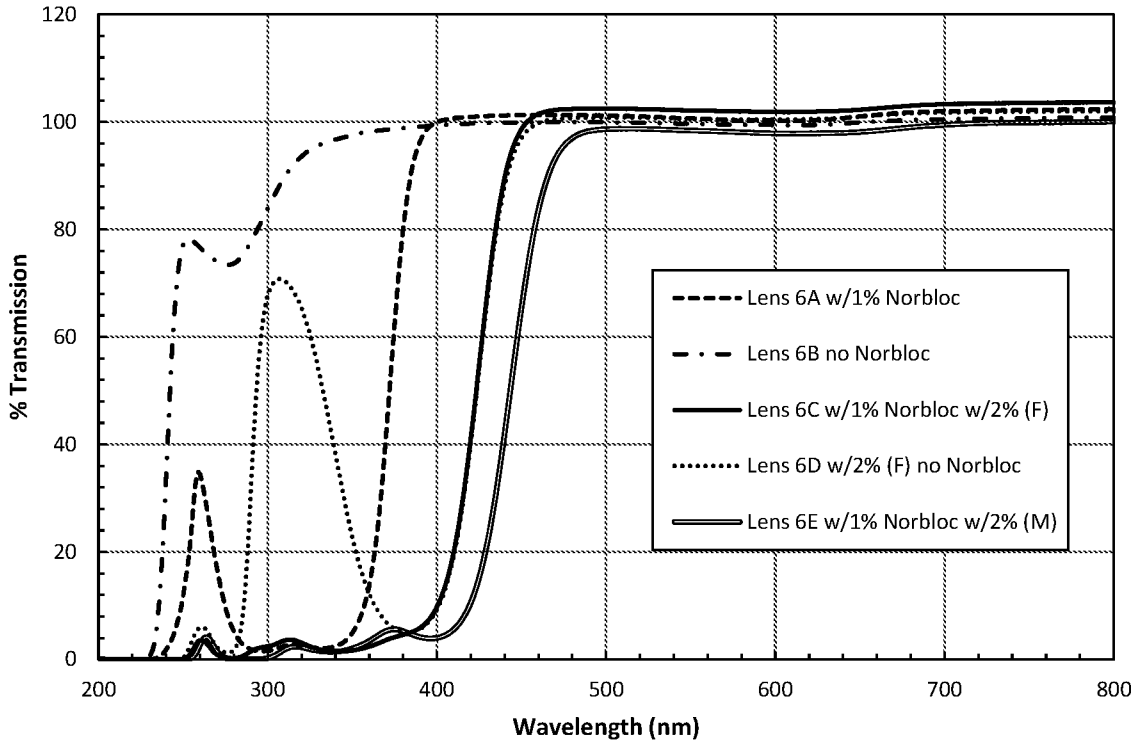


FIG. 3 – UV-VIS Transmission Spectra of Silicone Hydrogel Contact Lenses 4A and 5A-C


120
100
80
60
40
20
0
% Transmission
200
300
400
500
600
700
800
Wavelength (nm)
Lens 6A w/1% Norbloc
Lens 6B no Norbloc
Lens 6C w/1% Norbloc w/2% (F)
Lens 6D w/2% (F) no Norbloc
Lens 6E w/1% Norbloc w/2% (M)

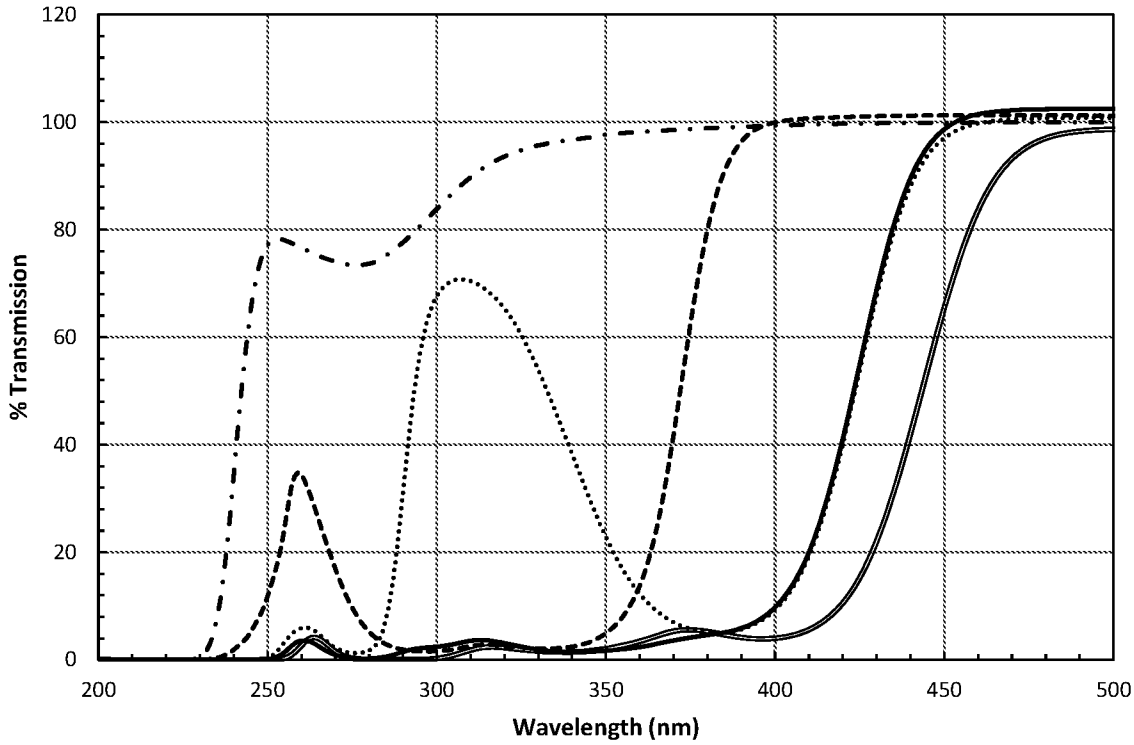


FIG. 4 – UV-VIS Transmission Spectra of Conventional Hydrogel Lenses 6A-6E