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(54) **SURFACE ACTIVE SEGMENTED BLOCK COPOLYMERS**

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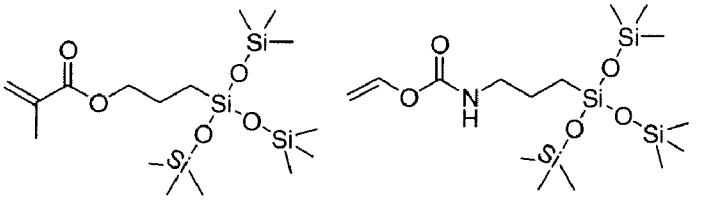
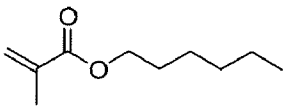
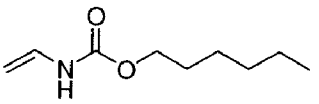
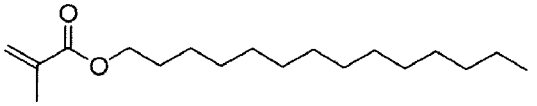
(57) **ABSTRACT**

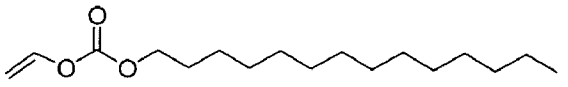
This invention is directed toward surface active segmented block copolymers useful to treat the surface of a substrate by means of surface active functionalities of the surface active segmented block copolymer material binding with complementary surface functionalities of the polymer substrate.

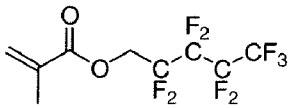


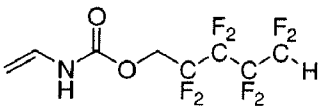


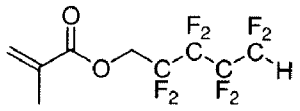


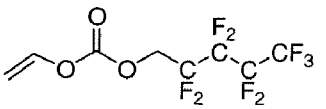












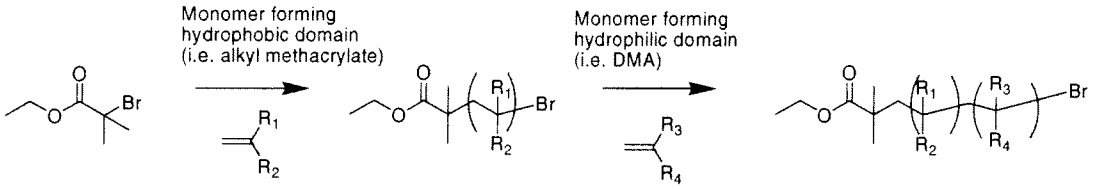


Figure 1.

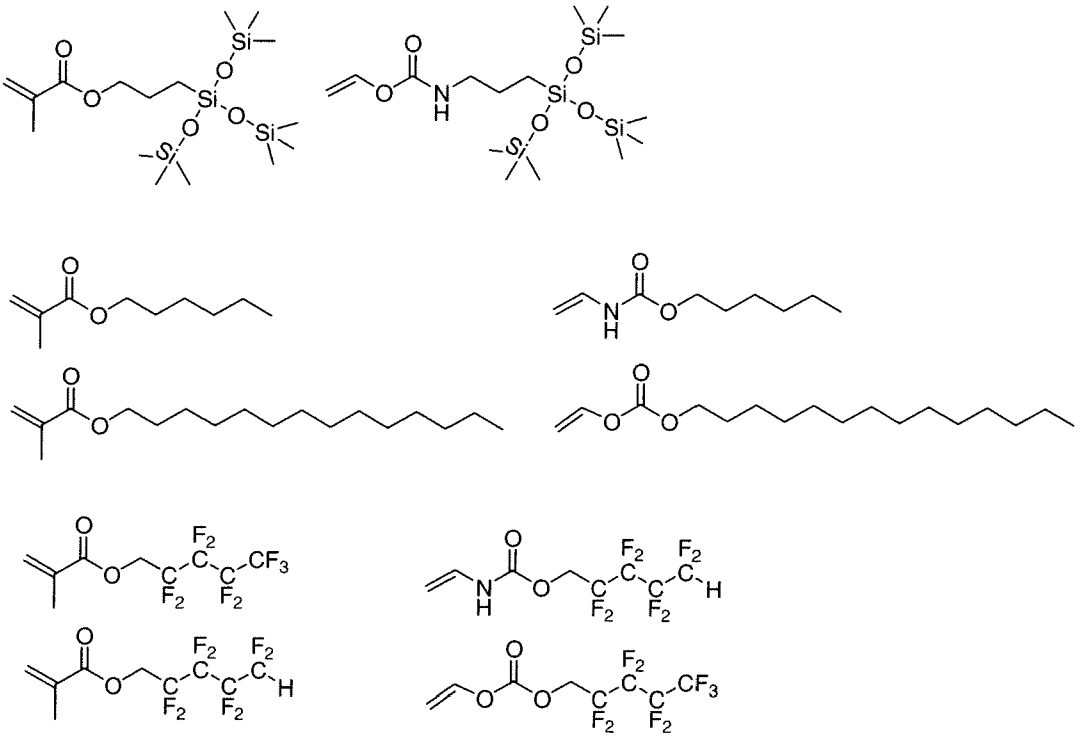


Figure 2.

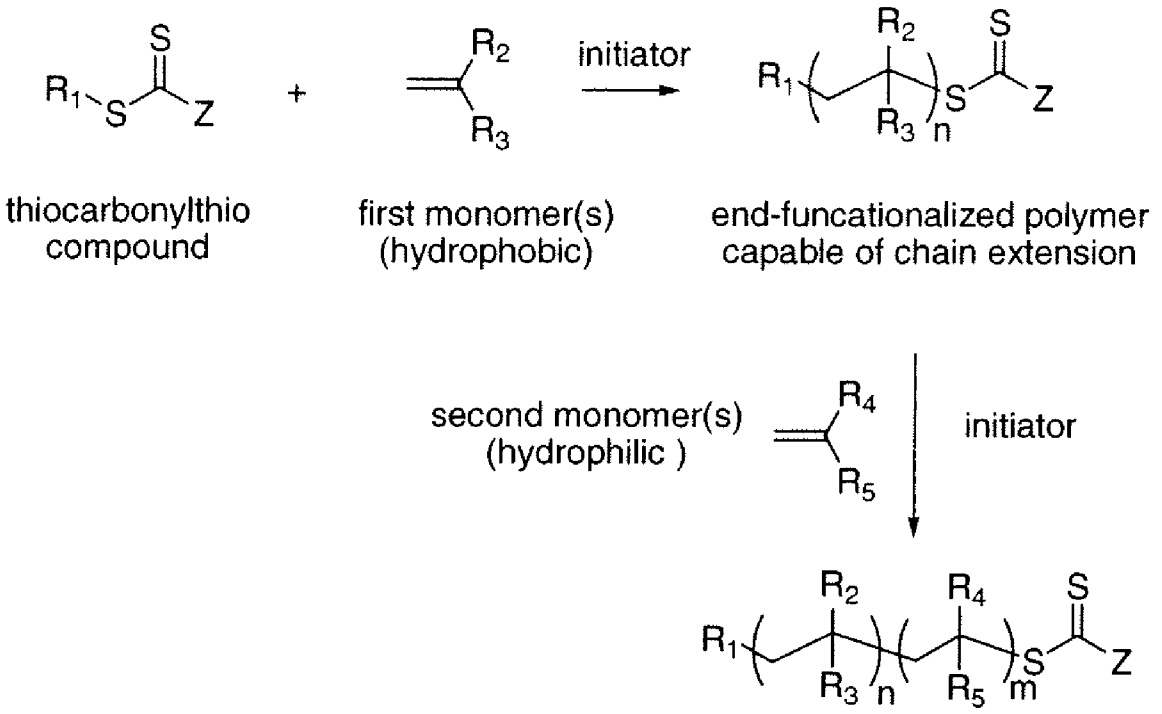

initiator
thiocarbonylthio compound
first monomer(s) (hydrophobic)
end-funcationalized polymer capable of chain extension
second monomer(s) (hydrophilic)
initiator

Figure 3.

SURFACE ACTIVE SEGMENTED BLOCK COPOLYMERS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Provisional Patent Application No. 61/016,844 filed Dec. 27, 2007; Provisional Patent Application No. 61/016,845 filed Dec. 27, 2007; Provisional Patent Application No. 61/016,841 filed Dec. 27, 2007; and Provisional Patent Application No. 61/016,843 filed Dec. 27, 2007.

FIELD OF INVENTION

[0002] This invention relates to a new class of tailored polymers useful as surface coatings for ophthalmic devices. These polymers can be specifically tailored using controlled radical polymerization processes and contain functional domains. Controlled radical polymerization allows the facile synthesis of segmented block copolymers with tunable chemical composition that, as a result, show different chemical properties than those prepared via conventional free radical polymerization. Surface active segmented block copolymers with hydrophobic domain(s) and hydrophilic domain(s) show good surface properties when applied to substrates.

