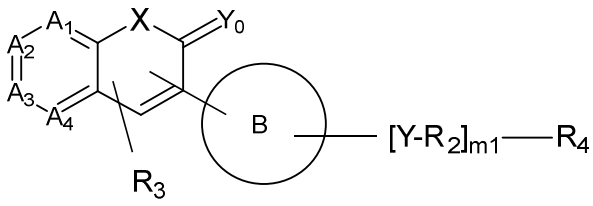
Patent claims

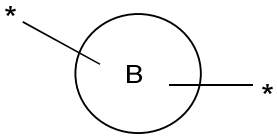
1. An ophthalmic device or a precursor article for manufacturing an ophthalmic device comprising at least one polymerized compound of formula (I)

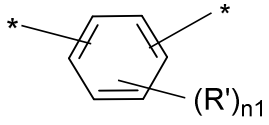


(I)

,

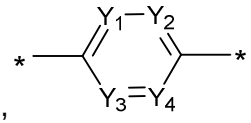
wherein

the divalent group  is selected from the group of formulae (B-1), (B-2), (B-3), (B-4) or (B-5)



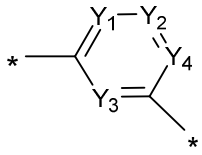
(B-1)

,



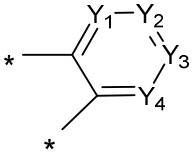
(B-2)

,



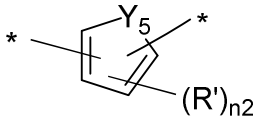
(B-3)

,



(B-4)

,



(B-5)

,

the asterisk * indicates the linkage to the remainder of formula (I);

Y_1, Y_2, Y_3, Y_4 are each independently of each other CR' or N, provided that only one of Y_1, Y_2, Y_3 and Y_4 is N and the others are CR';

Y_5 is O, S or NR_B;

R_B is selected from a linear or branched alkyl group having 1 to 10 C atoms or a linear or branched partially or fully fluorinated alkyl group having 1 to 10 C atoms;

X is O or S;

Y_0 is O or S;

A_1, A_2, A_3, A_4 are each independently of each other N, CR'' or C-Y-R_2-R_1, provided that in case m1 is 1 only one of A_1, A_2, A_3 and A_4 is N and the others are CR'' and provided that in case m1 is 0, only one of A_1, A_2, A_3 and A_4 is N, only one of A_1, A_2, A_3 and A_4 is C-Y-R_2-R_1 and the others are each independently CR'';

or

in case of m1 is 0, adjacent A_1-A_2, A_2-A_3 or A_3-A_4 are each independently of each other -N(R_2-R_1)-C(=O)- or -C(=O)-N(R_2-R_1)- and the remaining A_3, A_4, A_1 and A_2 are each independently of each other CR'';

Y is independently O, S, SO_2, or a bond;

m1 is 0 or 1;

n1 is 4;

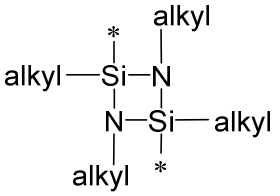
n2 is 2;

R' is at each occurrence independently selected from the group consisting of H, F, SF_5, CN, SO_2CF_3, a linear or branched, non-halogenated, partially or completely halogenated alkyl group having 1 to 20 C atoms, a non-halogenated, partially or completely halogenated cycloalkyl group having 3 to 6 C atoms, a linear or branched, non-halogenated, partially or completely halogenated alkoxy group having 1 to 20 C atoms and a linear or branched, non-halogenated, partially or completely halogenated thioalkyl group having 1 to 20 C atoms;

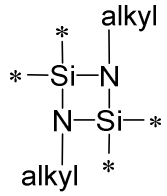
R'' is at each occurrence independently selected from the group consisting of H, F, Cl, Br, CN, SO_2CF_3, a linear or branched, non-halogenated, partially or completely halogenated alkyl group having 1 to 20 C atoms, a non-halogenated, partially or completely halogenated cycloalkyl group having 3 to 6 C atoms, a linear or branched, non-halogenated, partially or completely halogenated alkoxy group having 1 to 20 C atoms and a linear or

branched, non-halogenated and partially or completely halogenated thioalkyl group having 1 to 20 C atoms;

