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(71) Applicant *(for all designated States except US)*: **BAUSCH & LOMB INCORPORATED** [US/US]; One Bausch & Lomb Incorporated, Rochester, NY 14604-2701 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **SCHORZMAN, Derek** [US/US]; 5749 Goldfinch Ct., Ellicott City, MD 21043-6095 (US). **SALAMONE, Joseph, C.** [US/US]; 740 N.w. 6th Street, Boca Raton, FL 33486 (US).

(74) Agents: **THOMAS, John, E.** et al.; Bausch & Lomb Incorporated, One Bausch & Lomb Place, Rochester, NY 14604-2701 (US).

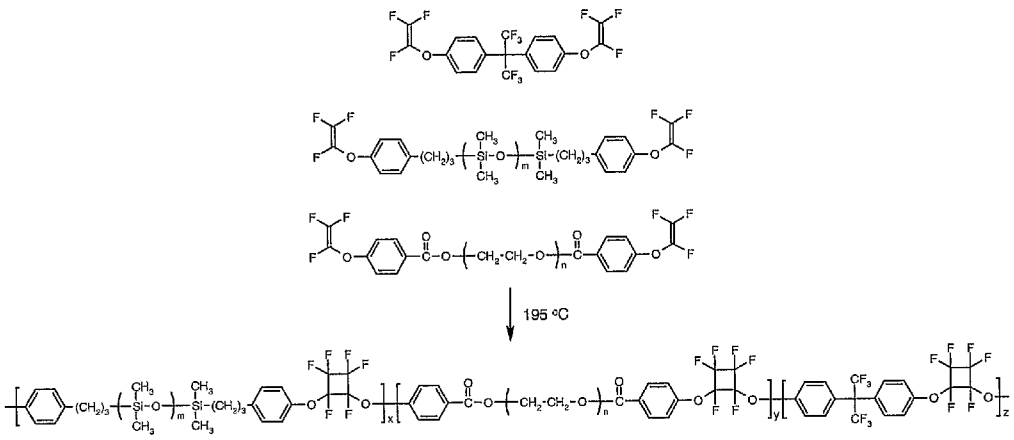
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(54) **Title:** POLYMERIZATION PRODUCTS AND BIOMEDICAL DEVICES CONTAINING SAME



(57) **Abstract:** Polymerization products formed from a monomeric mixture comprising (a) one or more first monomers of the general formula I: (I) wherein R^1 represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group; L is an optional linking group; A is CO_2Z, SO_2Z, PO_3Z, or OPO_3Z wherein Z is hydrogen or an alkali metal and n is an integer of 1 to about 1000; (b) one or more second crosslinking monomers comprising at least three trifluorovinyl groups and (c) one or more prepolymers comprising one or more trifluorovinyl groups are provided. Also provided are biomedical devices formed from such polymerization products.

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POLYMERIZATION PRODUCTS AND BIOMEDICAL DEVICES CONTAINING SAME

BACKGROUND OF THE INVENTION

Technical Field

The present invention generally relates to polymerization products useful as biomedical devices such as contact lenses or intraocular lenses.

Description of Related Art

In the field of biomedical devices such as contact lenses, various physical and chemical properties such as, for example, oxygen permeability, wettability, material strength and stability, must be carefully balanced in order to provide a useable contact lens. For example, since the cornea receives its oxygen supply exclusively from contact with the atmosphere, good oxygen permeability is a critical characteristic for any contact lens material. Wettability also is important in that, if the lens is not sufficiently wettable, it does not remain lubricated and therefore cannot be worn comfortably in the eye. Accordingly, the optimum contact lens would have at least both excellent oxygen permeability and excellent tear fluid wettability.

Contact lenses made from fluorinated materials have been investigated for a number of years. Such materials can generally be subdivided into two major classes, namely hydrogels and non-hydrogels. Hydrogels can absorb and retain water in an equilibrium state whereas non-hydrogels do not absorb appreciable amounts of water. Regardless of their water content, both hydrogel and non-hydrogel fluorinated contact lenses tend to have relatively hydrophobic, non-wettable surfaces.

By introducing fluorine-containing groups into contact lens polymers, the oxygen permeability can be significantly increased. For example, U.S. Patent No. 4,996,275 discloses using a mixture of comonomers including the fluorinated compound bis(1,1,1,3,3,3-hexafluoro-2-propyl)itaconate in combination with organosiloxane components. Fluorinating certain polysiloxane materials has been indicated to reduce the accumulation of deposits on contact lenses made from such materials. See, for example, U.S. Patent Nos. 4,440,918; 4,954,587; 4,990,582; 5,010,141 and 5,079,319. However, fluorinated polymers can suffer from one or more of the following drawbacks: difficult and/or expensive synthetic routes, poor processability, low refractive index,

poor wettability, poor optical clarity, poor miscibility with other monomers/reagents and toxicity.

The thermal polymerization products of trifluorovinyl-containing monomers, e.g., bis-trifluorovinyl monomers, to form perfluorocyclobutylene polymers are known. See, e.g., U.S. Patent Nos. 5,021,602; 5,023,380; 5,037,917; 5,037,918; 5,037,919; 5,066,746; 5,159,036; 5,159,037; 5,159,038, 5,162,468; 5,198,513; 5,210,265; 5,246,782; 5,364,547; 5,364,917 and 5,409,777. U.S. Patent Nos. 5,037,918; 5,066,746; 5,159,036; 5,159,037 and 5,246,782 further disclose the use of a "crosslinking initiating means" on perfluorocyclobutane polymers, subsequent to a completed step of polymerization, to obtain crosslinked polymers. U.S. Patent Publication No. 2002/0007083 discloses sulfonated perfluorovinyl functional monomers. However, there has been no recognition or appreciation that such materials can be employed in the manufacture of biomedical devices and particularly contact lens applications.

Accordingly, it would be desirable to provide improved biomedical devices formed from fluorinated polymerization products that exhibit suitable physical properties such as modulus and tear strength and chemical properties such as oxygen permeability and wettability for prolonged contact with the body while also being biocompatible.

SUMMARY OF THE INVENTION

In accordance with one embodiment of the present invention, a polymerization product is provided which comprises a monomeric mixture comprising one or more first monomers of the general formula I:

$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n \qquad (I);$$

wherein A, L, R^1, X and n are as defined herein, one or more second crosslinking monomers comprising at least three trifluorovinyl groups and one or more prepolymers having one or more trifluorovinyl groups.

In accordance with a second embodiment of the present invention, a biomedical device is provided comprising a polymerization product of a monomeric mixture comprising one or more monomers of the general formula I:

$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n \qquad (I)$$

wherein A, L, R^1, X and n are as defined herein.

In accordance with a third embodiment of the present invention, a contact lens is provided comprising a polymerization product of a monomeric mixture comprising one or more monomers of the of the general formula I:

$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n \qquad (I)$$

wherein A, L, R^1, X and n are as defined herein,.

BRIEF DESCRIPTION OF THE DRAWINGS

The figures set forth herein illustrate various embodiments of the present invention wherein:

Figure 1 is a poly(siloxane) containing star monomer which can be employed in the polymerization product of the present invention;

Figure 2 is a poly(siloxane) containing cyclic monomer which can be employed in the polymerization product of the present invention;

Figure 3 is a poly(siloxane) containing polycyclic monomer which can be employed in the polymerization product of the present invention.

Figure 4 illustrates a contact angle (θ) shown for the left side of the drop for measuring the Static Contact Angle (SCA) of Comparative Example A and Examples 2 and 3; and

Figure 5 illustrates the general reaction scheme of Example 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to polymerization products useful as biomedical devices intended for direct contact with body tissue or fluid. Representative examples of biomedical devices include, but are not limited to, artificial ureters, diaphragms, intrauterine devices, heart valves, catheters, denture liners, prosthetic devices, ophthalmic lens applications, where the lens is intended for direct placement in or on the eye, such as, for example, intraocular devices and contact lenses. A wide variety of types of contact lens materials can be produced herein ranging from hard, gas permeable lens materials; soft, hydrogel lens materials to soft, non-hydrogel lens materials. A particularly preferred contact lens is a rigid gas permeable lens.

The polymerization products of the present invention are advantageously formed from a monomeric mixture containing at least (a) one or more first monomers of the general formula I:

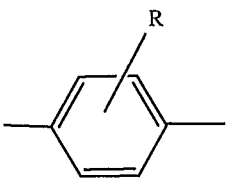
$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n \qquad (I)$$

wherein R^1 represents one or more inertly substituted groups; X is independently a group which links the R^1 group and the trifluorovinyl group; L is an optional linking group; n is from 1 to about 1000, preferably from 1 to about 100, more preferably from 1 to about 10 and most preferably from 1 to about 5 and A is CO_2Z, SO_2Z, PO_3Z, or OPO_3Z wherein Z is hydrogen or an alkali metal; (b) one or more second crosslinking monomers having at least three trifluorovinyl groups and (c) one or more prepolymers having one or more trifluorovinyl groups. As one skilled in the art would readily appreciate, the trifluorovinyl containing moiety can be present as one or more pendant groups in the monomer, e.g., in the case where R^1 is an alkylene group such as ethylene or in the case where R^1 is a polycyclic group, as well as an end group(s). By "inert" it is meant that the structures or substituents do not react undesirably with the perfluorovinyl groups or interfere undesirably with polymerization (e.g., perfluorocyclobutane formation) of the monomers.

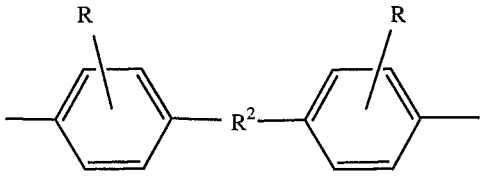
Representative R^1 groups include, by way of example, a substituted or unsubstituted C_1 to C_{30} hydrocarbyl group such as a substituted or unsubstituted C_1 to about C_{30} and preferably a substituted or unsubstituted C_1 to about C_{16} alkyl or an aromatic group optionally containing one or more heteroatoms; or a C_3 to about C_{25} cycloalkyl groups optionally containing one or more heteroatoms, substituted or unsubstituted siloxanyl group, or combinations thereof. In one embodiment, R^1 comprises one or more substituted or unsubstituted cyclic or polycyclic containing groups, e.g., one or more substituted or unsubstituted aromatic groups optionally containing one or more heteroatoms, and wherein the X group and the L or A group is bonded to the cyclic group in a position either ortho, meta, and/or para with respect to one another. Suitable aromatic group(s) can be of any molecular structure having aromatic character such as at least one six membered aromatic ring, optionally having any number of such six-membered rings fused together or connected by bonds or linking structures. For example, the aromatic groups can have from 1 to about 50 such substituted or unsubstituted aromatic rings, and preferably from 1 to about 10 substituted

or unsubstituted aromatic rings. If desired, when more than one cyclic containing group such as the aromatic groups are employed, the cyclic containing groups can be linked together with the same or different linking group, e.g., a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages.

