POLYSILOXANE-COMPRISING PERFLUOROALKYL ETHERS AND THE PREPARATION AND USE THEREOF

The present invention describes a free-radical-polymerizable macromer of the formula (I) based on an unsubstituted or symmetrically substituted perfluoroalkyl ether; a polymer comprising the product of the polymerization of a novel macromer, alone or together with at least one vinylic comonomer; a process for the preparation of a macromer and a polymer; mouldings, contact lenses, corneal implants and biomedical articles made from a polymer; and articles coated with a macromer of the formula (I) or a polymerization product thereof.

Contact-lens materials having a high fluorine content and a high siloxane content are known and proven since they generally have the high oxygen permeability necessary for a contact-lens material and in addition are mostly resistant to deposits of proteins and lipids from tear fluid, and are frequently also resistant to bacterial infestation. However, the following disadvantageous properties frequently have to be accepted: loss of comfort for the contact-lens wearer owing to mechanical rigidity, reduction in oxygen permeability if the water content of the material used is relatively high, and an excessively low refractive index for good optical properties. Contact-lens materials having relatively low refractive indices are thicker than those having relatively large refractive indices and are thus also less comfortable to wear. Furthermore, suction cup effects can occur on the lenses, restricting mobility on the eye.

Japanese Patent Application 04-168 116 (JSR) describes, for example, the preparation of oxygen-permeable polymers comprising the product of the copolymerization of, for example, methyl methacrylate with a macromer built up from a perfluoroalkyl ether, which may be bonded at each end to an unsaturated polymerizable group via one or more siloxanyl units and a plurality of bivalent hydrocarbon radicals. It is stated that these polymers can be used as ophthalmic material.

EP 0 379 462 describes ethylenically substituted macromers which contain perfluoroalkyl ether and polyalkyl ether segments and are used for the production of polymers and ophthalmic devices, such as intraocular implants and contact lenses, and furthermore crosslinked polymers with vinyl monomers.

It has been found that a novel and balanced composition gives a macromer which can be polymerized, if desired together with at least one vinylic comonomer (a), to give a material which is substantially free from the undesired properties indicated above.

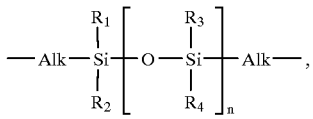
The present invention relates to a macromer of the formula (I)

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

where each P_1, 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 from 10 to 30; each Z, independently of the others, is a divalent radical having up to 12 carbon atoms or 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;

(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 proviso that each segment (a) or (b) has a segment (c) attached to it; and 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 from about 1000 to about 20,000, preferably in the range from about 3000 to about 15,000, particularly preferably in the range from about 5000 to about 12,000.

The total number of segments (a) and (b) in the polymer fragment Q is preferably in the range from 2 to about 11, particularly preferably in the range from 2 to about 9, and in particular in the range from 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).

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

Said 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—.