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[54] **METHODS OF FORMING AN EXTENDED WEAR OPHTHALMIC LENS HAVING A HYDROPHILIC SURFACE**

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[52] **U.S. Cl.** **523/106**; 523/107; 526/279; 528/32; 264/1.36; 427/2.24

[58] **Field of Search** 526/279; 523/106, 523/107; 427/2.24; 264/1.36; 528/32

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[57] **ABSTRACT**

An ophthalmic lens suited for extended-wear for periods of at least one day on the eye without a clinically significant amount of corneal swelling and without substantial wearer discomfort. The lens has a balance of oxygen permeability and ion or water permeability, with the ion or water permeability being sufficient to provide good on-eye movement, such that a good tear exchange occurs between the lens and the eye. A preferred lens is a copolymerization product of a oxyperm macromer and an ionoperm monomer. The invention encompasses extended wear contact lenses, which include a core having oxygen transmission and ion transmission pathways extending from the inner surface to the outer surface.

8 Claims, No Drawings

METHODS OF FORMING AN EXTENDED WEAR OPHTHALMIC LENS HAVING A HYDROPHILIC SURFACE

This application is a divisional of application Ser. No. 08/569,816, filed Dec. 8, 1995, which is a continuation-in-part of U.S. application Ser. No. 08/301,166, filed on Sep. 6, 1994, now abandoned. Priority is also claimed under 35 U.S.C. 119 for German Application No. 95810221.2 filed on Apr. 4, 1995 and Swiss Application No. 1496/95 filed on May 19, 1995.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates broadly to lenses and polymeric materials useful in optic and ophthalmic arts. More specifically, this invention relates to polymeric materials and treatment processes useful in the manufacture of contact lenses. Still more specifically, this invention relates to contact lenses useful as extended-wear contact lenses.

2. Description of the Related Art

A wide variety of research has been conducted in the field of biocompatible polymers. The definition of the term "biocompatible" depends on the particular application for which the polymer is designed. In the field of ophthalmic lenses, and in particular in the field of contact lenses, a biocompatible lens may be generally defined as one which will not substantially damage the surrounding ocular tissue and ocular fluid during the time period of contact. The phrase "ophthalmically compatible" more appropriately describes the biocompatibility requirements of ophthalmic lenses.

One ophthalmic compatibility requirement for contact lenses is that the lens must allow oxygen to reach the cornea in an amount which is sufficient for long-term corneal health. The contact lens must allow oxygen from the surrounding air to reach the cornea because the cornea does not receive oxygen from the blood supply like other tissue. If sufficient oxygen does not reach the cornea, corneal swelling occurs. Extended periods of oxygen deprivation causes the undesirable growth of blood vessels in the cornea. "Soft" contact lenses conform closely to the shape of the eye, so oxygen cannot easily circumvent the lens. Thus, soft contact lenses must allow oxygen to diffuse through the lens to reach the cornea.

Another ophthmic compatibility requirement for soft contact lenses is that the lens must not strongly adhere to the eye. Clearly, the consumer must be able to easily remove the lens from the eye for disinfecting, cleaning, or disposal. However, the lens must also be able to move on the eye in order to encourage tear flow between the lens and the eye. Tear flow between the lens and eye allows for debris, such as foreign particulates or dead epithelial cells, to be swept from beneath the lens and, ultimately, out of the tear fluid Thus, a contact lens must not adhere to the eye so strongly that adequate movement of the lens on the eye is inhibited.

While there exist rigid gas permeable ("RGP") contact lenses which have high oxygen permeability and which move on the eye, RGP lenses are typically quite uncomfortable for the consumer. Thus, soft contact lenses are preferred by many consumers because of comfort. Moreover, a contact lens which may be continuously worn for a period of a day or more (including wear during periods of sleeping) requires comfort levels which exclude RGP lenses as popular extended-wear candidates.

In order to balance the ophthalmic compatibility and consumer comfort requirements in designing a daily wear soft contact lens, polymers and copolymers of 2-hydroxyethyl methacrylate (HEMA) were developed. These hydrophilic polymers move well on the eye and provide sufficient oxygen permeability for daily wear. Certain soft contact lenses have been approved by the FDA for extended wear periods of up to about 6 nights of overnight wear and seven days of daily wear. However, the consumer cannot safely and comfortably wear these poly(HEMA) lenses for extended periods of seven days or more, because the oxygen permeability is insufficient. True extended wear (i.e., seven days or more) of these lenses may result, at a minimum, in corneal swelling and development of surface blood vessels in the cornea.

In order to improve oxygen permeability, polymers containing silicone groups were developed. A variety of siloxane-containing polymers have been disclosed as having high oxygen permeability. For example, see U.S. Pat. Nos. 3,228,741; 3,341,490; 3,996,187; and 3,996,189. However, polysiloxanes are typically highly lipophilic. The properties (e.g., lipophilicity, glass transition temperature, mechanical properties) of known polysiloxanes has resulted in contact lenses which adhere to the eye, inhibiting the necessary lens movement. In addition, polysiloxane lipophilicity promotes adhesion to the lens of lipids and proteins in the tear fluid, causing a haze which interferes with vision through the lens.

There have been attempts to blend the desirable hydrophilic properties of hydrophilic polymers, formed from monomers such as HEMA, with the desirable oxygen permeability of is polymers formed from siloxane-containing monomers. For example, see U.S. Pat. Nos. 3,808,178; 4,136,250; and 5,070,169. However, prior attempts at producing a true extended wear contact lens have been unsuccessfil, either because of the effect of the extended-wear lens on corneal health or because the lens would not move on the eye. Thus, there remains a need for an ophthamically compatible, transparent polymeric material which is suited to extended periods of continuous contact with ocular tissue and tear fluid.

OBJECTS AND SUMMARY OF THE INVENTION

An object of the invention is to provide a material having a balance of oxygen permeability, ion permeability, on-eye movement and tear exchange, all of which are sufficient for corneal health and wearer comfort during extended periods of continuous wear.

Another object of the invention is to provide an ophthalmic lens capable of extended continuous wear periods of at least 24 hours without substantial adverse impact on ocular health or consumer comfort, and more preferably, to provide a lens capable of continuous wear of 4 to 30 days or more without substantial adverse impact on ocular health or consumer comfort.

A further object of the invention is to provide an ophthalmic lens capable of extended continuous wear periods of at least 24 hours without substantial corneal swelling or consumer discomfort, and more preferably, to provide a lens capable of continuous wear of 4, 7, 14 or 30 days or more without substantial corneal swelling or consumer discomfort.

Yet another object of the invention is to provide methods of forming an extended-wear ophthalmic lens.

Still a further object of the invention is to provide methods of testing and classifying ophthalmic lenses as candidates for true extended-wear.

These and other objects of the invention are met by the various embodiments described herein.

One embodiment of the invention is an ophthalmic lens, suited to extended periods of wear in continuous, intimate contact with ocular tissue and tear fluid. The lens displays a balance of oxygen permeability and ion permeability sufficient to maintain good corneal health, adequate movement of the lens on the eye and wearer comfort during extended wear periods. The lens is formed by polymerization, preferably copolymerization, of (a) at least one oxyperm polymerizable material which is capable of polymerizing to form a polymer having a high oxygen permeability; and (b) at least one ionoperm polymerizable material which is capable of polymerizing to form a polymer having a high ion permeability. Preferably, the lens includes a core polymeric material and ophthalmically compatible surfaces. In a preferred embodiment, the surface is more hydrophilic and lipophobic than the core polymeric material.

Another embodiment of the invention is a method of forming an ophthalmic lens having high oxygen permeability and high ion permeability. The method includes the step of forming a core material, having an inner surface and an outer surface, such that at least one pathway for ion transport and at least one pathway for oxygen transport are present from the inner to the outer surface. In a preferred embodiment, the method includes treating the surface of the lens to render the surface more hydrophilic than the core.

A further embodiment of the invention is an ophthalmic lens comprising a polymeric material which has a high oxygen permeability and a high ion or water permeability, the polymeric material being formed from at least one polymerizable material including (a) at least one oxyperm segment and (b) at least one ionoperm segment. The lens displays a balance of oxygen permeability and ion permeability sufficient to maintain good corneal health, adequate movement of the lens on the eye and wearer comfort during extended wear periods.

Yet another embodiment of the invention is a method of using a contact lens having both an oxygen transmission pathway and an ion transmission pathway from inner to outer surface as an extended wear lens. The method includes (a) applying the lens to the ocular environment and (b) allowing the lens to remain in intimate contact with the ocular environment for a period of at least 24 hours without substantial adverse impact on corneal health or wearer comfort. A preferred method includes additional steps of (c) removing the lens from the ocular environment; (d) disinfecting the lens; (e) applying the lens to the ocular environment; and (f) allowing the lens to remain in intimate contact with the ocular environment for a period of at least an additional 24 hours. In a preferred embodiment, the lens is worn for a continuous period of at least seven days without substantial adverse impact on corneal health or wearer comfort.

OUTLINE OF DESCRIPTION OF THE PREFERRED EMBODIMENTS

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VI. METHODS OF MANUFACTURE OF LENSES

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One embodiment of the present invention is an ophthalmically compatible, transparent lens suited to extended periods of continuous contact with ocular tissue and tear fluids. A particularly preferred embodiment of the invention is an extended-wear vision correction lens suited for safe and comfortable long term wear without removal. In order to properly describe the invention and to delineate the metes and bounds of the claims, a set of basic terms will be defined at the outset.

I. DEFINITION OF TERMS

An "ophthalmic lens", as used herein, refers to lenses which are placed in intimate contact with the eye or tear fluid, such as contact lenses for vision correction (e.g., spherical, toric, bifocal), contact lenses for modification of eye color, ophthalmic drug delivery devices, ocular tissue protective devices (e.g., ophthalmic healing promoting lenses), and the like. A particularly preferred ophthalmic lens is an extended-wear contact lens, especially extended-wear contact lenses for vision correction.

A "polymerizable material which is capable of polymerizing to form a polymer having a high oxygen permeability", as used herein, refers to monomers, oligomers, macromers, and the like, and mixtures thereof, which are capable of polymerizing with like or unlike polymerizable materials to form a polymer which displays a relatively high rate of oxygen diffusion therethrough. For convenience of reference, these materials will be referred to herein as "oxyperm polymerizable materials" and the resultant polymers will be referred to herein as "oxyperm polymers".

The "oxygen transmissibility" of a lens, as used herein, is the rate at which oxygen will pass through a specific ophthalmic lens. Oxygen transmissibility, Dk/t, is conventionally expressed in units of barrers/mm, where t is the average thickness of the material [in units of mm] over the area being measured and "barrer" is defined as:

$$[(\text{cm}^3\ \text{oxygen})(\text{mm})/(\text{cm}^2)(\text{sec})(\text{mm Hg})]\times10^{-9}$$

The "oxygen permeability", Dk, of a lens material does not depend on lens thickness. Oxygen permeability is the rate at which oxygen will pass through a material. Oxygen permeability is conventionally expressed in units of barrers, where "barrer" is defined as:

$$[(\text{cm}^3\ \text{oxygen})(\text{mm})/(\text{cm}^2)(\text{sec})(\text{mm Hg})]\times10^{-10}$$

These are the units commonly used in the art. Thus, in order to be consistent with the use in the art, the unit "barrer" will have the meanings as defined above. For example, a lens having a Dk of 90 barrers ("oxygen permeability barrers") and a thickness of 90 microns (0.090 mm) would have a Dk/t of 100 barrers/mm ("oxygen transmissibility barrers"/mm).

A "polymerizable material which is capable of polymerizing to form a polymer having a high ion permeability", as used herein, refers to monomers, oligomers, macromers, and the like, and mixtures thereof, which are capable of polymerizing with like or unlike polymerizable materials to form a polymer which displays a relatively high rate of ion or water permeation therethrough. For convenience of reference, these materials will be referred to herein as "ionoperm polymerizable materials" and the resultant polymers will be referred to herein as "ionoperm polymers".

A "macromer", as used herein, refers to a polymerizable material which has a molecular weight of at least about 800 grams/mol. The term "macromer", as used herein, also encompasses oligomers.

A "monomer", as used herein refers to a polymerizable material which has a molecular weight of less than about 800 grams/mol.

A "phase", as used herein, refers to a region of substantially uniform composition which is a distinct and physically separate portion of a heterogeneous polymeric material. However, the term "phase" does not imply that the material described is a chemically pure substance, but merely that certain bulk properties differ significantly from the properties of another phase within the material. Thus, with respect to the polymeric components of a lens, an ionoperm phase refers to a region composed of essentially only ionoperm polymer (and water, when hydrated), while an oxyperm phase refers to a region composed of essentially only oxyperm polymer.

A "continuous phase", as used herein, refers to a region of substantially uniform composition which forms a continuous pathway from one surface of an article to another surface of an article.

"Co-continuous phases", as used herein, refers to at least two regions, each of substantially uniform composition which differs from the other, and each of which forms a continuous pathway from one surface of an article to another surface of an article. Thus, an ophthalmic lens having co-continuous phases of oxyperm polymer and ionoperm polymer will have two continuous pathways or sets of continuous pathways extending from the inner surface of the lens to the outer surface of the lens.

"Morphology", as used herein, refers to the structure and relationship of the phases of a material.

"Ophthalmically compatible", as used herein, refers to a material or surface of a material which may be in intimate contact with the ocular environment for an extended period of time without significantly damaging the ocular environment and without significant user discomfort. Thus, an ophthalmically compatible contact lens will not produce significant corneal swelling, will adequately move on the eye with blinking to promote adequate tear exchange, will not have substantial amounts of lipid adsorption, and will not cause substantial wearer discomfort during the prescribed period of wear.

"Ocular environment", as used herein, refers to ocular fluids (e.g., tear fluid) and ocular tissue (e.g., the cornea) which may come into intimate contact with a contact lens used for vision correction, drug delivery, wound healing, eye color modification, or other ophthalmic applications.

"Hydrophilic", as used herein, describes a material or portion thereof which will more readily associate with water than with lipids.

A "hydrophilic surface", as used herein, refers to a surface which is more hydrophilic and lipophobic than the bulk or core material of an article. Thus, an ophthalmic lens having a hydrophilic surface describes a lens having a core material having a certain hydrophilicity surrounded, at least in part, by a surface which is more hydrophilic than the core.

The "outer surface" of a lens, as used herein, refers to the surface of the lens which faces away from the eye during wear. The outer surface, which is typically substantially convex, may also be referred to as the front curve of the lens. The "inner surfa" of a lens, as used herein, refers to the surface of the lens which faces towards the eye during wear. The inner surface, which is typically substantially concave, may also be referred to as the base curve of the lens.

"TRIS", as used herein, refers to 3-methacryloxypropyltris(trimethylsiloxy) silane, which is represented by CAS No. 17096-07-0. The term "TRIS" also includes dimers of 3-methacryloxypropyltris (trimethylsiloxy) silane.

"Molecular weight" of a polymeric material (including monomeric or macromeric materials), as used herein, refers to the number-average molecular weight unless otherwise specifically noted or unless testing conditions indicate otherwise.

A. Oxyperm Polymerizable Materials

Oxyperm polymerizable materials include a wide range of materials which may be polymerized to form a polymer displaying a relatively high oxygen diffusion rate therethrough. In addition, these materials must be relatively ophthalmically compatible. These oxyperm polymerizable materials include, without limitation thereto, siloxane-containing macromers and monomers, fluorine-containing macromers and monomers, and carbon-carbon triple bond-containing macromers and monomers. The oxyperm macromer or monomer may also contain hydrophilic groups.

Preferred oxyperm polymers are those formed from a siloxane-containing macromer. Macromers having dialkyl siloxane groups, especially dimethyl siloxanes, are particularly preferred. These macromers are broadly referred to as poly(dimethyl siloxanes) (also, PDMS). The siloxane-containing macromer may also include hydrophilic groups. Examples of suitable siloxane-containing macromers include, without limitation thereto, the Materials A, B, C, and D as described herein.

The oxygen transmissibility (Dk/t) of the lens is preferably at least 70 barrers/mm, more preferably at least 75 barrers/mm, and most preferably at least 87 barrers/mm. The lens center thickness is typically more than about 30 microns, preferably about 30 to about 200 microns, more preferably about 40 to about 150 microns, even more preferably about 50 to about 120 microns, and most preferably about 60 to about 100 microns.