BACKGROUND OF THE INVENTION

[0003] Medical devices such as ophthalmic lenses are made from a wide variety of materials. In the contact lens field materials are broadly categorized into conventional hydrogels or silicone hydrogels. Recently, the use of silicone-containing materials (silicone hydrogels) has been preferred. These materials can vary greatly in water content. However, regardless of their water content, silicone materials tend to be relatively hydrophobic, non-wettable, and have a high affinity for lipids. Methods to modify the surface of silicone devices by increasing their hydrophilicity and improving their biocompatibility are of great importance.

[0004] A number of copolymers for surface coatings have been investigated. U.S. Pat. No. 6,958,169 discloses providing a medical device formed from a monomer mixture comprising a hydrophilic device-forming monomer including a copolymerizable group and an electron donating moiety, and a second device-forming monomer including a copolymerizable group and a surface active functional group; and, contacting a surface of the medical device with a wetting agent including a proton donating moiety reactive with the functional group provided by the second lens-forming monomer and that complexes with the electron donating moiety provided by the hydrophilic lens-forming monomer.

[0005] U.S. Pat. No. 6,858,310 discloses a method of modifying the surface of a medical device to increase its biocompatibility or hydrophilicity by coating the device with a removable hydrophilic polymer by means of reaction between reactive functionalities on the hydrophilic polymer with functionalities that are complementary on or near the surface of the medical device.

[0006] U.S. Pat. No. 6,599,559 discloses a method of modifying the surface of a medical device to increase its biocompatibility or hydrophilicity by coating the device with a removable hydrophilic polymer by means of reaction between reactive functionalities on the hydrophilic polymer which functionalities are complementary to reactive functionalities on or near the surface of the medical device.

[0007] U.S. Pat. No. 6,428,839 discloses a method for improving the wettability of a medical device, comprising the steps of: (a) providing a medical device formed from a monomer mixture comprising a hydrophilic monomer and a silicone-containing monomer, wherein said medical device has not been subjected to a surface oxidation treatment; (b) contacting a surface of the medical device with a solution comprising a proton-donating wetting agent, whereby the wetting agent forms a complex with the hydrophilic monomer on the surface of the medical device in the absence of a surface oxidation treatment step and without the addition of a coupling agent.

[0008] Many copolymers are currently made using conventional free radical polymerization techniques with the structure of the polymer being completely random or controlled by the reactivity ratios of the respective monomers. By using controlled free radical polymerization techniques one is able to assemble copolymers in a controlled fashion and, in turn, they show completely different solution and coating properties than copolymers prepared using conventional free radical polymerization techniques. Controlled free radical polymerization can be conducted by a variety of methods, such as ATRP (atom transfer radical polymerization) and RAFT (Reversible addition-fragmentation chain transfer polymerization).

[0009] There are a number of commercially available block copolymer surfactants that can function as antifoaming agents, wetting agents, dispersants, thickeners, and emulsifiers. One such surfactant class is the Pluronic® and Tetronic® block copolymers based on ethylene oxide and propylene oxide, available from BASF. Another class of surfactants is the Silwet® and Silsoft® block copolymers based on ethylene oxide and siloxane blocks, available from GE silicones. These block copolymers and a variety of others rely on ring opening polymerization methods to produce the blocks.

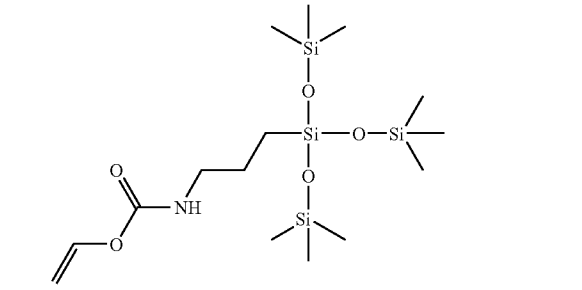
[0010] With the advent and rapid growth of RAFT polymerization in the late 1990's, block copolymers can now be prepared from a wide variety of vinyl based monomers. This opens up the toolbox for polymer chemists to synthesize countless number of block copolymer compositions. In addition, for the construction of surfactants there is a lot of chemical diversity in the selection of both the hydrophobic moieties and the hydrophilic moieties.

[0011] Surfactants or "surface active agents" lower the surface tension of water or other liquids and concentrate at the surface of the liquid. Surfactants have a common structural feature in which one portion of the surfactant molecule is highly polar or even ionic (hydrophilic or water loving) and the other portion is largely non-polar (hydrophobic or water fearing). The relationship of these two structural parts of the molecule with respect to each other controls the properties of the surfactant.

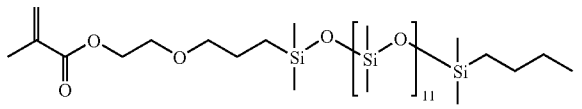
SUMMARY

[0012] This particular invention is related to the synthesis and preparation of specifically tailored block copolymer surfactants where both the lengths of the individual blocks, the chemical composition, and the sequence distribution are carefully controlled and the affinity of these surfactants for specific substrates can be guided by the "like prefers like" principle. For example, fluorocarbons interact with higher affinity to other fluorine-containing materials, as well as silicone containing blocks will interact with higher affinity to silicone containing materials. Therefore in one embodiment of this

invention, a block copolymer surfactant is prepared via RAFT polymerization that contains a hydrophilic block (NVP or DMA), and a fluorine containing hydrophobic block (perfluoroacrylate), where the surfactant is used to treat a fluorine containing substrate (i.e. Teflon or a fluoroelastomer). In another embodiment, a block copolymer surfactant is prepared via RAFT polymerization that contains a hydrophilic block (NVP or DMA), and a silicone containing hydrophobic block (TRIS-VC or M1-MCR-C12), where the surfactant is used to treat a silicone containing substrate (i.e. silicone hydrogel or a silicone elastomer).



TRIS-VC



M1-MCR-C12

[0013] In still another embodiment of this invention, a block copolymer surfactant is prepared via RAFT polymerization that contains a hydrophilic block (NVP or DMA), and a hydrocarbon containing hydrophobic block (Hexyl methacrylate or lauryl methacrylate), where the surfactant is used to treat a hydrocarbon based substrate (i.e. polyethylene or polypropylene).

[0014] In accordance with the present disclosure, the invention relates generally to surface active segmented block copolymers useful for forming coatings in the manufacture of medical devices. Examples of suitable devices include contact lenses, intraocular lenses, vascular stents, phakic intraocular lenses, aphakic intraocular lenses, corneal implants, catheters, implants, and the like. Therefore, disclosed in certain preferred embodiments as described herein is a surface active segmented block copolymer comprising a hydrophobic unit block comprising vinylically unsaturated polymerizable monomers and a hydrophilic block comprising vinylically unsaturated polymerizable monomers.

[0015] Surface active segmented block copolymers prepared through Atom Transfer Radical Polymerization ("ATRP") methods in accordance with the invention herein have the following generic formula (I):

$$R_1\text{-}[(A)_m]_p\text{-}[(B)_n]_q\text{—}X \quad (I)$$

wherein R_1 is the reactive residue of a moiety capable of acting as an initiator for Atom Transfer Radical Polymerization, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and X is a halogen capping group of the initiator for Atom Transfer Radical Polymerization. It should be noted, that there are many processes for the post polymerization removal or transformation of the halogen capping group of an initiator for Atom Transfer Radical Polymerization which are known to one of ordinary skill in the art. Therefore polymers prepared using ATRP according to the invention herein would include those where X is a halogen capping group of the initiator for Atom Transfer Radical Polymerization and those polymers that have undergone post polymerization removal or transformation of the halogen capping group of an initiator for Atom Transfer Radical Polymerization (i.e., derivatized reaction product). The polymers which contain halogen end-groups can be utilized in a host of traditional alkyl halide organic reactions. In one example, the addition of tributyltin hydride to the polymeric alkyl halide in the presence of a radical source (AIBN, or Cu(I) complex) leads to a saturated hydrogen-terminated polymer. In another example, by replacing tributyltin hydride with allyl tri-n-butylstannane, polymers with allyl end groups can be prepared. The terminal halogen can also be displaced by nucleophilic substitution, free-radical chemistry, or electrophilic addition catalyzed by Lewis acids to yield a wide variety of telechelic derivatives, such as alkenes, alkynes, alcohols, thiols, alkanes, azides, amines, phosphoniums, or epoxy groups, to mention a few.

