

Candidate's Answer Paper

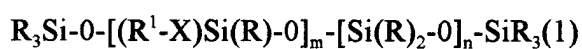
The present invention concerns novel polymers, processes for preparing said novel polymers, their use for the manufacture of transparent objects, in particular hard contact lenses. The present invention further concerns the production of said contact lenses.

The first materials used in the production of contact lenses were polymethyl methacrylate and, later, polymers of substituted alkyl methacrylates such as 2-hydroxyethyl methacrylate (**HEMA**). The latter monomers result, in general, in soft lenses which swell strongly in water.

The incorporation of fluoroalkyl (meth)acrylates and/or silicone macromers into such polymers heralded the breakthrough in achieving higher specific oxygen permeabilities, although this had the disadvantage of reducing lens hydrophilicity. Wearing comfort likewise suffered, as in many cases did the mechanical strength of the lenses. Polysiloxanes which contain polymerisable ethylenically unsaturated groups are also referred to as silicone, siloxane and polysiloxane macromers.

Document I describes silicone containing polymeric materials which range from "soft" to "hard" (using contact lens terminology), which are suitable to provide a silicone-containing lens the surface of which is permanently hydrophilic.

Document I discloses said silicon-containing material as being polymers comprising a polysiloxane monomer corresponding to the general formula (1)



Wherein the degree of polymerisation ($m + n$) ranges from 500 to 1000, and further may comprise styrenes or C_1 to C_{12} - alkyl, C_6 - to C_{12} - cycloalkyl or C_6 - to C_{12} - aralkyl acrylates or methacrylates. Document also discloses that small amounts of divinyl compounds or hydroxyalkyl, as well as C_6 - to C_{10} - fluoroalkyl acrylates and/or methacrylates, such as hydroxyethyl methacrylate and hexafluoroisopropyl methacrylate can also be used.

However, Document I is silent on the use of a polysiloxane monomer with a degree up to 150.

It was unexpectedly discovered that by changing the polymerisation degree of A in the art-known polymers to less than 150, one could obtain material which shows superior oxygen permeability and improved hydrophilicity as can be seen from a comparison between the results shown in Document I and the results shown in the experimental part of the present application.

The polymeric material avoids the disadvantages of the prior art and moreover provides material with superior characteristics over Document I.

The present invention discloses a polymer as shown in claim 1.

The present invention provides a polymer obtainable by polymerising components A, B, C and optionally D, the nature of which and the specific amounts of which will hereunder be discussed and is shown in claims.

It should be noted that the compounds used are in principle all known as such. Also the component A¹ mentioned hereunder is commercially available.

It should also be noted that even small amounts of unsuitable monomers cause deterioration of the optical quality of the polymers and sometimes in their other properties.

Component (A) consists mainly or totally of siloxane group-containing monomers, hereinafter referred to as reactive siloxanes (A'). To avoid any misunderstanding, please note that the term

The structure of the reactive siloxanes (A') correspond to formula

$R_3Si-O-[(R^1-X)Si(R)-O]_m-[Si(R)_2-O]_n-SiR_3$, wherein R, R¹ and X and m and n are as defined in claim 1. Our process does not require the presence of separate polymer blocks in the siloxane either. Whereas the number of siloxane units (= degree of polymerisation) in the silicone macromers used in **Document I** totals between 500 and 1000, the siloxane compounds we use have a degree of polymerisation of up to 150, preferably 100 to 150. This type of compound with such a limited degree of polymerisation is often described as an oligomer. In the reactive siloxanes (A') of formula (1) which we use, the R groups possess independently of one another the meanings C₁ to C₄ alkyl and/or phenyl. Here it is generally found that the hydrophilicity decreases as the number of C atoms in the R groups increases, i.e. that hydrophobicity already increases significantly when going from C₁ to C₄. The short-chained groups such as methyl and ethyl, and in particular methyl, are therefore preferred. The choice of these groups R also influences the optical properties.