The oxygen transmissibility of the extended-wear lens from the outer surface to the inner surface must be sufficient to prevent any substantial corneal swelling during the period of extended wear. It is known that the cornea swells approximately 3% to 4% during overnight periods of sleep when the eyelids are closed, as a result of oxygen deprivation. It is also known that wearing a typical contact lens, such as ACUVUE (Johnson & Johnson), for a period of about 8 hours (overnight wear) causes corneal swelling of about 11%. However, a preferred extended-wear contact lens will produce, after wear of about 24 hours, including normal sleep periods, corneal swelling of less than about 8%, more preferably less than about 6%, and most preferably less than about 4%. A preferred extended-wear contact lens will produce, after wear of about 7 days, including normal sleep periods, corneal swelling of less than about 10%, more preferably less than about 7%, and most preferably less than about 5%. Thus, the extended-wear lens must have oxyperm polymer in an amount sufficient to produce oxygen diffusion pathways from the outer surface to the inner surface of the lens which are sufficient to yield the above properties relating to corneal swelling. Preferably, the extended-wear lens has a continuous phase of oxyperm polymer extending from the outer surface to the inner surface of the lens.

B. Ionoperm Polymerizable Materials

Ionoperm polymerizable materials include a wide range of materials which may be polymerized to form a polymer displaying a relatively high ion diffusion rate therethrough. In addition, these materials must be relatively ophthalmically compatible. These ionoperm polymerizable materials include, without limitation thereto, acrylates and methacrylates, such as 2-hydroxyethyl methacrylate, acrylamide, methacrylamide, and dimethylacrylamide; poly (alkylene glycols), such as poly(ethylene glycol); N-vinyl pyrrolidones such as N-vinyl-2-pyrrolidone; and the like and mixtures thereof. Other ionoperm materials are disclosed in the specific embodiments of Materials A–D, described below.

C. Weight Ratios

The ratios of oxyperm to ionoperm polymerizable materials may vary substantially, depending on the selected balance of oxygen permeability and ion permeability for the chosen end-use of the molded polymeric article. Preferably, the volumetric ratio of oxyperm to ionoperm material (including water) in the fully hydrated lens is about 40 to about 60 to about 60 to about 40. However, weight percentages, based on the total weight of the lens, will be defined because weight percentages are more conveniently utilized in lens fabrication. Preferably, the extended-wear contact lenses having substantially only ionoperm and oxyperm materials will have about 60 to about 85 weight percent oxyperm polymerizable material and about 15 to about 40 weight percent ionoperm polymerizable material in the prepolymerization mixture, based on total polymerizable material weight. More preferably, the prepolymerization mixture will contain about 70 to about 82 weight percent oxyperm polymerizable material and about 18 to about 30 weight percent ionoperm polymerizable material, based on total polymerizable material weight.

A wide variety of additional polymerizable materials may be included in the mixture prior to polymerization. Cross-linking agents, such as ethylene glycol dimethacrylate (EGDMA), may be added to improve structural integrity and mechanical strength. Antimicrobial polymerizable materials such as poly(quaternary ammonium) salts may be added to inhibit microbial growth on the lens material. Also, additional ionoperm monomers or macromers and oxyperm polymerizable materials may be added to adjust the oxygen permeability and ion permeability of the final molded article. An especially advantageous polymerizable material is TRIS, which may act both to increase oxygen permeability and to improve the modulus of elasticity.

A preferred prepolymerization mixture will include (a) about 30 to 60 weight percent oxyperm macromer, (b) about 20 to 40 weight percent ionoperm polymerizable material, and (c) about 1 to 35 weight percent TRIS, based on the total lens weight. More preferably, the amount of TRIS is about 10 to 33 weight percent, based on the total prepolymerization mixture weight.

In a preferred embodiment, the prepolymerization mixture includes less than about 5 weight percent cross-linking agent, based on the total prepolymerization mixture weight. More preferably, the prepolymerization mixture includes less than about 2 weight percent cross-linking agent, based on the total prepolymerization mixture weight. Even more preferably, the prepolymerization mixture includes substantially no cross-linking agent. In a particularly preferred embodiment, the prepolymerization mixture includes no added cross-linking agent.

The previously described ranges for oxyperm polymerizable materials, ionoperm polymerizable materials, and TRIS are offered to enable the reader to better comprehend the invention. However, it should be noted that the specific weight or volume percentages of oxyperm and ionoperm polymerizable materials are not the most critical factors to consider in preparing a good extended-wear ophthalmic lens. More importantly, the lens must have sufficient ion permeability for good on-eye movement and sufficient oxygen permeability for good corneal health during the extended wear period.

D. Morphology

One requirement of the lens material is that the lens allow a high visible light transmission from the outer to inner surface of the lens. A lens morphology which includes large phase separated regions will reduce visible light transmission and cause substantial undesirable image distortion, thereby destroying the value of the lens as a vision correction device. Thus, the lens must have a morphology which allows at least about 80%, more preferably about 90%, visible light transmission and does not produce any significant undesirable image distortion.

In one preferred embodiment, the lens material has at least two phases: the phases including at least one oxyperm phase and at least one ionoperm phase. While there may be two distinct phases, it is believed that there may be a transition phase, or interphase, in which the material composition and the material properties are a blend of those of the oxyperm and ionoperm materials. Thus, there may exist a distinct oxyperm phase or plurality of distinct oxyperm phases, a distinct ionoperm phase or a plurality of distinct ionoperm phases, and an amphipathic phase mixture or blend of oxyperm and ionoperm phases. In one preferred embodiment, the glass transition temperature (Tg) of the oxyperm phase is less than about −115° Celsius.

The existence of separate oxyperm and ionoperm phases, rather than a complete blend of oxyperm and ionoperm phases, is believed to be advantageous in promoting the diffusion of oxygen and ions. Oxygen will diffuse predominantly through the oxyperm polymer, while the ionoperm polymer provides a higher barrier to oxygen diffusion. Similarly, ions will diffuse well through the ionoperm polymer, but the oxyperm polymer provides a higher resistance to ion diffusion. Thus, one homogeneous oxyperm/ionoperm phase will provide undesirable resistance to both oxygen and ion diffusion, while two separate oxyperm and ionoperm phases will provide low resistance pathways for transmission of both oxygen and ions or water. Thus, the ideal extended-wear lens has a pathway or series of pathways from the outer surface to the inner surface for transmission of oxygen therethrough, and an analogous continuous pathway or series of pathways for transmission of water or ions therethrough. In a particularly preferred embodiment, the lens has two co-continuous phases, one an oxyperm phase and the other an ionoperm phase, allowing for permeation of water or ions and oxygen between the front and base curves of the lens.

E. Bulk Water Content

The measurement of water content is difficult because the removal of adhered surface droplets, without affecting the bulk lens water content, is difficult. In addition, water may evaporate from the lens surface quickly, thereby lowering the water content from the equilibrium level. Accordingly, a discussion of the bulk water content of a lens warrants a discussion of the measurement technique used to determine the water content.

The preferred bulk water content of the hydrated lens will be a function of the lens material properties. The material properties are dependent on the prepolymerization macromers and monomers and polymerization conditions. Thus, the preferred water content for a lens including a fluorine-containing oxyperm material may be different from that of a lens including a siloxane-containing oxyperm material. Accordingly, while general ranges for bulk water content are offered for a better understanding of the invention, the invention is not generally limited to specific bulk water contents.

One method of measuring the water content of a lens formed in accordance with the present invention, referred to herein as the "Bulk Technique", is as follows. First the lens is thoroughly hydrated in a physiological saline solution, such that the water in the lens is in equilibrium with the surrounding water. Next the lens is gently blotted between two lint-free blotting cloths to remove surface moisture. The lens is quickly placed on an aluminum weighing pan and the first wet weight, W_1, is measured. Next, the aluminum pan with lens is placed in a oven at 36° C. for a period of at least 24 hours. After heat treating, the pan with lens is removed, placed in a desiccator, and allowed to cool to room temperature (about 22° C.). The pan with lens is weighed again to determine the dry weight, W_d. The lens is re-equilibrated in physiological saline solution and a second wet weight W_2 is determined thereon. The wet weights (W_1 and W_2) are averaged to yield an average wet weight, W_w. The bulk water content is determined by the following equation:

$$\text{Percent water content}=(W_w-W_d)/W_w\times100$$

A preferred lens bulk water content, determined by the "Bulk Technique", is less than about 32 weight percent. More preferably, the lens has a water content of about 10 to 30 weight percent, based on the total lens weight. A particularly preferred lens water content is about 15 to about 25 weight percent.

F. Ion and Water Permeability

Unexpectedly, it has been determined that the ion permeability through the lens correlates well with on-eye movement. As discussed earlier, it is known that on-eye movement of the lens is required to ensure good tear exchange, and ultimately, to ensure good corneal health. While the invention is not bound by theory presented herein, it may be useful to discuss some theory for a better understanding of ways to practice the invention.

It is theorized that water permeability is an exceptionally important feature for an extended-wear lens which includes oxyperm polymers such as those disclosed herein. Siloxane-containing oxyperm materials tend to adhere strongly to the eye, thereby stopping on-eye movement. The ability to pass water through the lens is believed to allow a siloxane-containing polymeric lens to move on the eye, where the movement occurs via forces exerted by water being squeezed out of the lens. The water permeability of the lens is also believed important in replenishing lens water content once pressure is removed. Further, the permeability of ions is believed to be directly proportional to the permeability of water. Thus, ion permeability is a predictor of on-eye movement.

However, regardless of whether the water permeability theory is a correct understanding of the actual on-eye movement phenomenon, it has been unexpectedly found that above a certain threshhold of ion permeability through a lens, from the inner surface of the lens to the outer, or vice versa, the lens will move on the eye, and below the threshhold the lens will adhere to the eye. Thus, the present innovative extended-wear contact lenses provide a balance between the relatively high oxygen permeability (and associated high binding capacity) of oxyperm materials with the low binding capacity (high on-eye movement) of ionoperm materials. It is believed that this is accomplished by providing a plurality of continuous ion transmission pathways for ion and water movement through the lens.

It should be noted that ions may move through the lens via these ion pathways by a number of means. For example, ions may diffuse through the lens because of concentration differences from one surface to another. Ions may also be forced through the ion pathways by the mechanical action of blinking, with the concomittent compression forces on the lens essentially squeezing water out of the lens. In addition, the charge nature of the surfaces may provide an electromotive force which drives ion permeation through the lens. At times, one of these driving forces may be larger than the others, while at other times the relative magnitude may reverse. This discussion is presented to clarify that the invention is not restricted by the method or driving force by which ions move through the lens.

Neither the measurement of water permeability nor ion permeability through an ophthalmic lens is considered a routine matter of testing in the industry. Accordingly, a discussion of the preferred ion or water permeability ranges warrants a discussion of the measurement techniques used to determine the permeability.

The water permeability of a lens may be determined from the rate of water permeation through the lens, from one surface to another surface. The water permeability of a lens may be determined by positioning a lens between two reservoirs holding solutions having known, and different, initial concentrations of radiolabeled water (e.g., tritiated water), and then measuring concentration of radiolabeled water in the "receiving" reservoir (the reservoir towards which the net flow of radiolabeled water is positive) as a function of time.

The relative ion permeability of a lens may be determined from the rate of ion permeation through the lens, from one surface to another surface. The rate of ion permeation may be determined by positioning a lens between two reservoirs holding solutions having known, and different, initial ion concentrations, and then measuring conductivity in the "receiving" reservoir (the reservoir towards which the net flow of ions is positive) as a function of time. The concentration of ions, such as sodium, can be measured accurately using a pH meter and an ion-selective electrode. Ions are believed to be transmitted through a lens, from inner to outer surfaces and vice versa, primarily by the diffusion of ions through water pathways in the lens. Ion permeability through a lens is believed to be directly proportional to water permeability through a lens.

1. Ionoflux Measurement Technique

The following technique, referred to herein as the "Ionoflux Technique", is a preferred method for determining the ion permeability of a lens. This technique may be used to determine the likelihood of adequate on-eye movement.

The "Ionoflux Technique" involves the use of a conductometer (LF 2000/C, catalog no. 300105, Wissenschaftlich-Technische Werkstitten GmbH (WTW), Germany), an electrode equipped with a temperature sensor (LR 01/T, catalog no. 302 520, WFW), a donor chamber containing a salt solution, a receiving chamber containing about 60 ml of deionized water, a stir bar and a thermostat.

The donor chamber is specially designed for sealing a contact lens thereto, so that the donor solution does not pass around the lens (i.e., ions may only pass through the lens). The donor chamber is composed of a glass tube which is threaded at the end which is immersed in the receiving solution. The glass tube includes a centrally located hole of about 9 mm in diameter. A lid, which is threaded to mate with the glass tube, holds a lens-retaining member which includes a centrally located hole of about 8 mm in diameter. The lens-retaining member includes a male portion adapted to mate with and seal the edges of the inner (concave) surface of a lens and a female portion adapted to mate with and seal the edges of the outer (convex) surface of a lens.

The lens to be measured is placed in the lens-retaining member, between the male and female portions. The male and female portions include flexible sealing rings which are positioned between the lens and the respective male or female portion. After positioning the lens in the lens-retaining member, the lens-retaining member is placed in the threaded lid. The lid is screwed onto the glass tube to define the donor chamber. The donor chamber is filled with 16 ml of 0.1 molar NaCl solution. The receiving chamber is filled with 60 ml of deionized water. The leads of the conductivity meter are immersed in the deionized water of the receiving chamber and a stir bar is added to the receiving chamber. The receiving chamber is placed in a thermostat and the temperature is held at about 35° C. Finally, the donor chamber is immersed in the receiving chamber.

Measurements of conductivity are taken every 20 minutes for about three hours, starting 10 minutes after immersion of the donor chamber into the receiving chamber. The Ionoflux Diffusion Coefficient, D, is determined by applying Fick's law as follows:

$$D=-n'/(A\times dc/dx)$$

where

n'=rate of ion transport [mol/min]

A=area of lens exposed [mm^2]

D=Ionoflux Diffusion Coefficient[mm^2/min]

dc=concentration difference [mol/L]

dx=thickness of lens [mm]

An Ionoflux Diffusion Coefficient of greater than about 6.4×10^{-6} mm^2/min is preferred for achieving sufficient on-eye movement. More preferably, the Ionoflux Diffusion Coefficient is greater than about 2.6×10^{-6} mm^2/min, while most preferably, the Ionoflux Diffusion Coefficient is greater than about 1.5×10^{-6} mm^2/min. It must be emphasized that the Ionoflux Diffusion Coefficient correlates with ion permeability through the lens, and thereby is a predictor of on-eye movement.

2. Ionoton Measurement Technique

The following technique, referred to herein as the "Ionoton Technique", is another preferred method for determining the relative ion permeability of a lens. The technique is based on measurement of the diffusion of sodium chloride through a lens.

The "Ionoton Technique" involves the use of a pH meter (Beckman, VWR catalog no. BK123142), a VSC-1 Diffusion Cell Drive Console (Crown-Bio, Somerville, N.J.), a DCB-100B Diffusion Cell (Crown-Bio), and a 6 cm sodium ion-specific electrode (Microelectronics, Londonderry, N.H., catalog no. MI-414P). The technique is not limited to the aforementioned instruments or materials; equivalent instruments or materials may be used.

First, a contact lens is mounted onto an orifice of the DCB-100B cell chamber, the donor chamber. Next, the connecting cell chamber (receptor chamber) is placed against the cell chamber containing the contact lens and tightly clamped on the clamp holder supplied with the VSC-1 Drive Console. Then, a phosphate-buffered saline (PBS, Mediatech catalog no. 21-031-LV) is placed into the receptor side of the cell chamber. Stir bars are added to each cell chamber. The 6 cm electrode is placed into the PBS saline receptor side. After the electrode has equilibrated in the PBS saline, the pH meter is placed in the mV function to establish the 0 mV point. PBS which has been saturated with sodium chloride is added to the donor chamber.

