methacrylic materials typically do not have an appropriate combination of strength, flexibility and non-tacky surface properties to permit IOLs to be inserted through an incision as small as that required for silicone IOLs.

Polyethylene glycol (PEG) dimethacrylates are known to improve glistening resistance of hydrophobic acrylic formulations. See, for example, U.S. Patent Nos. 5,693,095 and 6,353,069. Both the concentration and molecular weight of PEG dimethacrylates have an impact on glistening performance. Generally, use of higher molecular weight PEG dimethacrylates (1000 MW) yield copolymers with improved glistening performance at low PEG concentrations (10 – 15 wt%), as compared to lower molecular weight PEG dimethacrylates (<1000 MW). However, low PEG dimethacrylate concentrations are desirable to maintain a high refractive index copolymer. Addition of PEG dimethacrylates also tends to decrease the modulus and tensile strength of the resulting copolymer.

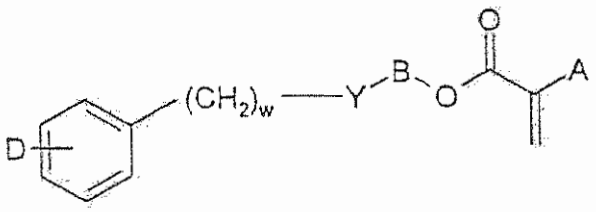
SUMMARY ~~OF THE INVENTION~~

Improved soft, foldable acrylic device materials which are particularly suited for use as IOLs, but which are also useful as other ophthalmic or otorhinolaryngological devices, such as contact lenses, keratoprostheses, corneal rings or inlays, otological ventilation tubes and nasal implants, have been discovered. These polymeric materials comprise a high molecular weight, reactive, linear polyethylene glycol component.

Among other factors, the present ~~invention~~disclosure is based on the finding that use of high molecular weight, reactive, linear polyethylene glycol components in acrylic intraocular lens formulations efficiently reduces or eliminates temperature-induced glistening formation in hydrophobic acrylic copolymers. The subject monomers allow synthesis of glistening resistant, low equilibrium water content, high refractive index IOLs.

In a first aspect, there is provided a polymeric ophthalmic or otorhinolaryngological device material comprising

a) 50-93% of a polymerizable monomer of the structure:



(I)

wherein: A is H or CH_3;

B is $(CH_2)_m$ or $[O(CH_2)_2]_z$;

m is 2-6;

z is 1-10;

Y is nothing, O, S, or NR', provided that if Y is O, S or NR', then B is $(CH_2)_m$;

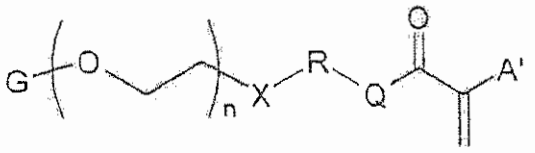
R' is H, CH_3, $C_{n'}H_{2n'+1}$, iso-OC_3H_7, C_6H_5, or $CH_2C_6H_5$;

n' = 1-10;

w is 0-6, provided that m + w ≤ 8; and

D is H, Cl, Br, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_6H_5, or $CH_2C_6H_5$;

b) 1-5% of a high molecular weight, linear polyethylene glycol component of the structure



(II)

wherein: X, X' independently = nothing, O, or NH;

R, R' independently = nothing or $(CH_2)_p$;

p = 1-3;

Q, Q' independently = nothing or $C(=O)NHCH_2CH_2O$;

A' = H or CH_3;

G = H, C_1-C_4 alkyl, $(CH_2)_mNH_2$, $(CH_2)_mCO_2H$, or

R'-X'-Q'-$C(=O)C(=CH_2)A'$; and

n = 45-225 when G = H, C_1-C_4 alkyl, $(CH_2)_mNH_2$, or $(CH_2)_mCO_2H$;

otherwise, n = 51-225; and

c) a polymerizable cross-linking agent,

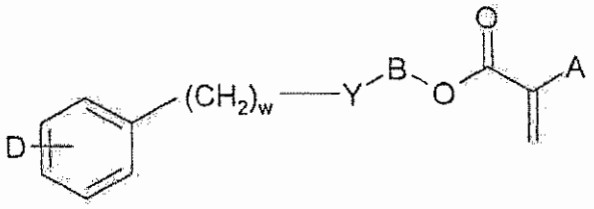
wherein the monomer of structure (II) has a polyethylene glycol component having a number average molecular weight of 2,000-8,000 Daltons.