R_1 is a trialkoxysilyl group or a dialkoxyalkylsilyl group where the alkyl and/or alkoxy groups are each independently linear or branched having 1 to 6 C atoms, or a silyl group of formula (1), (2) or (3) or a polymerizable group of formula (4),

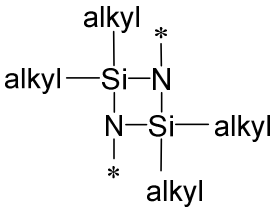


(1)

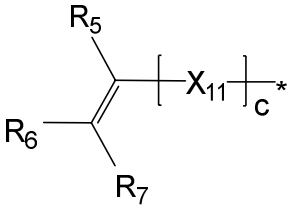


(2)

,



(3)



(4)

,

<u>wherein R_1 is polymerized and forms, or is part of the backbone of, the at least one polymerized compound of formula (I),</u>

wherein alkyl means at each occurrence independently of each other a linear or branched alkyl group having 1 to 6 C atoms and one of the asterisks "*" in each formula denotes a linkage to the linker $-R_2-$, $-R_2-Y-$ or $[Y-R_2-]_{m1}-$;

and wherein

X_{11} is selected from the group consisting of O, S, O-SO_2, SO_2-O, C(=O), OC(=O), C(=O)O, S(C=O) and (C=O)S,

R_5, R_6, R_7 are at each occurrence independently of each other selected from the group consisting of H, F, a linear or branched, non-fluorinated, partially or completely fluorinated alkyl group having 1 to 20 C atoms and an aryl with 6 to 14 C atoms and

c is 0 or 1;

$-R_2-$ is $-(C(R)_2)_o-$, or $-(C(R)_2)_p-X_8-(C(R)_2)_q-(X_9)_s-(C(R)_2)_r-(X_{10})_t-(C(R)_2)_u-$;

R is at each occurrence independently selected from the group consisting of H, F, a linear or branched alkyl group having 1 to 4 C atoms and a linear or branched partially or fully fluorinated alkyl group having 1 to 4 C atoms;

o is selected from the group consisting of 0 to 20,

X_8, X_9, X_{10} are at each occurrence independently O, S, SO_2, or NR_0,

s, t is 0 or 1,

p, q are at each occurrence independently selected from the group consisting of 1 to 10,

r, u are at each occurrence independently selected from the group consisting of 0 to 10, wherein the overall number of atoms for $–(C(R)_2)_p–X_8–(C(R)_2)_q–(X_9)_s–(C(R)_2)_r–(X_{10})_t-(C(R)_2)_u-$ is up to 20 atoms,

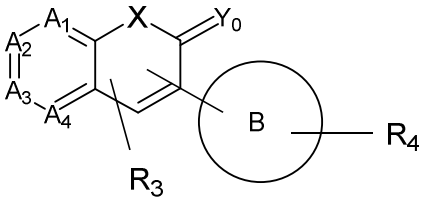
R_0 is at each occurrence independently selected from the group consisting of a linear or branched alkyl group having 1 to 4 C atoms and a linear or branched partially or fully fluorinated alkyl group having 1 to 4 C atoms;

R_3 is H, F, Cl, Br, CN or a linear or branched, non-halogenated, partially or completely halogenated alkyl group having 1 to 20 C atoms;

R_4 is R' in case m1 is 0 and

R_4 is R_1 in case m1 is 1.

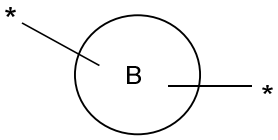
2. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to claim 1, wherein in polymerized compounds of formula (I), m1 is 0, and the at least one polymerized compound is of formula (I')



(I')

,

wherein R_1, $-R_2-$, Y, R_3, X, Y_0, R', R'' and



have a meaning as indicated in claim 1 and

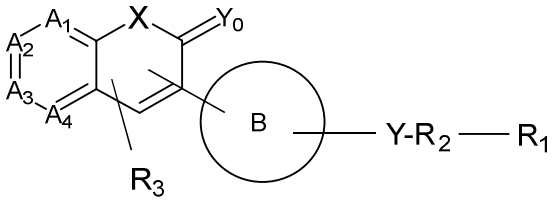
A_1, A_2, A_3, A_4 are each independently of each other N, CR'' or C-Y-R_2-R_1, provided that only one of A_1, A_2, A_3 and A_4 is N, only one of A_1, A_2, A_3 and A_4 is C-Y-R_2-R_1 and the others are each independently CR'';

or

adjacent A_1-A_2, A_2-A_3 or A_3-A_4 are each independently of each other -N(R_2-R_1)-C(=O)- or -C(=O)-N(R_2-R_1)- and the remaining A_3, A_4, A_1 and A_2 are each independently of each other CR''; and

R_4 is H or R'.