The millivolt signal is recorded at 5, 10, 15, 30, 60, 120, and 180 minute intervals. The millivolt signal is converted to a sodium ion concentration by a standard curve of sodium ion concentration vs. millivolt signal. The Ionoton Ion Permeability Coefficient, P, is then determined in accordance with the following equation:

$$\ln(1-2C(t)/C(0))=-2APt/Vd$$

where:

C(t)=concentration of sodium ions at time t in the receiving cell

C(0)=initial concentration of sodium ions in donor cell

A=membrane area, i.e., lens area exposed to cells

V=volume of cell compartment (3.0 ml)

d=average lens thickness in the area exposed

P=permeability coefficient

The average thickness of the lens in the exposed test area may be determined by averaging a number of readings, e.g., 10 readings, with a low-pressure thickness-measuring instrument, such as a Mitotoya micrometer VL-50, or equivalents thereof. The Ionoton Ion Permeability Coefficient, P, having units of cm^2/second, may be determined from the slope of a plot of time (t) v. $\ln(1-2C(t)/C(0))\times(-2At/Vd)$.

An Ionoton Ion Permeability Coefficient, P, of greater than about 0.2×10^{-6} cm^2/sec is preferred, while greater than about 0.3×10^{-6} cm^2/sec is more preferred and greater than about 0.4×10^{-6} cm^2/sec is most preferred. It must be emphasized that the Ionoton Ion Permeability Coefficient correlates with ion permeability through the lens, and thereby is a predictor of on-eye movement.

3. Hydrodell Water Permeability Technique

The following technique, referred to herein as the "Hydrodell Technique", is a preferred method for determining the water permeability of a lens. This technique may be used to determine the likelihood of adequate on-eye movement.

The Hydrodell Technique involves the measurement of the rate of transfer of the radiolabeled solutes THO (^{3}H-HO or tritiated water) and ^{14}C-glucose across the contact lens using a two-chamber apparatus. ^{14}C-glucose is used in this measurement technique to reveal any leak in the system during testing. The lens is mounted between chambers, which are stirred at a controllable rate. Chamber I contains a solution with a high concentration of labeled solute. Chamber II, the "receiving chamber", contains an identical solution but without the labeled solute. Samples of the solution in chambers I and II are taken at intervals over the test period. The radioactivity in the samples is measured. The permeability of the lens is calculated from the measured radioactivity, the sample times, the chamber volumes and the lens area exposed to the solutions. A more detailed description of the Hydrodell Technique follows.

a. Solution Preparation

Dulbecco's phosphate buffered saline (DPBS) is prepared by first dissolving, sequentially, about 160 g sodium chloride NaCl), about 4 grams potassium chloride (KCl), about 23 grams disodium hydrogen orthophosphate (Na_2HPO_4), about 4 grams potassium dihydrogen orthophosphate (KH_2PO_4), and about 10 grams sodium azide in a liter of reverse-osmosis (MilliQ) water. Then, the pH is adjusted to about 7.3 by adding appropriate amounts of HCl. Finally, the buffer solution is diluted to 1:20 (50 ml buffer solution with 950 ml reverse-osmosis water), and allowed to degas either in a screw-capped container overnight or under vacuum.

A Cold Glucose buffer solution is prepared by adding about 0.1 grams D-glucose to one liter of DPBS, followed by sterilization via filtration through a 0.2 µl millipore filter and storage at 4° C. until use.

The Chamber I solution is prepared by adding about 6 µl THO (TR53, 1.0 mCi/ml activity, available from Amersham Australia, located in North Ryde NSW Australia) and about 16 µl ^{14}C-glucose (in ethanol, available from Amersham Australia) to about 12 ml of the Cold Glucose buffer solution. Preferably, this solution is used within about 24 hours of preparation. The Chamber II solution is DPBS.

b. Apparatus Preparation

The chambers have a volume sufficient to hold about 12 ml of solution during testing. While the exact shape of the chambers is not critical, both chambers have rectangular cross-sections for ease of construction. The chambers may be made from a variety of water-proof rigid materials, preferably clear (e.g., acrylic plates, FX Plastics, Marrickville NSW Australia) so that samples may be observed during testing. Each chamber has a circular aperture of about 7 mm diameter appropriate for mounting a lens between the chambers for contact with solutions held within the chambers. Some affixing means, such as a set of mounting bolts, are necessary to securely affix one chamber to the other with the lens mounted in between.

A test contact lens is mounted symmetrically over the aperture of Chamber II. Folds and wrinkles are manually removed from the lens. Chamber I is positioned adjacent the aperture and mounted lens of Chamber II, and the chambers are secured to one another using mounting bolts.

About 12 ml (V_2) of DPBS is placed in Chamber II. About 12 ml of the Chamber I labeled solution is placed in Chamber I, at which point time t=0 is established. Stirrers are added to both chambers and the stirrer speed is set at about 1200 rpm.

c. Sampling

Sampling generally starts at time t_0=5 minutes. The final sample time, t_f, is usually at about 50 minutes for high water content lenses and about 120 minutes for low water content lenses, although these times are not critical.

At time t_0=5 minutes, two samples of about 0.2 ml volume are pipetted from Chamber I, and two 0.2 ml aliquots of DPBS are added to Chamber I to restore the volume. These samples are placed into plastic counting tubes with about 4 ml Ultima Gold™ cocktail (available from Packard Instrument Co., Meriden, Conn.) and about 0.9 ml DPBS.

Also at time t_0, one sample of about 1.0 ml volume is pipetted from Chamber II and one 1.0 ml aliquot of DPBS is added to Chamber II to restore the volume. The sample is placed into a plastic counting tube with about 4 ml Ultima Gold™ cocktail.

At intermediate times between t_0 and t_f (e.g., every 10 minutes), one sample of about 1.0 ml volume is pipetted from Chamber II and one 1.0 ml aliquot of DPBS is added to Chamber II to restore the volume. Each sample is placed into a plastic counting tube with about 4 ml Ultima Gold™ cocktail.

At time t_f, two samples of about 0.2 ml volume are pipetted from Chamber I. These samples are placed into plastic counting tubes with about 4 ml Ultima Gold™ cocktail and about 0.9 ml DPBS.

Also at time t_f, two samples of about 1.0 ml volume are pipetted from Chamber II. These samples are placed into plastic counting tubes with about 4 ml Ultima Gold™ cocktail.

d. Measurements

The activity of the samples are measured by liquid scintillation counting, or other appropriate technique. Liquid scintillation counting may be advantageously accomplished by using protocol number 6 for $^3H/^{14}C$ on a Tri-Carb Liquid Scintillation Analyzer (1900TR, available from Packard Instrument Co.).

Three standards containing about 10^4 to 10^5 cpm THO in reversed-osmosis (MilliQ) water are prepared. Three standards containing about 10^4 to 10^5 cpm ^{14}C glucose in reversed-osmosis (MiliQ) water are also prepared. A blank containing MilliQ water is prepared.

The scintillation analyzer settings are LLA=0 KeV and ULA=12 KeV for ^3H ("1") in channel 1 and LLB=12 KeV and ULB=156 KeV for ^{14}C ("2") in channel 2. The standards and blank are counted three times during each counting of samples, and the counts are averaged. The following denote the relevant measured sample activities:

b_1=measured activity of blank sample in channel 1

b_2=measured activity of blank sample in channel 2

S'_{11}=measured activity of standard ^3H sample in channel 1

S'_{12}=measured activity of standard ^{14}C sample in channel 2

S'_{21}=measured activity of standard ^3H sample in channel 1

S'_{22}=measured activity of standard ^{14}C sample in channel 2

y_1=measured activity of test sample (both ^3H and ^{14}C) in channel 1

y_2=measured activity of test sample (both ^3H and ^{14}C) in channel 2

e. Water Permeability Calculation

In order to calculate the actual activity of a sample, the measured activities of the isotopes, ^3H and ^{14}C, must first be corrected to remove the cross-contamination error due to the presence of both isotopes in one sample. Without explaining the mathematical derivations, the following stepwise procedure is offered as an example of one method of determining water permeability from the above measurements:

(1) Calculate S_{11}, S_{12}, S_{21}, and S_{22}, from the following equations:

$$S_{11}=S'_{11}-b_1$$

$$S_{12}=S'_{12}-b_1$$

$$S_{21}=S'_{21}-b_2$$

$$S_{22}=S'_{22}-b_2$$

(2) Calculate a_{12} and a_{21} from the following equations:

$$a_{12}=S_{12}/S_{22}$$

$$a_{21}=S_{21}/S_{11}$$

(3) Calculate corrected concentrations of ^3H ("1") and ^{14}C ("2") from the following equations:

$$c_1=[(y_1-b_1)-a_{12}(y_2-b_2)]/(1-a_{12}a_{21})V$$

$$c_2=|(y_2-b_2)-a_{21}(y_1-b_1)|/(1-a_{12}a_{21})V$$

where V is the volume of the test sample.

(4) Calculate water permeability for an interval from t_1 to t_2 as follows:

$$P=V_{II}|c_{II}(t_2)-c_{II}(t_1)|/A(c_I-c_{II})(t_1-t_2)$$

where V_{II} is the volume of Chamber II, $c_{II}(t_2)$ is the concentration of ^3H in Chamber II at time t_2, $c_{II}(t_1)$ is the concentration of ^3H in Chamber II at time t_1. A is the area of lens exposure, c_I is the average concentration of ^3H in Chamber I over the time period t_1 to t_2 and c_{II} is the average concentration of ^3H in Chamber II over the time period t_1 to t_2.

The ophthalmic lenses of one embodiment of the present invention have a Hydrodell Water Permeability Coefficient of greater than about 0.2×10^{-6} cm^2/sec. The ophthalmic lenses in a preferred embodiment of the invention have Hydrodell Water Permeability Coefficient of greater than about 0.3×10^{-6} cm^2/sec. The ophthalmic lenses in a preferred embodiment of the invention have Hydrodell Water Permeability Coefficient of greater than about 0.4×10^{-6} cm^2/sec.

G. Oxygen Transmissibility and Permeability

As mentioned earlier, the cornea receives oxygen primarily from the corneal surface which is exposed to the environment, in contrast to other tissues which receives oxygen from blood flow. Thus, an ophthalmic lens which may be worn on the eye for extended periods of time must allow sufficient oxygen to permeate through the lens to the cornea to sustain corneal health. One result of the cornea receiving an inadequate amount of oxygen is that the cornea will swell. In a preferred embodiment, the oxygen transmissibility of the present ophthalmic lenses is sufficient to prevent any clinically significant amount of corneal swelling from occurring.

A preferred ophthalmic lens material will have an oxygen transmissibility, Dk/t, of at least 70 (cm^3 oxygen)(mm)/mm-cm^2×(sec/mm Hg)×10^{-9} or |barrers/mm|, more preferably at least 75 barrers/mm, and most preferably at least 87 barrers/mm.

The oxygen permeability of a lens and oxygen taansmissibility of a lens material may be determined by the following technique. Oxygen fluxes (J) are measured at 34 C in a wet cell (i.e., gas streams are maintained at about 100% relative humidity) using a Dk1000 instrument (available from Applied Design and Development Co., Norcross, Ga.), or similar analytical instrument. An air stream, having a known percentage of oxygen (e.g., 21%), is passed across one side of the lens at a rate of about 10 to 20 cm^3/min., while a nitrogen stream is passed on the opposite side of the lens at a rate of about 10 to 20 cm^3/min. The barometric pressure surrounding the system, $P_{measured}$, is measured. The thickness (t) of the lens in the area being exposed for testing is determined by measuring about 10 locations with a Mitotoya micrometer VL-50, or similar instrument, and averaging the measurements. The oxygen concentration in the nitrogen stream (i.e., oxygen which diffuses through the lens) is measured using the DK1000 instrument. The oxygen permeability of the lens material, D_k, is determined from the following formula:

$$D_k=Jt/(P_{oxygen})$$

where

J=oxygen flux [microliters O_2/cm^2-minute]

$P_{oxygen}=(P_{measured}-P_{water\ vapor})\times(\%O_2$ in air stream) |mm Hg|=partial pressure of oxygen in the air stream

$P_{measured}$=barometric pressure |mm Hg|

$P_{water\ vapor}$=0 mm Hg at 34 C (in a dry cell) |mm Hg|

$P_{water\ vapor}$=40 mm Hg at 34 C (in a wet cell) |mm Hg|

t=average thickness of the lens over the exposed test area |mm|

where D_k is expressed in units of barrers, i.e., |(cc oxygen)(mm)/cm^2|×|sec/mm Hg|×10^{-10}.

The oxygen transmissibility (D_k/t) of the material may be calculated by dividing the oxygen permeability (D_k) by the average thickness (t) of the lens.

H. Mechanical On-eye Movement Parameters

On-eye movement of a lens may be predicted from the mechanical properties of a lens, the ion or water permeability through the lens, or both the mechanical properties and ion or water permeability. In fact, on-eye movement may be predicted more accurately from a combination of mechanical properties and ion or water permeability.

1. Tensile Modulus and Short Relaxation Time

Tensile mechanical testing may be performed on lens materials to determine mechanical properties. A procedure for preparing a test sample from a lens for subsequent mechanical testing includes the following steps:

1. Cut a parallel-sided strip through the center of the lens. A suitable width for the strip is about 3.1 mm.
2. Immerse the test strip in a phosphate-buffered saline solution (approximating ocular fluid osmolality) for a period of about 24 hours before testing.
3. Conduct mechanical testing with the test strip immersed in phosphate-buffered saline at ambient temperature (about 23° C.).

Tensile modulus may be measured by applying a strain rate of about 100% per minute to the test strip and recording the resultant stress. However, the procedure may be used at differing strain rates.

Stress relaxation is measured by applying a constant strain of about 5% to the test strip and recording the resultant stress for about 5 minutes. A useful mechanical testing instrument for this type of testing is the Vitrodyne V-200 from Liveco Biomechanical Instruments, located in Burlington, Vt.

In order to analyze stress relaxation data, a three element Maxwell-Wiechert model (a spring and two spring-dashpot elements in parallel) may be assumed for the polymer material. For this model the stress relaxation modulus is given by the following equation:

$$E(t)=E_0+E_1\ \exp\ (-t/t_1)+E_2\ \exp\ (-t/t_2)$$

Stress v. time curves may be normalized to the maximum (initial) stress induced in the samples. These curves may be analyzed by a variety of commercially available software (for example, ORIGIN software) by fitting the double exponential equation:

$$y(t)=y_0+A_1\ \exp\ (-t/t_1)+A_2\ \exp\ (-t/t_2)$$

in order to obtain the stress relaxation parameters y_0, t_1, A_1, t_2, and A_2.

It has been determined that the tensile modulus (modulus of elasticity, E) and the short relaxation time constant (t_1) correlate well with on-eye movement. In order to have appropriate on-eye movement, a lens preferably has a tensile modulus of less than about 3 MPa. More preferably, E is about 0.4 to about 2.5 MPa while a particularly preferred E is about 0.5 to about 1.5 MPa.

A preferred short relaxation time constant (t_1) is greater than about 3.5 seconds. More preferably, t_1 is greater than about 4 seconds, while a particularly preferred t_1, is greater than about 4.5 seconds.

2. Tangent Delta

Lenses may also be evaluated by dynamic mechanical analysis (DMA) methods. It has been determined that a factor known as tan δ (i.e., tangent delta), also known as mechanical loss factor, correlates well with on-eye movement. It has been observed that lens materials which move on the eye exhibit a distinct increase in tan δ with increasing frequency from about 0.1 to 10 Hz when these materials are tested by dynamic mechanical analysis. The tan δ of a preferred lens material is above about 0.2 at 0.1 Hz and increases to about 0.25 or more at about 10 Hz. A tan δ of about 0.3 or greater at 10 Hz is more preferred, while a tan δ of about 0.5 or greater at 10 Hz is even more preferred.

DMA measurements may be determined in accordance with the following procedure. A disk of lens material having a diameter of about 3.0 mm and a thickness of about 0.50 mm is formed. The disk is placed in a Perkin-Elmer DMA-7 instrument. The disk is immersed in a solution buffered to a pH of about 7.2 and held isothermally for a period of about 10 minutes or more prior to testing, at a temperature of about 23° to 35° C. The instrument is set to a compression measuring mode and the strain on the sample is adjusted to about 2% to 4%, depending on the sample response. The amplitude of compression is about 2 to 4 μm. Measurements of the modulus of elasticity and tan δ are taken at frequencies of about 0.1, about 1, and about 10 Hz.

3. Parameter Combinations

In order to assure appropriate movement of the lens on the eye, one may select materials which have a combination of the above-discussed properties. Therefore, a preferred group of extended-wear contact lens materials have (a) a modulus of elasticity (E) of about 1.5 MPa or less, (b) a short time relaxation constant (t_1) of greater than about 4 seconds, and (c) an Ionoton Ion Permeability Coefficient of greater than about 0.3×10^{-6} cm^2/sec and/or an Ionoflux Diffusion Coefficient greater than about 6.4×10^{-6} mm^2/min.