Examples of aromatic groups for use herein include, but are not limited to, the following structures:

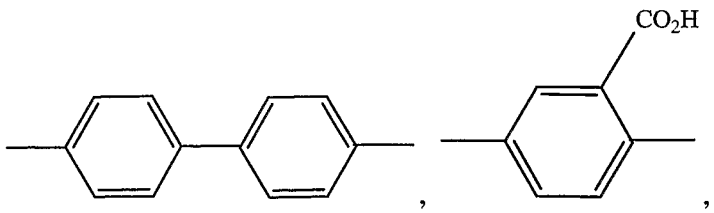


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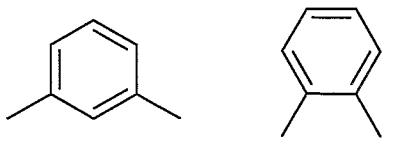
and the like

wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, or a C_1-C_{20} alkoxy group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups; R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages and wherein the X group and the L or A group may independently be bonded to the aromatic group either ortho, meta and/or para with respect one another. Representative examples of such aromatic groups include, but are not limited to,

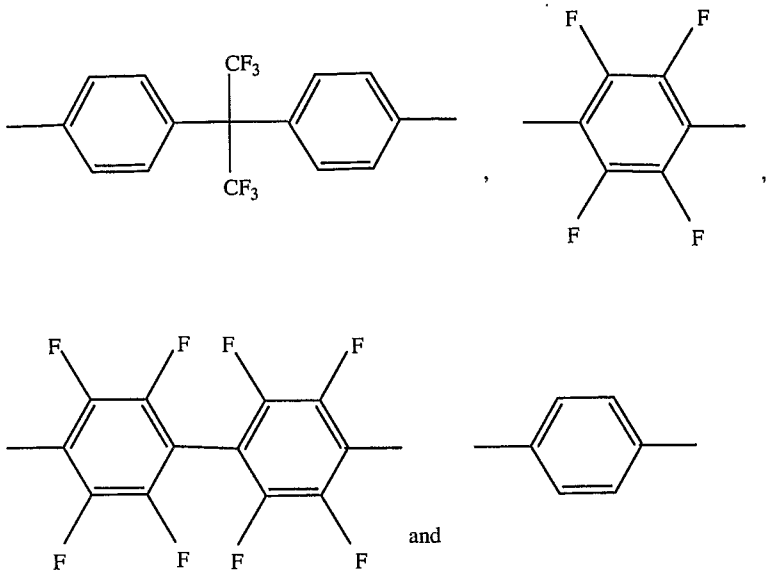


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,



and the like.

Although the aromatic groups of R^1 are shown as being bonded in the para position, all positions on the aromatic ring are contemplated herein, e.g., ortho, meta, para and combinations thereof. In another embodiment, R^1 comprises one or more substituted or unsubstituted cyclic or polycyclic siloxane containing groups.

The X groups can be the same or different and include, but are not limited to, a bond, an oxygen atom, a sulfur atom, a carboxylic or thiocarboxylic ester group, an amide group, a sulfone, a sulfoxide, a carbonate, a carbamate, a perfluoroalkylene, a perfluoroalkylene ether, an alkylene, an acetylene, a phosphine, a carbonyl or thio carbonyl group, seleno, telluro, nitrido, a silanediyl group, a trisilanediyl group, a tetrasilanetetrayl group, a siloxanediyl group, a disiloxanediyl group, a trisiloxyldiyl group, a trisilazanyl group, a silythio group, a boranediyl group; and the like and combinations thereof. Optional linking group L can be, by way of example, a straight or branched C_1-C_{30} alkyl group, a C_3-C_{30} cycloalkyl group, a C_5-C_{30} aryl group, an ether group, a C_1-C_{20} ester group, an amide group, a siloxanyl, an arylsiloxanyl or a fluorosiloxanyl

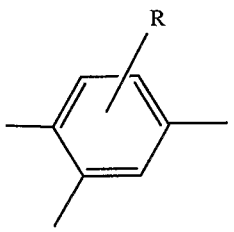
The foregoing monomers of formula I are either commercially available from such sources as, for example, Tetramer Technologies through Oakwood Products (West Columbia, SC), or can be prepared by methods known in the art and does not constitute a part of the present invention. See, e.g., Topping et al., *Polym. Prepr.*, 43(1), PP. 486-487 (2002)

In the practice of this invention, the polymers are crosslinked which involves chemical reactions that interconnect polymer molecules. As these reactions proceed, a polymer network is formed. Early in a crosslinking process, there are molecules having a wide variety of molecular weights such that the molecular weight increases with increasing extent of crosslinking.

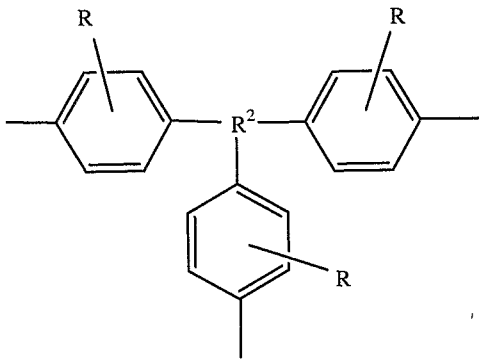
Suitable crosslinking monomers in forming the polymerization products herein include, but are not limited to, crosslinking monomers having three or more trifluorovinyl groups, crosslinking monomers having three or more trifluorovinyl ether groups, crosslinking monomers having three or more trifluorovinyl aromatic ether groups, and the like and mixtures thereof. In one embodiment, suitable crosslinking monomers are represented by the general formula II:

$$F_2C=CF\text{-}X\text{-}R^3\text{-}(X\text{-}CF=CF_2)_z \qquad (II)$$

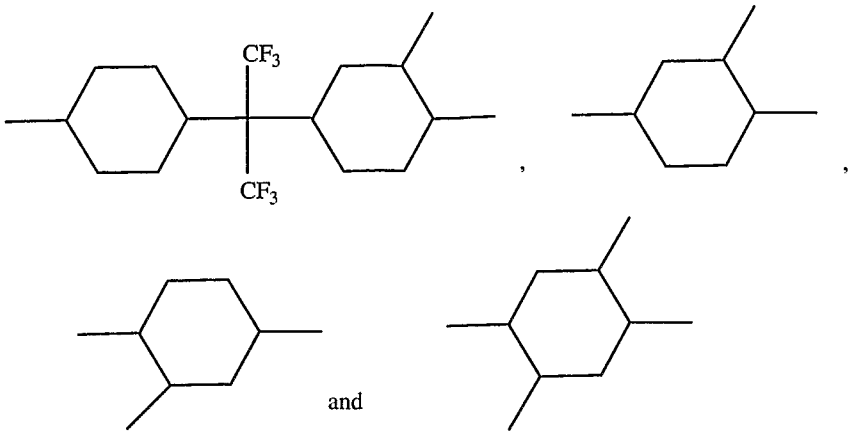
wherein R^3 represents one or more inertly substituted groups as defined above for R^1, X independently is a group which links the inertly substituted groups and the trifluorovinyl group and has the aforestated meanings and z is from 2 to about 1000, preferably from 2 to about 100, more preferably from 2 to about 10 and most preferably from 2 to about 5. Representative examples of R^3 include, but are not limited to, aromatic groups of the general formula



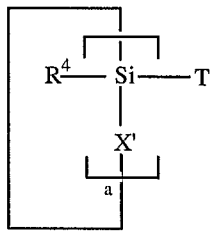
, and



wherein R and R^2 have the aforestated meanings and wherein each X group may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another. Alternatively, R^3 can be one or more substituted or unsubstituted C_3-C_{25} cycloalkyl groups optionally containing one or more heteroatoms. Representative examples of such cycloalkyl groups are of the formulae

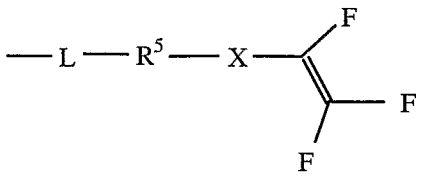


In an alternative embodiment, suitable crosslinking monomers are represented by the general formula III:



(II)

wherein R^4 is independently hydrogen, a substituted or unsubstituted C_1-C_{30} alkyl, a substituted or unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted a C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, or a substituted or unsubstituted C_6-C_{30} heteroarylalkyl; X' has the aforestated meanings for X and preferably is an oxygen atom; a is from 3 to about 100 and preferably from 3 to about 10; and T is the same or different and is of the general formula:



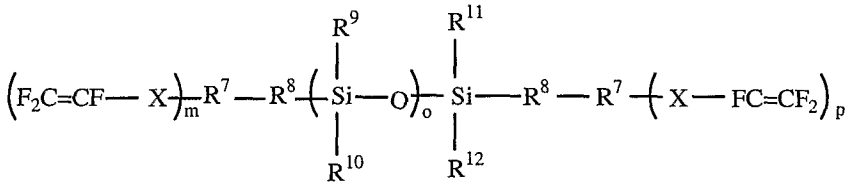
wherein R^5 independently represents one or more inertly substituted groups as defined above for R^1; and each X and L has the aforestated meanings. In the case where R^5 is a cyclic or polycyclic group, the X group and either the L group or Si atom may independently be bonded to the cyclic group in a position either ortho, meta and/or para

with respect to one another. Specific examples of the foregoing trifluorovinyl containing monomers of formula III are set forth in Figures 1-3.

In another embodiment, the crosslinked polymers can be obtained from at least a monomeric mixture containing at least one or more C_1-C_{20} tris(trifluorovinyloxyaryl)alkanes such as 1,1,1-tris(4'-[trifluorovinyloxy]phenyl)ethane.

The foregoing crosslinking monomers are either commercially available from such sources as, for example, Tetramer Technologies through Oakwood Products (West Columbia, SC), or can be prepared by any method known in the art which links molecular structures having perfluorovinyl groups to other molecular structures or which form perfluorovinyl groups and does not constitute a part of the present invention. See, e.g., U.S. Patent No. 5,023,380, the contents of which are incorporated by reference herein.

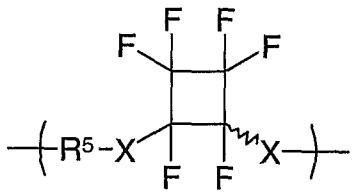
The monomeric mixtures can further include one or more prepolymers having one or more trifluorovinyl groups. Suitable prepolymers include, but are not limited to, poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and the like and mixtures thereof. For example, the poly(siloxane) prepolymers can be represented by the general formula



wherein m and p are independently integers from 1 to about 1000, preferably 1 to about 100, more preferably from 1 to about 10 and most preferably from 1 to about 5; o is an integer from 1 to about 1000; R^7 independently represents one or more inertly substituted groups as defined above for R^1; X is independently a group which links the inertly substituted groups and the trifluorovinyl group and has the aforestated meanings; R^8 is independently an amide group, a C_1-C_{20} ester group, an ether group, an ureido, a substituted or unsubstituted C_3-C_{30} cyclicalkyl, or a C_1-C_{30} alkylene or haloalkylene group optionally containing ether or ester linkages; and R^9, R^{10}, R^{11} and R^{12} are independently hydrogen, a straight or branched C_1-C_{30} alkyl group, a C_1-C_{30} fluoroalkyl group, one or more substituted or unsubstituted aromatic groups, a C_1-C_{20} ester group, an ether group, an ureido group, an amide group, an amine group, a substituted or

unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, a substituted or unsubstituted C_6-C_{30} heteroarylalkyl, fluorine, a vinyl group, a C_5-C_{30} fluoroaryl, or a hydroxyl group.

The foregoing monomeric mixtures can be polymerized by heating the monomeric mixture to a temperature and for a time sufficient to form crosslinked polymerization products having one or more perfluorocyclobutane groups in the backbone of the polymer. By heating the monomeric mixture, the dimerizable perfluorovinyl groups react with another such group to form one or more perfluorocyclobutane groups represented by the general formula:



Thus, the resulting polymerization products can have one or more perfluorocyclobutane groups, and includes oligomers which have from about 2 to about 100 repeating units. The molecular weight of the resulting polymerization products can vary widely, e.g., a number average molecular weight of at least about 100 and can range from about 100 to about 1,000,000. It is to be understood that depending on the molecular structure connecting the perfluorocyclobutane groups, the number of perfluorocyclobutane groups can vary from as few as one up to thousands. The process of forming polymers or oligomers herein is general and capable of forming biomedical devices having wide ranges of utility. The physical and chemical properties of the resulting products are highly dependent on the choice of the molecular structure between the perfluorocyclobutane groups as well as the number of perfluorocyclobutane groups. Whereas polyaddition of perfluorovinyl groups to form perfluoroaliphatic polymers (like poly(tetrafluoroethylene)), not generally having perfluorocyclobutane groups, takes place in the presence of free radicals or free radical generating catalysts, dimerization to form perfluorocyclobutane groups takes place thermally.