[0016] Surface active segmented block copolymers prepared through Reversible addition-fragmentation chain transfer polymerization ("RAFT") methods in accordance with the invention herein have the following generic formula (II):

$$R_1\text{-}[(A)_m]_p\text{-}[(B)_n]_q\text{—}R_2 \quad (II)$$

wherein R_1 is a radical forming residue of a RAFT agent or free radical initiator, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is I to 10,000, p and q are natural numbers, and R_2 is a thio carbonyl thio fragment of the chain transfer agent. RAFT agents based upon thio carbonyl thio chemistry are well known to those of ordinary skill in the art and would include, for example, xanthates, trithiocarbonates and dithio esters. It should be noted, that there are many processes for the post polymerization removal or transformation of the thio carbonyl thio fragment of the chain transfer agent which are known to one of ordinary skill in the art. Therefore polymers prepared using RAFT agent according to the invention herein would include those where R_2 is a thio carbonyl thio fragment of the chain transfer agent and those polymers that have undergone post polymerization removal or transformation of the thio carbonyl thio fragment of the chain transfer agent (i.e., a derivatized reaction product). One example of such a transformation is the use of free radical reducing agents to replace the thio carbonyl thio group with hydrogen. Others include thermolysis of the end group or conversion of the thio carbonyl thio groups to thiol groups by aminolysis. A wide variety of telechelic derivatives can be prepared, such as alkenes, alkynes, alcohols, thiols, alkanes, azides, amines, phosphoniums, or epoxy groups, to mention a few.

[0017] Surface active segmented block copolymers prepared through reversible addition-fragmentation chain transfer polymerization ("RAFT") methods in accordance with the invention herein have the following generic formula (III):

$$R1\text{-}[(B)n]q\text{-}[(A)m]p\text{-}R2\text{-}[(A)m]p\text{-}[(B)n]q\text{-}R1 \quad (III)$$

wherein R1 is a radical forming residue of a RAFT agent or free radical initiator, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and R2 is a thio carbonyl group.

[0018] For each of the polymers of generic formula I, II and III the order of the block units is not critical and the surface active segmented block copolymer can contain more than two

blocks. Therefore the surface active segmented block copolymers can be multiblock copolymers and include repetition of one or more blocks. As examples please see the nonlimiting representations below, each of which is intended to fall within generic formula I, II and III:

$$-(A)_m-(B)_n- \quad (1)$$

$$-(B)_n-(A)_m- \quad (2)$$

$$-(A)_m-(B)_n-(A)_m- \quad (3)$$

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** is a schematic example of atom-transfer radical polymerization (ATRP) used to make a segmented block copolymer in which there is an oligomeric block of the hydrophobic unit at one end of the polymer followed by a large hydrophilic block;

[0020] FIG. **2** is the structural formula of various monomers which may be used to provide the hydrophobic unit of the segmented block copolymers of the invention herein;

[0021] FIG. **3** is a reaction schematic showing how RAFT polymerization can be used to polymerize block copolymers with surface active domains.

DETAILED DESCRIPTION

[0022] The present invention relates generally to surface active segmented block copolymers. The surface active segmented block copolymers are useful in various compositions including ophthalmic compositions comprising the surface active segmented block copolymers for use in providing surface coatings in the manufacture of medical devices. Therefore, disclosed in certain preferred embodiments as described herein is a surface active segmented block copolymer comprising a hydrophobic unit block comprising vinylically unsaturated polymerizable monomers and a hydrophilic block comprising vinylically unsaturated polymerizable monomers. In preferred embodiments, the present invention relates to medical devices surface coated with surface active segmented block copolymers. It should be understood that the term "surface" as used to describe surface coating is not to be limited to meaning "at least one complete surface". Surface coverage does not have to be even or complete to be effective for surface coating. The surface active segmented block copolymers of the present invention are useful as coatings for biocompatible materials including both soft and rigid materials commonly used for ophthalmic lenses, including contact lenses.

[0023] Surface active segmented block copolymers prepared through Atom Transfer Radical Polymerization ("ATRP") methods in accordance with the invention herein have the following generic formula (I):

$$R_1-[(A)_m]_p-[(B)_n]_q—X \quad (I)$$

wherein R_1 is the reactive residue of a moiety capable of acting as an initiator for Atom Transfer Radical Polymerization, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and X is a halogen capping group of the initiator for Atom Transfer Radical Polymerization. It should be noted that there are many processes for the post polymerization removal or transformation of the halogen capping group of an initiator for Atom Transfer Radical Polymerization which are known to one of ordinary skill in the art. Therefore polymers prepared using ATRP according to the invention herein would include those where X is a halogen capping group of the initiator for Atom Transfer Radical Polymerization and those polymers that have undergone post polymerization removal or transformation of the halogen capping group of an initiator for Atom Transfer Radical Polymerization (i.e., derivatized reaction product). The polymers which contain halogen end-groups can be utilized in a host of traditional alkyl halide organic reactions. In one example, the addition of tributyltin hydride to the polymeric alkyl halide in the presence of a radical source (AIBN, or Cu(I) complex) leads to a saturated hydrogen-terminated polymer. In another example, by replacing tributyltin hydride with allyl tri-n-butylstannane, polymers with allyl end groups can be prepared. The terminal halogen can also be displaced by nucleophilic substitution, free-radical chemistry, or electrophilic addition catalyzed by Lewis acids to yield a wide variety of telechelic derivatives, such as alkenes, alkynes, alcohols, thiols, alkanes, azides, amines, phosphoniums, or epoxy groups, to mention a few.

[0024] Surface active segmented block copolymers prepared through Reversible addition-fragmentation chain transfer polymerization ("RAFT") methods in accordance with the invention herein have the following generic formula (II):

$$R_1-[(A)_m]_p-[(B)_n]_q—R_2 \quad (II)$$

wherein R_1 is a radical forming residue of a RAFT agent or free radical initiator, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and R_2 is a thio carbonyl thio fragment of the chain transfer agent with the proviso that when A is an ionic block, B will be a nonionic block. It should be noted that there are many processes for the post polymerization removal or transformation of the thio carbonyl thio fragment of the chain transfer agent which are known to one of ordinary skill in the art. Therefore polymers prepared using RAFT agent according to the invention herein would include those where R_2 is a thio carbonyl thio fragment of the chain transfer agent and those polymers that have undergone post polymerization removal or transformation of the thio carbonyl thio fragment of the chain transfer agent (i.e., a derivatized reaction product). One example of such a transformation is the use of free radical reducing agents to replace the thio carbonyl thio group with hydrogen. Others include thermolysis of the end group or conversion of the thio carbonyl thio groups to thiol groups by aminolysis. A wide variety of telechelic derivatives can be prepared, such as alkenes, alkynes, alcohols, thiols, alkanes, azides, amines, phosphoniums, or epoxy groups, to mention a few.

[0025] Surface active segmented block copolymers prepared through reversible addition-fragmentation chain transfer polymerization ("RAFT") methods in accordance with the invention herein have the following generic formula (III):

$$R1-[(B)n]q-[(A)m]p-R2-[(A)m]p-[(B)n]q-R1 \quad (III)$$

wherein R1 is a radical forming residue of a RAFT agent or free radical initiator, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and R2 is a thio carbonyl thio group.

[0026] For each of the polymers of generic formula I, II and III the order of the block units is not critical and the surface active segmented block copolymer can contain more than two blocks. Therefore the surface active segmented block copolymers can be multiblock copolymers and include repetition of

one or more blocks. As examples please see the nonlimiting representations below, each of which is intended to fall within generic formula I, II and III:

$$-(A)_m-(B)_n- \quad (1)$$

$$-(B)_n-(A)_m- \quad (2)$$

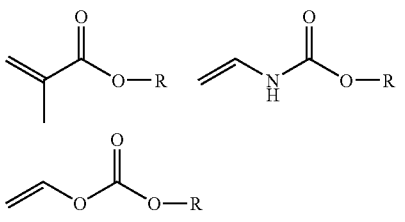
$$-(A)_m-(B)_n-(A)_m- \quad (3)$$

[0027] The present invention provides materials useful for surface modifying contact lenses and like medical devices through the use of surface active functionality. Although only contact lenses will be referred to hereinafter for purposes of simplicity, such reference is not intended to be limiting since the subject method is suitable for surface modification of other medical devices such as phakic and aphakic intraocular lenses and corneal implants as well as contact lenses. The preferred surface active segmented block copolymers in the present invention are selected based on the polymeric material to be coated.

[0028] The surface active segmented block copolymer comprises a hydrophobic unit block. The hydrophobic unit block can be made of vinylically unsaturated polymerizable monomers. Examples of hydrophobic vinylically unsaturated polymerizable monomers would include alkyl acrylates such as hexyl methacrylate and lauryl methacrylate, fluoroacrylates such as octofluoropentamethacrylate and 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl methacrylate (TDFM) and polysiloxanylalkyl (meth)acrylic monomers such as TRIS-VC and M1-MCR-C12. The hydrophobic unit block can be varied and is selected based upon the intended use of the surface active segmented block copolymers. That is, the hydrophobic unit block of the surface active segmented block copolymers is selected to provide a composition that is complementary with the surface of the device.