I. Examples of Suitable Materials

1. Material "A"

One embodiment of a suitable core material of the present ophthalmic lenses is a copolymer formed from the following monomeric and macromeric components:

(a) about 5 to about 94 dry weight percent of a macromer having the segment of the formula

CP—PAO—DU—ALK—PDMS—ALK—DU—PAO—CP

where

PDMS is a divalent poly(disubstituted siloxane),

ALK is an alkylene or alkylenoxy group having at least 3 carbon atoms,

DU is a diurethane-containing group,

PAO is a divalent polyoxyalkylene, and

CP is selected from acrylates and methacrylates,

wherein said macromer has a number-average molecular weight of 2000 to 10,000;

(b) about 5 to about 60 weight percent methacryloxypropyltris(trimethylsiloxy)silane;

(c) about 1 to about 30 weight percent of an acrylate or methacrylate monomer; and

(d) 0 to 5 weight percent cross-linking agent,

with the weight percentages being based upon the dry weight of the polymer components.

A preferred polysiloxane macromer segment is defined by the formula

CP—PAO—DU—ALK—PDMS—ALK—DU—PAO—CP

where

PDMS is a divalent poly(disubstituted siloxane);

CP is an isocyanatoalkyl acrylate or methacylate, preferably isocyanatoethyl methacrylate, where the urethane group is bonded to the terminal carbon on the PAO group;

PAO is a divalent polyoxyalkylene (which may be substituted), and is preferably a polyethylene oxide, i.e., $(-CH_2-CH_2-O-)_mCH_2CH_2-$ where m may range from about 3 to about 44, more preferably about 4 to about 24;

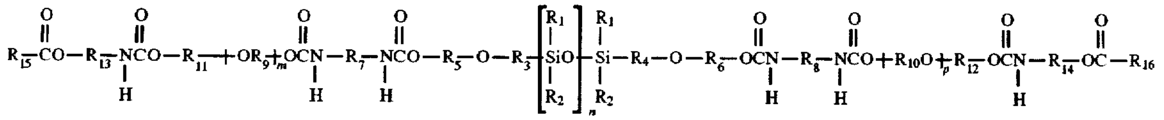
DU is a diurethane, preferably including a cyclic structure,

where an oxygen of the urethane linkage (1) is bonded to the PAO group and an oxygen of the urethane linkage (2) is bonded to the ALK group;

and ALK is an alkylene or alkylenoxy group having at least 3 carbon atoms, preferably a branched alkylene group or an alkylenoxy group having 3 to 6 carbon atoms, and most preferably a sec-butyl (i.e., $-CH_2CH_2CH(CH_3)-$) group or an ethoxypropoxy group (e.g., $-O-(CH_2)_2-O-(CH_2)_3-$).

It will be noted that the DU group can be formed from a wide variety of diisocyanates or triisocyanates, including aliphatic, cycloaliphatic or aromatic polyisocyanates. These isocyanates include, without limitation thereto, ethylene diisocyanate; 1,2-diisocyanatopropane; 1,3-diisocyanatopropane; 1,6-isocyanatohexane; 1,2-diisocyanatocyclohexane; 1,3-diisocyanatocyclohexane; 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl) methane; bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatophenyl)methane; 1,2- and 1,4-toluene diisocyanate; 3,3-dichloro4,4'-diisocyanatobiphenyl; tris(4-isocyanatophenyl)methane; 1,5-diisocyanaphthalene; hydrogenated toluene diisocyanate; 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (i.e., isophorone diisocyanate); 1,3,5-tris(6-isocyanatohexyl) biuret; 1,6-diisocyanato-2,2,4-(2,4,4)-trimethylhexane; 2,2'-diisocyanatodiethyl fumarate; 1,5-diisocyanato-1-carboxypentane; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and 2,3-diisocyanatonaphthalene; 2,4- and 2,7-diisocyanato-1-methylnaphthalene; 1,4-diisocyanatomethylcyclohexane; 1,3-diisocyanato-6(7)-methylnaphthalene; 4,4'-diisocyanatobiphenyl; 4,4'-diisocyanato-3,3'-dimethoxybisphenyl; 3,3'- and 4,4'-diisocyanato-2,2'-dimethylbisphenyl; bis(4-isocyanatophenyl) ethane; bis(4-isocyanatophenyl ether); 1,2- or 1,4-toluene diisocyanate; and mixtures thereof. Preferably DU is formed from isophorone diisocyanate or toluene diisocyanate, and more preferably, isophorone diisocyanate, where one isomeric diurethane structure of isophorone diisocyanate is defined above.

A preferred Material A macromer segment has the following formula:



$$R_{15}-\overset{O}{\overset{\|}{C}}O-R_{13}-\underset{\underset{H}{|}}{N}\overset{O}{\overset{\|}{C}}O-R_{11}-(OR_9)_m-O\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}-R_7-\underset{\underset{H}{|}}{N}\overset{O}{\overset{\|}{C}}O-R_5-O-R_3-\left[\begin{matrix}R_1\\|\\SiO\\|\\R_2\end{matrix}\right]_n-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{Si}}-R_4-O-R_6-O\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}-R_8-\underset{\underset{H}{|}}{N}\overset{O}{\overset{\|}{C}}O-(R_{10}O)_p-R_{12}-O\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}-R_{14}-O\overset{O}{\overset{\|}{C}}-R_{16}$$

wherein:

R_1 and R_2 are lower alkyl (C_1–C_6), preferably C_1–C_3 alkyl, more preferably methyl;

R_3, R_4, R_5, and R_6 are lower alkylene (C_1–C_6), preferably C_1–C_3 alkylene, more preferably C_2–C_3 alkylene, and preferably, where the total number of carbon atoms in R_3 and R_5, or R_4 and R_6 is greater than 4;

R_7 and R_8 are linear or branched alkylene or an bivalent cycloalkylene, preferably bivalent cycloalkylene;

R_9, R_{10}, R_{11}, and R_{12} are C_1–C_2 alkylene, preferably C_2 alkylene;

R_{13} and R_{14} are lower alkylene (C_1–C_6), preferably C_1–C_3 alkylene, more preferably ethylene; and

R_{15} and R_{16} are linear or branched lower alkenylene, preferably C_2–C_3 alkenylene;

m and p, independently of one another, may range from about 3 to about 44, more preferably about 4 to about 24; and

n may range from about 13 to about 80, more preferably, about 20 to about 50, and even more preferably about 24 to about 30.

The polysiloxane macromer may be synthesized by the following preferred process. At about room temperature (about 20°–25° C.), poly(dimethylsiloxane) dialkanol having hydroxyalkyl (e.g., hydroxy-sec-butyl) or hydroxyalkoxy (e.g., hydroxyethylpropoxy) end groups and having a molecular weight of about 2000 to 3000 (preferably about 2200, i.e., having about 28 repeating siloxane groups) is reacted with isophorone diisocyanate at about a 1:2 molar ratio, using about 0.2 weight percent (based on polydimethylsiloxane) dibutyltin dilaurate added as a catalyst. The reaction is carried out for about 36 to 60 hours. To this mixture is added poly(ethylene glycol) having a molecular weight of about 400 to 1200 (more preferably about 500 to 700) at about a 2:1 or 2.1:1 molar ratio with respect to the PDMS, about 0.4 to 0.5 weight percent dibutyltin dilaurate (based on polyethylene glycol weight), and chloroform sufficient to ensure substantial mixture homogeneity. The mixture is agitated for about 12 to 18 hours, then held at a temperature of about 44° to 48° C. for about 6 to 10 hours. Excess chloroform is evaporated therefrom at about room temperature to produce a composition having about 50 weight percent solids. Then, isocyanatoethyl methacrylate is added to the mixture in about a 2:1 to 2.3:1 molar ratio with respect to PDMS. The mixture is agitated at room temperature for about 15 to 20 hours. The resulting solution contains a polysiloxane macromer having the composition described above and a number-average molecular weight of about 2000 to 10,000, more preferably about 3000 to 5000.

An advantageous polymeric material formed from the Material A macromer of the present invention is a copolymer of the aforementioned Material A macromer; an acrylated or methacrylated siloxane monomer, preferably methacryloxypropyltris (trimethylsiloxy) silane (referred to herein as "Tris"); a hydrophilic monomer, preferably 2-hydroxyethyl methacrylate (HEMA); and preferably, a cross-linking agent such as ethylene glycol dimethacrylate (EGDMA). The final copolymer composition includes about 10 to 90, preferably 70 to 90, weight percent polysiloxane macromer; about 5 to 60, preferably about 8 to 20, weight percent siloxane monomer; about 1 to 30, preferably about 1 to 5, weight percent acrylate or methacrylate monomer; and 0 to about 5, preferably up to about 2 weight percent cross-linking agent (e.g., EGDMA) based on a total dry copolymer weight. A more preferred composition includes about 80 to 84 polysiloxane macromer, about 12 to 15 weight percent TRIS, about 3 to about 4 weight percent 2-hydroxyethyl methacrylate, and about 0.7 to about 1.2 weight percent ethylene glycol dimethacrylate.

The advantageous copolymers of the present invention may be formed from the previously-described polysiloxane macromer in the following manner. A monomeric solution is formed by adding Tris, HEMA, DAROCUR® 1173 (a photoinitator available from Ciba-Geigy Corporation), and optionally, EGDMA to the polysiloxane macromer solution. The resulting polymer precursor solution preferably contains about 83 to about 95 weight percent polysiloxane macromer solution, about 5 to about 10 weight percent Tris, about 0.5 to about 5 weight percent HEMA, about 0.1 to about 1.0 weight percent DAROCUR® 1173, and about 0.1 to about 1.0 weight percent EGDMA. More preferably, the monomer solution contains about 87 to about 93 weight percent polysiloxane macromer solution, about 7 to about 8 weight percent Tris, about 2 to about 4 weight percent EEMA, about 0.3 to about 0.7 weight percent DAROCUR® 1173, and about 0.3 to about 0.7 weight percent EGDMA. The monomer solution is preferably agitated for about 8 to about 24 hours prior to the polymerization step.

Contact lenses may be prepared from the monomer solution by applying the monomer solution to appropriate lens molds and applying sufficient ultraviolet (UV) radiation to initiate polymerization. The ultraviolet light may be applied for a period of a few minutes to about 5 hours, depending on the intensity of light applied. Subsequent to polymerization, the contact lens may be extracted with a solvent, e.g., isopropanol, to remove unreacted monomers.

Thus, generally, one embodiment of the present invention is a method of forming a molded polymeric article suitable for ophthalmic applications (especially a contact lens), including the following steps:

(a) contacting a poly(dialkylsiloxane) dialkanol with a diisocyanate compound in the presence of a first catalyst at conditions sufficient to cause reaction of said dialkanol with said diisocyanate, thereby forming a first mixture;

(b) contacting said first mixture with poly(alkylene glycol), a second catalyst, and sufficient solvent to ensure mixture homogeneity, thereby forming a second mixture;

(c) evaporating sufficient solvent from said second mixture to generate a third mixture having a solids content of about 40 to 60 weight percent;

(d) adding isocyanatoalkyl methacrylate to said third mixture, thereby forming a fourth mixture containing a polysiloxane macromer;

(e) adding to said fourth mixture 3-methacryloxypropyltris(trimethylsiloxy)silane

(TRIS), a hydrophilic monomer, a cross-linking agent and a photoinitiator, thereby forming a fifth mixture;

(f) placing said fifth mixture into a mold; and

(g) applying sufficient radiation to copolymerize said monomers, thereby forming said polymeric material into a molded polymeric article.

The hydrophilic copolymers of the present invention are especially advantageous in the formation of "soft" contact lenses. In the use of the copolymers in the contact lens field, the lenses have a water content of about 10 to about 50 weight percent, more preferably about 10 to about 30 weight percent, and most preferably about 15 to about 22 weight percent, based on total hydrophilic polymer weight. Preferably, the fully-hydrated contact lens has an oxygen transmissibility (D_k/t) of greater than 70 barrers/mm (i.e., $[(\text{cc oxygen})(\text{mm})/\text{cm}^2]\times[\text{sec/mm Hg}]\times 10^{-10}$), more preferably greater than about 75 barrers/mm, and most preferably greater than about 87 barrers/mm.

2. Material "B"

Polysiloxane-comprising perfluoroalkyl ethers

The Material "B" macromer is defined by formula (I):

$$P_1—(Y)_m—(L—X_1)p—Q—(X_1—L)_p—(Y)_m—P_1 \qquad (I)$$

where

each P1, independently of the others, is a free-radical-polymerizable group;

each Y, independently of the others, is —CONHCOO—, —CONHCONH—, —OCONHCO—, —NHCONHCO—, —NHCO—, —CONH—, —NHCONH—, —COO—, —OCO—, —NHCOO— or —OCONH—;

m and p, independently of one another, are 0 or 1;

each L, independently of the others, is a divalent radical of an organic compound having up to 20 carbon atoms;

each X_1, independently of the others, is —NHCO—, —CONH—, —NHCONH—, —COO—, —OCO—, —NHCOO— or —OCONH—; and

Q is a bivalent polymer fragment consisting of the segments:

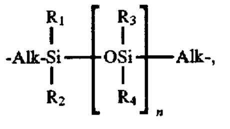
(a) $—(E)_k—Z—CF_2—(OCF_2)_x—(OCF_2CF_2)_y—OCF_2—Z—(E)_k—$,

where x+y is a number in the range of 10 to 30;

each Z, independently of the others, is a divalent radical having up to 12 carbon atoms or Z is a bond;

each E, independently of the others, is $—(OCH_2CH_2)_q—$, where q has a value of from 0 to 2, and where the link —Z—E— represents the sequence $—Z—(OCH_2CH_2)_q—$; and

k is 0 or 1;



$$\text{-Alk-}\underset{R_2}{\overset{R_1}{\text{Si}}}\left[\text{O}\underset{R_4}{\overset{R_3}{\text{Si}}}\right]_n\text{Alk-}, \qquad (b)$$

where

n is an integer from 5 to 100;

Alk is alkylene having up to 20 carbon atoms;

80–100% of the radicals R_1, R_2, R_3 and R_4, independently of one another, are alkyl and 0–20% of the radicals R_1, R_2, R_3 and R_4, independently of one another, are alkenyl, aryl or cyanoalkyl; and

(c) $X_2—R—X_2$,

where R is a divalent organic radical having up to 20 carbon atoms, and

each X_2, independently of the others, is —NHCO—, —CONH—, —NHCONH—, —COO—, —OCO—, —NHCOO— or OCONH—;

with the provisos that there must be at least one of each segment (a), (b), and (c) in Q, that each segment (a) or (b) has a segment (c) attached to it, and that each segment (c) has a segment (a) or (b) attached to it.

The number of segments (b) in the polymer fragment Q is preferably greater than or equal to the number of segments (a). The ratio between the number of segments (a) and (b) in the polymer fragment Q is preferably 3:4, 2:3, 1:2 or 1:1. The molar ratio between the number of segments (a) and (b) in the polymer fragment Q is more preferably 2:3, 1:2 or 1:1.

The mean molecular weight of the polymer fragment Q is in the range of about 1000 to about 20000, preferably in the range of about 3000 to about 15000, particularly preferably in the range of about 5000 to about 12000.

The total number of segments (a) and (b) in the polymer fragment Q is preferably in the range of 2 to about 11, particularly preferably in the range of 2 to about 9, and in particular in the range of 2 to about 7. The smallest polymer unit Q is preferably composed of one perfluoro segment (a), one siloxane segment (b) and one segment (c).

In a preferred embodiment of the polymer fragment Q, which preferably has a composition in the abovementioned ratios, the polymer fragment Q is terminated at each end by a siloxane segment (b).

The compositions in a bivalent polymer fragment Q always correspond above and below to a mean statistical composition. This means that, for example, even individual block copolymer radicals containing identical recurring units are included, so long as the final mean statistical composition is as specified.

X_1 is preferably —NHCONH—, —NHCOO— or —OCONH—, particularly preferably —NHCOO— or —OCONH—.

The $X_2—R—X_2$ segment is preferably a radical derived from a diisocyanate, where each X_2, independently of the other, is NHCONH—, —NHCOO— or —OCONH—, in particular —NHCOO— or —OCONH—.