When a perfluorovinyl group is dimerizable, dimerization is preferably favored over other thermal reactions either kinetically or in equilibrium. As one skilled in the art would readily appreciate, the perfluorovinyl groups on a monomer can be separated by at least one atom or group of atoms which does not facilitate isomerization. The atom or group of atoms can include at least one aromatic group or can include an aliphatic or cycloalkyl group. However, aromatic groups are usually preferred due their ease of manufacturing monomers. Furthermore, when the perfluorovinyl groups are attached to aliphatic carbons or separated from aliphatic carbons by single atoms such as, for example, oxygen, the perfluorovinyl groups are preferably primary or secondary because tertiary perfluorovinyl groups are generally sterically hindered with respect to formation of perfluorocyclobutane rings, and more preferably the perfluorovinyl groups are primary because secondary perfluorovinyl groups tend to rearrange. Preferably, to avoid rearrangement and facilitate polymer formation the monomers have structures such that the resulting polymers have hydrocarbyl groups, e.g., one or more substituted or unsubstituted aromatic rings, perfluorocyclobutane rings and at least one non-carbon atom, e.g., oxygen, silicon, boron, phosphorus, nitrogen, selenium, tellurium and/or sulfur atom (each optionally substituted) in the backbones.

Suitable temperatures for forming one or more perfluorocyclobutane rings can differ according to the structure of the monomer(s). In general, temperatures can range from about 50°C to about 400°C and preferably from about 75°C to about 300°C for formation of perfluorocyclobutane rings. Temperatures above about 450°C are usually avoided because perfluorocyclobutane groups are generally thermally unstable above such temperatures. In another embodiment, a temperature of from about 100°C to about 230°C is generally most preferred for cyclization of perfluorovinyl aromatic or aliphatic ethers or sulfides, while a temperature of from about 50°C to 80°C is needed to form perfluorocyclobutane groups when the perfluorovinyl group is attached directly to an aromatic ring. A suitable time can vary according to the temperature used and the structure of the monomer. Generally, the time period for the polymerization can range from about 1 hour to about 100 hours and preferably from about 10 hours to about 40 hours.

Alternatively, in the case when the trifluorovinyl containing monomers are capable of radical initiated addition polymerization, conditions conducive to free radical

polymerization, e.g. presence of oxygen, ozone, peroxygen compounds and other free radical generating compounds, are avoided so that the trifluorovinyl groups will dimerize into perfluorocyclobutane groups rather than undergoing addition polymerization. Compounds known in the art for stabilization against free radical polymerization are alternatively used. Similarly, when the trifluorovinyl groups are capable of addition polymerization in the presence of anions or cations, compounds which supply such anions or cations are avoided. For example, fluoride ions (e.g. from carbonyl fluorides), chloride, hydroxide, phenoxide and the like are avoided. To avoid such compounds as carbonyl fluorides, oxidative conditions such as the presence of oxygen, hypochlorite, dichromate, permanganate and the like are avoided because the perfluorovinyl groups are known to oxidize to form carbonyl fluorides. Perfluorovinyl ethers, thioethers, sulfones, sulfoxides and the like are relatively stable with regard to addition polymerization and oxidation; and, therefore, such precautions are generally unnecessary when such perfluorovinyl compounds are used.

The monomeric mixtures are suitably neat or, optionally, in admixture with other materials such as in a solution, an emulsion, a dispersion or in any other form which can provide a polymerization product.

Suitable solvents are those which are inert to the conditions encountered in the polymerization reaction and include, but are not limited to, xylene, mesitylene and perfluorotetradecahydrophenanthrene. At atmospheric pressure, preferred solvents are those which attain temperatures of about 170°C to about 250°C such as, for example, dichlorobenzene, trichlorobenzene, diphenyl oxide and perfluorotetradecahydrophenanthrene. When a solvent is used, the concentration of monomers in solvent is advantageously from about 0.1 to about 99.9 weight percent and preferably from about 10 to about 90 weight percent by weight monomer.

Polymerization or dimerization suitably takes place at any pressure. Pressures are generally chosen such that the monomers and any solvents and/or dispersing media remain liquid at the temperatures used for polymerization. When the monomers or other materials evaporate at temperatures used, then it is generally preferable to maintain a pressure at least sufficient to maintain the materials liquid.

Alternatively, the foregoing monomeric mixtures may be polymerized by free radical polymerization by exposing the mixture to heat and/or radiation, e.g., ultraviolet

light (UV), visible light, or high energy radiation, to produce biomedical devices such as contact lenses according to conventional methods. A polymerization initiator may be included in the mixture to facilitate the polymerization step. Representative free radical thermal polymerization initiators are organic peroxides such as, for example, acetal peroxide, lauroyl peroxide, decanoyl peroxide, stearoyl peroxide, benzoyl peroxide, tertiarylbutyl peroxypivalate, peroxydicarbonate, and the like and mixtures thereof. Representative UV initiators are those known in the field such as, for example, benzoin methyl ether, benzoin ethyl ether, Darocure 1173, 1164, 2273, 1116, 2959, 3331 (EM Industries) and Igracure 651 and 184 (Ciba-Geigy), and the like and mixtures thereof. Generally, the initiator will be employed in the monomeric mixture at a concentration at about 0.1 to about 5 percent by weight of the total mixture.

The biomedical devices of the present invention, e.g., contact lenses or intraocular lenses, can be prepared by polymerizing the foregoing monomeric mixtures containing at least one or more of the monomers of formula I to form a product that can be subsequently formed into the appropriate shape by, for example, lathing, injection molding, compression molding, cutting and the like. Alternatively, the reaction mixture may be placed in a mold and subsequently cured into the appropriate product.

For example, in producing contact lenses, the initial monomeric mixture may be polymerized in tubes to provide rod-shaped articles, which are then cut into buttons. The buttons may then be lathed into contact lenses. Alternately, the contact lenses may be cast directly in molds from the monomeric mixtures, e.g., by spincasting and static casting methods. Spincasting methods are disclosed in U.S. Patent Nos. 3,408,429 and 3,660,545, and static casting methods are disclosed in U.S. Patent Nos. 4,113,224, 4,197,266, and 5,271,875. Spincasting methods involve charging the monomeric mixture to a mold, and spinning the mold in a controlled manner while exposing the monomer mixture to a radiation source such as UV light. Static casting methods involve charging the monomeric mixture between two mold sections, one mold section shaped to form the anterior lens surface and the other mold section shaped to form the posterior lens surface, and curing the monomeric mixture while retained in the mold assembly to form a lens, for example, by free radical polymerization of the monomeric mixture. Examples of free radical reaction techniques to cure the lens material include thermal radiation, infrared radiation, electron beam radiation, gamma radiation, ultraviolet (UV)

radiation, and the like; or combinations of such techniques may be used. U.S. Patent No. 5,271,875 describes a static cast molding method that permits molding of a finished lens in a mold cavity defined by a posterior mold and an anterior mold. As an additional method, U.S. Patent No. 4,555,732 discloses a process where an excess of a monomeric mixture is cured by spincasting in a mold to form a shaped article having an anterior lens surface and a relatively large thickness, and the posterior surface of the cured spincast article is subsequently lathed to provide a contact lens having the desired thickness and posterior lens surface.

When polymerizing the monomeric mixture by the thermal technique discussed above, a resin or metal material that is capable of withstanding high temperatures, i.e., thermally stable, should be employed as a contact lens mold. For example, in injection molding, the resin should have a heat deflection temperature of at least 350°C and a hardness of at least 100 on the Rockwell Hardness Scale (M scale). Suitable resins include, but are not limited to, engineering plastics based on polyetherimide resins (e.g., ULTEM™ available from General Electric Co., Polymers Product Dept.); polyamide-imide plastics (e.g., TORLON available from Amoco Performance Products); polyphenylene sulfide plastics (e.g., RYTON™ available from Phillips Petroleum Co.); polysulfone and polyarylsulfone plastics (e.g., UDEL™ and RADEL™ available from Amoco Performance Products); polythalamide plastics (e.g., AMODEL available from Amoco Performance Products); polyketone plastics (e.g., KADEL™ available from Amoco Performance Products); various liquid crystal polymer resins (e.g., XYDAR™ available from Amoco Performance Products) and the like.

Optionally, the monomeric mixtures herein may include additional components according to the specific type of lens being produced. For example, when producing rigid gas-permeable (RGP) materials, the monomeric mixture may include in addition to the foregoing trifluorvinyl containing monomers, one or more agents such as strengthening agents or UV absorbing or dye monomers.

When producing a hydrogel lens, the monomeric mixture may also include at least a diluent that is ultimately replaced with water when the polymerization product is hydrated to form a hydrogel. Generally, the water content of the hydrogel is greater than about 5 wt. % and more commonly between about 10 to about 80 wt. %. The amount of diluent used should be less than about 50 wt. % and in most cases, the diluent content

will be less than about 30 wt. %. However, in a particular polymer system, the actual limit will be dictated by the solubility of the various monomers in the diluent. In order to produce an optically clear copolymer, it is important that a phase separation does not occur between the comonomers and the diluent, or the diluent and the final copolymer.

Furthermore, the maximum amount of diluent which may be used will depend on the amount of swelling the diluent causes the final polymers. Excessive swelling will or may cause the copolymer to collapse when the diluent is replaced with water upon hydration. Suitable diluents include, but are not limited to, ethylene glycol; glycerine; liquid poly(ethylene glycol); alcohols; alcohol/water mixtures; ethylene oxide/propylene oxide block copolymers; low molecular weight linear poly(2-hydroxyethy lmethacrylate)s; glycol esters of lactic acid; formamides; ketones; dialkylsulfoxides; butyl carbitol; and the like and mixtures thereof. If necessary, it may be desirable to remove residual diluent from the lens before edge-finishing operations which can be accomplished by evaporation at or near ambient pressure or under vacuum. An elevated temperature can be employed to shorten the time necessary to evaporate the diluent. The time, temperature and pressure conditions for the solvent removal step will vary depending on such factors as the volatility of the diluent and the specific monomeric components, as can be readily determined by one skilled in the art. If desired the monomeric mixture used to produce the hydrogel lens may further include additional crosslinking agents as well as wetting agents known in the prior art for making hydrogel materials.

The contact lenses obtained herein may be subjected to optional machining operations. For example, the optional machining steps may include buffing or polishing a lens edge and/or surface. Generally, such machining processes may be performed before or after the product is released from a mold part, e.g., the lens is dry released from the mold by employing vacuum tweezers to lift the lens from the mold, after which the lens is transferred by means of mechanical tweezers to a second set of vacuum tweezers and placed against a rotating surface to smooth the surface or edges. The lens may then be turned over in order to machine the other side of the lens.

The lens may then be transferred to individual lens packages containing a buffered saline solution. The saline solution may be added to the package either before or after transfer of the lens. Appropriate packaging designs and materials are known in

the art. A plastic package is releasably sealed with a film. Suitable sealing films are known in the art and include foils, polymer films and mixtures thereof. The sealed packages containing the lenses are then sterilized to ensure a sterile product. Suitable sterilization means and conditions are known in the art and include, for example, autoclaving.