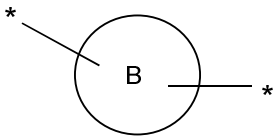
3. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to claim 1, wherein m1 is 1, and the at least one polymerized compound is of formula (I'')



(I'')

,

wherein R_1, $-R_2-$, Y, R_3, X, Y_0, R', R'' and

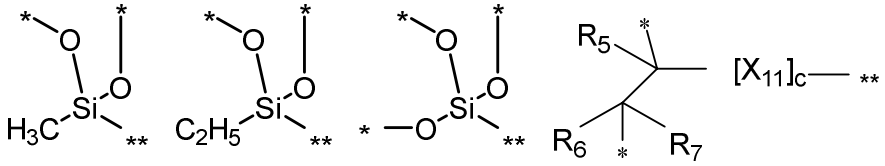


have a meaning as indicated in claim 1 and

A_1, A_2, A_3, A_4 are each independently of each other N or CR'' provided that only one of A_1, A_2, A_3 and A_4 is N and the others are CR''.

4. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 3, comprising an oligomer, polymer or copolymer comprising a constitutional unit M^0 based on formulae (I), (I') or (I'') wherein R_1 on each occurrence is polymerized, R_1 thus forms the regioregular, alternated, regiorandom, statistical, block or random oligomer or polymer backbone or is part of the copolymer backbone.

5. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 4, wherein said R_1 in <u>each occurrence is polymerized and</u> is of formulae (1-p), (2-p), (3-p) or (4-p)

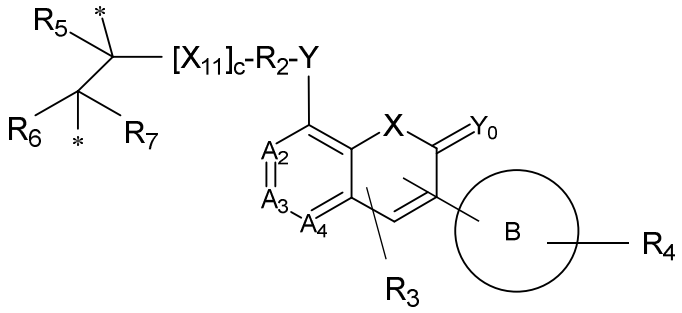


(1-p) , (2-p) , (3-p) , (4-p) ,

where the asterisk "*" within formulae (1-p) to (4-p) denotes a linkage to the adjacent repeating unit in the polymer chain or oligomer chain or to a terminal end group, the asterisk "**" within formulae (1-p) to (4-p) denotes the linkage to the remainder of formulae (I), (I') or (I'') and R_5, R_6, R_7, X_{11} and c has a meaning according to claim 1.

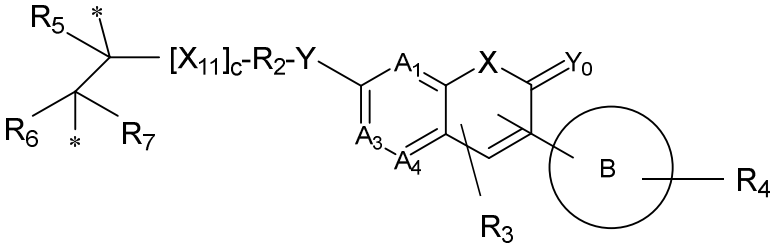
6. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 5, wherein the constitutional unit M^0 is of formulae (M^0-I'-a), (M^0-I'-b), (M^0-I'-c), (M^0-I'-d),

(M^0-I'-e), (M^0-I'-f), (M^0-I'-g), (M^0-I'-h), (M^0-I'-i) or (M^0-I''),



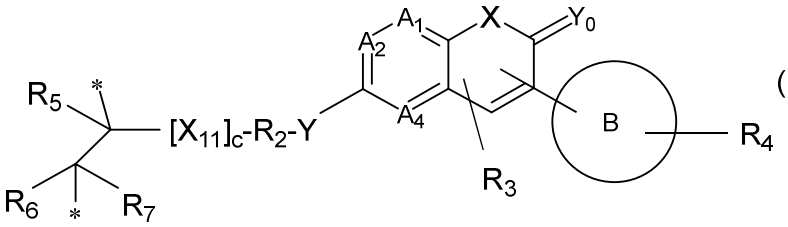
(M^0-I'-a)