Z is preferably a bond, lower alkylene or —CONH-arylene, in which the —CO— moiety is linked to a CF_2 group. Z is particularly preferably lower alkylene, in particular methylene.

q is preferably 0, 1, 1.5 or 2, particularly preferably 0 or 1.5.

The perfluoroalkoxy units OCF_2 and OCF_2CF_2 with the indices x and y in segment (a) can either have a random distribution or be in the form of blocks in a chain. The sum of the indices x+y is preferably a number in the range of 10 to 25, particularly preferably of 10 to 15. The ratio x:y is preferably in the range of 0.5 to 1.5, in particular in the range of 0.7 to 1.1.

A free-radical-polymerizable group P_1 is, for example, alkenyl, alkenylaryl or alkenylarylenealkyl having up to 20 carbon atoms. Examples of alkenyl are vinyl, allyl, 1-propen-2-yl, 1-buten-2-, -3- and 4-yl, 2-buten-3-yl, and the isomers of pentenyl hexenyl, octenyl, decenyl and undecenyl. Examples of alkenylaryl are vinylphenyl, vinylnaphthyl or allylphenyl. An example of alkenylarylenealkyl is o-, m-, or p-vinylbenzyl.

P_1 is preferably alkenyl or alkenylaryl having up to 12 carbon atoms, particularly preferably alkenyl having up to 8 carbon atoms, in particular alkenyl having up to 4 carbon atoms.

Y is preferably —COO—, —OCO—, —NHCONH—, —NHCOO—, —OCONH—, NHCO— or —CONH—, particularly preferably —COO—, —OCO—, NHCO— or —CONH—, and in particular, —COO— or —OCO—.

In a preferred embodiment, the indices, m and p, are not simultaneously zero. If p is zero, m is preferably 1.

L is preferably alkylene, arylene, a saturated bivalent cycloaliphatic group having 6 to 20 carbon atoms, arylenealkylene, alkylenearylene, alkylenearylenealkylene or arylenealkylenearylene.

Preferably, L is a divalent radical having up to 12 carbon atoms, particularly preferably a divalent radical having up to 8 carbon atoms. In a preferred embodiment, L is furthermore alkylene or arylene having up to 12 carbon atoms. A particularly preferred embodiment of L is lower alkylene, in particular lower alkylene having up to 4 carbon atoms.

The divalent radical R is, for example, alkylene, arylene, alkylenearylene, arylenealaylene or arylenealkylenearylene having up to 20 carbon atoms, a saturated bivalent cycloaliphatic group having 6 to 20 carbon atoms or cycloalkylenealkylenecycloalkylene having 7 to 20 carbon atoms.

In a preferred embodiment, R is alkylene, arylene, alkylenearylene, arylenealaylene or arylenealkylenearylene having up to 14 carbon atoms or a saturated divalent cycloaliphatic group having 6 to 14 carbon atoms. In a particularly preferred embodiment, R is alkylene or arylene having up to 12 carbon atoms or a saturated bivalent cycloaliphatic group having 6 to 14 carbon atoms.

In a preferred embodiment, R is alkylene or arylene having up to 10 carbon atoms or a saturated bivalent cycloaliphatic group having 6 to 10 carbon atoms.

In a particularly preferred meaning, R is a radical derived from a diisocyanate, for example from hexane 1,6-diisocyanate, 2,2,4-trimethylhexane 1,6-diisocyanate, tetramethylene diisocyanate, phenylene 1,4-diisocyanate, toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, m- or p-tetramethylxylene diisocyanate, isophorone diisocyanate or cyclohexane 1,4-diisocyanate.

In a preferred meaning, n is an integer from 5 to 70, particularly preferably 10 to 50, in particular 14 to 28.

In a preferred meaning, 80–100%, preferably 85–100%, in particular 90–100%, of the radicals R_1, R_2, R_3 and R_4 are, independently of one another, lower alkyl having up to 8 carbon atoms, particularly preferably lower alkyl having up to 4 carbon atoms, especially lower alkyl having up to 2 carbon atoms. A further particularly preferred embodiment of R_1, R_2, R_3 and R_4 is methyl.

In a preferred meaning, 0–20%, preferably 0–15%, in particular 0–10%, of the radicals R_1, R_2, R_3 and R_4 are, independently of one another, lower alkenyl, unsubstituted or lower alkyl- or lower alkoxy-substituted phenyl or cyano (lower alkyl).

Arylene is preferably phenylene or naphthylene, which is unsubstituted or substituted by lower alkyl or lower alkoxy, in particular 1,3-phenylene, 1,4-phenylene or methyl-1,4-phenylene, 1,5-naphthylene or 1,8-naphthylene.

Aryl is a carbocyclic aromatic radical which is unsubstituted or substituted preferably by lower alkyl or lower alkoxy. Examples are phenyl, tolyl, xylyl, methoxyphenyl, t-butoxyphenyl, naphthyl and phenanthryl.

A saturated bivalent cycloaliphatic group is preferably cycloalkylene, for example cyclohexylene or cyclohexylene (lower alkylene), for example cyclohexylenemethylene, which is unsubstituted or substituted by one or more lower alkyl groups, for example methyl groups, for example trimethylcyclohexylenemethylene, for example the bivalent isophorone radical.

For the purposes of the present invention, the term "lower" in connection with radicals and compounds, unless defined otherwise, denotes, in particular, radicals or compounds having up to 8 carbon atoms, preferably having up to 4 carbon atoms.

Lower alkyl has, in particular, up to 8 carbon atoms, preferably up to 4 carbon atoms, and is, for example, methyl, ethyl, propyl, butyl, tert-butyl, pentyl, hexyl or isohexyl.

Alkylene has up to 12 carbon atoms and can be straight-chain or branched. Suitable examples are decylene, octylene, hexylene, pentylene, butylene, propylene, ethylene, methylene, 2-propylene, 2-butylene, 3-pentylene, and the like.

Lower alkylene is alkylene having up to 8 carbon atoms, particularly preferably up to 4 carbon atoms. Particularly preferred meanings of lower alkylene are propylene, ethylene and methylene.

The arylene unit in alkylenearylene or arylenealkylene is preferably phenylene, unsubstituted or substituted by lower alkyl or lower alkoxy, and the alkylene unit therein is preferably lower alkylene, such as methylene or ethylene, in particular methylene. These radicals are therefore preferably phenylenemethylene or methylenephenylene.

Lower alkoxy has, in particular, up to 8 carbon atoms, preferably up to 4 carbon atoms, and is, for example, methoxy, ethoxy, propoxy, butoxy, tert-butoxy or hexyloxy.

Arylenealkylenearylene is preferably phenylene(lower alkylene)phenylene having up to 8, in particular up to 4, carbon atoms in the alkylene unit, for example phenyleneethylenephenylene or phenylenemethylenephenylene.

The macromers of the formula (I) can be prepared by processes known per se, for example as follows:

In a first step, a perfluoropolyalkyl ether derivative of formula (IV):

$$X_3—(E)_k—Z—CF_2—(OCF_2)_x—(OCF_2CF_2)_y—OCF_2—Z—(E)_k—X_3 \qquad (IV)$$

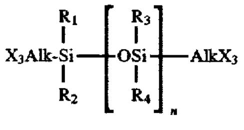
in which X_3 is —OH, —NH_2, —COOH, —COCl, —NCO or —$COOR_5$, where —$COOR_5$ is generally an activated ester in which R_5 is alkyl or aryl which is unsubstituted or substituted by halogen or cyano, and the variables Z, E, k, x and y are as defined above, is preferably reacted with two equivalents of a bifunctional radical of formula (V):

$$X_4—R—X_4 \qquad (V)$$

in which R is as defined above and X_4 is a functional radical which is coreactive with an X_3 and is preferably —OH—, —NH_2, COOH, —COCl, —$COOR_5$ or —NCO; in the presence or absence of a suitable catalyst, where the reaction of X_3 with X_4 gives a group X_2; after which a reactive derivative of formula (VI):

$$X_4—R—X_2—(E)_k—Z—CF_2—(OCF_2)_x—(OCF_2CF_2)_y—OCF_2—Z—(E)_k—X_2—R—X_4) \qquad (VI)$$

is obtained which is then preferably reacted with two equivalents of an α,ω-substituted siloxane of formula (VII):

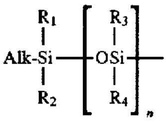


$$X_3Alk\text{-}\underset{R_2}{\overset{R_1}{Si}}—\left[O\underset{R_4}{\overset{R_3}{Si}}\right]_n—AlkX_3 \qquad (VII)$$

where the variables R_1, R_2, R_3, R_4, n, X_3 and Alk are as defined above, in the presence or absence of a suitable catalyst, giving a compound of formula (VIII):

$$X_3—Sil—X_2—R—X_2—PFPE—X_2—R—X_2—Sil—X_3 \qquad (VIII)$$

in which PFPE is $(E)_k$—Z—CF_2—$(OCF_2)_x$—$(OCF_2CF_2)_y$—OCF_2—Z—$(E)_k$, Sil is the siloxane radical



$$\mathrm{Alk}-\overset{R_1}{\underset{R_2}{\mathrm{Si}}}-\left[\mathrm{O}\overset{R_3}{\underset{R_4}{\mathrm{Si}}}\right]_n-\mathrm{Alk}$$

and the other variables are as defined above; after which the reactive intermediate of the formula (VIII) is preferably reacted with two equivalents of a compound of the formula (IXa) or (IXb):

$$P_1—(Y)_m—L—X_4 \qquad \text{(IXa)}$$

$$P_1—Y_2 \qquad \text{(IXb)}$$

in the presence or absence of a catalyst, to give the macromer of the formula (I):

$$P_1—(Y)_m—(L—X_1)_p—Q—(X_1—L)_p—(Y)_m—P_1 \qquad \text{(I)}$$

in which Y_2 is a functional radical which is coreactive with X_3 and is preferably —OH, —NH_2, —COOH, —COCl, —$COOR_5$, —CONCO or —NCO, and the variables are as defined above, and in which X_1 is formed from the reaction of X_3 with X_4 and Y is formed from the reaction of Y_2 with X_3.

The starting materials of formula (IV) for the preparation of the perfluoroalkyl ethers are known and many are commercially available. For example, U.S. Pat. No. 3,810,875 and European Patent No. 0211237 (U.S. Pat. No. 4,746,575) describe such compounds. Ausimont, Italy, markets perfluoroalkyl ether dimethanols under the name Fomblin, for example Fomblin ZDOL and Fomblin ZDOL-TX. Further Fomblin derivatives of the formula (IV) are commercially available, including, for example, Fomblin ZDISOC, in which the radical —Z—X_3 in the formula (IV) is CONH—$C_6H_3(CH_3)$—NCO; Fomblin ZDEAL, in which the radical Z—X_3 in the formula (IV) is —$COOR_5$; and Fomblin ZDIAC, in which the radical —Z—X_3 in the formula (IV) is —COOH.

Bifunctional radicals having a substitution pattern as per formula (V) exist in large numbers and are commercially available. Examples include, without limitation thereto: diisocyanates, such as isophorone diisocyanate and 2,2,4-trimethylhexane 1,6-diisocyanate; diols, such as glycol and cyclohexane-1,2-diol; dicarboxylic acids, such as adipic acid and maleic acid; diamines, such as ethylenediamine and hexamethylenediamine, diesters, such as diethyl phthalate and dibutyl malonate; derivatives containing various functional groups, such as 2-aminoethanol, monomethyl malonate, glycolic acid, salicylic acid, glycine and glycine methyl ester.

Preference is given to bifunctional derivatives of the formula (V) which have different reactivities irrespective of the nature of their functional radicals X_4. In the case of identical radicals X_4, this is achieved, for example, through different steric requirements in the direct vicinity of a radical X_4. Examples thereof are isophorone diisocyanate, 2,2,4-trimethylhexane 1,6-diisocyanate and toluene 2,4-diisocyanate. The advantage of using bifunctional derivatives of formula (V) of different reactivity is that the chain length of polymer Q (number of segments (a), (b) and (c)) is easily adjustable and controllable.

α,ω-substituted siloxanes of formula (VII) are likewise commercially available, for example α,ω-hydroxypropyl-terminated polydimethylsiloxane KF6001 from Shin-Etsu.

The novel compounds can be prepared in the presence or absence of a solvent. It is advantageous to use a substantially inert solvent, i.e., one which does not participate in the reaction. Suitable examples thereof are ethers, such as tetrahydrofuran (THF), diethyl ether, diethylene glycol dimethyl ether or dioxane, halogenated hydrocarbons, such as chloroform or methylene chloride, bipolar aprotic solvents, such as acetonitrile, acetone, dimethylformamide (DMF) or dimethyl sulfoxide (D)MSO), hydrocarbons, such as hexane, petroleum ether, toluene or xylene, and furthermore pyridine or N-methylmorpholine.

In the preparation of novel compounds, the reactants are advantageously employed in stoichiometric amounts. The reaction temperature can be, for example, from −30° C. to 150° C., preferably from 0° to room temperature. The reaction times are in the range of about 15 minutes to 7 days, preferably about 12 hours. If necessary, the reaction is carried out under argon or nitrogen as protective gas. In urethane-forming reactions, a suitable catalyst, for example, so dibutyltin dilaurate (DBTDL), is advantageously added.

The present Material "B" furthermore relates to a polymer comprising a product of the polymerization of at least one compound of formula (I) as defined above and, if desired, at least one vinylic comonomer (a). In a preferred composition of a novel copolymer, the proportion by weight of a compound of formula (I) is in the range of 100 to 0.5%, in particular in the range of 80 to 10%, preferably in the range of 70 to 30%, based on the total polymer.

In a preferred polymer comprising a product of the polymerization of at least one compound of the formula (I), comonomer (a) is absent and the polymer is a homopolymer.

A comonomer (a) present in the novel polymer can be hydrophilic or hydrophobic or a mixture thereof. Suitable comonomers are, in particular, those which are usually used in the production of contact lenses and biomedical materials. A hydrophobic comonomer (a) is taken to mean a monomer which typically gives a homopolymer which is insoluble in water and can absorb less than 10% by weight of water. Analogously, a hydrophilic comonomer (a) is taken to mean a monomer which typically gives a homopolymer which is soluble in water or can absorb at least 10% by weight of water. Suitable hydrophobic comonomers (a) are, without limitation thereto, C_1–C_{18}alkyl and C_3–C_{18}cycloalkyl acrylates and methacrylates, C_3–C_{18}alkylacrylamides and -methacrylamides, acrylonitrile, methacrylonitrile, vinyl C_1–C_{18}alkanoates, C_2–C_{18}alkenes, C_2–C_{18}haloalkenes, styrene, (lower alkyl)styrene, lower alkyl vinyl ethers, C_2–C_{10}perfluoroalkyl acrylates and methacrylates and correspondingly partially fluorinated acrylates and methacrylates, C_3–C_{12}perfluoroalkylethylthiocarbonylaminoethyl acrylates and methacrylates, acryloxy- and methacryloxyalkylsiloxanes, N-vinylcarbazole, C_1–C_{12}alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like.

Preference is given, for example, to acrylonitrile, C_1–C_4alkyl esters of vinylically unsaturated carboxylic acids having 3 to 5 carbon atoms or vinyl esters of carboxylic acids having up to 5 carbon atoms.

Examples of suitable hydrophobic comonomers (a) are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl acrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyltoluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl methacrylate, tristrimethylsilyloxysilylpropyl methacrylate (TRIS), 3-methacryloxy propylpentamethyldisiloxane and bis(methacryloxypropyl) tetramethyldisiloxane.

Preferred examples of hydrophobic comonomers (a) are methyl methacrylate, TRIS and acrylonitrile.

Suitable hydrophilic comonomers (a) are, without this being an exhaustive list, hydroxyl-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, (lower alkyl)acrylamides and -methacrylamides, ethoxylated acrylates and methacrylates, hydroxyl-substituted (lower alkyl)acrylamides and -methacrylamides, hydroxyl-substituted lower alkyl vinyl ethers, sodium vinylsulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinyl-2-pyrrolidone, 2-vinyloxazoline, 2-vinyl-4,4'-dialkyloxazolin-5-one, 2- and 4-vinylpyridine, vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms, amino(lower alkyl)- (where the term "amino" also includes quaternary ammonium), mono(lower alkylamino)(lower alkyl) and di(lower alkylamino)(lower alkyl) acrylates and methacrylates, allyl alcohol and the like. Preference is given, for example, to N-vinyl-2-pyrrolidone, acrylamide, methacrylamide, hydroxyl-substituted lower alkyl acrylates and methacrylates, hydroxy-substituted (lower alkyl) acrylamides and -methacrylamides and vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms.