[0029] Selection of the hydrophobic unit monomer of the block copolymer is determined by the surface of the device. For example, if the surface active molecule on the surface of the device contains perfluorinated hydrocarbons, a monomer containing fluoroalkyl substituents (i.e. octafluoropentyl methacrylate) can be a hydrophobic unit monomer of the surface active segmented block copolymer. If the surface active molecule on the surface of the device contains siloxane functionality, silicone containing monomers (i.e. TRIS-methacrylate or TRIS-VC) can be a hydrophobic unit monomer of the surface active segmented block copolymer. A wide variety of suitable combinations of functional group containing monomers of the hydrophobic unit complementary to the surface of the device will be apparent to those of ordinary skill in the art.

[0030] Generic structures of hydrophobic units would include the following:



wherein R can consist of alkyl, fluoroalkyl, siloxy, or branched silicone.

[0031] Non-limiting examples would include methacryloxypropyl tris(trimethyl-siloxy)silane or tris(trimethylsiloxy)silylpropyl methacrylate, 3-(trimethylsilyl)propyl vinyl carbonate; 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane]; 3-[tris(tri-methylsiloxy)silyl]propyl vinyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; hexyl methacrylate, dodecyl methacrylate, lauryl methacrylate, hexyl vinyl carbamate, hexyl vinyl carbonate, octafluoropentamethacrylate, and octafluoropenta vinyl carbamate.

[0032] The hydrophobic unit block of the surface active segmented block copolymers is oligomeric or polymeric and is sized to provide suitable association with the surface of the medical device to be coated. Therefore the variable m of formula I, II or III can be between 1 and about 1000, preferably between 1 and about 100, most preferably between 1 and about 30.

[0033] In addition to the hydrophobic unit, the surface active segmented block copolymers of the invention herein will also contain hydrophilic domain(s) showing good surface properties when the block copolymer is coated onto the substrates. The hydrophilic domain(s) can be made of vinylically unsaturated polymerizable monomers such as, HEMA, glycerol methacrylate, methacrylic acid ("MAA"), acrylic acid ("AA"), methacrylamide, acrylamide, N,N'-dimethylmethacrylamide, or N,N'-dimethylacrylamide; copolymers thereof; hydrophilic prepolymers, such as ethylenically unsaturated poly(alkylene oxide)s, cyclic lactams such as N-vinyl-2-pyrrolidone ("NVP"), or derivatives thereof. Still further examples are the hydrophilic vinyl carbonate or vinyl carbamate monomers. Hydrophilic monomers can be nonionic monomers, such as 2-hydroxyethyl methacrylate ("HEMA"), 2-hydroxyethyl acrylate ("HEA"), 2-(2-ethoxyethoxy)ethyl (meth)acrylate, glyceryl (meth)acrylate, poly (ethylene glycol (meth)acrylate), tetrahydrofurfuryl (meth) acrylate, (meth)acrylamide, N,N'-dimethylmethacrylamide, N,N'-dimethylacrylamide("DMA"), N-vinyl-2-pyrrolidone (or other N-vinyl lactams), N-vinyl acetamide, and combinations thereof. Still further examples of hydrophilic monomers are the vinyl carbonate and vinyl carbamate monomers disclosed in U.S. Pat. No. 5,070,215, and the hydrophilic oxazolone monomers disclosed in U.S. Pat. No. 4,910,277. The contents of these patents are incorporated herein by reference. The hydrophilic monomer also can be an anionic monomer, such as 2-methacryloyloxyethylsulfonate salts. Substituted anionic hydrophilic monomers, such as from acrylic and methacrylic acid, can also be utilized wherein the substituted group can be removed by a facile chemical process. Non-limiting examples of such substituted anionic hydrophilic monomers include trimethylsilyl esters of (meth) acrylic acid, which are hydrolyzed to regenerate an anionic carboxyl group. The hydrophilic monomer also can be a cationic monomer selected from the group consisting of 3-methacrylamidopropyl-N,N,N-trimethyammonium salts, 2-methacryloyloxyethyl-N,N,N-trimethylammonium salts, and amine-containing monomers, such as 3-methacrylamidopropyl-N,N-dimethyl amine. Other suitable hydrophilic monomers will be apparent to one skilled in the art.

[0034] The hydrophilic monomer block will be sized to provide the desirable surface coating property of the surface active segmented block copolymer. The size of the hydrophilic oligomeric or polymeric block may vary depending

upon the substrate to be coated and the intended use. Therefore the variable n of formula I, II or III can be between 1 and about 10000, preferably between about 10 and about 1000, and more preferably between about 20 and about 300.

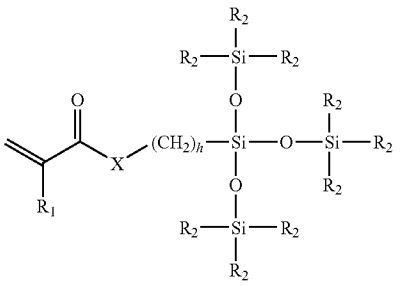
[0035] Atom-transfer radical polymerization (ATRP) can be used to prepare segmented block copolymers in which the molecular weight of each of the blocks and the entire polymer can be precisely controlled. As shown in FIG. **1**, atom-transfer radical polymerization (ATRP) can be used to make a segmented block copolymer in which there is a block of the hydrophobic unit at one end of the polymer followed by a large hydrophilic block. It should be understood that the order of addition of the monomer comprising the hydrophobic unit domain and the monomer comprising the hydrophilic domain is not critical. A large number of monomers are available for the assembly of polymers (For example, see FIG. **2**). Reversible addition-fragmentation chain transfer polymerization (RAFT) can also be used to prepare segmented block copolymers in which the molecular weight of each of the blocks and the entire polymer can be precisely controlled (see FIG. **3**).

[0036] The surface active segmented block copolymers of the invention herein are useful in providing coatings for substrates. Examples of substrate materials useful with the present invention are taught in U.S. Pat. No. 5,908,906 to Künzler et al.; U.S. Pat. No. 5,714,557 to Künzler et al.; U.S. Pat. No. 5,710,302 to Künzler et al.; U.S. Pat. No. 5,708,094 to Lai et al.; U.S. Pat. No. 5,616,757 to Bambury et al.; U.S. Pat. No. 5,610,252 to Bambury et al.; U.S. Pat. No. 5,512,205 to Lai; U.S. Pat. No. 5,449,729 to Lai; U.S. Pat. No. 5,387,662 to Künzler et al.; U.S. Pat. No. 5,310,779 to Lai and U.S. Pat. No. 6,891,010 to Künzler et al.; which patents are incorporated by reference as if set forth at length herein.

[0037] The present invention contemplates the use of surface active segmented block copolymers with medical devices including both "hard" and "soft" contact lenses. As disclosed above, the invention is applicable to a wide variety of materials. Hydrogels in general are a well-known class of materials that comprise hydrated, cross-linked polymeric systems containing water in an equilibrium state. Silicon containing hydrogels generally have water content greater than about 5 weight percent and more commonly between about 10 to about 80 weight percent. Such materials are usually prepared by polymerizing a mixture containing at least one silicon containing monomer and at least one hydrophilic monomer. Typically, either the silicon containing monomer or the hydrophilic monomer functions as a crosslinking agent (a crosslinker being defined as a monomer having multiple polymerizable functionalities) or a separate crosslinker may be employed. Applicable silicon containing monomeric units for use in the formation of silicon containing hydrogels are well known in the art and numerous examples are provided in U.S. Pat. Nos. 4,136,250; 4,153,641; 4,740,533; 5,034,461; 5,070,215; 5,260,000; 5,310,779; and 5,358,995.

[0038] Examples of applicable silicon-containing monomeric units include bulky polysiloxanylalkyl (meth)acrylic monomers. An example of bulky polysiloxanylalkyl (meth) acrylic monomers are represented by the following Formula IV:

(IV)

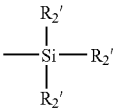


wherein:

[0039] X denotes —O— or —NR—;

[0040] each R_1 independently denotes hydrogen or methyl;

[0041] each R_2 independently denotes a lower alkyl radical, phenyl radical or a group represented by

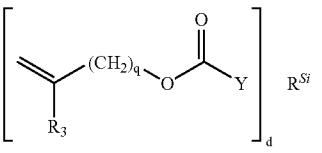


[0042] wherein each $R'_{2'}$ independently denotes a lower alkyl or phenyl radical; and h is 1 to 10. Some preferred bulky monomers are methacryloxypropyl tris(trimethyl-siloxy)silane or tris(trimethylsiloxy)silylpropyl methacrylate, sometimes referred to as TRIS.

[0043] Another class of representative silicon-containing monomers includes silicon containing vinyl carbonate or vinyl carbamate monomers such as: 1,3-bis[4-vinyloxycarbonyloxy)butyl]tetramethyl-disiloxane; 3-(trimethylsilyl) propyl vinyl carbonate; 3-(vinyloxycarbonylthio)propyl-[tris (trimethylsiloxy)silane]; 3-[tris(tri-methylsiloxy)silyl] propyl vinyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; t-butyldimethylsiloxyethyl vinyl carbonate; trimethylsilylethyl vinyl carbonate; and trimethylsilylmethyl vinyl carbonate.