,



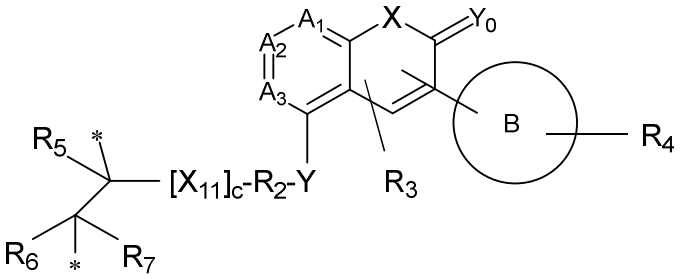
(M^0-I'-b)

,

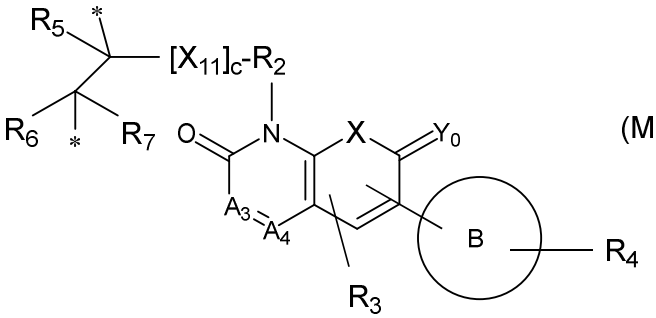


(M^0-I'-c)

,

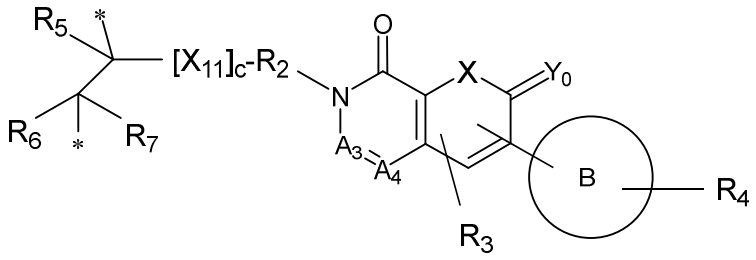


(M^0-I'-d)



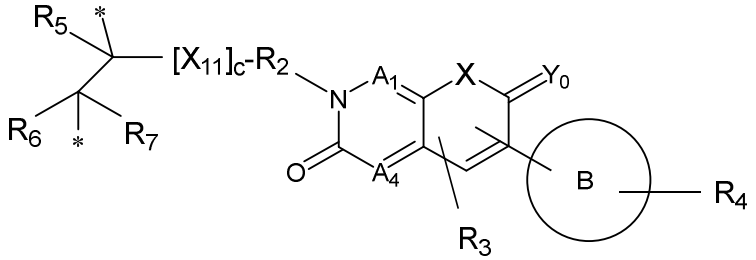
(M^0-I'-e)

,



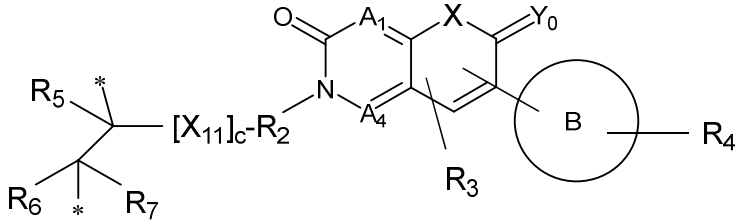
(M⁰-I'-f)

,



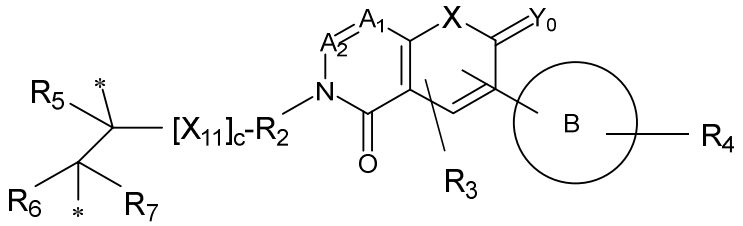
(M⁰-I'-g)