Examples of suitable hydrophilic comonomers (a) are hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate, hydroxypropyl acrylate, trimethylammonium 2-hydroxy propylmethacrylate hydrochloride (Blemer® QA, for example from Nippon Oil), dimethylaminoethyl methacrylate (DMAEMA), dimethylaminoethylmethacrylamide, acrylamide, methacrylamide, N,N-dimethylacrylamide (DMA), allyl alcohol, vinylpyridine, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-vinyl-2-pyrrolidone (NVP), acrylic acid, methacrylic acid and the like.

Preferred hydrophilic comonomers (a) are trimethylammonium 2-hydroxy propylmethacrylate hydrochloride, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, trimethylammonium 2-hydroxypropylmethacrylate hydrochloride, N,N-dimethylacrylamide and N-vinyl-2-pyrrolidone.

The novel polymers are synthesized in a manner known per se from the corresponding monomers (the term monomer here also including a macromer according to the definition of the formula (I)) by a polymerization reaction customary to the person skilled in the art. Usually, a mixture of the abovementioned monomers is warmed with addition of a free-radical former. Examples of such free-radical formers are azoisobutyronitrile (AIBN), potassium peroxodisulfate, dibenzoyl peroxide, hydrogen peroxide and sodium percarbonate. If, for example, said compounds are warmed, free radicals form with homolysis, and can then initiate, for example, a polymerization.

A polymerization reaction can particularly preferably be carried out using a photoinitiator. In this case, the term photopolymerization is used. In the photopolymerization, it is appropriate to add a photoinitiator which can initiate free-radical polymerization and/or crosslinking by using light. Examples thereof are customary to the person skilled in the art; suitable photoinitiators are, in particular, benzoin methyl ether, 1-hydroxycyclohexylphenyl ketone, Darocur and Irgacur products, preferably Darocur® 1173 and Irgacur® 2959. Also suitable are reactive photoinitiators, which can be incorporated, for example, into a macromer, or can be used as a specific comonomer (a). Examples thereof are given in European Patent No. 0632329. The photopolymerization can then be initiated by actinic radiation, for example light, in particular UV light having a suitable wavelength. The spectral requirements can, if necessary, be controlled appropriately by addition of suitable photosensitizers.

A polymerization can be carried out in the presence or absence of a solvent. Suitable solvents are in principle all solvents which dissolve the monomers used, for example water, alcohols, such as lower alkanols, for example ethanol or methanol, furthermore carboxamides, such as dimethylformamide, dipolar aprotic solvents, such as dimethyl sulfoxide or methyl ethyl ketone, ketones, for example acetone or cyclohexanone, hydrocarbons, for example toluene, ethers, for example THF, dimethoxyethane or dioxane, halogenated hydrocarbons, for example trichloroethane, and also mixtures of suitable solvents, for example mixtures of water and an alcohol, for example a water/ethanol or water/methanol mixture.

A polymer network can, if desired, be reinforced by addition of a crosslinking agent, for example a polyunsaturated comonomer (b). In this case, the term crosslinked polymers is used. The invention, therefore, furthermore relates to a crosslinked polymer comprising the product of the polymerization of a macromer of the formula (I), if desired with at least one vinylic comonomer (a) and with at least one comonomer (b).

Examples of typical comonomers (b) are allyl (meth) acrylate, lower alkylene glycol di(meth)acrylate, poly(lower alkylene) glycol di(meth)acrylate, lower alkylene di(meth) acrylate, divinyl ether, divinyl sulfone, di- and trivinylbenzene, trimethylolpropane tri(meth)acrylate, pentaerythrritol tetra(meth)acrylate, bisphenol A di(meth) acrylate, methylenebis(meth)acrylamide, triallyl phthalate and diallyl phthalate.

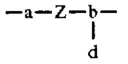
The amount of comonomer (b) used is expressed in a proportion by weight based on the total polymer and is in the range from 20 to 0.05%, in particular in the range from 10 to 0.1%, preferably in the range from 2 to 0.1%.

3. Material "C"

Material "C" polymers are formed by polymerizing polymerizable macromers which contain free hydroxyl groups. Macromers which are built up, for example, from an amino-alkylated polysiloxane which is derivatized with at least one polyol component containing an unsaturated polymerizable side chain are disclosed. Polymers can be prepared on the one hand from the macromers according to the invention by homopolymerization. The macromers mentioned furthermore can be mixed and polymerized with one or more hydrophilic and/or hydrophobic comonomers. A special property of the macromers according to the invention is that they function as the element which controls microphase separation between selected hydrophilic and hydrophobic components in a crosslinked end product. The hydrophilic/hydrophobic microphase separation is in the region of less than 300 nm. The macromers are preferably crosslinked at the phase boundaries between, for example, an acrylate comonomer on the one hand and an unsaturated polymerizable side chain of polyols bonded to polysiloxane on the other hand, by covalent bonds and additionally by reversible physical interactions, for example hydrogen bridges. These are formed, for example, by numerous amide or urethane groups. The continuous siloxane phase which exists in the phase composite has the effect of producing a surprisingly high permeability to oxygen.

The present embodiment of the invention relates to a macromer comprising at least one segment of the formula

(I):



(I)

$$-a-Z-\underset{\textstyle d}{\underset{|}{b}}-$$

in which

(a) is a polysiloxane segment,

(b) is a polyol segment which contains at least 4 C atoms,

Z is a segment (c) or a group X_1,

(c) is defined as X_2—R—X_2, wherein

R is a bivalent radical of an organic compound having up to 20 C atoms and

each X_2 independently of the other is a bivalent radical which contains at least one carbonyl group,

X_1 is defined as X_2, and

(d) is a radical of the formula (II):

$$X_3—L—(Y)_k—P_1 \qquad \text{(II)}$$

in which

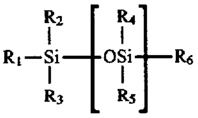
P_1 is a group which can be polymerized by free radicals;

Y and X_3 independently of one another are a bivalent radical which contains at least one carbonyl group;

k is 0 or 1 and

L is a bond or a divalent radical having up to 20 C atoms of an organic compound.

A polysiloxane segment (a) is derived from a compound of the formula (III):



(III)

$$R_1-\underset{R_3}{\overset{R_2}{\overset{|}{\underset{|}{Si}}}}-\left[O\underset{R_5}{\overset{R_4}{\overset{|}{\underset{|}{Si}}}}\right]-R_6$$

in which

n is an integer from 5 to 500;

99.8–25% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are alkyl and 0.2–75% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are partly fluorinated alkyl, aminoalkyl, alkenyl, aryl, cyanoalkyl, alk—NH—alk—NH_2 or alk—$(OCH_2)_m$—(OCH_2)p—OR_7,

R_7 is hydrogen or lower alkyl, alk is alkylene, and

m and p independently of one another are an integer from 0 to 10, one molecule containing at least one primary amino or hydroxyl group.

The alkylenoxy groups —$(OCH_2CH_2)_m$ and —$(OCH_2)_p$ in the siloxane of the formula (III) are either distributed randomly in a ligand alk—$(OCH_2CH_2)_m$—$(OCH_2)_p$—OR_7 or are distributed as blocks in a chain.

A polysiloxane segment (a) is linked a total of 1–50 times, preferably 2–30 times, and in particular 4–10 times, via a group Z with a segment (b) or another segment (a), Z in an a-Z-a sequence always being a segment (c). The linkage site in a segment (a) with a group Z is an amino or hydroxyl group reduced by one hydrogen.

In a preferred embodiment, a polysiloxane segment is derived from a compound of the formula (III) in which the radicals R_1, R_2, R_3, R_4, R_5 and R_6 are a total of 1–50 times, more preferably 2–30 times, and in particular 4–10 times, independently either terminally or pendently aminoalkyl or hydroxyalkyl, the other variables being as defined above.

In a preferred embodiment, a polysiloxane segment is derived from a compound of the formula (III) in which 95–29% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are alkyl and 5–71% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are partly fluorinated alkyl, aminoalkyl, alkenyl, aryl, cyanoalkyl, alk—NH—alk—NH_2 or alk—$(OCH_2CH_2)_m$—$(OCH_2)_p$—OR_7, and in which the variables are as defined above.

In a preferred meaning, n is an integer from 5 to 400, more preferably 10 to 250 and particularly preferably 12 to 125.

In a preferred meaning, the two terminal radicals R_1 and R_6 are aminoalkyl or hydroxyalkyl, the other variables being as defined above.

In another preferred meaning, the radicals R_4 and R_5 are 1–50 times, more preferably 2–30 times and in particular 4–10 times pendently aminoalkyl or hydroxyalkyl and the other variables are as defined above.

In another preferred meaning, the radicals R_1, R_2, R_3, R_4, R_5 and R_6 are a total of 1–50 times, more preferably 2–30 times and in particular 4–10 times, independently both terminally and pendently aminoalkyl or hydroxyalkyl and the other variables are as defined above.

If Z is X_1, X_1 is a bivalent group which contains at least one carbonyl group. A carbonyl group mentioned is flanked in any manner, if appropriate, by —O—, —CONH—, —NHCO— or —NH—.

Examples of bivalent groups Z are typically carbonyls, esters, amides, urethanes, ureas or carbonates.

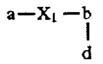
X_1 is preferably an ester, amide, urethane or urea group, in particular an ester or amide group.

X_2 is defined in the same way as X_1 and is preferably an ester, amide, urethane, carbonate or urea group, more preferably an ester, amide, urethane or urea group and in particular an amide, urethane or urea group.

If Z in formula (I) is X_1, a polyol segment b is preferably understood as meaning a polyol derived from a carbohydrate, carbohydrate monolactone or carbohydrate dilactone. A carbohydrate is understood as meaning a mono-, di-, tri-, tetra-, oligo- or polysaccharide. A carbohydrate lactone is understood as meaning the lactone of an aldonic or uronic acid. An aldonic or uronic acid is, for example, a carboxylic acid formed by oxidation of a mono-, di-, tri-, tetra-, oligo- or polysaccharide. Examples of aldonic acid lactones are gluconolactone, galactonolactone, lactobionolactone or maltoheptaonolactone; examples of uronic acid lactones are glucuronic acid lactone, mannuronic acid lactone or iduronic acid lactone. An example of a carbohydrate dilactone is D-glucaro-1,4:6,3-dilactone.

A carbohydrate lactone reacts, for example, with a primary amino group or a hydroxyl group of segment (a) to form a covalent amide or ester bond of the type X_1. Such linkages are the constituent of a further preferred embodiment of macromers according to the invention. Such macromers have an alternating distribution of segments of type (a) and (b) which are interrupted by X_1.

This embodiment of the invention preferably relates to a macromer of the formula (IV):

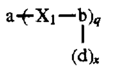


(IV)

$$a-X_1-\underset{\textstyle d}{\underset{|}{b}}$$

in which the variables are as defined above.

An embodiment of the invention furthermore preferably relates to a macromer according to formula (V):



(V)

$$a(-X_1-\underset{\textstyle (d)_x}{\underset{|}{b}})_q$$

in which

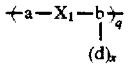
the polysiloxane segment (a) contains q pendent ligands x is 0, 1 or 2,

q has an average numerical value of 1–20, preferably 1–10, and in particular 1–5,

and

the segments (b) in a macromer according to the formula (V) are linked in total (per molecule) with up to 20, preferably with up to 15, and in particular with up to 6 polymerizable segments (d).

An embodiment of the invention furthermore preferably relates to a macromer according to formula (VI):



$$\left[a - X_1 - \underset{(d)_x}{\underset{|}{b}} \right]_q \qquad \text{(VI)}$$

in which

a linear sequence is present,

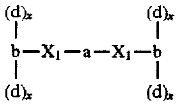
x is 0, 1 or 2,

q has an average numerical value of 1–20, preferably 1–10, and in particular 1–5,

and

the segments (b) in a macromer according to the formula (VI) are linked in total (per molecule) with up to 20, preferably with up to 15, and in particular with up to 6 polymerizable segments (d).

An embodiment of the invention furthermore very preferably relates to a macromer according to formula (VII):



$$\begin{array}{c} (d)_x \\ | \\ b \\ | \\ (d)_x \end{array} - X_1 - a - X_1 - \begin{array}{c} (d)_x \\ | \\ b \\ | \\ (d)_x \end{array} \qquad \text{(VII)}$$

in which x is 0, 1 or 2, and

the average number of segments (d) per molecule of the formula (VII) is preferably in the range from 2 to 5, and very preferably is in the range from 3 to 4.

A polyol segment (b) is derived from a polyol which carries no lactone group if the group Z is a segment (c). Examples of such polyols are a 1,2-polyol, for example the reduced monosaccharides, for example mannitol, glucitol, sorbitol or iditol, a 1,3-polyol, for example polyvinyl alcohol (PVA), which is derived from partly or completely hydrolysed polyvinyl acetate, and furthermore amino-terminal PVA telomers, aminopolyols, aminocyclodextrins, aminomono-, -di-, -tri-, -oligo- or -polysaccharides or cyclodextrin derivatives, for example hydroxypropylcyclodextrin. An abovementioned carbohydrate dilactone can be reacted, for example, with preferably 2 equivalents of an amino-terminal PVA telomer to give a polyol macromer which carries, in the central part the carbohydrate compound derived from the dilactone. Such polyols of this composition are likewise understood to be a suitable polyol.

As illustrated in formula (I), a segment (b) carries at least one vinylic polymerizable segment (d), a linkage of a segment (d) via the bivalent radical X_3 thereof to an amino or hydroxyl group, of a segment (b), reduced by a hydrogen atom being intended.

A vinylic polymerizable segment (d) is incorporated either terminally or pendently preferably 1–20 times, more preferably 2–15 times, and in particular 2–6 times, per macromer molecule according to the invention.

A vinylic polymerizable segment (d) is incorporated terminally and also pendently as desired (as a terminal/pendent mixture) preferably 1–20 times, more preferably 2–15 times and in particular 2–6 times, per macromer molecule according to the invention.

A group P_1 which can be polymerized by free radicals is, for example, alkenyl, alkenylaryl or alkenylarylenealkyl having up to 20 C atoms. Examples of alkenyl are vinyl, allyl, 1-propen-2-yl, 1-buten-2- or -3- or -4-yl, 2-buten-3-yl and the isomers of pentenyl, hexenyl, octenyl, decenyl or undecenyl. Examples of alkenylaryl are vinylphenyl, vinylnaphthyl or allylphenyl. An example of alkenylarylenealkyl is vinylbenzyl.

P_1 is preferably alkenyl or alkenylaryl having up to 12 C atoms, more preferably alkenyl having up to 8 C atoms and in particular alkenyl having up to 4 C atoms.

L is preferably alkylene, arylene, a saturated bivalent cycloaliphatic group having 6 to 20 carbon atoms, arylenealkylene, alkylenearylene, alkylenearylenealaylene or arylenealkylenearylene. In a preferred meaning, L furthermore is preferably a bond.

In a preferred meaning, L is a divalent radical having up to 12 C atoms, and more preferably a divalent radical having up to 8 C atoms. In a preferred meaning, L furthermore is allylene or arylene having up to 12 C atoms. A very preferred meaning of L is lower alkylene, in particular lower alkylene having up to 4 C atoms.

Y is preferably a carbonyl, ester, amide or urethane group, in particular a carbonyl, ester or amide group, and very preferably a carbonyl group.

In another preferred meaning, Y is absent, i.e., k is 0.

In a preferred meaning, X_3 is a urethane, urea, ester, amide or carbonate group, more preferably a urethane, urea, ester or amide group, and in particular a urethane or urea group. A vinylic polymerizable segment (d) is derived, for example, from acrylic acid, methacrylic acid, methacryloyl chloride, 2-isocyanatoethyl methacrylate (IEM), allyl isocyanate, vinyl isocyanate, the isomeric vinylbenzyl isocyanates or adducts of hydroxyethyl methacrylate (HEMA) and 2,4-tolylene diisocyanate (TDI) or isophorone diisocyanate (IPDI), in particular the 1:1 adduct. The invention furthermore preferably relates to a macromer in which a segment (d) is incorporated either terminally or pendently or as a terminal/pendent mixture 5 times. The invention furthermore preferably relates to a macromer in which a segment (d) is incorporated terminally 5 times.