As one skilled in the art will readily appreciate other steps may be included in the molding and packaging process described above. Such other steps can include, for example, coating the formed lens, surface treating the lens during formation (e.g., via mold transfer), inspecting the lens, discarding defective lenses, cleaning the mold halves, reusing the mold halves, and the like and combinations thereof.

The following examples are provided to enable one skilled in the art to practice the invention and are merely illustrative of the invention. The examples should not be read as limiting the scope of the invention as defined in the claims. Various homopolymer and copolymer films were formed and characterized by standard testing procedures such as:

1. Modulus (g/mm^2) and elongation were measured per ASTM 1708 employing an Instron (Model 4502) instrument where the film sample was immersed in borate buffered saline; an appropriate size of the film sample was gauge length 22 mm and width 4.75 mm, where the sample further has ends forming a dogbone shape to accommodate gripping of the sample with clamps of the Instron instrument, and a thickness of 200 ± 50 microns.

2. Tensile strength (g/mm^2) was measured per ASTM test method D1708a.

3. Oxygen permeabilities (also referred to as Dk) were determined by the following procedure. Other methods and/or instruments may be used as long as the oxygen permeability values obtained therefrom are equivalent to the described method. The oxygen permeability of the films were measured by the polarographic method (ANSI Z80.20-1998) using an O2 Permeometer Model 201T instrument (Createch, Albany, California USA) having a probe containing a central, circular gold cathode at its end and a silver anode insulated from the cathode. Measurements are taken only on pre-inspected

pinhole-free, flat film samples of three different center thicknesses ranging from 150 to 600 microns. Center thickness measurements of the film samples may be measured using a Rehder ET-1 electronic thickness gauge. Generally, the film samples have the shape of a circular disk. Measurements are taken with the film sample and probe immersed in a bath containing circulating phosphate buffered saline (PBS) equilibrated at 35°C+/- 0.2°. Prior to immersing the probe and film sample in the PBS bath, the film sample is placed and centered on the cathode premoistened with the equilibrated PBS, ensuring no air bubbles or excess PBS exists between the cathode and the film sample, and the film sample is then secured to the probe with a mounting cap, with the cathode portion of the probe contacting only the film sample. For silicone films, it is frequently useful to employ a Teflon polymer membrane, e.g., having a circular disk shape, between the probe cathode and the film sample. In such cases, the Teflon membrane is first placed on the pre-moistened cathode, and then the film sample is placed on the Teflon membrane, ensuring no air bubbles or excess PBS exists beneath the Teflon membrane or film sample. Once measurements are collected, only data with correlation coefficient value (R^2) of 0.97 or higher should be entered into the calculation of Dk value. At least two Dk measurements per thickness, and meeting R^2 value, are obtained. Using known regression analyses, oxygen permeability (Dk) is calculated from the film samples having at least three different thicknesses. Any film samples hydrated with solutions other than PBS are first soaked in purified water and allowed to equilibrate for at least 24 hours, and then soaked in PHB and allowed to equilibrate for at least 12 hours. The instruments are regularly cleaned and regularly calibrated using RGP standards. Upper and lower limits are established by calculating a +/- 8.8% of the Repository values established by William J. Benjamin, et al., *The Oxygen Permeability of Reference Materials*, Optom Vis Sci 7 (12s): 95 (1997), the disclosure of which is incorporated herein in its entirety:

MATERIAL NAME	Repository Values	Lower Limit	Upper Limit
Fluoroperm 30	26.2	24	29
Menicon EX	62.4	56	66
Quantum II	92.9	85	101

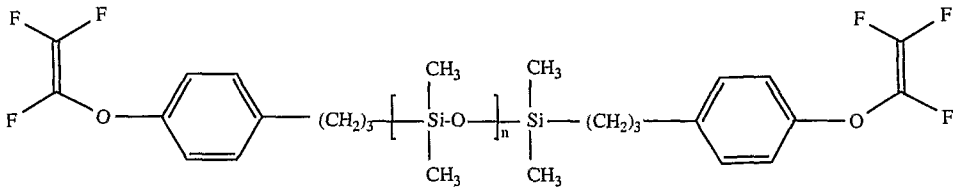
4. Refractive index was measured per typical methods on hydrated samples using a refractometer.

5. Static Contact Angle (SCA) - The instrument used for this measurement was an AST Products Video Contact Angle System (VCA) 2500XE. This instrument utilizes a low-power microscope that produces a sharply defined image of the water drop, which is captured immediately on the computer screen. Surface Tension of the water used for analysis was periodically measured by the dynamic contact angle method and averaged 73 dynes/cm. The water was 80µl drawn into the VCA system microsyringe, and 0.6µl drops were dispensed from the syringe onto the sample. The contact angle is calculated by placing five markers along the circumference of the drop as shown below. The software generated a curve representing the circumference of the drop and calculated the contact angle of the drop with respect to the surface on both sides of the drop. The contact angle (θ) is shown for the left side of the drop as shown in Figure 4. All films were received in water, and soaked in HPLC water for 15 minutes prior to analysis. Sections of the films were placed onto a clean glass slide and allowed to dry overnight in a nitrogen dry box. Five drops of water were used to measure the contact angle of each sample.

In the following examples, the properties of such films derived from polymerization products are described.

EXAMPLE 1

This example illustrates the preparation of a 3-(4-[trifluorovinyloxy]phenyl)propyl terminated poly(dimethylsiloxane) having a number average molecular weight (M_n) of 1128, a weight average molecular weight of 1523 and a polydispersity (PD) of 1.35 (as determined using SEC and by comparison to standards of known molecular weight) and of the formula



wherein n is an average of 8.

To a solution of hydride terminated poly(dimethylsiloxane) obtained from Aldrich Chemical Co. (Milwaukee, WI) (average M_n 580 g/mol, 3.47 g) and 4-(trifluorovinyloxy)allylbenzene (3.87 g, 17.9 mmol) prepared from 1-bromo-4-(trifluorovinyloxy)benzene obtained from Oakwood Products, Inc. (West Columbia, SC) using procedures set forth in the literature (e.g., *Polymer Preprints*, 39(1), p. 530 (1998)) in tetrahydrofuran/1,4-dioxane (2:1 v/v, 36 mL) was added 10% solution of platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylenes (0.01 mL) and the solution was heated 15 hours at 60°C. The solvents were removed from the cooled solution at reduced pressure and the crude product was purified via column chromatography (0-50% dichloromethane/pentane, silica gel, 5 x 5 cm) to provide a product as a colorless oil (3.95 g, 66%): ^{1}H NMR ($CDCl^3$, 400 MHz) δ 7.15 (d, J = 8 Hz, 4 H), 7.00 (d, J = 8 Hz, 4 H), 2.60 (t, J = 8 Hz, 4 H), 1.66-1.60 (m, 4 H), 0.57 (t, J = 8 Hz, 4 H), 0.07 (s, approximately 63 H).

COMPARATIVE EXAMPLE A AND EXAMPLES 2 AND 3

Poly(perfluorocyclobutane) with 4-(trifluorovinyloxy)benzoic acid as wetting agent

Various proportions of 4-(trifluorovinyloxy)benzoic acid (TA) obtained from Oakwood Products, Inc., 3-(4-[trifluorovinyloxy]phenyl)propyl terminated poly(dimethylsiloxane) (T_2D_8) of Example 1 and 1,1,1-(4-[trifluorovinyloxy]phenyl)ethane (T_3) obtained from Oakwood Products, Inc. (West Columbia, SC) were dissolved with stirring and gentle heat. The weight ratio of T_2D_8 to

T_3 was held constant at 50:50 for all samples and the amount of TA was varied. The warm solution was clamped between silanized glass plates using Teflon tape spacer and heated under a nitrogen atmosphere at approximately 195°C for 20 hours. The cooled, transparent, tack-free films were removed from the glass plates and further analyzed. Equilibrium water uptake was measured by measuring mass increase of film after soaking in deionized water (DI) up to 67 hour. Multiple static contact angle (SCA) measurements were conducted and reported. These results are set forth below in Table 1.

TABLE 1

Wetting properties of T_2D_8/T_3 films with TA wetting agent

Comp. Ex./Ex.	A	2	3
TA (w/w %)	0	3.4	8.7
SCA (°)	104(1)	91(2)	95(2)
Water (w/w %)	0.0	1.8	2.2

Number in parenthesis represents standard deviation for last digit

The observed decrease in contact angle and increase in water content indicates increased surface wettability/hydrophilicity.

EXAMPLE 4

Copolymerization of T end-capped poly(alkyl ether), poly(siloxane), and poly(PFCB) prepolymers.

A monomeric mixture was prepared by dissolving 0.42 g of 4-(trifluorovinyloxy)benzoate terminated poly(ethylene glycol) (1) having a M_n of 1006, a weight average molecular weight (M_w) of 1234 and a PD of 1.23, 3-(4-[trifluorovinyloxy]phenyl)propyl terminated poly(dimethylsiloxane) (2) of Example 1, and 0.43 g (1.11 mmol) of 2,2-bis(4-[trifluorovinyloxy]phenyl)-1,1,1,3,3,3-hexafluoropropane (3), with stirring and gentle heating. The warm solution (insoluble at ambient temperature) was clamped between silanized glass plates with a Teflon tape spacer and heated at 195°C for 40 hours under nitrogen purge to afford a viscous, transparent oil (1.28 g, 100%); SEC (THF, PS standards). The reaction scheme of this example is generally set forth in Figure 5 wherein m and n and x, y, and z are such that the copolymer has a M_n=3641, M_w=14664, and PD=4.03. The weight average molecular

weight (M_w) was measured at various points during curing. These results are set forth below in Table 2.

TABLE 2

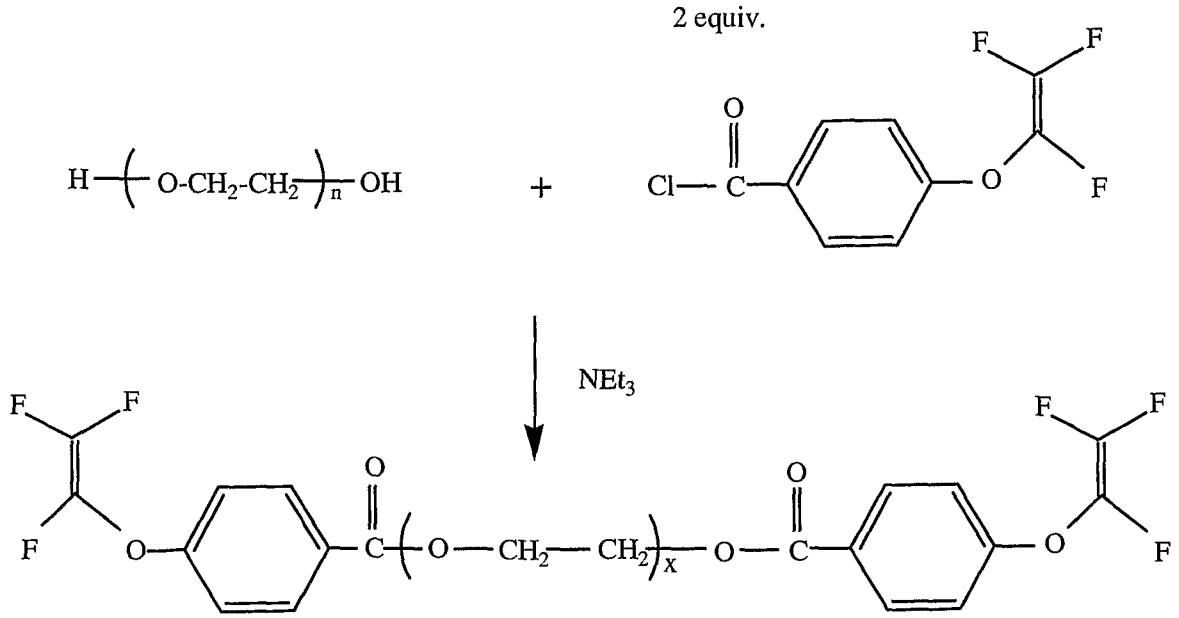
Cure time (h)	Weight average molecular weight (g/mol)			
	1	2	3	
	Copolymer			
0	1234	2054	N/A	N/A
20	4993	8478	4133	6836
40	7668	15914	7498	14664