The number of R¹-X- groups in which an ethylenically unsaturated group R¹ is bonded to a silicon atom of the reactive siloxane by a urethane group X is at least 1 in our invention.

Hence m should be ≥ 1 .

Their number should not however exceed 25 % of the total number of all the silicon-bonded organic groups (R and R¹-X-). As the examples below show, products with particularly good swelling and mechanical strength characteristics are obtained if these unsaturated groups account for between 5 and 10 % of all these groups R and R¹-X-. For the preparation of these reactive siloxanes reference has only to be made to our example 1 and to **Document I**.

These reactive siloxanes are polymerised with comonomers the major proportion of which are methacrylic acid alkyl esters (= alkyl methacrylates) (B). Because of the properties required in the polymer, only the C₁ to C₅ alkyl methacrylates are used. Of these the ethyl, and particularly the methyl ester, are preferred, as the polymers obtained are softer the longer the alkyl group of the methacrylic acid ester and the higher the proportion of these longer-chained alkyl esters.

Also polymerised as further key components are hydroxy group-containing alkyl acrylates and/or methacrylates (C) in order to increase hydrophilicity. Methacrylic esters and acrylic esters of alkane diols, which contain a free hydroxy group are to be mentioned in this connection. Preferably hydroxyethyl or hydroxypropyl methacrylates are used.

The desired high mechanical strength is most easily obtained by using cross-linked polymers. If therefore the reactive siloxanes are not already providing sufficient cross-linkage through several ethylenically unsaturated R¹-X- groups, further polyethylenically unsaturated monomers are also added to the reaction mixture as cross-linking agents (D). The only compounds suitable for use as such cross-linking agents are compounds having at least two polymerisable ethylenically unsaturated groups, such as neopentylglycol diacrylate or dimethacrylate, to name but two.

Increasing cross-linkage while leaving the monomer composition otherwise unchanged makes the polymer harder and reduces its swelling capacity.

To obtain polymers that meet our requirements the monomers are copolymerised in the following proportions: component (A) in amounts of 15 to 40 % by weight, the alkyl methacrylates (B) in amounts of 40 to 80 % by weight, the hydroxy group-containing (meth)acrylates (C) in amounts of 2 to 10 % by weight and the cross-linking agents (D) in amounts of up to 10 % by weight. Of crucial importance for the polymer thus obtained is that the degree of cross-linking is such that the polymer does not swell in water by more than 10 vol. %, so as to ensure that the polymer, and the contact lens obtained from it, has sufficient dimensional stability. On the other hand, the Shore-D hardness should not exceed 85. This figure is a simple indication of the limit value for the required mechanical strength.

In component (A), a part of the reactive siloxanes (A') can be replaced by fluoroalkyl methacrylates (A'') of which the fluoroalkyl groups contain 2 to 10 C atoms. The amount of these fluorinated monomers should not exceed 10 % by weight of the total amount of the components (A) to (D). The longer the fluoroalkyl group, and the higher the total amount of this fluorinated monomer (A'') and of the reactive siloxane (A'), the less hydrophilic is the polymer. Under no circumstances, therefore, should the total amount of this component (A), i.e. (A')+(A''), exceed 40 % by weight, as hydrophilicity will otherwise fall below an acceptable limit value. This limit value is defined by the contact angle (see **Document I**) which must be at least 100°.

The monomers are admixed in the above proportions and 0.001 to 0.5 % by weight of initiator (E) is added. No other substances, e.g. solvents, are added to the mixture. The monomer mixture must already be glass-clear and streak-free. Numerous tests have shown that monomer mixtures that are not streak-free always produce polymers which are unsuitable for us because of their unsatisfactory optical properties.