,



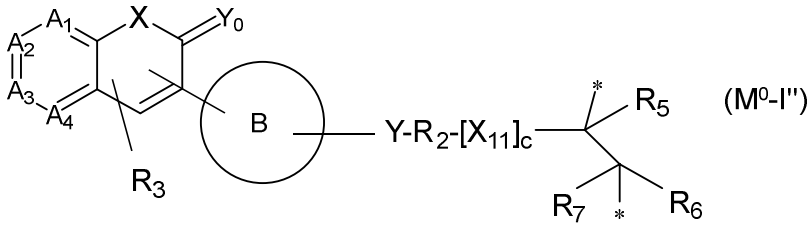
(M⁰-I'-h)

,



(M⁰-I'-i)

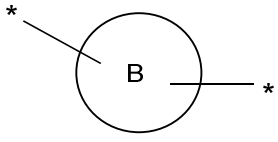
,



(M⁰-I'')

,

where R_1, $-R_2-$, X, Y_0, Y, A_1, A_2, A_3, A_4, R_3, R_4, R_5, R_6, R_7, X_{11}, c and



have a meaning according to claim 1 and R_4 is R' and where the asterisk "*" denotes at each occurrence a linkage to the

adjacent repeating unit in the polymer chain or oligomer chain or to a terminal end group.

7. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 6, comprising in addition to the at least one polymerized compound of formulae (I), (I') or (I'') or the constitutional unit M^0 of formulae (M^0-I'-a), (M^0-I'-b), (M^0-I'-c), (M^0-I'-d), (M^0-I'-e), (M^0-I'-f), (M^0-I'-g), (M^0-I'-h), (M^0-I'-i) or (M^0-I'') at least one further polymerized monomer selected from the group consisting of styrene, ethoxyethyl methacrylate (EOEMA), methyl methacrylate (MMA), methyl acrylate, n-alkyl acrylates (the n-alkyl group comprising 2-20 C-atoms), n-alkyl methacrylates (the n-alkyl group comprising 2-20 C-atoms), i-alkyl acrylates (the i-alkyl group comprising 3-20 C-atoms), i-alkyl methacrylates (the i-alkyl group comprising 3-20 C-atoms), ethoxyethoxy ethylacrylate (EEEA), 2-hydroxyethyl methacrylate (HEMA), tetrahydrofuryl methacrylate (THFMA), glycidylmethacrylate (GMA), 16-hydroxyhexadecyl acrylate, 16-hydroxyhexadecyl methacrylate, 18-hydroxyoctadecyl acrylate, 18-hydroxyoctadecyl methacrylate, 2-phenoxyethyl acrylate (EGPEA), heptafluorobutyl acrylate, heptafluorobutyl methacrylate, hexafluorobutyl acrylate, hexafluorobutyl methacrylate, hexafluoroisopropyl acrylate, hexafluoroisopropyle methacrylate, octafluoropentyl acrylate, octafluoropentyl methacrylate, petanfluoropropyl acrylate, pentafluoropropyl methacrylate, tetrafluoropropyl methacrylate, trifluoroethyl acrylate, trifluoroethyl methacrylate, Bisphenol A diacrylate-1 EO/Phenol (BPADA), 2-[3'-2'H-benzotriazol- 2'-yl)-4'-hydroxyphenyl]ethyl methacrylate (BTPEM) or ehtyleneglycoldimethacrylate.

8. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to claim 7, wherein the at least one further polymerized monomer is selected from methyl methacrylate, 2-

hydroxyethyl methacrylate, 2-phenoxyethyl acrylate, ethoxyethoxy ethylacrylate, 8-methylnonyl methacrylate, *n*-butyl methacrylate, 2-ethyl hexylmethacrylate or a mixture thereof.

9. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 8, wherein $-R_2-$ is at each occurrence independently $–(C(R)_2)_o–$ and R and o have a meaning as indicated in claim 1.

10. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 9, wherein X is O and Y_0 is O.

11. The ophthalmic device or the precursor article for manufacturing an ophthalmic device according to any oneof claims 1 to 10, wherein polymerized R_1 is at each occurrence independently derived from an acryl or methacryl radical.

12. The precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 11, wherein said precursor article is a blank which may be transformed into an eye implant, preferably an intraocular lens.