[0044] An example of silicon-containing vinyl carbonate or vinyl carbamate monomers are represented by Formula V:

(V)



wherein:

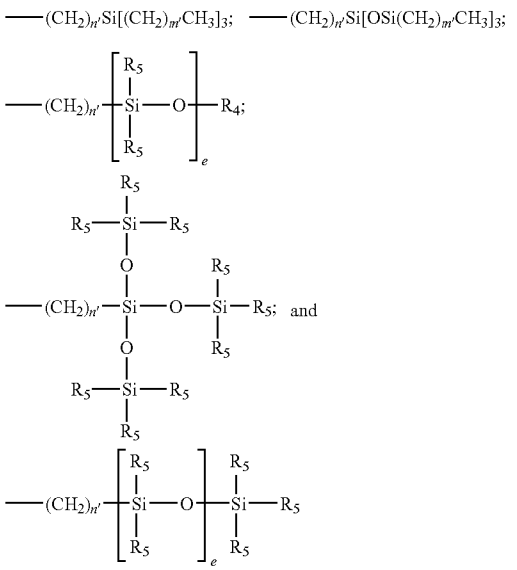
[0045] Y' denotes —O—, —S— or —NH—;

[0046] R^{Si} denotes a silicon containing organic radical;

[0047] R_3 denotes hydrogen or methyl;

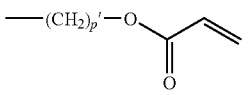
[0048] d is 1, 2, 3 or 4; and q is 0 or 1.

[0049] Suitable silicon containing organic radicals R^{Si} include the following:



wherein:

[0050] R_4 denotes

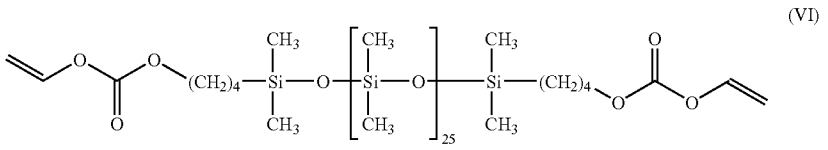


wherein p' is 1 to 6;

[0051] R_5 denotes an alkyl radical or a fluoroalkyl radical having 1 to 6 carbon atoms;

[0052] e is 1 to 200; n' is 1, 2, 3 or 4; and m' is 0, 1, 2, 3, 4 or 5.

[0053] An example of a particular species within Formula V is represented by Formula VI.



(VI)

[0054] Another class of silicon-containing monomers includes polyurethane-polysiloxane macromonomers (also sometimes referred to as prepolymers), which may have hard-soft-hard blocks like traditional urethane elastomers. They may be end-capped with a hydrophilic monomer such as HEMA. Examples of such silicon containing urethanes are disclosed in a variety of publications, including Lai, Yu-Chin, "The Role of Bulky Polysiloxanylalkyl Methacrylates in Polyurethane-Polysiloxane Hydrogels," *Journal of Applied Polymer Science,* Vol. 60, 1193-1199 (1996). PCT Published Application No. WO 96/31792 discloses examples of such monomers, which disclosure is hereby incorporated by reference in its entirety. Further examples of silicon containing urethane monomers are represented by Formulae VII and VIII:

$$E(*D*A*D*G)_a*D*A*D*E'; \text{ or} \quad \text{(VII)}$$

$$E(*D*G*D*A)_a*D*G*D*E'; \quad \text{(VIII)}$$

wherein:

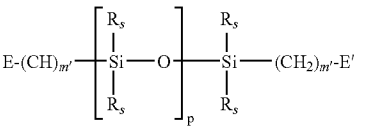
[0055] D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 6 to 30 carbon atoms;

[0056] G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 1 to 40 carbon atoms and which may contain ether, thio or amine linkages in the main chain;

[0057] * denotes a urethane or ureido linkage;

[0058] a is at least 1;

[0059] A denotes a divalent polymeric radical of Formula IX:



(IX)

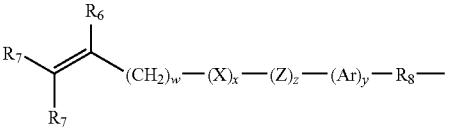
[0060] wherein:

[0061] each R_S independently denotes an alkyl or fluoro-substituted alkyl group having 1 to 10 carbon atoms which may contain ether linkages between carbon atoms;

[0062] m' is at least 1; and

[0063] p is a number which provides a moiety weight of 400 to 10,000;

[0064] each of E and E' independently denotes a polymerizable unsaturated organic radical represented by Formula X:



(X)

wherein:

[0065] R_6 is hydrogen or methyl;

[0066] R_7 is hydrogen, an alkyl radical having 1 to 6 carbon atoms, or a —CO—Y—R_9 radical wherein Y is —O—, —S— or —NH—;

[0067] R_8 is a divalent alkylene radical having 1 to 10 carbon atoms;

[0068] R_9 is a alkyl radical having 1 to 12 carbon atoms;

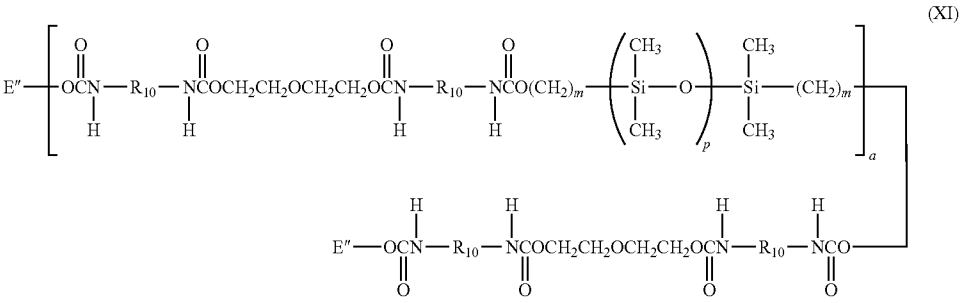
[0069] X denotes —CO— or —OCO—;

[0070] Z denotes —O— or —NH—;

[0071] Ar denotes an aromatic radical having 6 to 30 carbon atoms;

[0072] w is 0 to 6; x is 0 or 1; y is 0 or 1; and z is 0 or 1.

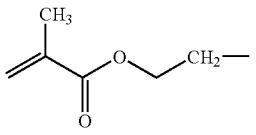
[0073] A more specific example of a silicon containing urethane monomer is represented by Formula (XI):



(XI)

[0074] wherein m is at least 1 and is preferably 3 or 4, a is at least I and preferably is 1,

[0075] p is a number which provides a moiety weight of 400 to 10,000 and is preferably at least 30, R_{10} is a diradical of a diisocyanate after removal of the isocyanate group, such as the diradical of isophorone diisocyanate, and each E" is a group represented by:



[0076] A preferred silicon containing hydrogel material comprises (in the bulk monomer mixture that is copolymerized) 5 to 50 percent, preferably 10 to 25 percent, by weight of one or more silicon containing macromonomers, 5 to 75 percent, preferably 30 to 60 percent, by weight of one or more polysiloxanylalkyl (meth)acrylic monomers, and 10 to 50 percent, preferably 20 to 40 percent, by weight of a hydrophilic monomer. In general, the silicon containing macromonomer is a poly(organosiloxane) capped with an unsaturated group at two or more ends of the molecule. In addition to the end groups in the above structural formulas, U.S. Pat. No. 4,153,641 to Deichert et al. discloses additional unsaturated groups, including acryloxy or methacryloxy. Fumarate-containing materials such as those taught in U.S. Pat. Nos. 5,512,205; 5,449,729; and 5,310,779 to Lai are also useful substrates in accordance with the invention. Preferably, the silane macromonomer is a silicon-containing vinyl carbonate or vinyl carbamate or a polyurethane-polysiloxane having one or more hard-soft-hard blocks and end-capped with a hydrophilic monomer.

[0077] Suitable hydrophilic monomers form hydrogels, such as silicon-containing hydrogel materials useful in the present invention. Examples of useful monomers include amides such as dimethylacrylamide, dimethylmethacrylamide, cyclic lactams such as n-vinyl-2-pyrrolidone and poly (alkene glycols) functionalized with polymerizable groups. Examples of useful functionalized poly(alkene glycols) include poly(diethylene glycols) of varying chain length containing monomethacrylate or dimethacrylate end caps. In a preferred embodiment, the poly(alkene glycol) polymer contains at least two alkene glycol monomeric units. Still further examples are the hydrophilic vinyl carbonate or vinyl carbamate monomers disclosed in U.S. Pat. No. 5,070,215, and the hydrophilic oxazolone monomers disclosed in U.S. Pat. No. 4,910,277. Other suitable hydrophilic monomers will be apparent to one skilled in the art.