The diradical R is, for example, alkylene, arylene, alkylenearylene, arylenealkylene or arylenealkylenearylene having up to 20 carbon atoms, a saturated bivalent cycloaliphatic group having 6 to 20 carbon atoms or cycloalklenealkylenecycloalkylene having 7 to 20 carbon atoms.

In a preferred meaning, R is alkylene, arylene, alkylenearylene, arylenealkylene or arylenealkylenearylene having up to 14 carbon atoms or a saturated bivalent cycloaliphatic group having 6 to 14 carbon atoms.

In a preferred meaning, R is alkylene, arylene, alkylenearylene or arylenealkylene having up to 14 carbon atoms, or a saturated bivalent cycloaliphatic group having 6 to 14 carbon atoms. In a preferred meaning, R is alkylene or arylene having up to 12 carbon atoms, or a saturated bivalent cycloaliphatic group having 6 to 14 carbon atoms.

In a preferred meaning, R is alkylene or arylene having up to 10 carbon atoms, or is a saturated bivalent cycloaliphatic group having 6 to 10 carbon atoms.

In a very preferred meaning, a segment (c) is derived from a diisocyanate, for example from hexane 1,6-diisocyanate, 2,2,4-trimethylhexane 1,6diisocyanate, tetramethylene diisocyanate, phenylene 1,4-diisocyanate, toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, m- or p-tetramethylxylene diisocyanate, isophorone diisocyanate or cyclohexane 1,4-diisocyanate.

A preferred embodiment of segment (c) is furthermore derived from a diisocyanate in which the isocyanate groups have different reactivities. The different reactivity is influenced, in particular, by the spatial requirements and/or electron density in the neighbourhood of an isocyanate group.

The average molecular weight of a macromer according to the invention is preferably in the range from about 300 to about 30,000, very preferably in the range from about 500 to about 20,000, more preferably in the range from about 800 to about 12,000, and particularly preferably in the range from about 1000 to about 10,000.

A preferred embodiment of the macromer has a segment sequence of the formula (VIII):

$$b—Z—a—\{c—a\}_r—(Z—b)_t \qquad \text{(VIII)}$$

in which

- r is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3;
- t is 0 or 1, and preferably 1;
- a linear (c—a) chain which may or may not be terminated by a segment (b) is present (t=1); and
- the above preferences apply to the total number of segments (d), which are preferably bonded to a segment (b).

A preferred embodiment of the macromer has a segment sequence of formula (IX):

$$b—Z—a—\{c—a—(Z—b)_t\}_r \qquad \text{(IX)}$$

in which

- the sequence (c—a)—(Z—b)t hangs pendently r times on the segment (a) and may or may not be terminated by a segment (b);
- r is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3;
- t is 0 or 1, and is preferably 1;
- Z is a segment (c) or a group X_1; and
- the above preferences apply to the total number of segments (d), which are preferably bonded to a segment (b).

Another preferred embodiment of the macromer has a segment sequence of formula (X):

$$b—c—\{a—c\}_s—B \qquad \text{(X)}$$

in which

- s is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3;
- B is a segment (a) or (b); and
- the above preferences apply to the number of segments (d), which are bonded to a segment (b).

Another preferred embodiment of the macromer has a segment sequence of the formula (X):

$$B—(c—b)_s—Z—a—(b)_t \qquad \text{(XI)}$$

in which

- the structures are linear,
- s is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3;
- B is a segment (a) or (b);
- t is 0 or 1, and
- the above preferences apply to the number of segments (d), which are bonded to a segment (b).

The ratio of the number of segments (a) and (b) in a macromer according to the Material "C" embodiment of the invention is preferably in a range of (a):(b)=3:4, 2:3, 1:2, 1:1, 1:3 or 1:4. The total sum of segments (a) and (b) or, where appropriate, (a) and (b) and (c) is in a range from 2 to 50, preferably 3 to 30, and in particular in the range from 3 to 12.

Alkyl has up to 20 carbon atoms and can be straight-chain or branched. Suitable examples include dodecyl, octyl, hexyl, pentyl, butyl, propyl, ethyl, methyl, 2-propyl, 2-butyl or 3-pentyl.

Arylene is preferably phenylene or naphthylene, which is unsubstituted or substituted by lower alkyl or lower alkoxy, in particular 1,3-phenylene, 1,4-phenylene or methyl-1,4-phenylene; or 1,5-naphthylene or 1,8-naphthylene.

Aryl is a carbocyclic aromatic radical, which is unsubstituted or substituted by preferably lower alkyl or lower alkoxy. Examples are phenyl, toluyl, xylyl, methoxyphenyl, t-butoxyphenyl, naphthyl or phenanthryl.

A saturated bivalent cycloaliphatic group is preferably cycloalkylene, for example cyclohexylene or cyclohexylene-lower alkylene, for example cyclohexylenemethylene, which is unsubstituted or substituted by one or more lower alkyl groups, for example methyl groups, for example trimethylcyclohexylenemethylene, for example the bivalent isophorone radical. The term "lower" in the context of this invention in connection with radicals and compounds, unless defined otherwise, means, in particular, radicals or compounds having up to 8 carbon atoms, preferably having up to 4 carbon atoms.

Lower alkyl has, in particular, up to 8 carbon atoms, preferably up to 4 carbon atoms, and is, for example, methyl, ethyl, propyl, butyl, tert-butyl, pentyl, hexyl or isohexyl.

Alkylene has up to 12 carbon atoms and can be straight-chain or branched. Suitable examples include decylene, octylene, hexylene, pentylene, butylene, propylene, ethylene, methylene, 2-propylene, 2-butylene or 3-pentylene.

Lower alkylene is alkylene having up to 8, and particularly preferably having up to 4 carbon atoms. Particularly preferred examples of lower alkylenes are propylene, ethylene and methylene.

The arylene unit of alkylenearylene or arylenealkylene is preferably phenylene, which is unsubstituted or substituted by lower alkyl or lower alkoxy, and the alkylene unit of this is preferably lower alkylene, such as methylene or ethylene, in particular methylene. Such radicals are therefore preferably phenylenemethylene or methylenephenylene.

Lower alkoxy has, in particular, up to 8 carbon atoms, preferably up to 4 carbon atoms, and is, for example, methoxy, ethoxy, propoxy, butoxy, tert-butoxy or hexyloxy.

Partly fluorinated alkyl is understood as meaning alkyl in which up to 90%, preferably up to 70%, and in particular up to 50%, of the hydrogens are replaced by fluorine.

Arylenealkylenearylene is preferably phenylene-lower alkylene-phenylene having up to 8, and in particular having up to 4 carbon atoms in the alkylene unit, for example phenylenethylenephenylene or phenylenemethylenephenylene.

A monosaccharide in the context of the present invention is understood as meaning an aldopentose, aldohexose, aldotetrose, ketopentose or ketohexose.

Examples of an aldopentose are D-ribose, D-arabinose, D-xylose or D-lyose; examples of an aldohexose are D-allose, D-altrose, D-glucose, D-mannose, D-gulose, D-idose, D-galactose, D-talose, L-fucose or L-rhamnose; examples of a ketopentose are D-ribulose or D-xylulose; examples of a tetrose are D-erythrose or threose; and examples of a ketohexose are D-psicose, D-fructose, D-sorbose or D-tagatose. Examples of a disaccharide are trehalose, maltose, somaltose, cellobiose, gentiobiose, saccharose, lactose, chitobiose, N,N-diacetylchitobiose, palatinose or sucrose. Raffinose, panose or maltotriose may be mentioned as an example of a trisaccharide. Examples of an oligosaccharide are maltotetraose, maltohexaose, chitoheptaose and furthermore cyclic oligosaccharides, such as cyclodextrins.

Cyclodextrins contain 6 to 8 identical units of α-1,4-glucose. Some examples are α-, β- and γ-cyclodextrin, derivatives of such cyclodextrins, for example hydroxypropylcyclodextrins, and branched cyclodextrins.

The macromers according to this embodiment of invention can be prepared by processes known per se, for example as follows.

In a first step, a polysiloxane containing at least one primary amino- or hydroxyalkyl group is reacted with a carbohydrate lactone, an amide or ester bond being formed and a compound of the formula (XIIa) or (XIIb) being formed:

$$(a—Z—b)_q \quad (XIIa)$$

$$a—(Z—b)_q \quad (XIIb)$$

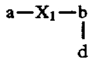
in which the variables are as defined above and Z is a group X1,

after which the compound (XII) is reacted with an unsaturated polymerizable compound of the formula (XIII):

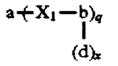
$$X_4—L—(Y)_k—P_1 \quad (XIII)$$

in which X_4 is a group which is coreactive with a hydroxyl or amino group of segment (b), an X_3 group of a segment (d) according to formula (II) being formed from such a reaction, where X_4 is preferably —COOH, —$COOR_{10}$, —COCl or —NCO, in which R_{10} is alkyl, or is aryl which is unsubstituted or substituted by lower alkyl or lower alkoxy, and the other variables are as defined above,

after which a macromer according to the formula (IV) or (V) is formed



$$a—X_1—\underset{\displaystyle d}{\underset{|}{b}} \quad (IV)$$



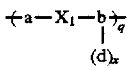
$$a\text{+}X_1—\underset{\displaystyle (d)_x}{\underset{|}{b}})_q \quad (V)$$

in which the segments (d) are incorporated terminally or pendently.

Another process starts from a polysiloxane (a) which contains terminal primary amino- or hydroxyalkyl groups and is reacted with a carbohydrate dilactone to form linear structures of the formula (XIV):

$$\text{+}a—X_1—b\text{+}_q \quad (XIV)$$

in which the variables are as defined and preferred above, after which a compound of the formula (XIV) is reacted with a compound of the formula (XIII) analogously to the above process to give a macromer of the formula (VI):



$$\text{+}a—X_1—\underset{\displaystyle (d)_x}{\underset{|}{b}}\text{+}_q \quad (VI)$$

in which the variables are as defined and preferred above.

Another process starts from a polysiloxane (a) which contains terminal primary amino- or hydroxyalkyl groups and is initially reacted with a bifunctional compound of the formula (XV):

$$X_4—R—X_4 \quad (XV)$$

in which X_4 is a group which is coreactive with a hydroxyl or amino group of segment (a), an X_2 group of a segment (c) being formed from such a reaction, where X_4 is preferably —COOH, —$COOR_{10}$, —COCl or —NCO, in which R_{10} is alkyl, or aryl which is unsubstituted or substituted by lower alkyl or lower alkoxy, and R is as defined above,

after which this intermediate is reacted with a polyol which carries no lactone group to give a compound of the formula (XVI):

$$b—c—\{a—c\}_s—b \ (XVI)$$

in which the variables are as defined and preferred above, after which the compound of the formula (XVI) is reacted with a compound of the formula (XIII) to give a macromer of the formula (X):

$$b—c—\{a—c\}_s—B \ (X)$$

in which s is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3;

B is a segment (a) or (b); and the above preferences apply to the number of segments (d) which are bonded to a segment (b).

Another process starts from a bifunctional compound of the formula (XV):

$$X_4—R—X_4 \quad (XV)$$

which is reacted with an excess of polysiloxane (a) to give an —a—(c—a)$_r$— sequence, in which the above meanings apply, after which, in a second step, the intermediate is reacted with a polyol which carries no lactone to give a compound of the formula (XVII):

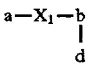
$$b—Z—a—\{c—a\}_r—Z—b \ (XVII)$$

after which the compound (XVII) is reacted with the compound (XIII) to give a macromer of the formula (VIII):

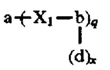
$$b—Z—a—\{c—a\}_r—(Z—b)_t \quad (VIII)$$

in which r is an integer from 1 to 10, preferably from 1 to 7, and in particular from 1 to 3; t is 0 or 1, and is preferably 1; in which a linear (c—a) chain, which may or may not be terminated by a segment (b), is present (t=1); and the above preferences apply to the total number of segments (d), which are preferably bonded to a segment (b).

Another process starts from a carbohydrate lactone which is reacted in a first step with a compound of the formula (XIII), the lactone function being retained, after which the intermediate is reacted with a polysiloxane containing at least one amino or hydroxyl group to give a compound of the formula (IV) or (V):



$$a—X_1—\underset{\displaystyle d}{\underset{|}{b}} \quad (IV)$$



$$a\text{+}X_1—\underset{\displaystyle (d)_x}{\underset{|}{b}})_q \quad (V)$$

in which q is typically 1 or 2, and in which the above meanings and preferences otherwise apply, and the segments (d) are incorporated terminally or pendently.

The present embodiment of the invention furthermore relates to the intermediates which are novel and which occur during synthesis of the macromers according to the invention.

The invention therefore furthermore relates to a compound of the formula (XIIa):

$$(a—Z—b)_q \qquad \text{(XIIa)}$$

in which q is greater than 1,

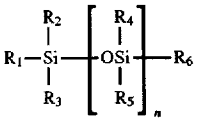
(a) is derived from a polysiloxane as defined by formula (I) above and

(b) is derived from a carbohydrate dilactone.

An embodiment of the invention furthermore relates to a compound of the formula (XIIb)

$$a—(Z—b)_q \qquad \text{(XIIb)}$$

in which Z, (b) and q are as defined and preferred above, but with the proviso that a segment (a) is derived from a compound of the formula (III):



$$R_1—\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_3}{|}}{Si}}—\left[\overset{\overset{\displaystyle R_4}{|}}{\underset{\underset{\displaystyle R_5}{|}}{OSi}}\right]_n—R_6 \qquad \text{(III)}$$

in which n is an integer from 5 to 500;

99.8–25% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are alkyl and

0.2–75% of the radicals R_1, R_2, R_3, R_4, R_5 and R_6 independently of one another are partly fluorinated alkyl, aminoalkyl, alkenyl, aryl, cyanoalkyl, alk—NH—Alk—NH_2 or alk—$(OCH_2CH_2)_m$—$(OCH_2)_p$—OR_7 in which R_7 is hydrogen or lower alkyl, alk is alkylene and

m and p independently of one another are an integer from 0 to 10, one molecule containing at least one primary amino or hydroxyl group and at least one partly fluorinated alkyl group.

The invention furthermore relates to a compound of the formula (XVI):

$$b—c—\{a—c\}_s—b \qquad \text{(XVI)}$$

in which a segment (b) is derived from a polyol which carries no lactone and the other variables are as defined and preferred above.

An embodiment of the invention furthermore relates to a compound of the formula (XVII):

$$b—Z—a—\{c—a\}_r—Z—b \qquad \text{(XVII)}$$

in which a segment (b) is derived from a polyol which carries no lactone and the other variables are as defined and preferred above.

A siloxane (a) containing at least one primary amino or hydroxyl group is, for example, commercially obtainable. Examples are KF-6002, KF-8003, X-22-161C (Shin Etsu) or GP4 (Genesee). Other siloxanes can be synthesized with the aid of published processes.

A polyol (b) required for the synthesis is as a rule commercially obtainable. Examples are gluconolactone or lactobionolactone. Otherwise, they can be synthesized with the aid of a published process.

The compounds according to the invention can be prepared in the presence or absence of a solvent. A solvent which is largely inert, i.e., does not participate in the reaction, is advantageously used. Suitable examples of these are ethers, such as tetrahydrofuran (THF), 1,2-dimethoxyethane, diethylene glycol dimethyl ether or dioxane, halogenated hydrocarbons, such as chloroform or methylene chloride, bipolar aprotic solvents, such as acetonitrile, acetone, dimethylformaride (DMF) or dimethyl sulfoxide (DMSO), hydrocarbons, such as toluene or xylene, and furthermore pyridine or N-methylmorpholine.

The reactants are advantageously employed in stoichiometric amounts for the preparation of the compounds according to the invention. The reaction temperature can be, for example, from −30° C. to 150° C. The range from 0° C. to 40° C. is a preferred temperature range. The reaction times here are in the range from about 15 minutes to 7 days, preferably in the region of about 12 hours. If necessary, the reaction is carried out under argon or nitrogen as an inert gas. A suitable catalyst is advantageously added for urethane-forming reactions, for example dibutyltin dilaurate (DBTDL).

The present invention furthermore relates to a polymer comprising a polymerization product of at least one macromer according to the invention as defined above and, if appropriate, at least one vinylic comonomer (a).

The preferred composition of a polymer according to the invention comprises a weight content, with respect to the total polymer, of a macromer according to the invention in the range from 100 to 0.5%, in particular in the range from 80 to 10%, and preferably in the range from 70 to 30%.