13. A process of forming an ophthalmic device or a precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 12, said process comprising the steps of:
- providing a composition comprising at least one compound of formulae (I), (I') or (I'') as described in one or more of claims 1 to 3, 9 and 10 and/or an oligomer or polymer as described in one or more of claims 4 to 8 and 11 but having at least one reactive group left for polymerization and optionally further monomers different from compounds of formulae (I), (I') or (I'') and/or crosslinking agents and/or UV absorbers and/or

radical initiators; and

- subsequently forming the ophthalmic device or precursor article of said composition.

14. A process of changing the optical properties of an ophthalmic device or a precursor article for manufacturing an ophthalmic device according to any one of claims 1 to 12, said process comprising the steps of:

- providing an ophthalmic device or a precursor article according to claim 13, and

- subsequently exposing said ophthalmic device or said precursor article to irradiation having a wavelength of at least 200 nm and at most 1500 nm.

15. An ophthalmic device or precursor article for manufacturing an ophthalmic device obtained by the process according to claim 14.

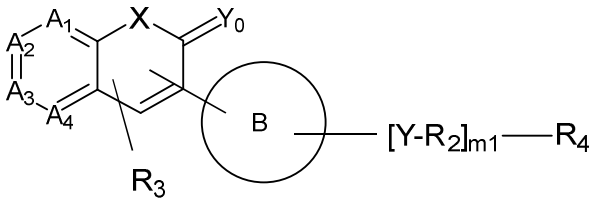
16. An oligomer, polymer or copolymer comprising at least one polymerized compound of formula (I) as described in claim 1.

17. The copolymer according to claim 16 comprising, in addition to the polymerized compounds of formula (I), at least one further polymerized monomer selected from the group consisting of styrene, ethoxyethyl methacrylate (EOEMA), methyl methacrylate (MMA), methyl acrylate, n-alkyl acrylates (the n-alkyl group comprising 2-20 C-atoms), n-alkyl methacrylates (the n-alkyl group comprising 2-20 C-atoms), i-alkyl acrylates (the i-alkyl group comprising 3-20 C-atoms), i-alkyl methacrylates (the i-alkyl group comprising 3-20 C-atoms), ethoxyethoxy ethylacrylate (EEEA), 2-hydroxyethyl methacrylate (HEMA), tetrahydrofuryl methacrylate (THFMA), glycidylmethacrylate (GMA), 16-hydroxyhexadecyl acrylate, 16-hydroxyhexadecyl methacrylate, 18-hydroxyoctadecyl acrylate, 18-hydroxyoctadecyl methacrylate, 2-phenoxyethyl acrylate (EGPEA), heptafluorobutyl

acrylate, heptafluorobutyl methacrylate, hexafluorobutyl acrylate, hexafluorobutyl methacrylate, hexafluoroisopropyl acrylate, hexafluoroisopropyle methacrylate, octafluoropentyl acrylate, octafluoropentyl methacrylate, petanfluoropropyl acrylate, pentafluoropropyl methacrylate, tetrafluoropropyl methacrylate, trifluoroethyl acrylate, trifluoroethyl methacrylate, Bisphenol A diacrylate-1 EO/Phenol (BPADA), 2-[3'-2'H-benzotriazol- 2'-yl)-4'-hydroxyphenyl]ethyl methacrylate (BTPEM) and ehtyleneglycoldimethacrylate.

18. A composition for polymerization comprising at least one compound of formulae (I), (I') or (I'') as described in any one of claims 1 to 3, 9 and 10, and/or an oligomer or polymer according to claim 16 or 17 having at least one reactive group left for polymerization, and/or a crosslinking agent, and/or a UV absorber, and/or a radical initiator, and optionally, further monomers different from compounds of formulae (I), (I') or (I'').

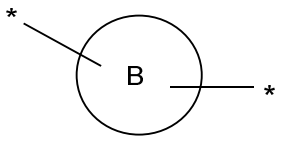
19. A compound of formula (I)



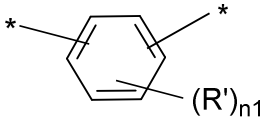
(I)

,

wherein

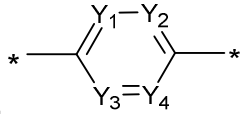
the divalent group 

is selected from the group of formulae (B-1), (B-2), (B-3), (B-4) or (B-5)