To prevent bubbles of entrapped gas being formed in the mixture, this is briefly placed in a vacuum prior to starting the polymerisation. After degassing, polymerisation under inert gas is then started either thermally (using peroxide group-containing radical-forming initiators) or photochemically (by means of photo-initiators). The polymers can be regarded as being identical, irrespective of the method used for initiating the reaction. The degree of polymerisation of the polymers is kept in the required range by using the above-stated amount of initiator and ensuring that the reaction temperature does not rise beyond 60° C.

Usually polymerisation for the production of contact lenses is performed in a mould with a space approximately the same shape as the lens, so that lens blanks are produced directly. This ensures good reaction heat dissipation and further reduces the likelihood of the formation of streaks. To reduce this still further, polymerisation is preferably started photochemically. This obviates the need for external heat and it prevents the reaction mixture overheating.

Furthermore this method of polymerisation in the mould simplifies subsequent processing and avoids excessive material loss. The blanks are then machined to achieve their exact shape, following which the surfaces are polished. The more dimensionally stable the polymer is, the simpler these stages in processing are. These stages are common knowledge among skilled practitioners.

The following examples are intended to explain the invention to you in greater detail. We refer you to the description in the attached **Document I** for further details of the methods of measurement used.

Example 1

As described in the **Document I**, a reactive siloxane with three polymerisable methacrylate groups bonded to siloxane groups was made from a dimethyl siloxane oligomer having a degree of polymerisation of 100 which contained three hydroxyethyl groups per molecule, diisocyanate and hydroxyethyl methacrylate (**HEMA**).

Table 1

Ex.	Comonomers (wt.%, balance to 100%: reactive siloxane)	Appearance	O ₂ -DK	Contact angle	Shore-D hardness	Swelling (Vol.%)
2	MMA (60) HEMA (4)	clear	34	110°	73	6.9
3	MMA (66) HEMA (4)	clear	28	117°	75	7.4
4	MMA (73) HEMA (4)	clear	17	123°	80	8.7
5*	MMA (87) HEMA (4)	clear	7.5	124°	83	9.5
6	MMA (60) NPDA (4) HEMA (4)	clear	25	117°	77	5.9
7	MMA (60) FPMA (4) HEMA (4)	clear	33	101°	70	7.5
8	MMA (60) HEMA (4)	clear	34	110°	79	5.2
9	MMA (66) HEMA (4)	clear	28	118°	81	5.6
10	MMA (73) HEMA (4)	clear	16	123°	83	5.9

MMA = methyl methacrylate
 FPMA = hexafluoroisopropyl methacrylate

HEMA = 2-hydroxyethyl methacrylate
 NPDA = neopentylglycol diacrylate
 "clear" means glass-clear in each case

* Comparison test

Examples 2-7

The reactive siloxane produced in example 1 was copolymerised with the monomers listed in table 1 into 0.1 mm thick films following addition of 0.2 % by weight of a UV photo-initiator commercially available as "UVInit A" by irradiation with UV light between plates of quartz glass which have been treated so as to be non-sticking. Measurements of the specific oxygen permeability (O₂-DK) were carried out on these films. Using the same method, 1 mm thick sheets were made from each monomer mixture and used to determine their water wettability.

In a similar way, and as described in **Document I**, samples for hardness measurements were also made and examined.

Water swelling was determined by measuring the increase in volume of samples after standing for 48 hours in distilled water at 20° C. The samples were produced by the method described for the hardness measurement. The value for Shore-D hardness should never be less than 70. Below this limit the polymers are too soft. The results are summarised in table 1.

Examples 8-10

In a manner analogous to example 1, a reactive siloxane was produced which had a degree of polymerisation of 100 and contained polymerisable methacrylate groups, their number being 10 % of all the organic groups bonded to siloxane groups. This reactive siloxane was used to repeat examples 2, 3 and 4. The results are shown in table 1.

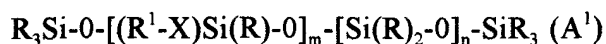
Tests with various commercially available photo-initiators or monomer-soluble peroxide group-containing radical-forming initiators consistently produced polymers with negligibly small amounts of residual monomers.