Device Forming Additives and Comonomers

[0078] The monomer mix may, further as necessary and within limits not to impair the purpose and effect of the present invention, comprise various additives such as antioxidant, coloring agent, ultraviolet absorber and lubricant.

[0079] The monomer mix may be prepared by using, according to the end-use and the like of the resulting shaped polymer articles, one or at least two of the above comonomers and oligomers and, when occasions demand, one or more crosslinking agents.

[0080] Where the shaped polymer articles are for example medical products, in particular a contact lens, the monomer mix is suitably prepared from one or more of the silicon compounds, e.g. siloxanyl (meth)acrylate, siloxanyl (meth) acrylamide and silicon containing oligomers, to obtain contact lenses with high oxygen permeability.

[0081] The monomer mix may include additional constituents such as crosslinking agents, internal wetting agents, hydrophilic monomeric units, toughening agents, and other constituents as is well known in the art.

[0082] Although not required, the monomer mix may include toughening agents, preferably in quantities of less than about 80 weight percent e.g. from about 5 to about 80 weight percent, and more typically from about 20 to about 60 weight percent. Examples of suitable toughening agents are described in U.S. Pat. No. 4,327,203. These agents include cycloalkyl acrylates or methacrylates, such as: methyl acrylate and methacrylate, t-butylcyclohexyl methacrylate, iso-

propylcyclopentyl acrylate, t-pentylcycloheptyl methacrylate, t-butylcyclohexyl acrylate, isohexylcyclopentyl acrylate and methylisopentyl cyclooctyl acrylate. Additional examples of suitable toughening agents are described in U.S. Pat. No. 4,355,147. This reference describes polycyclic acrylates or methacrylates such as: isobornyl acrylate and methacrylate, dicyclopentadienyl acrylate and methacrylate, adamantyl acrylate and methacrylate, and isopinocamphyl acrylate and methacrylate. Further examples of toughening agents are provided in U.S. Pat. No. 5,270,418. This reference describes branched alkyl hydroxyl cycloalkyl acrylates, methacrylates, acrylamides and methacrylamides. Representative examples include: 4-t-butyl-2-hydroxycyclohexyl methacrylate (TBE); 4-t-butyl-2-hydroxycyclopentyl methacrylate; methacryloxyamino-4-t-butyl-2-hydroxycyclohexane; 6-isopentyl-3-hydroxycyclohexyl methacrylate; and methacryloxyamino-2-isohexyl-5-hydroxycyclopentane.

[0083] In particular regard to contact lenses, the fluorination of certain monomers used in the formation of silicon containing hydrogels has been indicated to reduce the accumulation of deposits on contact lenses made therefrom, as described in U.S. Pat. Nos. 4,954,587, 5,079,319, 5,010,141 and 6,891,010. Moreover, the use of silicon containing monomers having certain fluorinated side groups, i.e. —(CF_2)—H, have been found to improve compatibility between the hydrophilic and silicon containing monomeric units, as described in U.S. Pat. Nos. 5,387,662 and 5,321,108.

[0084] As stated above, surface structure and composition determine many of the physical properties and ultimate uses of solid materials. Characteristics such as wetting, friction, and adhesion or lubricity are largely influenced by surface characteristics. The alteration of surface characteristics is of special significance in biotechnical applications where biocompatibility is of particular concern. Thus, it is desired to provide a silicon containing hydrogel contact lens with an optically clear, hydrophilic surface film that will not only exhibit improved wettability, but which will generally allow the use of a silicon containing hydrogel contact lens in the human eye for extended period of time. In the case of a silicon containing hydrogel lens for extended wear, it be further desirable to provide an improved silicon-containing hydrogel contact lens with an optically clear surface film that will not only exhibit improved lipid and microbial behavior, but which will generally allow the use of a silicon-containing hydrogel contact lens in the human eye for an extended period of time. Such a surface treated lens would be comfortable to wear in actual use and allow for the extended wear of the lens without irritation or other adverse effects to the cornea.

[0085] It also may be desirable to apply these surface enhancing coatings to implantable medical devices such as intraocular lens materials to reduce the attachment of lens epithelial cells to the implanted device and to reduce friction as the intraocular lens passes through an inserter into the eye. It may also be desirable to apply these surface enhancing coatings to surgical instruments such as intraocular lens inserters and endoscopic instruments.

[0086] Methods of coating the substrate would include dip coating of the substrate into a solution containing the surface modifying agent. The solution containing the surface modifying agent may contain substantially the surface modifying agent in solvent or may contain other materials such as cleaning and extracting materials. Other methods could include spray coating the device with the surface modifying agent. Alternatively, the substrate and the other surface modifying agent may be subjected to autoclave conditions. In certain embodiments, the substrate and the surface modifying agent may be autoclaved in the packaging material that will contain the coated substrate. Once the contact between the substrate and the surface modifying agent has occurred, the remaining surface modifying agent could be substantially removed and packaging solution would be added to the substrate packaging material. Sealing and other processing steps would then proceed as they usually do. Alternatively, the surface modifying agent could be retained in the substrate packaging material during storage and shipping of the substrate device to the end user.

[0087] A general method of coating is now described. Medical devices, such as commercial SofLens59™ contact lenses, are removed from the packaging and soaked in purified water for at least 15 minutes prior to being placed in polymer solution. It should be recognized by persons skilled in the art that the quantities of a solution disclosed herein may be adjusted under specific circumstances to accommodate the size of the medical device. Glass vials are labeled and filled with about 4 ml of a polymer solution, and a lens is placed in each vial. When two polymer solutions are used for coating, they are mixed together immediately prior to placing in the vials. The vials are capped with silicone stoppers and crimped aluminum caps, then placed in an autoclave for one 30-minute cycle. The treated lenses are allowed to cool for a minimum of 3 hours, then removed from the vials and rinsed at least three times with deionized water. The rinsed lenses are then placed into new vials containing 4 ml of borate buffered saline (phosphate for samples undergoing bacterial adhesion testing) and autoclaved for one 30-minute cycle for sterilization.

[0088] Other types of contact lenses, such as those comprising other hydrogel materials can be treated with coating polymers, as disclosed above. In one embodiment, PureVision™ contact lenses comprising Balafilcon A hydrogel material, disclosed in U.S. Pat. No. 5,260,000, which is incorporated herein by reference, are surface-treated with a coating polymer as disclosed above. (PureVision™ contact lenses are available from Bausch and Lomb Incorporated, Rochester, N.Y.) In one aspect, PureVision™ contact lenses are first treated with a plasma discharge generated in a chamber containing air. A packaging solution for surface treatment comprised segmented block poly(TRIS-b-DMA) is added to a blister package before the lens is placed in and sealed around the perimeter of the receptacle with lidstock, The blister containing the lens is then autoclaved for one 30-minute cycle for sterilization.

[0089] In another method, a fluoro-silicone hydrogel contact lenses are packaged in a container that includes a receptacle portion to hold the contact lens and a sterile packaging solution comprising a segmented block poly(OFPMA-b-DMA). Examples of the container are conventional contact lens blister packages. This receptacle, containing the contact lens immersed in the solution, is hermetically sealed, for example, by sealing lidstock on the package over the receptacle. For example, the lidstock is sealed around a perimeter of the receptacle.

[0090] The solution and the contact lens are sterilized while sealed in the package receptacle. Examples of sterilization techniques include subjecting the solution and the contact lens to thermal energy, microwave radiation, gamma radiation or ultraviolet radiation. A specific example involves heating the solution and the contact lens, while sealed in the

package container, to a temperature of at least 100° C., more preferably at least 120° C., such as by autoclaving.

[0091] The packaging solution is an aqueous solution that includes the surface active segmented block copolymer, preferably in an amount of 0.02 to 5.0 weight percent, based on total weight of the packaging solution. The specific amount of surface active segmented block copolymer will vary depending on the substrate and the copolymer, but generally, the surface active segmented block copolymer will be present in an amount within this range.

[0092] The packaging solutions preferably have a pH of about 6.0 to 8.0, more preferably about 6.5 to 7.8, and most preferably 6.7 to 7.7. Suitable buffers include monoethanolamine, diethanolamine, triethanolamine, tromethamine (tris (hydroxymethyl)aminomethane, Tris), Bis-Tris, Bis-Tris Propane, borate, citrate, phosphate, bicarbonate, amino acids, and mixtures thereof. Examples of specific buffering agents include boric acid, sodium borate, potassium citrate, citric acid, Bis-Tris, Bis-Tris Propane, and sodium bicarbonate. When present, buffers will generally be used in amounts ranging from about 0.05 to 2.5 percent by weight, and preferably from 0.1 to 1.5 percent by weight.

[0093] The packaging solutions may further include a tonicity adjusting agent, optionally in the form of a buffering agent, for providing an isotonic or near-isotonic solution having an osmolality of about 200 to 400 mOsm/kg, more preferably about 250 to 350 mOsm/kg. Examples of suitable tonicity adjusting agents include sodium and potassium chloride, dextrose, glycerin, calcium and magnesium chloride. When present, these agents will generally be used in amounts ranging from about 0.01 to 2.5 weight percent and preferably from about 0.2 to about 1.5 weight percent.