EXAMPLE 5

Synthesis of end-capped poly(ethylene oxide) prepolymer (prepolymer 1)

A solution of 4-(trifluorovinyloxy)benzoyl chloride (1.85 g, 7.8 mmol) prepared from 1-bromo-4-(trifluorovinyloxy)benzene obtained from Oakwood Products, Inc. (West Columbia, SC) using procedures set forth in the literature (e.g., *Polymer Preprints*, 43(1), p. 487 (2002)) in tetrahydrofuran (5 mL) was treated with a solution of poly(ethylene oxide) having a M_n of 300 (0.78 g, 2.6 mmol) and triethylamine (1.21 mL, 8.7 mmol) in tetrahydrofuran (5 mL) dropwise under inert atmosphere. After 15 hours at ambient temperature, the reaction mixture was diluted in dichloromethane (30 mL), washed with $NaHCO_3$(aq) (0.25 M, 1x25 mL), dried over Na_2SO_4, filtered, and solvents were removed under reduced pressure. The crude oil was purified by column chromatography (3x3 cm, silica gel, 0-50% dichloromethane/pentane) and solvents removed under reduced pressure to afford the product as a viscous oil (0.42 g, 23%): ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, 4 H, J=8 Hz), 7.11 (d, 4 H, J=8 Hz), 4.48 (br, 4 H), 3.79 (br, 4 H), 3.61 (br, 22.3 H); SEC (THF, PS standards): M_n=1006 g/mol, M_w=1234 g/mol, and a PD 1.23. This reaction is generally shown below in Scheme 1.

SCHEME 1

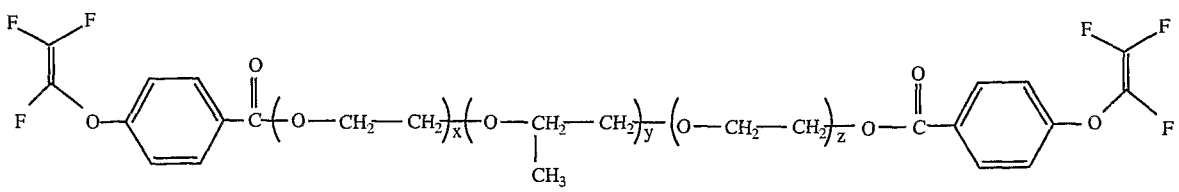


wherein x is approximately 7.

EXAMPLE 6

Synthesis of end-capped poly(ethylene oxide-*block*-propylene oxide-*block*-ethylene oxide) prepolymer (prepolymer 2)

Polyoxamer 108 supplied as Pluronic F38 (4700 g/mol, 3.45 g), obtained from BASF Co. (Florham Park, NJ) was reacted using substantially the same procedure described in Example 5 to afford the product as a solid (2.01 g, 54%): GPC (THF, PS standards): M_n = 9637 g/mol, M_w = 8761 g/mol, PD = 1.10; ^{1}H NMR ($CDCl_3$, 400 MHz); δ 8.08 (d, J=8Hz, 4H), 7.13 (d, J=8 Hz, 4H), 4.54 (t, J=5 Hz, 4H), 3.82-3.37 (m, 530 H), 1.15-1.11 (m, 60 H). The final product is represented by the following formula:

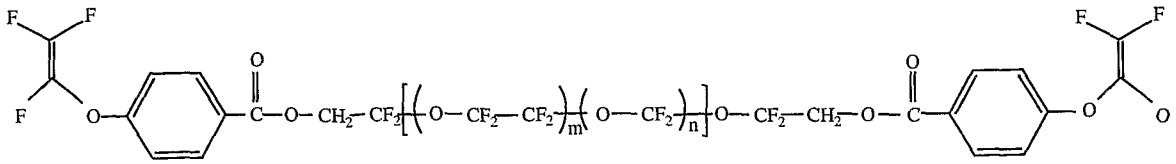


wherein x is y and z are such that the product has a M_n = 9637 g/mol, M_w = 8761 g/mol, and PD=1.1.

EXAMPLE 7

Synthesis of end-capped poly(perfluoroalkyl ether) prepolymer (prepolymer 3)

Fomblin Z DOL 2000 (a hydroxy terminated poly(perfluoroethylene containing glycol)) (2000 g/mol) obtained from Solvay Solexis (Thorofare, NJ) was reacted using substantially the same procedure described in Example 5 except using dichloromethane instead of tetrahydrofuran as solvent to afford the product as a viscous oil (0.58 g, 17%): GPC (THF, PS standards): M_n = 1604 g/mol, M_w = 1656 g/mol, PD = 1.05 g/mol; ^{1}H NMR ($CDCl_3$, 400 MHz); δ 8.08 (d, J=8 Hz, 4 H), 7.15 (d, J=8Hz, 4H), 4.67 (m, 4.70-4.64, 4H). The final product is represented by the following formula:



EXAMPLE 8

Samples of the materials from Examples 5-7 were clamped between silanized glass plates with Teflon spacers and heated under nitrogen atmosphere at 195°C for various times. In each case the isolated products were oils of varied viscosities. The linear polymers were dissolved in tetrahydrofuran (5 mg/mL) and analyzed via GPC (relative to PS standards) to demonstrate increase in molecular weight as a function of thermal cure time. The molecular weight analysis of the polymerized products are set forth below in Table 3.

TABLE 3

Molecular Weight Analysis of Thermal Trifluorovinylarylether end-capped Poly(alkyl ether) Polymerization at 195°C as Determined by SEC

Cure time (h)	Prepolymer 1		Prepolymer 2		Prepolymer 3	
	M_n (g/mol)	PD	M_n (g/mol)	PD	M_n (g/mol)	PD
0	1006	1.23	9637	1.10	1604	1.05
20	2123	2.35	13205	1.43	2815	1.45
40	2945	2.60	19529	1.82	4707	1.71

EXAMPLE 9

Synthesis of 2,4,6,8,10-pentamethyl-2,4,6,8,10-penta(3-[4-trifluorovinyloxyphenyl]propyl)cyclopentasiloxane (cyclo-$(TD)_5$)

A solution of 2,4,6,8,10-pentamethylcyclopentasiloxane (0.34 g, 1.13 mmol) and 4-(trifluorovinyloxy)allylbenzene (1.83 g, 8.55 mmol) in 2:1 tetrahydrofuran/1,4-dioxane (17 mL) was treated with 10% platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylenes (0.09 mL) and heated at 60°C for 15 hours. The cooled solution was concentrated under reduced pressure and purified via column chromatography (0-50% ethyl ether/pentane, silica gel, 3 x 10 cm) to afford the product as a viscous oil (57 mg, 4%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (br, 2 H), 6.99 (br, 2 H), 2.55 (br, 2 H), 1.59 (br, 2 H), 0.5 (br, 2 H), 0.02 (br, 3H). The final product is shown in Figure 2.

EXAMPLE 10

Homopolymerization of cyclo-$(TD)_5$

The product prepared in Example 9 was clamped between two silanized glass plates with Teflon tape spacer and heated at 195°C under a nitrogen purge for 20 hours to result in a transparent, insoluble, tack-free film: DSC, T_g 94°C.

EXAMPLE 11

Crosslinking of 3-(4-trifluorovinyloxyphenyl)propyl terminated poly(dimethylsiloxane) (T_2D_8) using cyclo-$(TD)_5$.

The product of Example 9 (25 parts) and 3-(4-[trifluorovinyloxy]phenyl)propyl terminated poly(dimethylsiloxane) of Example 1 (75 parts) were dissolved with gentle heat and agitation and polymerized as in Example 10 to result in a transparent, insoluble, tack-free film: DSC, no transitions observed –100 to 300°C.

EXAMPLE 12

Thermal cast molding of poly(perfluorocyclobutane) films

The monomeric mixture of Example 2 is melted with gentle heating and clamped between glass plates with Teflon® tape spacers of varied thicknesses. The assemblies can be sealed in a heating oven with a constant N_2 purge and heated for 20 hours at 195°C. The cooled films can then be removed from the plates and believed to yield a transparent, colorless, glassy film. The films can be further cut into wafers for oxygen permeability and refractive index determination:

EXAMPLE 13

Thermal cast molding of poly(perfluorocyclobutane) button

The monomeric mixture of Example 2 is added to a flat-bottomed, 15 mm diameter glass test tube. The vessel can be sealed in a heating oven with a constant N_2 purge and heated for 68 hours at 155°C. The cooled vessel is removed from the oven and test tube and believed to yield a transparent, colorless, glassy button for lathing into a Rigid, Gas-Permeable (RGP) contact lens.

EXAMPLE 14

Thermal cast molding of poly(perfluorocyclobutane) films

The monomeric mixture of Example 3 is melted with gentle heating and clamped between glass plates with Teflon® tape spacers of varied thicknesses. The assemblies can be sealed in a heating oven with a constant N_2 purge and heated for 20 hours at 195°C. The cooled films can then be removed from the plates and believed to yield a transparent, colorless, glassy film. The films can be further cut into wafers for oxygen permeability and refractive index determination.

EXAMPLE 15

Thermal cast molding of poly(perfluorocyclobutane) button

The monomeric mixture of Example 3 is added to a flat-bottomed, 15 mm diameter glass test tube. The vessel is sealed in a heating oven with a constant N_2 purge and heated for 68 hours at 155°C. The cooled vessel is removed from the oven and test tube and believed to yield a transparent, colorless, glassy button for lathing into a Rigid, Gas-Permeable (RGP) contact lens.

It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore the above description should not be construed as limiting, but merely as exemplifications of preferred embodiments. For example, the functions described above and implemented as the best mode for operating the present invention are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this invention. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the features and advantages appended hereto.

WHAT IS CLAIMED IS:

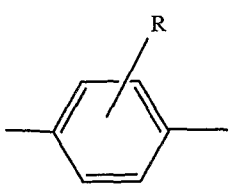
1. A polymerization product of a monomeric mixture comprising (a) one or more first monomers of the general formula:

$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n$$

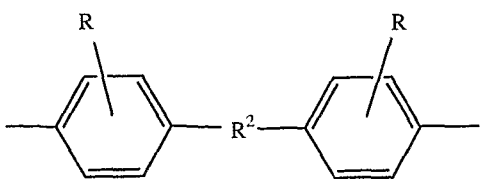
wherein R^1 represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group; L is an optional linking group and is independently a straight or branched C_1-C_{30} alkyl group, a C_3-to C_{30} cycloalkyl group, a C_5-C_{30} aryl group, an ether group, a C_1-C_{20} ester group, an amide group , a siloxanyl, an arylsiloxanyl or a fluorosiloxanyl; A is CO_2Z, SO_2Z, PO_3Z, or OPO_3Z wherein Z is hydrogen or an alkali metal and n is an integer of 1 to about 1000; (b) one or more second crosslinking monomers comprising at least three trifluorovinyl groups and (c) one or more prepolymers comprising one or more trifluorovinyl groups.