Incidentally these polymers can also be used for other applications for which good transparency and water wettability are essential, such as for containers or for optical lenses.

Claims

1. A polymer obtainable by polymerising

- (a) 15 to 40% by weight of component A, which consist mainly or totally of a siloxane containing monomer of formula



wherein $m \geq 1$ and wherein the degree of polymerisation ($m + n$) is up to about 150, wherein each R independently means C_1 - C_4 alkyl or phenyl,

wherein R^1 is an ethylenically unsaturated group, X is $R^3-O-CO-NH-R^5-NH-CO-O-R^4$, each of R^3 and R^4 being a linear or branched (divalent) alkylene residue and R^5 is a linear or cyclic alkylene residue, wherein the number of R^1 -X- groups is ten or equal to 25% of the total number of all silicon-bonded groups, the remainder of A being A" which is a fluoroalkyl methylacrylates of which the fluoroalkyl groups contain 2 to 10 C atoms in an amount which should not exceed 10% by weight of the total amount of the components (A) to (D);

- (b) 40 to 80% by weight of component B which is a C_1 to C_5 alkyl methacrylate;
- (c) 2 to 10% by weight of component C which is a hydroxy group containing alkylacrylate and/or methylacrylate;
- (d) 0 to 10% by weight of component D which is a compound having at least two polymerisable ethylenically unsaturated groups, the sum of components always being 100% apart from a maximum of 0.5 of impurities due to initiator.
2. A polymer according to claim 1 wherein the degree of polymerisation ($m + n$) ranges from about 100 to about 150.
3. A polymer according to any of claims 1 or 2, wherein R is methyl or ethyl, particularly methyl.
4. A polymer according to any of the preceding claims wherein the number of R^1 -X- groups account for between 5 and 10% of all the groups R and R^1 -X.
5. A polymer according to any of the preceding claims wherein R^1 is $CH_2=C(R^2)-CO-O-$, wherein R^2 is hydrogen or methyl.
6. A polymer according to any of the preceding claims wherein B is ethyl methacrylate or methyl methacrylate.
7. A polymer according to any of the preceding claims wherein C is hydroxyethyl or hydroxypropyl methacrylate.
8. A polymer according to any of the preceding claims wherein component D is neopentylglycol diacrylate or dimethylacrylate.

9. A transparent object consisting of a polymer as claimed in claim 1.
10. A transparent object as claimed in claim 9, wherein said object is a container.
11. A transparent object as claimed in claim 9 wherein said object is an optical lens.
12. A transparent object as claimed in claim 9 wherein said object is a contact lens.
13. Use of a polymer as claimed in claim 1 for the preparation of a transparent object as claimed in claims 9 to 12.
14. A process for preparing a polymer as claimed in claim 1 by
 - (a) preparing a glass-clear and streak-free mixture of monomers;
 - (b) subsequently adding 0.001 to 0.5% by weight of initiator E being either a peroxide group-containing radical forming initiator or a photoinitiator;
 - (c) degassing;
 - (d) starting the polymerisation under inert gas, ensuring that the reaction temperature does not rise beyond 60°C.
15. A process for preparing a polymer as claimed in claim 14, wherein E is a photoinitiator and the polymerisation is started photochemically.
16. A process for preparing a contact lens, by performing the processes claimed in claims 14 or 15 in a mould with a space approximately the same shape as the lens thus obtaining lens blanks which are then machined to achieve their exact shape, following which the surfaces are polished.

Notes:

1. The application will have to be filed soon in view of the conference of next week.
2. I have tried to carefully stick to the instructions of the client concerning the amounts, because of the danger that some products deviating from the client's instructions would be unworkable.
3. I have opted for a product-by-process claim because the components A, B, C etc are compounds which are as they go into the reaction mixture and not as they are once polymerisation took place.
4. I entered the wording "about" 150 for the polymerisation degree, because polymerisation degree is not an accurate number (statistical).