In a second aspect, there is provided an ophthalmic or otorhinolaryngological device comprising the polymeric device material as defined above wherein the ophthalmic or otorhinolaryngological device is selected from the group consisting of intraocular lenses; contact lenses; keratoprostheses; corneal inlays or rings; otological ventilation tubes; and nasal implants.

Claims:

1. A polymeric ophthalmic or otorhinolaryngological device material comprising

a) 50-93% of a polymerizable monomer of the structure:



(I)

wherein: A is H or CH_3;

B is $(CH_2)_m$ or $[O(CH_2)_2]_z$;

m is 2-6;

z is 1-10;

Y is nothing, O, S, or NR', provided that if Y is O, S or NR', then B is $(CH_2)_m$;

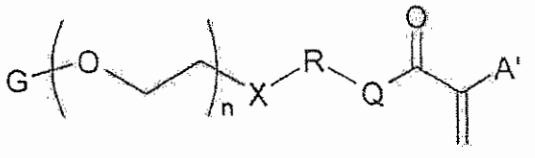
R' is H, CH_3, $C_{n'}H_{2n'+1}$, iso-OC_3H_7, C_6H_5, or $CH_2C_6H_5$;

n' = 1-10;

w is 0-6, provided that m + w ≤ 8; and

D is H, Cl, Br, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_6H_5, or $CH_2C_6H_5$;

b) 1-5% of a high molecular weight, linear polyethylene glycol component of the structure



(II)

wherein: X, X' independently = nothing, O, or NH;

R, R' independently = nothing or $(CH_2)_p$;

p = 1-3;

Q, Q' independently = nothing or $C(=O)NHCH_2CH_2O$;

A' = H or CH_3;

G = H, C_1-C_4 alkyl, $(CH_2)_mNH_2$, $(CH_2)_mCO_2H$, or

R'-X'-Q'-$C(=O)C(=CH_2)$A'; and

n = 45-225 when G = H, C_1-C_4 alkyl, $(CH_2)_mNH_2$, or $(CH_2)_mCO_2H$;

otherwise, n = 51-225; and

c) a polymerizable cross-linking agent,

wherein the monomer of structure (II) has a polyethylene glycol component having a number average molecular weight of 2,000-8,000 Daltons.

2. The polymeric device material of Claim 1 wherein the monomer of structure (I) is selected from the group consisting of: 2-ethylphenoxy acrylate; phenyl acrylate; benzyl acrylate; 2-phenylethyl acrylate; 3-phenylpropyl acrylate; 4-phenylbutyl acrylate; 4-methylphenyl acrylate; 4-methylbenzyl acrylate; 2-2-methylphenylethyl acrylate; 2-3-methylphenylethyl acrylate; 2-4-methylphenylethyl acrylate; 2-(4-propylphenyl)ethyl acrylate; 2-(4-(1-methylethyl)phenyl)ethyl acrylate; 2-(4-methoxyphenyl)ethyl acrylate; 2-(4-cyclohexylphenyl)ethyl acrylate; 2-(2-chlorophenyl)ethyl acrylate; 2-(3-chlorophenyl)ethyl acrylate; 2-(4-chlorophenyl)ethyl acrylate; 2-(4-bromophenyl)ethyl acrylate; 2-(3-phenylphenyl)ethyl acrylate; 2-(4-phenylphenyl)ethyl acrylate; 2-(4-benzylphenyl)ethyl acrylate; 2-ethylphenoxy methacrylate; phenyl methacrylate; benzyl methacrylate; 2-phenylethyl methacrylate; 3-phenylpropyl methacrylate; 4-phenylbutyl methacrylate; 4-methylphenyl methacrylate; 4-methylbenzyl methacrylate; 2-2-methylphenylethyl methacrylate; 2-3-methylphenylethyl methacrylate; 2-4-methylphenylethyl methacrylate; 2-(4-propylphenyl)ethyl methacrylate; 2-(4-(1-methylethyl)phenyl)ethyl methacrylate; 2-(4-methoxyphenyl)ethyl methacrylate; 2-(4-cyclohexylphenyl)ethyl methacrylate; 2-(2-chlorophenyl)ethyl methacrylate; 2-(3-chlorophenyl)ethyl methacrylate; 2-(4-chlorophenyl)ethyl methacrylate; 2-(4-bromophenyl)ethyl methacrylate; 2-(3-phenylphenyl)ethyl methacrylate, 2-(4-phenylphenyl)ethyl methacrylate; and 2-(4-benzylphenyl)ethyl methacrylate.

3. The polymeric device material of Claim 1 wherein for the monomer of structure (I): B is $(CH_2)_m$, m is 2-5, Y is nothing or O, w is 0-1, and D is H.