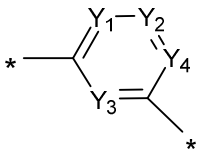
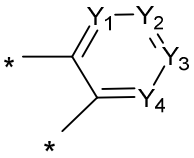
(B-1)

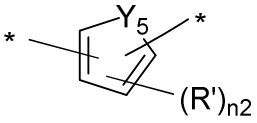
,



(B-2)

,


(B-3)

(B-4)


(B-5)

the asterisk * indicates the linkage to the remainder of formula (I);

Y_1, Y_2, Y_3, Y_4 are each independently of each other CR' or N, provided that only one of Y_1, Y_2, Y_3 and Y_4 is N and the others are CR';

Y_5 is O, S or NR_B;

R_B is selected from a linear or branched alkyl group having 1 to 10 C atoms or a linear or branched partially or fully fluorinated alkyl group having 1 to 10 C atoms;

A_1, A_2, A_3, A_4 are each independently of each other N, CR'' or C-Y-R_2-R_1, provided that in case m1 is 1 only one of A_1, A_2 and A_3 is N and the others and A_4 are CR'' and provided that in case m1 is 0, only one of A_1, A_2 and A_3 is N, only one of A_1, A_2, A_3 and A_4 is C-Y-R_2-R_1 and the others are each independently CR'';

or

in case of m1 is 0, adjacent A_1-A_2, A_2-A_3 or A_3-A_4 are each independently of each other -N(R_2-R_1)-C(=O)- or -C(=O)-N(R_2-R_1)- and the remaining A_3, A_4, A_1 and A_2 are each independently of each other CR'';

Y is independently O, S, SO_2, or a bond;

m1 is 0 or 1;

n1 is 4;

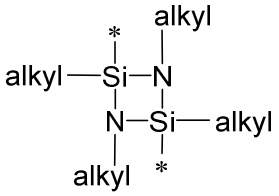
n2 is 2;

R' is at each occurrence independently selected from the group consisting of H, F, SF_5, CN, SO_2CF_3, a linear or branched, non-halogenated, partially or completely halogenated alkyl group

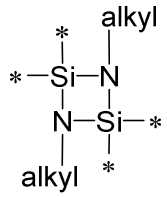
having 1 to 20 C atoms, a non-halogenated, partially or completely halogenated cycloalkyl group having 3 to 6 C atoms, a linear or branched, non-halogenated, partially or completely halogenated alkoxy group having 1 to 20 C atoms and a linear or branched, non-halogenated, partially or completely halogenated thioalkyl group having 1 to 20 C atoms;

R'' is at each occurrence independently selected from the group consisting of H, F, Cl, Br, CN, SO_2CF_3, a linear or branched, non-halogenated, partially or completely halogenated alkyl group having 1 to 20 C atoms, a non-halogenated, partially or completely halogenated cycloalkyl group having 3 to 6 C atoms, a linear or branched, non-halogenated, partially or completely halogenated alkoxy group having 1 to 20 C atoms and a linear or branched, non-halogenated and partially or completely halogenated thioalkyl group having 1 to 20 C atoms;

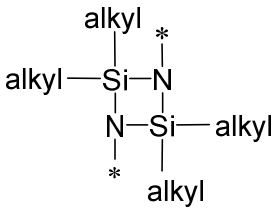
R_1 is a trialkoxysilyl group or a dialkoxyalkylsilyl group where the alkyl and/or alkoxy groups are each independently linear or branched having 1 to 6 C atoms, or a silyl group of formula (1), (2) or (3) or a polymerizable group of formula (4),



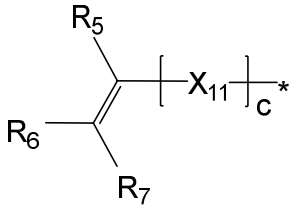
(1),



(2),



(3),



(4),

wherein alkyl means at each occurrence independently of each other a linear or branched alkyl group having 1 to 6 C atoms and one of the the asterisks “*” in each formula denotes a linkage to the linker $-R_2-$, $-R_2-Y-$ or $[Y-R_2-]_{m1}-$;

and wherein

X_{11} is selected from the group consisting of O, S, O-SO_2, SO_2-O, C(=O), OC(=O), C(=O)O, S(C=O) and (C=O)S,

R_5, R_6, R_7 are at each occurrence independently of each other selected from the group consisting of H, F, a linear or branched, non-fluorinated, partially or completely fluorinated alkyl group having 1 to 20 C atoms and an aryl with 6 to 14 C atoms and

c is 0 or 1;