[0094] Optionally, the packaging solutions may include an antimicrobial agent, but it is preferred that the solutions lack such an agent.

[0095] The surface active segmented block copolymers useful in certain embodiments of the present invention may be prepared according to syntheses well known in the art and according to the methods disclosed in the following examples. Surface modification of contact lenses using one or more surface modifying agents in accordance with the present invention is described in still greater detail in the examples that follow.

EXAMPLES

Example A

Synthesis of NVP-b-LMA Copolymer

[0096] To a 100-mL 2-neck round bottom flask equipped with a magnetic stir bar, 2 septa and an SS sparging needle was added 44 mg of AIBN, 10.0-g (0.090 mol) of N-vinylpyrrolidone (NVP), 0.20-g (0.00090 mol) of ethyl-α-(O-ethylxanthyl) propionate (EEXP) and 20-mL of 1,4-dioxane. The solution was sparged with nitrogen for 30-min. at RT before heating the flask in an oil bath to 60° C. The solution was sparged throughout the entire course of the polymerization. After 6 hours at 60° C., a 1 mL aliquot was removed from the flask and precipitated in 50 mL of ethyl ether. A quantity of lauryl methacrylate (LMA) (2.64-mL, 0.0090 mol) was then added to the flask in one portion via pipette. The solution was maintained at 60° C. overnight. The now hazy solution was cooled to RT and was added dropwise into 2.5-L of stirred ethyl ether. The precipitate was isolated by filtration and dried in vacuo at RT affording 6.08-g (49%) of white solid. The 6-hour aliquot was isolated in similar fashion.

[0097] The block copolymer product was characterized by proton NMR (CDCl3) and GPC. Resonances attributable to the alkyl protons of LMA were observed at approximately 0.8 and 1.25 ppm (not present in spectrum of the PVP aliquot). GPC was performed using a PLgel RESIpore column and DMF+1.0 M LiBr as solvent with calibration using PVP standards. Mn for the PVP aliquot was determined to be 11,650 Daltons (target=11,340 Daltons) with a polydispersity of 1.44. Mn for the block copolymer was determined to be 18,650 Daltons (target=13,900 Daltons) with a polydispersity of 1.63.

Example B

Synthesis of NVP-b-TRIS-VC (Two Step)

[0098] AIBN (23.2 mgs; 1.41×10^{-4} mol) was added to a 100 mL Schlenk flask equipped with a magnetic stirring bar. To the flask was added 147 mgs (7.05×10^{-4}) of ethyl-α-(O-ethylxanthyl)propionate (EEXP) dissolved in a small amount of dioxane. Dioxane (15 ml) and N-vinylpyrrolidone (NVP) [15 ml; 0.141 mol] were added to the Schlenk flask, which was then sealed and purged with N_2 for 30 minutes. The flask was placed in an oil bath (60° C.) for 24 hours. After cooling to RT, 20 ml of THF was added to the flask and the reaction was precipitated into diethyl ether while stirring vigorously. The precipitate was isolated by filtration and dried in vacuo yielding 14.148 grams of white solid (PVP MacroRAFT agent).

[0099] The second block (TRIS-VC) was added to the PVP MacroRAFT agent in a second reaction. Ten grams of PVP MacroRAFT agent (approx. 1.67×10^{-3} mol) was added to a 100 mL Schlenk flask along with 20 mL of 1,4-dioxane and a stir bar. 14.127-g (3.3×10^{-2} mol) of TRIS-VC and 54.8 mgs of AIBN (3.33×10^{-4} mol) were then added to the flask which was sealed and purged with N_2 for 60 minutes. The reaction was then heated for 11 hours in a 60° C. oil bath. The reaction mixture was dissolved in methanol (creating a dispersion). Dialysis tubes (Spectra/por 6, MWCO 3500) were filled with the solution and submerged in IL of methanol solvent with slow stirring. The solvent was changed after 4 h, 19.5 h, and 41.5 h. The tubes were removed at 48 h and the methanol was removed with a rotary evaporator. The resulting polymer was dried in a vacuum oven.

[0100] Both the PVP MacroRAFT agent and the block copolymer of NVP and TRIS-VC were characterized by proton NMR (CDCl3) and GPC. The calculated molecular weight of the block copolymer (MW=10,640 PD=1.30) is higher than the PVP MacroRAFT agent (MW=6,760). In addition, the NMR spectrum of the block copolymer shows peaks present from the TRIS-VC block at 0.0 ppm and 0.3 ppm and distinct peaks from the PVP segments between 1.0-2.5 ppm and 3.0-4.0 ppm. From the integrations it is estimated that the ratio of NVP:TRIS-VC is approximated at 29:1 by NMR.

Example C

Synthesis of NVP-b-TRIS-VC (Sequential Addition)

[0101] NVP (10 ml; 0.09 mol.), Xanthate (0.094 g, 4.5×10^{-4} mol.), AIBN (15 mg, 9.0×10−5 mol.), and 1,4 dioxane (10 ml) were added to Schlenk flask. The flask was sealed and purged with N2 for 1 hour. The flask was then heated at 60° C.

for 22 hours. In a separate flask, TRIS-VC (3.81 g, 8.99×10−3 mol.), AIBN (15 mg, 9.0×10−5 mol.) and 1,4-dioxane (4 ml) were combined, and then the flask was sealed and purged with N2 for 1 hour. This solution was then carefully added to the PVP reaction under N2. The flask was then heated for another 21 hours. Conversion of TRIS-VC was measured to be 35% by NMR. After cooling, methanol was added and the solution dialyzed (Spectra/por 6, MWCO 3500). The tubes were removed at 40 h and the methanol removed. The polymer was dried in a vacuum oven. The 1H NMR spectrum indicates a composition of approximately 4% of TRIS-VC, a similar value to the block copolymer in example B (ratio of NVP: TRIS-VC is approximated at 29:1).

[0102] Note* This approach should yield a block copolymer that has the change from one segment to the other less well-defined as the first block copolymer discussed above. The second block may actually be a statistical copolymerization of the TRIS-VC and any remaining NVP that had not been polymerized at the time of the TRIS-VC addition. The second "block", is therefore compositionally heterogeneous. A polymerization that yields a statistical copolymerization or compositionally heterogeneous block as the second block would also be considered to be a reactive segmented block copolymer according to the invention herein.

Example D

Synthesis of Various DMA-b-Hydrophobic Monomer (Sequential Addition)

[0103]

Reaction	DMA (mL)	DMA (mol)	CTR (mgs)	CTR (mol)	Hydrophobic Methacrylate (ml)	HM (mol)
2748-152	10	0.097	175	0.00048	1.40	0.0049
2748-153	10	0.097	175	0.00048	2.12	0.0073
2748-154	10	0.097	350	0.00097	2.12	0.0073
2748-155	10	0.097	350	0.00097	2.80	0.0097
2748-156	10	0.097	88	0.00024	1.12	0.0039
2748-157	10	0.097	88	0.00024	1.70	0.0058

*For reactions-152, -154, and -156 the hydrophobic methacrylate was 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl methacrylate (TDFM).
*For reactions-153, -155, and -157 the hydrophobic methacrylate was lauryl methacrylate (LMA).

[0104] Note: All reactions were carried out in a similar fashion using the amounts shown in the table above. Reaction 2748-152 is described below as an example of the procedure used. Weighed 175 mgs (0.48 mmol) of S-1-Dodecyl-S-(α, α'-dimethyl-α"-acetic acid) trithiocarbonate and 35 mgs of AIBN into a 250 ml round bottom flask. Added 10 ml (97 mmol) of N,N-Dimethylacrylamide (DMA) and 30 ml of dioxane to the flask, sealed flask with a septum and then purged with argon to deoxygenate for 30 mins. Placed flask in an oil bath (50° C.) for 6.0 hrs. In a separate container, 1.40 ml (4.9 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl methacrylate (TDFM) was bubbled with argon for 30 mins., then added to the flask after 6.0 hrs. *Note: A small aliquot was taken from the flask immediately before TDFM addition and precipitated into diethyl ether. The reaction was stopped 16 hours after TDFM addition (22 hrs total reaction time). The final product was precipitated out of the reaction mixture into diethyl ether. Precipitate contained a cloudy layer in the diethyl ether that was decanted off and a precipitate that settled that was collected and dried in the vacuum oven.