2. The polymerization product of Claim 1, wherein in the first monomer R^1 comprises a substituted or unsubstituted cyclic or polycyclic containing group optionally containing one or more heteroatoms or a substituted or unsubstituted cyclic or polycyclic siloxane containing group; X is independently a bond, an oxygen atom, a sulfur atom, a carboxylic or thiocarboxylic ester group, an amide group, a sulfone, a sulfoxide, a carbonate, a carbamate, a perfluoroalkylene, a perfluoroalkylene ether, an alkylene, an acetylene, a phosphine, a carbonyl or thio carbonyl group; seleno; telluro; nitrido; a silanediyl group, a trisilanediyl group, a tetrasilanetetrayl group, a siloxanediyl group, a disiloxanediyl group, a trisiloxyldiyl group, a trisilazanyl group, a silythio group, or a boranediyl group and n is from 1 to about 10.

3. The polymerization product of Claim 1, wherein in the first monomer X is O; R^1 is an aromatic group selected from the group consisting of



, and



wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-,

OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, or a C_1-C_{20} alkoxy group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and n is from 1 to about 10 and wherein the X group and either the L or A group may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

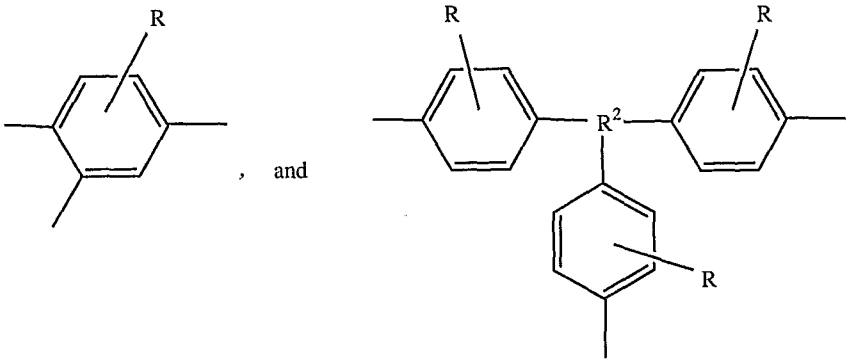
4. The polymerization product of Claim 1, wherein the second crosslinking monomer comprises one or more monomers of the general formula

$$F_2C=CF\text{-}X\text{-}R^3\text{-}(X\text{-}CF=CF_2)_z$$

wherein R^3 represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group and m is an integer of 2 to about 1000.

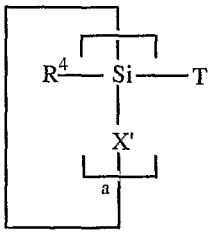
5. The polymerization product of Claim 4, wherein R^3 comprises a substituted or unsubstituted cyclic or polycyclic containing group optionally containing one or more heteroatoms or a substituted or unsubstituted, cyclic or polycyclic siloxane containing group; X is independently a bond, an oxygen atom, a sulfur atom, a carboxylic or thiocarboxylic ester group, an amide group, a sulfone, a sulfoxide, a carbonate, a carbamate, a perfluoroalkylene, a perfluoroalkylene ether, an alkylene, an acetylene, a phosphine, a carbonyl or thio carbonyl group; seleno; telluro; nitrido; a silanediyl group, a trisilanediyl group, a tetrasilanetetrayl group, a siloxanediyl group, a disiloxanediyl group, a trisiloxyldiyl group, a trisilazanyl group, a silythio group, or a boranediyl group and z is from 1 to about 10.

6. The polymerization product of Claim 4, wherein each X is O; R^3 is an aromatic group selected from the group consisting of



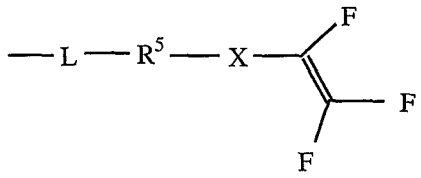
wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, $NR^{13}{}_2$ or $N\,R^{13}{}_3^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, or a C_1-C_{20} alkoxy group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and wherein each X group may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another and z is from 1 to about 10.

7. The polymerization product of Claim 1, wherein the second crosslinking monomer is of the general formula:



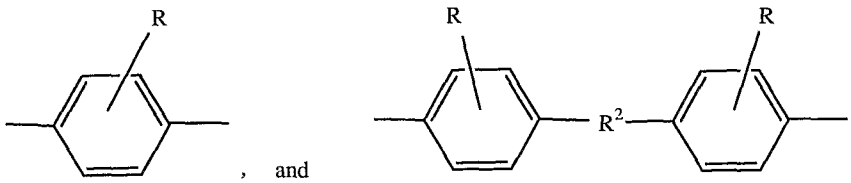
wherein R^4 is independently hydrogen, a substituted or unsubstituted C_1-C_{30} alkyl, a substituted or unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted a C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, or a substituted or unsubstituted C_6-C_{30}

heteroarylalkyl; X' is an oxygen atom; a is from 3 to about 100; and T is independently of the general formula:



wherein R^5 is independently one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group and L is an optional linking group and is independently a straight or branched C_1-C_{30} alkyl group, a C_3-to C_{30} cycloalkyl group, a C_5-C_{30} aryl group, an ether group, a C_1-C_{20} ester group, an amide group, a siloxanyl, an arylsiloxanyl or a fluorosiloxanyl.

8. The polymerization product of Claim 7, wherein R^4 is a substituted or unsubstituted C_1-C_{30} alkyl; X is O and R^5 is an aromatic group selected from the group consisting of

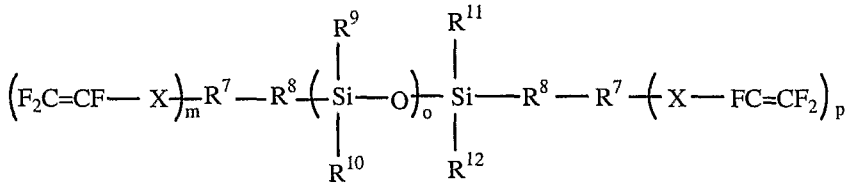


wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2 SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $N\,R^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, or a C_1-C_{20} alkoxy group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages and wherein the X group and either the L group or Si atom may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

9. The polymerization product of Claim 1, wherein one or more prepolymers are selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether)

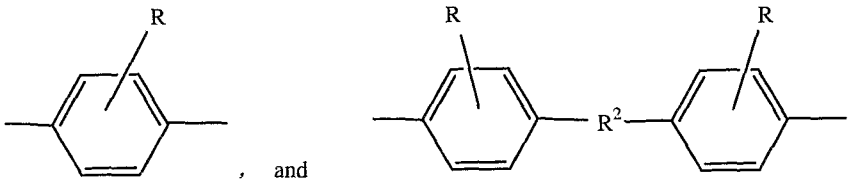
prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

10. The polymerization product of Claim 1, wherein the prepolymer is one or more poly(siloxane) prepolymers of the general formula:



wherein m, o and p are independently integers from 1 to about 1000; R^7 independently represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group; R^8 is independently an amide group, a C_1-C_{20} ester group, an ether group, an ureido, a substituted or unsubstituted C_3-C_{30} cyclicalkyl, or a C_1-C_{30} alkylene or haloalkylene group optionally containing ether or ester linkages; and R^9, R^{10}, R^{11} and R^{12} are independently hydrogen, a straight or branched C_1-C_{30} alkyl group, a C_1-C_{30} fluoroalkyl group, one or more substituted or unsubstituted aromatic groups, a C_1-C_{20} ester group, an ether group, an ureido group, an amide group, an amine group, a substituted or unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, a substituted or unsubstituted C_6-C_{30} heteroarylalkyl, fluorine, a vinyl group, a C_5-C_{30} fluoroaryl, or a hydroxyl group.

11. The polymerization product of Claim 10, wherein each X is O; each R^7 is independently an aromatic group selected from the group consisting of



wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-,

OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, or a C_1-C_{20} alkoxy group,, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and wherein the X and R^8 groups may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another and n and p is from 1 to about 10.

12. The polymerization product of Claim 1, wherein in the first monomer X is O, R^1 comprises a cyclic or polycyclic group optionally containing one or more heteroatoms and A is CO_2Z; the second crosslinking monomer comprises at least three trifluorovinyl aromatic ether groups and the one or more prepolymers are selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

13. The polymerization product of Claim 1, wherein in the first monomer X is O, R^1 comprises a cyclic or polycyclic group optionally containing one or more heteroatoms and A is SO_2Z; the second crosslinking monomer comprises at least three trifluorovinyl aromatic ether groups and one or more prepolymers are selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

14. The polymerization product of Claim 1, which is a thermal polymerization product.

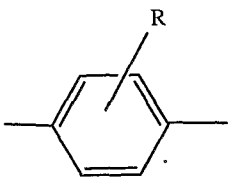
15. A biomedical device comprising a polymerization product of a monomeric mixture comprising one or more first monomers of the general formula:

$$A\text{-}L\text{-}R^1\text{-}(X\text{-}CF{=}CF_2)_n$$

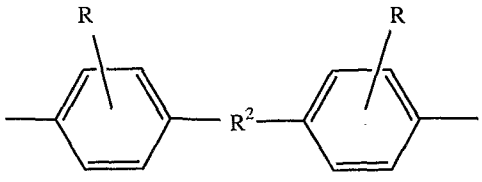
wherein R^1 represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group; L is an optional linking group and is independently a straight or branched C_1-C_{30} alkyl group, a C_3-to C_{30} cycloalkyl group, a C_5-C_{30} aryl group, an ether group, a C_1-C_{20} ester group, an amide group , a siloxanyl, an arylsiloxanyl or a fluorosiloxanyl; A is CO_2Z, SO_2Z, PO_3Z, or OPO_3Z wherein Z is hydrogen or an alkali metal and n is an integer from 1 to about 1000.

16. The biomedical device of Claim 15, wherein in the first monomer R^1 comprises a substituted or unsubstituted cyclic or polycyclic containing group optionally containing one or more heteroatoms or a substituted or unsubstituted cyclic or polycyclic siloxane containing group; X is independently a bond, an oxygen atom, a sulfur atom, a carboxylic or thiocarboxylic ester group, an amide group, a sulfone, a sulfoxide, a carbonate, a carbamate, a perfluoroalkylene, a perfluoroalkylene ether, an alkylene, an acetylene, a phosphine, a carbonyl or thio carbonyl group; seleno; telluro; nitrido; a silanediyl group, a trisilanediyl group, a tetrasilanetetrayl group, a siloxanediyl group, a disiloxanediyl group, a trisiloxyldiyl group, a trisilazanyl group, a silythio group, or a boranediyl group and n is from 1 to about 10.

17. The biomedical device of Claim 15, wherein in the first monomer X is O; R^1 is an aromatic group selected from the group consisting of



, and



wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and n is from 1 to about 10 and wherein the

X group and either the L or A group may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

18. The biomedical device of Claim 15, wherein the monomeric mixture further comprises (b) one or more second crosslinking monomers comprising at least three trifluorovinyl groups and (c) one or more prepolymers comprising one or more trifluorovinyl groups.