In a preferred polymer comprising a polymerization product of at least one macromer according to the invention, comonomer (a) is absent and the polymer is preferably a homopolymer.

A comonomer (a) which is contained in a polymer according to the invention can be hydrophilic or hydrophobic or a mixture of both. Suitable comonomers include, in particular, those which are usually used for the preparation of contact lenses and biomedical materials. A hydrophobic comonomer (a) is understood as meaning monomers which typically give, as a homopolymer, polymers which are water-insoluble and can absorb less than 10% by weight of water.

Analogously, a hydrophilic comonomer (a) is understood as meaning a monomer which typically gives, as a homopolymer, a polymer which is water-soluble or can absorb at least 10% by weight of water.

Suitable hydrophobic comonomers (a) include, without this list being exhaustive, C_1–C_{18}alkyl and C_3–C_{18}cycloalkyl acrylates and methacrylates, C_3–C_{18}alkylacrylamides and -methacrylamides, acrylonitrile, methacrylonitrile, vinyl C_1–C_{18}alkanoates, C_2–C_{18}alkenes, C_2–C_{18}haloalkenes, styrene, lower alkyl styrene, lower alkyl vinyl ethers, C_2–C_{10}perfluoroalkyl acrylates and methacrylates or correspondingly partly fluorinated acrylates and methacrylates, C_3–C_{12}perfluoroalkyl-ethyl-thiocarbonylaminoethyl acrylates and meylates, acryloxy- and methacryloxy-alkylsiloxanes, N-vinylcarbazole and C_1–C_{12}alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like. Preferred comonomers are, for example, acrylonitrile, C_1–C_4alkyl esters of vinylically unsaturated carboxylic acids having 3 to 5 carbon atoms, or vinyl esters of carboxylic acids having up to 5 carbon atoms.

Examples of suitable hydrophobic comonomers (a) include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, isobutyl acrylate (IBA), isooctyl acrylate (OA), isodecyl acrylate (DA), cyclohexyl acrylate, 2-ethylhexyl acrylate (EHA), methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl acrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyl toluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl (meth)acrylate (HFBMA and HFBA), tris-trimethylsilyloxy-silyl-propyl methacrylate (TRIS), 3-methacryloxypropylpentamethyldisiloxane and bis (methacryloxypropyl) tetramethyldisiloxane. Preferred examples of hydrophobic comonomers (a) are methyl methcrylate, IBA, HFBA, HFBMA, OA, EHA, DA, TRIS and acrylonitrile.

Suitable hydrophilic comonomers (a) include, without this list being conclusive, hydroxyl-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, lower allylacrylamides and -methacrylamides, ethoxylated acrylates and methacrylates, hydroxyl-substituted lower alkylacrylamides and -methacrylamides, hydroxyl-substituted lower alkyl vinyl ethers, sodium vinylsulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinyl-2-pyrrolidone, 2-vinyloxazoline, 2-vinyl4,4'-dialkyloxazolin-5-one, 2- and 4-vinylpyridine, vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms, amino-lower alkyl (where the term "amino" also includes quaternary ammonium), mono-lower alkylamino-lower alkyl and di-lower alkylamino-lower alkyl acrylates and methacrylates, allyl alcohol and the like. Preferred comonomers are, for example, N-vinyl-2-pyrrolidone, acrylamide, methacrylamide, hydroxyl-substituted lower alkyl acrylates and methacrylates, hydroxyl-substituted lower alkylacrylamides and -methacrylamides and vinylically unsaturated carboxylic acids having a total of 3 to 5 carbon atoms.

Examples of suitable hydrophilic comonomers (a) include hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate, hydroxypropyl acrylate, trimethylammonium-2-hydroxypropyl methacrylate hydrochloride (Blemer® QA, for example from Nippon Oil), dimethylaminoethyl meth acrylate (DMAEMA), dimethylaminoethyl methacrylamide, acrylamide, methacrylamide, N,N-dimethylacrylamide (DMA), allyl alcohol, vinylpyridine, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-vinyl-2-pyrrolidone (NVP), acrylic acid, methacrylic acid and the like.

Preferred hydrophilic comonomers (a) are 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, trimethylammonium-2-hydroxypropyl methacrylate hydrochloride, N,N-dimethylacrylamide and N-vinyl-2-pyrrolidone.

The polymers according to the invention are built up in a manner known per se from the corresponding monomers (the term monomers here also including a macromer according to the invention) by a polymerization reaction with which the expert is familiar. Usually, a mixture of the abovementioned monomers is heated, with the addition of an agent which forms free radicals. Such an agent which forms free radicals is, for example, azoisobutronitrile (AIBN), potassium peroxodisulfate, dibenzoyl peroxide, hydrogen peroxide or sodium percarbonate. If the compounds mentioned are heated, for example, free radicals are then formed, by homolysis, and can then, for example, initiate a polymerization.

A polymerization reaction can particularly preferably be carried out using a photoinitiator. Photopolymerization is the term used in this case. For photopolymerization, a photoinitiator which can initiate free radical polymerization and/or crosslinking by the use of light is suitably added. Examples of this are familiar to the expert, and specifically, suitable photoinitiators are benzoin methyl ether, 1-hydroxycyclohexyl phenyl ketone and Darocur and Irgacur types, preferably Darocur 1173® and Darocur 2959®. Reactive photoinitiators which can be incorporated, for example, into a macromer or can be used as a special comonomer (a) are also suitable. Examples of these are to be found in EP 632 329. The photopolymerization can then be triggered off by actinic radiation, for example light, in particular UV light of a suitable wavelength. The spectral requirements can be controlled accordingly, if appropriate, by addition of suitable photosensitizers.

Polymerization can be carried out in the presence or absence of a solvent. Suitable solvents are in principle all solvents which dissolve the monomers used, for example water, alcohols, such as lower alkanols, for example ethanol or methanol, and furthermore carboxylic acid amides, such as dimethylformamide, dipolar aprotic solvents, such as dimethyl sulfoxide or methyl ethyl ketone, ketones, for example acetone or cyclohexanone, hydrocarbons, for example toluene, ethers, for example TBF, dimethoxyethane or dioxane, and halogenated hydrocarbons, for example trichloroethane, and also mixtures of suitable solvents, for example mixtures of water with an alcohol, for example a water/ethanol or a water/methanol mixture.

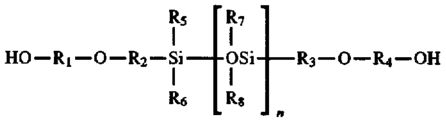
If appropriate, a polymer network can be intensified by addition of a so-called crosslinking agent, for example a polyunsaturated comonomer (b). The invention furthermore relates to a polymer comprising the polymerization product of a macromer according to the invention with, if appropriate, at least one vinylic comonomer (a) and with at least one comonomer (b).

Examples of typical comonomers (b) are, for example, allyl(meth)acrylate, lower alkylene glycol di(meth)acrylate, poly lower alkylene glycol di(meth)acrylate, lower alkylene di(meth)acrylate, divinyl ether, divinyl sulfone, di- or trivinylbenzene, trimethylolpropane tri(methylacrylate, pentaerythritol tetra(meth)acrylate, bisphenol A di(meth) acrylate, methylenebis(meth)acrylamide, triallyl phthalate or diallyl phthalate.

The amount of comonomer (b) used is expressed in the weight content with respect to the total polymer and is in the range from 20 to 0.05%, in particular in the range from 10 to 0.1%, and preferably in the range from 2 to 0.1%.

4. "Material D"

Another advantageous embodiment of the present invention relates to the use of a siloxane-containing macromer which is formed from a poly(dialkylsiloxane) dialkoxyalkanol having the following structure:



$$HO-R_1-O-R_2-\underset{R_6}{\overset{R_5}{Si}}-\left[\underset{R_8}{\overset{R_7}{OSi}}\right]_n-R_3-O-R_4-OH$$

where n is an integer from about 5 to about 500, preferably about 20 to 200, more preferably about 20 to 100;

the radicals R_1, R_2, R_3, and R_4, independently of one another, are lower alkylene, preferably C_1–C_6 alkylene, more preferably C_1–C_3 alkylene, wherein in a preferred embodiment, the total number of carbon atoms in R_1 and R_2 or in R_3 and R_4 is greater than 4; and

R_5, R_6, R_7, and R_8, independently of one another, are lower alkyl, preferably C_1–C_6 alkyl, more preferably C_1–C_3 alkyl.

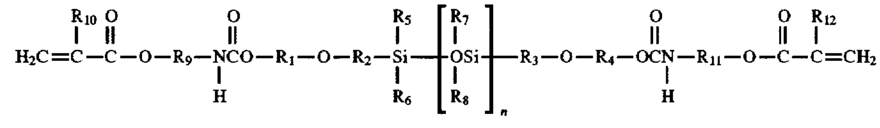
The general structure of the Material D macromer follows:

ACRYLATE—LINK—ALK—O—ALK—PDAS—ALK—O—ALK—LINK—ACRYLATE

where the ACRYLATE is selected from acrylates and methacrylates; LINK is selected from urethanes and diurethane linkages, ALK—O—ALK is as defined above (R_1—O—R_2 or R_3O—R_4), and PDAS is a poly(dialkylsiloxane).

For example, a Material D macromer may be prepared by reacting isophorone diisocyanate, 2-hydroxyethyl (meth) acrylate and a poly(dialkylsiloxane) dialkoxyalkanol in the presence of a catalyst.

A preferred Material D macromer may be prepared by reacting a slight excess of isocyanatoalkyl methacrylate, especially isocyanatoethyl methacrylate (IEM), with a poly (dialkylsiloxane) dialkoxyalkanol, preferably poly (dimethylsiloxane) dipropoxyethanol, in the presence of a catalyst, especially an organotin catalyst such as dibutyltin dilaurate (DBTL). The primary resulting structure is as follows:



$$H_2C{=}\overset{R_{10}}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-R_9-\underset{\underset{H}{|}}{N}CO-R_1-O-R_2-\underset{\underset{R_6}{|}}{\overset{R_5}{\overset{|}{Si}}}-\left[\underset{\underset{R_8}{|}}{\overset{R_7}{\overset{|}{OSi}}}\right]_n-R_3-O-R_4-O\overset{O}{\overset{\|}{C}}\underset{\underset{H}{|}}{N}-R_{11}-O-\overset{O}{\overset{\|}{C}}-\overset{R_{12}}{\overset{|}{C}}{=}CH_2$$

where

R_9 and R_{11} are alkylene; preferably $C_{1\text{-}6}$ alkylene, more preferably ethylene;

R_{10} and R_{12} are methyl or hydrogen.

The "Material D" prepolymer mixture may be formed by mixing the aforementioned siloxane-containing macromer with one or more hydrophilic monomers and a thermoinitiator or a photoinitiator such as Darocur® 1173. A solvent, such as hexanol, is preferably added to homogenize the mixture. Preferably, an appropriate amount of TRIS is added to lower the modulus of elasticity to a desired level. The ionoperm monomer or monomers may be selected from any of the aforementioned ionoperm or hydrophilic monomers. Preferably, the ionoperm monomer is selected from the group consisting of acrylates, methacrylates, acrylamides, methacrylamides and mixtures thereof. More preferably, the ionoperm monomers are selected from dimethylacrylamide (DMA) and methacrylic acid (MAA).

A preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes about 35 to 60% Material D macromer; about 6 to 25% TRIS; about 15 to 35% ionoperm monomer; about 0.1 to 1% photoinitiator; and about 10 to 20% solvent. A more preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes the following: about 40 to 55% Material D macromer; about 8 to 16% TRIS; about 20 to 30% dimethylacrylamide; about 0.2 to 2% methacrylic acid; about 0.1 to 1% photoinitiator; and about 10 to 20% solvent. A particularly preferred "Material D" prepolymer mixture, in weight percentages based on total mixture weight, includes the following: about 44 to 50% Material D macromer; about 10 to 12% TRIS; about 22 to 26% dimethylacrylamide; about 0 to 1% methacrylic acid; about 0.2 to 0.6% photoinitiator; and about 10 to 20% solvent.

The prepolymer mixture may be formed into lenses and other ophthalmic devices by any of a number of techniques known in the art and disclosed herein. Preferably, the prepolymer mixture is conveyed into a concave half of a lens mold, the convex mold half is mated with the concave mold half, and an appropriate amount of radiation is applied to initiate polymerization. While ultraviolet (UV) radiation is preferred, a number of other energy sources known in the art so and disclosed herein may also be used.

The Material D ophthalmic lens is preferably a polymerization product of the following macromeric and monomeric components, based on total weight of polymerizable material:

(a) about 45 to about 65 percent Material D macromer;

(b) about 5 to about 25 percent TRIS; and

(c) about 20 to about 40 percent ionoperm monomer.

The Material D ophthalmic lens is more preferably a polymerization product of the following macromeric and monomeric components, based on total weight of polymerizable material:

(a) about 50 to about 60 percent Material D macromer;

(b) about 10 to about 20 percent TRIS; and

(c) about 25 to about 35 percent ionoperm monomer.

In a preferred embodiment, the Material D ophthalmic lens is a polymerization product of the following macromeric and monomeric components, based on total weight of polymerizable material:

(a) about 50 to about 60 percent Material D macromer;

(b) about 10 to about 20 percent TRIS;

(c) about 25 to about 35 percent DMA; and

(d) up to about 2 percent MAA.

In another preferred embodiment, about 0.2 to 1.0 weight percent MAA is used, together with the components (a), (b), and (c) in the above-cited amounts.

III. OPHTHALMICALLY COMPATIBLE SURFACES

The ophthalmic lenses of the present invention have a surface which is biocompatible with ocular tissue and ocular fluids during the desired extended period of contact. In one preferred embodiment, the ophthalmic lenses of the present invention include a core material, as defined above, surrounded, at least in part, by a surface which is more hydrophilic and lipophobic than the core material. A hydrophilic surface is desirable in order to enhance the compatibility of the lens with the ocular tissues and tear fluids. As surface hydrophilicity increases, undesirable attraction and adherence of lipids and proteinaceous matter typically decreases. There are factors other than surface hydrophilicity, such as immunological response, which may contribute to deposit accumulation on the lens. Deposition of lipids and proteinaceous matter causes haze on the lens, thereby reducing visual clarity. Proteinaceous deposits may also cause other problems, such as irritation to the eye. After extended periods of continuous or intermittent wear, the lens must be removed from the eye for cleaning, i.e., deposit removal. Therefore, increased surface hydrophilicity, and concomittent reductions in deposits of biological matter, allows increased wear time.

"Surface treatment processes", as used herein, refers to processes to render a surface more ophthalmically compatible, in which, by means of contact with a vapor or liquid, and/or by means of application of an energy source (1) a coating is applied to the surface of an article, (2) chemical species are adsorbed onto the surface of an article, (3) the chemical nature (e.g., electrostatic charge) of chemical groups on the surface of an article are altered, or (4) the surface properties of an article are otherwise modified.

There are a variety of methods disclosed in the art for rendering a surface of a material hydrophilic. For example, the lens may be coated with a layer of a hydrophilic polymeric material. Alternatively, hydrophilic groups may be grafted onto the surface of the lens, thereby producing a monolayer of hydrophilic material. These coating or grafting processes may be effected by a number of processes, including without limitation thereto, exposing the lens to plasma gas or immersing the lens in a monomeric solution under appropriate conditions.

Another set of methods of altering the surface properties of a lens involves treatment prior to polymerization to form the lens. For example, the mold may be treated with a plasma (i.e., an ionized gas), a static electrical charge, irradiation, or other energy source, thereby causing the prepolymerization mixture immediately adjacent the mold surface to differ in composition from the core of the prepolymerization mixture.

A preferred class of surface treatment processes are plasma processes, in which an ionized gas is applied to the

substantially altered and wearer comfort is acceptable during a period of extended, continuous contact with ocular tissue and ocular fluids.

The preferred extended-wear contact lenses of the present invention are those which are comfortable over the period of extended wear. If the lens diameter is too small, the eyelids will not cover any portion of the lens when the eye is open. Thus, the eyelids will contact the edge of the lens each time the eyelid is closed. This repeated eyelid-lens interaction typically causes irritation, wearer discomfort, and lens dislodgement. Accordingly, the preferred contact lens diameters are those which are sufficiently large to minimize eyelid-lens interaction and the associated irritation. Preferably, the contact lens has a diameter of about 12 to