[0105] For all of the reactions, both the first precipitate and the block copolymer of DMA and hydrophobic methacrylate (either TDFM or LMA) were characterized by proton NMR (CDCl3) and GPC (DMF as eluent). The GPC chromatograms all show a shift in the elution peaks to shorter times (higher MW) after the addition of the hydrophobic methacrylate blocks. In addition, the NMR spectra of the block copolymers for samples -152,-154, and -156 above show a broad peak at around 4.5 ppm corresponding to the methylene group adjacent to the methacrylate of 3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl methacrylate (TDFM). The NMR of the block copolymers for samples -153,-155, and -157 show peaks for the —CH3 group (0.8 ppm) and —CH2-groups (1.3 ppm) of the alkyl chain of lauryl methacrylate

Example E

Synthesis of a Matrix of GMA-b-DMA Copolymers where the MW of Each of the Blocks is Varied

[0106]

TABLE 5

Reaction	DMA (mL)	DMA (mol)	CTR (mgs)	CTR (mol)	GMA (mL)	GMA (mol)	MW DMA block (theoretical)	MW GMA block (theoretical)
2748-114	20	0.194	350	0.00097	2.0	0.0146	19,800	2,140
2748-115	20	0.194	350	0.00097	4.0	0.0293	19,800	4,275
2748-116	20	0.194	350	0.00097	8.0	0.0586	19,800	8,550
2748-117	20	0.194	700	0.00194	2.0	0.0146	9,900	1,070
2748-118	20	0.194	700	0.00194	4.0	0.0293	9,900	2,140
2748-119	20	0.194	700	0.00194	8.0	0.0586	9,900	4,275
2748-120	10	0.097	700	0.00194	2.0	0.0146	4,950	1,070
2748-121	10	0.097	700	0.00194	4.0	0.0293	4,950	2,140
2748-122	10	0.097	700	0.00194	8.0	0.0586	4,950	4,275

*~33 mgs of AIBN were added to all of the reactions

[0107] *Note: All reactions were carried out in a similiar fashion using the amounts shown in the table above. Reaction 2748-1114 is described below as an example of the procedure used.

Weighed 350 mgs (0.97 mmol of S-1-Dodecyl-S-(□, □'-dimethyl-□"-acetic acid) trithiocarbonate and 33 mgs of AIBN into a 250 ml round bottom flask. Added 20 ml (194 mmol) of N,N-Dimethylacrylamide (DMA) and 60 ml of dioxane to the flask, sealed flask with a septum and then purged with argon to deoxygenate for 30 mins. Placed flask in an oil bath (50° C.) for 6.0 hrs. In a separate container, 2.0 ml (14.66 mmol) of glycidyl methacrylate (GMA) was bubbled with argon for 30 mins, then added before GMA addition and precipitated into diethyl ether. The reaction was stopped 15 hours after GMA addition (19.5 hrs total reaction time). The final product was precipitated out of the reaction mixture into diethyl ether.

[0108] Both the first precipitate and the block copolymer of DMA and GMA were characterized by proton NMR (CDCl3) and GPC. The GPC shows a shift in the elution peak to shorter times (higher MW) after the addition of the GMA block. In addition, the NMR spectra of the block copolymer show peaks for the glycidol methacrylate contributions at 3.7 ppm and 4.3 ppm. GPC data for these polymers using DMF as an eluent are shown below, using both PMMA standards and PVP standards as calibrants. Although the trends in MW are the same, PMMA standards show MW's much closer to the theoretically expected value for polyDMA.

TABLE 6

	PMMA Standards		PVP Standards	
Sample	Mw	Mn	Mw	Mn
2748-114	20,270	15,320	432,500	207,100
2748-115	—	—	534,200	219,500
2748-116	—	—	681,500	282,000
2748-117	8,950	6,430	147,800	71,700
2748-118	—	—	182,400	74,100
2748-119	—	—	245,900	72,300
2748-120	4,000	2,540	48,600	16,100
2748-121	—	—	70,100	15,000
2748-122	—	—	145,100	20,0

Example F

Packaging a Lens with a Surfactant

[0109] An aqueous packaging solution containing 1% by weight of the silicone-containing surfactant NVP-b-TRIS-VC of Example 1 dissolved in a borate buffered saline at a pH of 7.2 is placed in a polypropylene blister package. Next, a balafilcon A contact lens is immersed in the aqueous packaging solution in the polypropylene blister package. The package is sealed with foil lidstock and then autoclaved for 30 minutes at 121° C.

[0110] While there is shown and described herein certain specific structures and compositions of the present invention, it will be manifest to those skilled in the art that various modifications may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to particular structures herein shown and described except insofar as indicated by the scope of the appended claims.

What is claimed is:

1. A surface active segmented block copolymer comprising a hydrophobic unit block comprising vinylically unsaturated polymerizable monomers and a hydrophilic block comprising vinylically unsaturated polymerizable monomers.

2. The surface active segmented block copolymer of claim **1** wherein the hydrophobic unit comprises a vinylically unsaturated polymerizable monomer selected from the group consisting of methacryloxypropyl tris(trimethyl-siloxy)silane or tris(trimethylsiloxy)silylpropyl methacrylate, 3-(trimethylsilyl)propyl vinyl carbonate; 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane]; 3-[tris(tri-methylsiloxy)silyl] propyl vinyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl allyl carbamate; 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; hexyl methacrylate, dodecyl methacrylate, lauryl methacrylate, hexyl vinyl carbamate, hexyl vinyl carbonate, octafluoropentamethacrylate, octafluoropenta vinyl carbamate, and mixtures thereof.

3. The surface active segmented block copolymer of claim **1** wherein the hydrophilic block comprises vinylically unsaturated polymerizable monomers selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol methacrylate, methacrylic acid, acrylic acid, methacrylamide, acrylamide, N,N'-dimethylmethacrylamide, N,N'-dimethylacrylamide; ethylenically unsaturated poly(alkylene oxide) s, cyclic lactams, N-vinyl-2-pyrrolidone, hydrophilic vinyl carbonate, hydrophilic vinyl carbamate monomers, 2-hydroxyethyl acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, glyceryl (meth)acrylate, poly(ethylene glycol (meth) acrylate), tetrahydrofurfuryl (meth)acrylate, N-vinyl acetamide, copolymers, derivatives and combinations thereof.

4. The surface active segmented block copolymer of claim **1** wherein the block of the hydrophobic unit comprises between 1 and about 1,000 units.

5. The surface active segmented block copolymer of claim **1** wherein the block of the hydrophobic unit comprises between 1 and about 100 units.

6. The surface active segmented block copolymer of claim **1** wherein the block of the hydrophobic unit comprises between 1 and about 30 units.

7. The surface active segmented block copolymer of claim **1** wherein the hydrophilic block comprises between 1 and about 10,000 units.

8. The surface active segmented block copolymer of claim **1** wherein the hydrophilic block comprises between about 10 and about 1,000 units.

9. The surface active segmented block copolymer of claim **1** wherein the hydrophilic block comprises between about 20 and about 300 units.

10. A surface active segmented block copolymer having the following generic formula (I):

$$R1\text{-}[(A)m]p\text{-}[(B)n]q\text{-}X \quad (I)$$

wherein R1 is a reactive residue of a moiety capable of acting as an initiator for Atom Transfer Radical Polymerization, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and X is a halogen capping group of an initiator for Atom Transfer Radical Polymerization or a derivatized reaction product.

11. A surface active segmented block copolymers having the following generic formula (II):

$$R1\text{-}[(A)m]p\text{-}[(B)n]q\text{-}R2 \quad (II)$$

wherein R1 is a radical forming residue of a RAFT agent or free radical initiator, A is a hydrophobic unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and

q are natural numbers, and R2 is a thio carbonyl thio fragment of the chain transfer agent or a derivatized reaction product.

12. A surface active segmented block copolymers having the following generic formula (III):

$$R1\text{-}[(B)n]q\text{-}[(A)m]p\text{-}R2\text{-}[(A)m]p\text{-}[(B)n]q\text{-}R1 \quad (III)$$

wherein R1 is a radical forming residue of a RAFT agent or free radical initiator, A is a chemical binding unit block, B is a hydrophilic unit block, m is 1 to 10,000, n is 1 to 10,000, p and q are natural numbers, and R2 is a thio carbonyl thio group.

13. The surface active segmented block copolymer of claim **10** wherein one of the chemical binding unit block or the hydrophilic block is a statistical copolymerization or compositionally heterogeneous block.

14. The surface active segmented block copolymer of claim **11** wherein one of the chemical binding unit block or the hydrophilic block is a statistical copolymerization or compositionally heterogeneous block.

15. The surface active segmented block copolymer of claim **12** wherein one of the chemical binding unit block or the hydrophilic block is a statistical copolymerization or compositionally heterogeneous block.

16. The surface active segmented block copolymer of claim **10** wherein the hydrophobic unit block comprises vinylically unsaturated polymerizable monomers and the hydrophilic block comprises vinylically unsaturated polymerizable monomers.

17. The surface active segmented block copolymer of claim **11** wherein the hydrophobic unit block comprises vinylically unsaturated polymerizable monomers and the hydrophilic block comprises vinylically unsaturated polymerizable monomers.

18. The surface active segmented block copolymer of claim **12** wherein the hydrophobic unit block comprises vinylically unsaturated polymerizable monomers and the hydrophilic block comprises vinylically unsaturated polymerizable monomers.

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