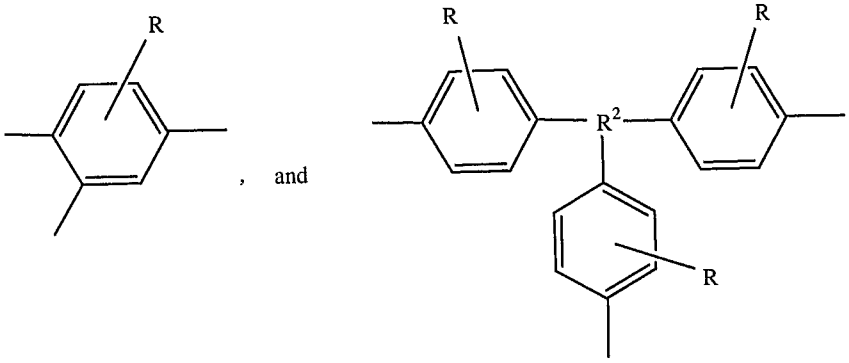
19. The biomedical device of Claim 18, wherein the second crosslinking monomer comprises one or more monomers of the general formula

$$F_2C=CF\text{-}X\text{-}R^3\text{-}(X\text{-}CF=CF_2)_z$$

wherein R^3 represents one or more inertly substituted groups; X is independently a group which links the R^3 group and the trifluorovinyl group and z is an integer of 2 to about 1000.

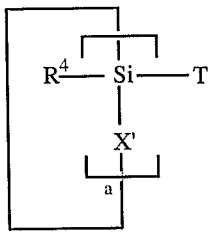
20. The biomedical device of Claim 19, wherein R^3 comprises a substituted or unsubstituted cyclic or polycyclic containing group optionally containing one or more heteroatoms or a substituted or unsubstituted, cyclic or polycyclic siloxane containing group; X is independently a bond, an oxygen atom, a sulfur atom, a carboxylic or thiocarboxylic ester group, an amide group, a sulfone, a sulfoxide, a carbonate, a carbamate, a perfluoroalkylene, a perfluoroalkylene ether, an alkylene, an acetylene, a phosphine, a carbonyl or thio carbonyl group; seleno; telluro; nitrido; a silanediyl group, a trisilanediyl group, a tetrasilanetetrayl group, a siloxanediyl group, a disiloxanediyl group, a trisiloxyldiyl group, a trisilazanyl group, a silythio group, or a boranediyl group and z is from 1 to about 10.

21. The biomedical device of Claim 19, wherein each X is O; R^3 is an aromatic group selected from the group consisting of

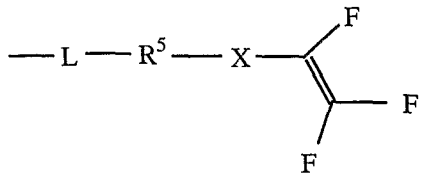


wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and m is from 1 to about 10 and wherein each X group may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

22. The biomedical device of Claim 18, wherein the second crosslinking monomer comprises one or more monomers of the general formula:

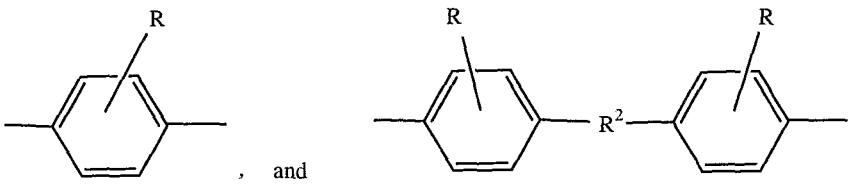


wherein X' is an oxygen atom; R^4 is independently hydrogen, a substituted or unsubstituted C_1-C_{30} alkyl, a substituted or unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted a C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, or a substituted or unsubstituted C_6-C_{30} heteroarylalkyl; a is from 3 to about 100; and T is independently of the general formula:



wherein R^5 is independently one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group and L is an optional linking group and is independently a straight or branched C_1-C_{30} alkyl group, a C_3-to C_{30} cycloalkyl group, a C_5-C_{30} aryl group, an ether group, a C_1-C_{20} ester group, an amide group, a siloxanyl, an arylsiloxanyl or a fluorosiloxanyl.

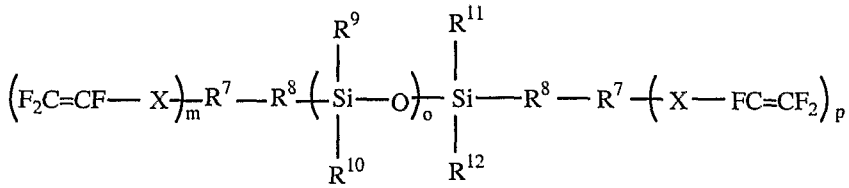
23. The biomedical device of Claim 22, wherein R^4 is a substituted or unsubstituted C_1-C_{30} alkyl; X is O and R^5 is an aromatic group selected from the group consisting of



wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, or two R groups together with the carbon atom to which they are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and wherein the X group and either the L group or Si atom may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

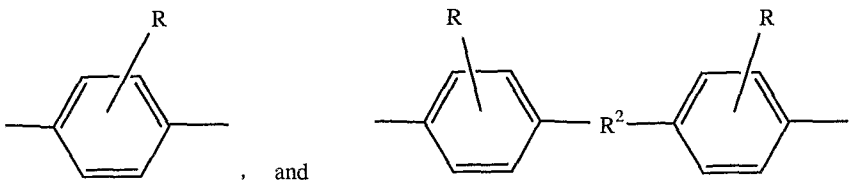
24. The biomedical device of Claim 18, wherein the one or more prepolymers are selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

25. The biomedical device of Claim 18, wherein the prepolymer comprises one or more poly(siloxane) prepolymers of the general formula:



wherein m, o and p are independently integers from 1 to about 1000; R^7 independently represents one or more inertly substituted groups; X is independently a group which links the inertly substituted groups and the trifluorovinyl group; R^8 is independently an amide group, a C_1-C_{20} ester group, an ether group, an ureido, a substituted or unsubstituted C_3-C_{30} cyclicalkyl, or a C_1-C_{30} alkylene or haloalkylene group optionally containing ether or ester linkages; and R^9, R^{10}, R^{11} and R^{12} are independently hydrogen, a straight or branched C_1-C_{30} alkyl group, a C_1-C_{30} fluoroalkyl group, one or more substituted or unsubstituted aromatic groups, a C_1-C_{20} ester group, an ether group, an ureido group, an amide group, an amine group, a substituted or unsubstituted C_1-C_{30} alkoxy, a substituted or unsubstituted C_3-C_{30} cycloalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkylalkyl, a substituted or unsubstituted C_3-C_{30} cycloalkenyl, a substituted or unsubstituted C_5-C_{30} aryl, a substituted or unsubstituted C_5-C_{30} arylalkyl, a substituted or unsubstituted C_5-C_{30} heteroaryl, a substituted or unsubstituted C_3-C_{30} heterocyclic ring, a substituted or unsubstituted C_4-C_{30} heterocyclylalkyl, a substituted or unsubstituted C_6-C_{30} heteroarylalkyl, fluorine, a vinyl group, a C_5-C_{30} fluoroaryl, or a hydroxyl group.

26. The biomedical device of Claim 25, wherein each X is O; each R^7 is independently an aromatic group selected from the group consisting of



wherein R is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, a C_1-C_{20} carboxylic acid group, a C_1-C_{20} ester group, a C_1-C_{20} alkoxy group, CO_2^-, SO_3^-, PO_3^-, OPO_3^{2-}, F, Br, I, NR^{13}_2 or $NR^{13}_3{}^+$ wherein R^{13} is independently hydrogen, a C_1-C_{20} alkyl group, a hydroxyl group, or two R groups together with the carbon atom to which they

are bonded are joined together to form a cyclic structure optionally containing one or more heterocyclic groups and R^2 is a bond, a C_1-C_{20} alkylene or haloalkylene group optionally containing ether or ester linkages; and n and p is from 1 to about 10 and wherein the X and R^8 groups may independently be bonded to the aromatic group either ortho, meta and/or para with respect to one another.

27. The biomedical device of Claim 15, wherein in the first monomer X is O, R^1 comprises a cyclic or polycyclic group optionally containing one or more heteroatoms and A is CO_2Z; and the monomeric mixture further comprises a second crosslinking monomer comprising at least three trifluorovinyl aromatic ether groups and one or more prepolymers selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

28. The biomedical device of Claim 15, wherein in the first monomer X is O, R^1 comprises a cyclic or polycyclic group optionally containing one or more heteroatoms and A is SO_2Z; and the monomeric mixture further comprises a second crosslinking monomer comprising at least three trifluorovinyl aromatic ether groups and one or more prepolymers selected from the group consisting of poly(siloxane) prepolymers, poly(alkyl ether) prepolymers, poly(aromatic ether) prepolymers, poly(perfluorocyclobutane) prepolymers, copolymers thereof and mixtures thereof.