-R_2- is $–(C(R)_2)_o–$, or $–(C(R)_2)_p–X_8–(C(R)_2)_q–(X_9)_s–(C(R)_2)_r–(X_{10})_t-(C(R)_2)_u-$;

R is at each occurrence independently selected from the group consisting of H, F, a linear or branched alkyl group having 1 to 4 C atoms and a linear or branched partially or fully fluorinated alkyl group having 1 to 4 C atoms;

o is 0 to 20,

X_8, X_9, X_{10} are at each occurrence independently O, S, SO_2, or NR_0,

s, t is 0 or 1,

p, q are at each occurrence independently selected from the group consisting of 1 to 10,

r, u are at each occurrence independently selected from the group consisting of 0 to 10, wherein the overall number of atoms for $–(C(R)_2)_p–X_8–(C(R)_2)_q–(X_9)_s–(C(R)_2)_r–(X_{10})_t-(C(R)_2)_u-$ is up to 20 atoms,

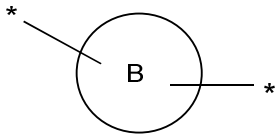
R_0 is at each occurrence independently selected from the group consisting of a linear or branched alkyl group having 1 to 4 C atoms and a linear or branched partially or fully fluorinated alkyl group having 1 to 4 C atoms;

R_3 is H, F, Cl, Br, CN or a linear or branched, non-halogenated, partially or completely halogenated alkyl group having 1 to 20 C atoms;

R_4 is R' in case m1 is 0;

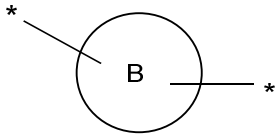
R_4 is R_1 in case m1 is 1 and

provided that in case of m1 is 0, Y is O or S, A_2 is C-Y-R_2-R_1,

the divalent group 

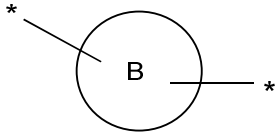
is in position 3 and is selected from formulae (B-3) and (B-4) where Y_4 within formula (B-3) is N and where Y_3 in formula (B-4) is N, c is 1;

provided that in case of m1 is 1, A_2 is CR'' and R'' is a linear or branched, non-halogenated, partially or completely halogenated alkoxy group having 1 to 20 C atoms and a linear or branched, non-halogenated and partially or completely halogenated thioalkyl group having 1 to 20 C atoms,

the divalent group 

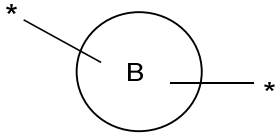
is in position 3 and is selected from formula (B-3), Y_2 within formula (B-3) is CR' and R' is H, Y_4 within formula (B-3) is N, and Y is a bond, O or S, c is 1;

provided that in case of m1 is 1, Y is a bond, c is 0, R_3 is Cl and

the divalent group 

is in position 3, o is 5 to 20;

provided that in case of m1 is 0, Y is a bond or O, c is 0, R_3 is Cl and

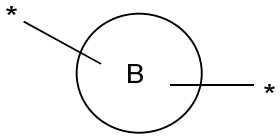
the divalent group 

is in position 3, o is 7 to 20;

provided that in case of m1 is 0, X is O, Y_0 is O and Y is a bond, c is 1 and X_{11} is O, S, O-SO_2, SO_2-O, OC(=O), C(=O)O, S(C=O) and (C=O)S;

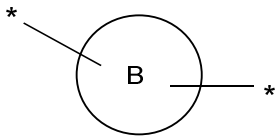
provided that in case of m1 is 1, X is O and Y_0 is O, o is 5 to 20;

provided that in case of m1 is 1, c is 0, Y is a bond or O and

the divalent group 

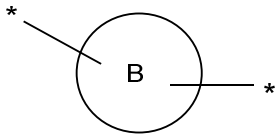
is in position 3, o is 11 to 20;

provided that in case of m1 is 1, A_1 or A_3 is N, Y is a bond, c is 0,

the divalent group 

is in position 3, o is 7 to 20 and

provided that in case of m1 is 0, X is O, Y_0 is O, Y is O or S, c is 0, A_2 is C-Y-R_2-R_1, A_3 is Br, A_1 is N,

the divalent group 

is in position 4 and is selected from formulae (B-1), (B-3) and (B-4), o is 2 to 20.