4. The polymeric device material of Claim 3 wherein the monomer of structure (I) is selected from the group consisting of: 2-phenylethyl acrylate; 4-phenylbutyl acrylate; 5-phenylpentyl acrylate; 2-benzyloxyethyl acrylate; 3-benzyloxypropyl acrylate; 2-phenylethyl methacrylate; 4-phenylbutyl methacrylate; 5-phenylpentyl methacrylate; 2-benzyloxyethyl methacrylate; and 3-benzyloxypropyl methacrylate.

5. The polymeric device material of Claim 1 wherein the amount of monomer of structure (I) is 75-90% (w/w).

6. The polymeric device material of Claim 1 wherein for the monomer of structure (II):
X, X' independently = nothing or O;
R, R' = nothing;
Q, Q' independently = nothing or $C(=O)NHCH_2CH_2O$;
A' = H or CH_3;
G = C_1-C_4 alkyl or R'-X'-Q'-$C(=O)C(=CH_2)A'$; and
n = 45-180 when G = C_1-C_4 alkyl; otherwise, n = 51-225.

7. The polymeric device material of Claim 1 wherein the monomer of structure (II) has a polyethylene glycol component having a number average molecular weight of 2,000-6,000 Daltons.

8. The polymeric device material of Claim 7 wherein the monomer of structure (II) has a polyethylene glycol component having a number average molecular weight of 2,500-6,000 Daltons.

9. The polymeric device material of Claim 1 wherein the amount of monomer of structure (II) is 2-5% (w/w).

10. The polymeric device material of Claim 9 wherein the amount of monomer of structure (II) is 2-4% (w/w).

11. The polymeric device material of Claim 1 wherein the cross-linking monomer is selected from the group consisting of: ethylene glycol dimethacrylate; diethylene glycol dimethacrylate, triethylene glycol dimethacrylate; tetraethylene glycol dimethacrylate; allyl methacrylate; 1,3-propanediol dimethacrylate; 2,3-propanediol dimethacrylate; 1,6-

hexanediol dimethacrylate; 1,4-butanediol dimethacrylate; $CH_2=C(CH_3)C(=O)O-(CH_2CH_2O)_p-C(=O)C(CH_3)=CH_2$ where p = 1-50; and $CH_2=C(CH_3)C(=O)O(CH_2)_tO-C(=O)C(CH_3)=CH_2$ where t = 3-20; and their corresponding acrylates.

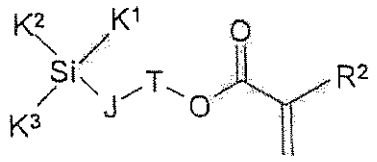
12. The polymeric device material of Claim 11 wherein the cross-linking monomer is selected from the group consisting of ethylene glycol dimethacrylate; diethylene glycol dimethacrylate; triethylene glycol dimethacrylate; triethylene glycol diacrylate; 1,4-butanediol diacrylate; and $CH_2=C(CH_3)C(=O)O-(CH_2CH_2O)_p-C(=O)C(CH_3)=CH_2$ where p is such that the number-average molecular weight is about 400, about 600, or about 1000.

13. The polymeric device material of Claim 1 further comprising an ingredient selected from the group consisting of polymerizable UV absorbers and polymerizable colorants.

14. The polymeric device material of Claim 13 comprising 0.1-5% (w/w) of a polymerizable UV absorber and 0.01-0.5% (w/w) of a polymerizable colorant.

15. The polymeric device material of Claim 1 wherein the polymeric device material has an equilibrium water content of less than 2.0 weight % across the temperature range of 16-45°C.

16. The polymeric device material of Claim 1 wherein the polymeric device material further comprises a siloxane monomer of the structure:



(III)

wherein

R^2 is H or CH_3;

T is nothing, $O(CH_2)_b$, or $OCH_2CH(OH)CH_2$;

b is 1-3;

J is $(CH_2)_z$; and

K^1, K^2, and K^3 independently are CH_3, C_6H_5, or $OSi(CH_3)_3$.

17. The polymeric device material of Claim 1 wherein the polymeric device material further comprises 2-hydroxyethyl methacrylate.

18. An ophthalmic or otorhinolaryngological device comprising the polymeric device material of Claim 1 wherein the ophthalmic or otorhinolaryngological device is selected from the group consisting of intraocular lenses; contact lenses; keratoprostheses; corneal inlays or rings; otological ventilation tubes; and nasal implants.

19. The ophthalmic or otorhinolaryngological device of Claim 18 wherein the ophthalmic or otorhinolaryngological device is an intraocular lens.