29. The biomedical device of Claim 15, which is an ophthalmic lens.

30. The biomedical device of Claim 15, wherein the ophthalmic lens is a contact lens.

31. The biomedical device of Claim 30, wherein the contact lens is a rigid gas permeable lens.

FIGURE 1

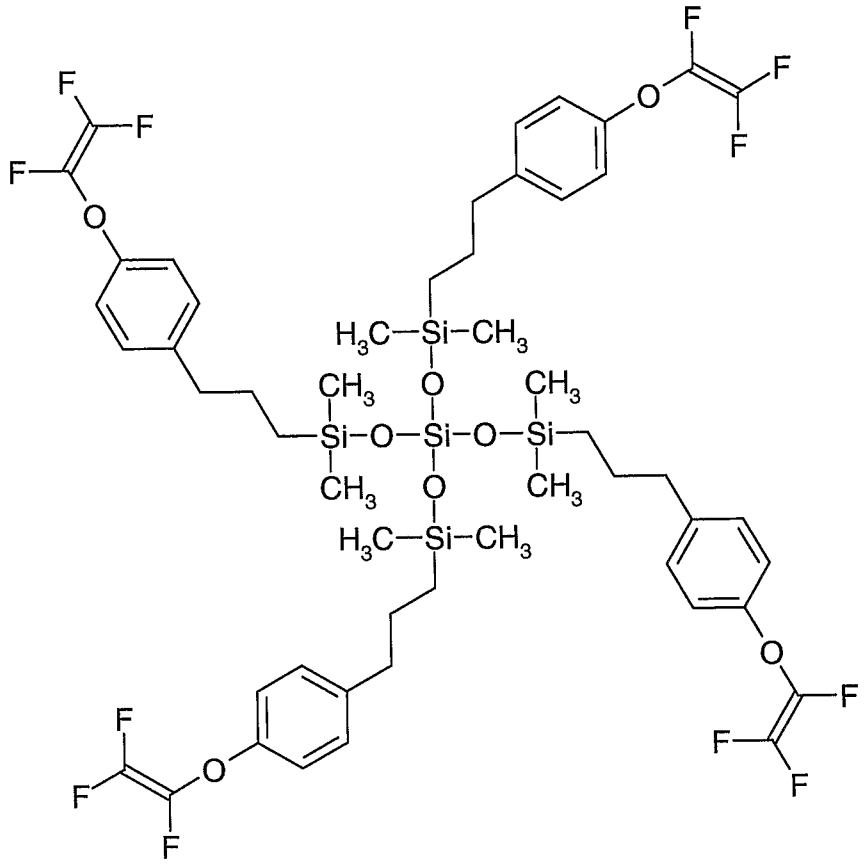

F
F
F
O
F
F
F
O
H3C—Si—CH3
CH3
O
CH3
Si—O—Si—O—Si
CH3
O
CH3
H3C—Si—CH3
O
F
F
F
F
F
O
F
F
F

FIGURE 2

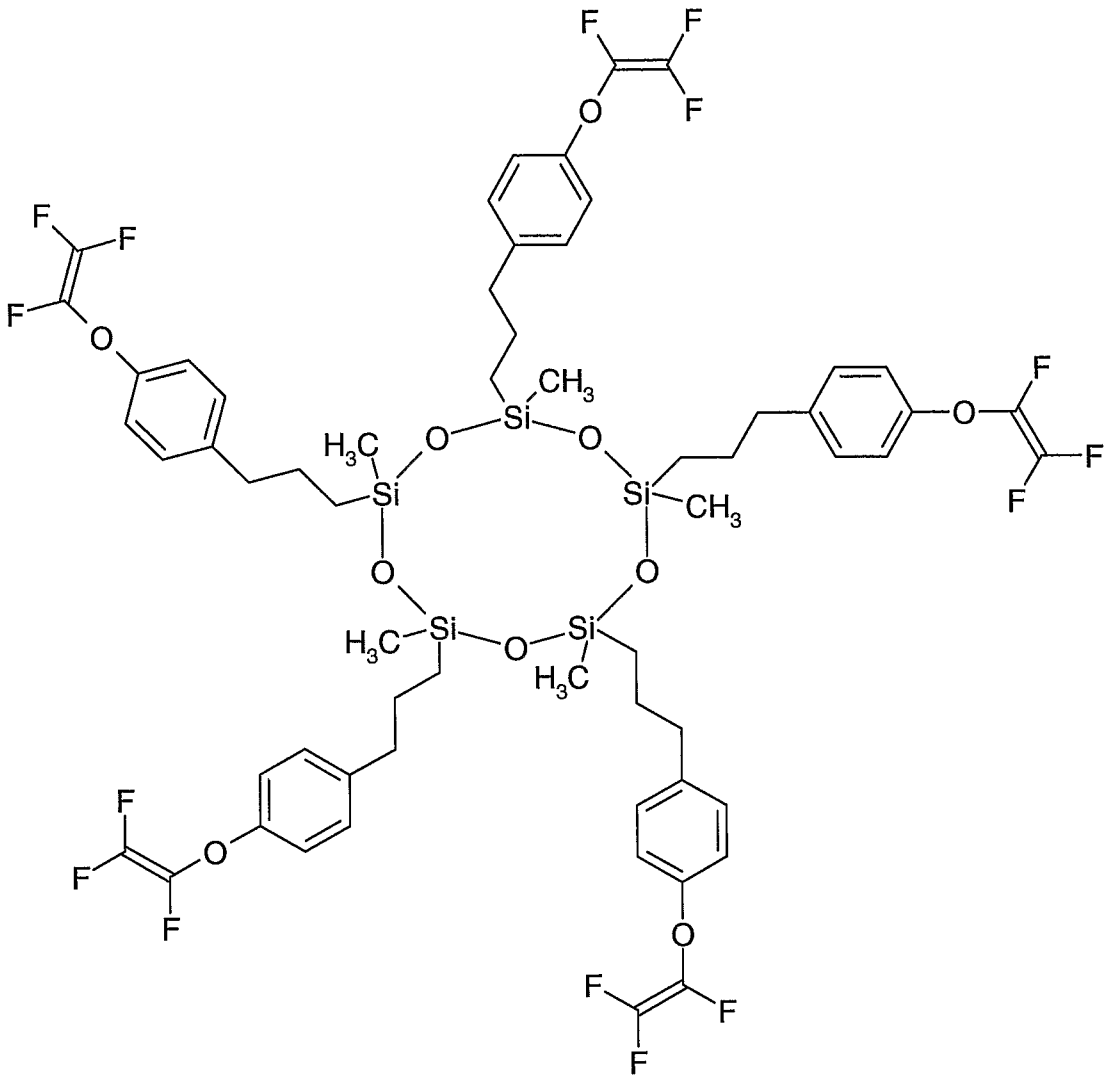


FIGURE 3

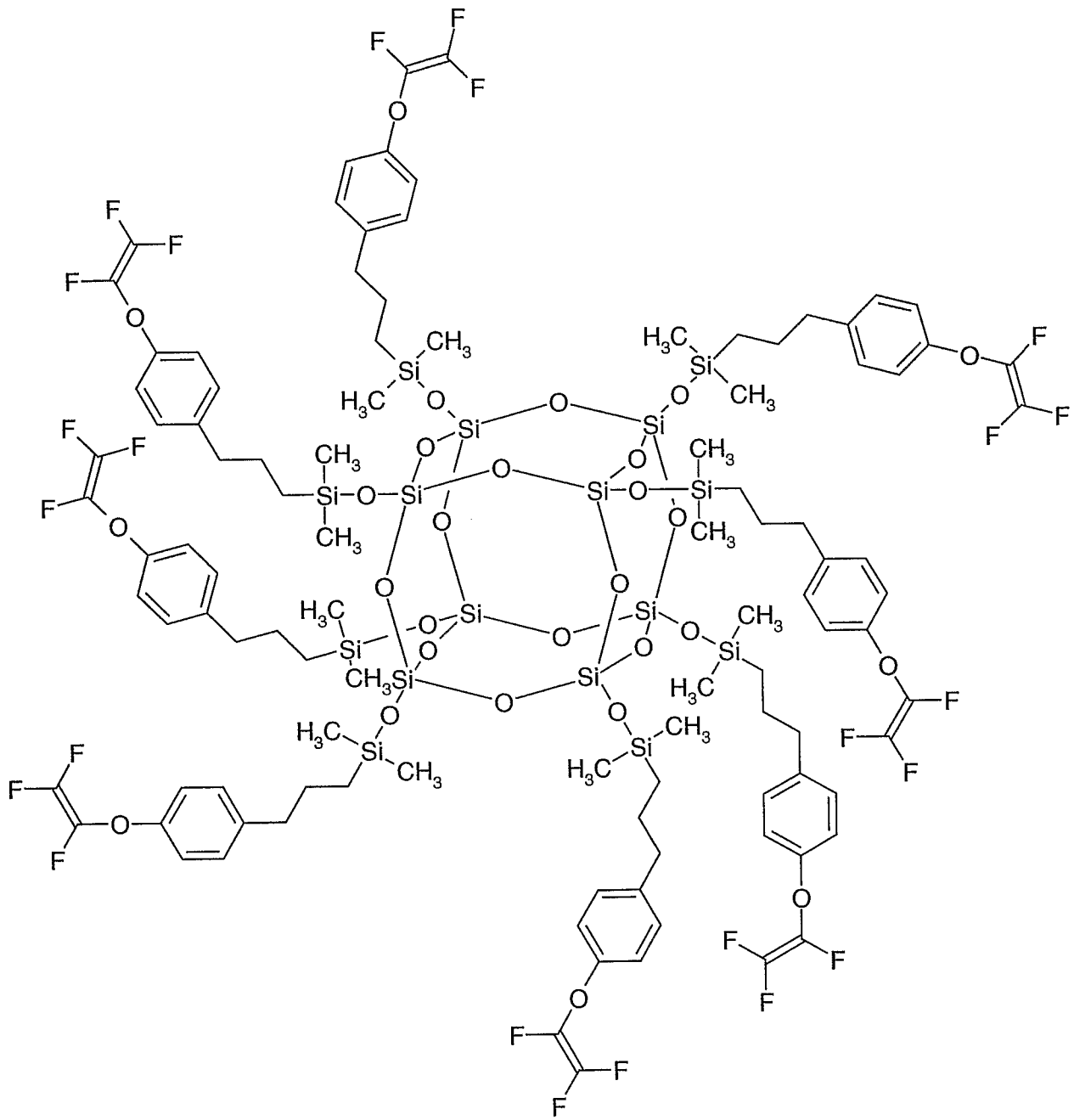


FIGURE 4

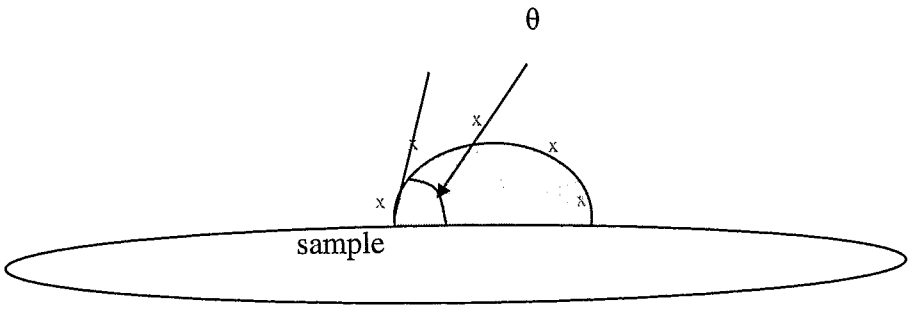
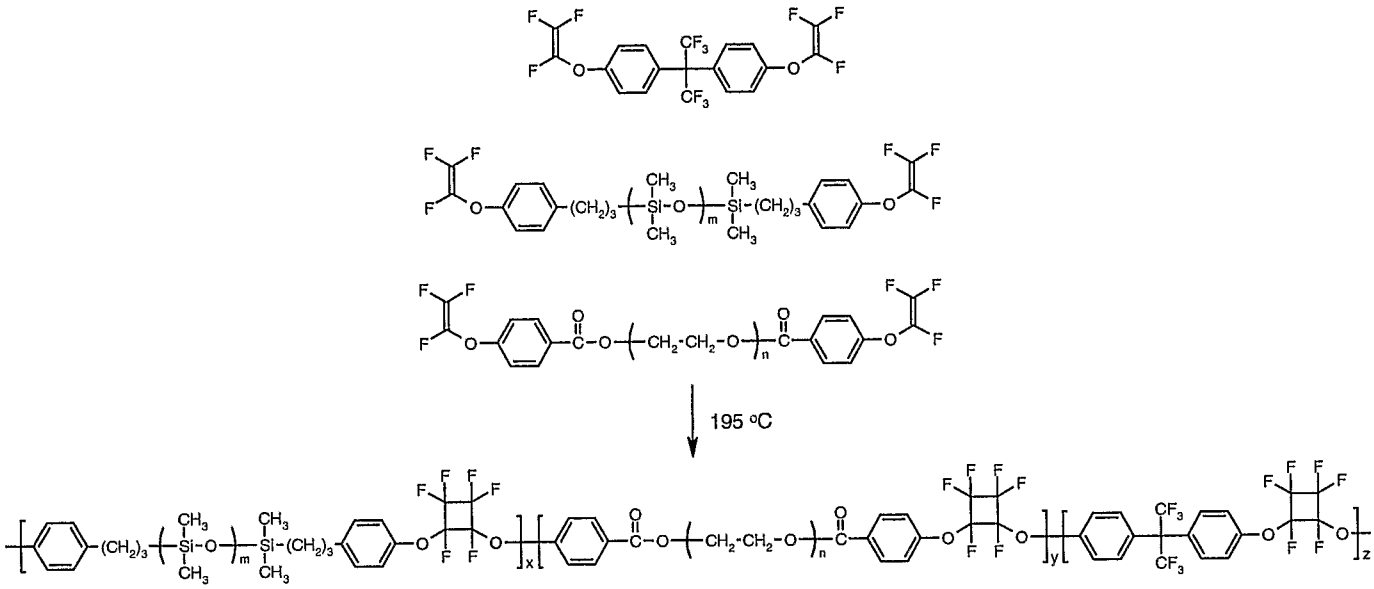


FIGURE 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/024679

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B1/04 C08F214/18 C08F236/00 C08F290/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G02B C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 066 746 A (CLEMENT KATHERINE S [US] ET AL) 19 November 1991 (1991-11-19) cited in the application the whole document	1-31
A	SHARON WONG, HONG MA, AND ALEX K.-Y. JEN, RICK BARTO AND CURTIS W. FRANK: "Perfluorocyclobutane-Based Polyester(arylene ether)s for Applications in Integrated Optics" MACROMOLECULES, vol. 37, 23 June 2004 (2004-06-23), pages 5578-5585, XP002403645 the whole document	1-31

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 October 2006	03/11/2006
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Degrendel, Magali

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/024679

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5066746 A	19-11-1991	NONE	