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(54) Title: OPTICAL MATERIAL DERIVED FROM A POLYMERIZABLE COMPOUND CONTAINING ALKYNYLENE AND THIOL FUNCTIONS

(57) Abstract: The invention relates to an optical material having a refractive index higher than or equal to 1.50 obtained by polymerization of a polymerizable composition comprising at least one polymerizable compound having at least two mercapto -SH groups, and at least one alkynylene -C≡C- group connected on each side to a carbon atom.



Optical material derived from a polymerizable compound containing alkynylene and thiol functions

The present invention relates to optical materials having improved optical and mechanical properties, which can be used in particular in optical substrates such as ophthalmic lenses, having generally a middle or high refractive index. The present invention is also directed to polymerizable compounds and a method of making the optical material.

BACKGROUND AND SUMMARY OF THE INVENTION

Plastic materials have been developed as alternatives and replacements for glass in applications such as optical lenses, fiber optics, windows, and automotive, nautical and aviation industries. As compared to inorganic glass, organic polymeric materials are advantageous in terms of light weight, high impact resistance, ease of molding and dyeability.

However, the refractive indices of many polymeric materials are lower than that of glass. Optically transparent plastic materials having a higher refractive index are of major interest since they allow the manufacture optical articles such as lenses of lower thickness for an equivalent corrective power.

Using thiol-ene chemistry, i.e., an organic reaction between a thiol and an alkene to form a thioether, polymers with both high glass transition temperature and high refractive indexes are often difficult to achieve with simple, cheap and commercially available monomers. For example, polymerization of a stoichiometric mixture of pentaerythritol tetrakis (mercaptopropionate) and pentaerythritol tetraacrylate provides a polymer having limited glass transition temperature (13°C) and refractive index (1.545). The known methods to improve the optical and mechanical properties of polymers obtained by thiol-ene reactions are not suitable, as they involve the use of very specific monomers that include highly polarizable bonds such as carbon-metal or phosphorus-chalcogens.

US 2016/376453 discloses a curable composition comprising a polythiol constituent, an alkene-containing and/or alkyne-containing constituent, and an epoxy-containing constituent. The polythiol constituent can derive from a mercaptan-containing terpene or terpenoid, a mercaptan-containing cyclic alkene, a mercaptan-containing polycyclic alkene, a linear alkene, a mercaptan-containing alkyne, a mercaptan-containing unsaturated fatty acid, a mercaptan-containing unsaturated fatty ester, or a mercaptan-containing polyalkene. The cured composition is used for making cell phone cases or expanded polystyrene foam. However, several chemicals need to be synthesized then blended to obtain the polymerizable composition.

The article "Hyperbranched Polymers by Thiol-Yne Chemistry: From Small Molecules to Functional Polymers", D. Konkolewicz et al., J. Am. Chem. Soc. 2009, 131, 50, 18075-18077 describes the homopolymerization of monomers comprising one terminal alkyne function and one thiol function, such as propargyl 3-mercaptopropionate. A catalytic amount of photoinitiator and

UV radiation are used to add two thiols across one alkyne bond at room temperature, resulting in hyperbranched polymers.

The article "Hyperbranched Polymers with High Degrees of Branching and Low Dispersity Values: Pushing the Limits of Thiol-Yne Chemistry", A. B. Cook et al, Macromolecules 2016, 49, 4, 1296-1304 discloses the homopolymerization of monomers comprising one terminal alkyne function and one thiol function, or the copolymerization of such monomers with multifunctional core molecules (poly-ene or poly-yne monomers), in the presence of photoinitiator and under UV irradiation, resulting in the formation of hyperbranched thiol-yne polymers.

Thus, there is a need in the art to develop a polymeric material having an adequate refractive index and good impact resistance/strength for practical use in optical articles, at a reasonable cost.

The present invention relates to an optical material having a refractive index higher than or equal to 1.50 obtained by polymerization of a polymerizable composition comprising at least one polymerizable compound A having at least two mercapto -SH groups, and at least one alkynylene -C≡C- group connected on each side to a carbon atom.

The present invention provides highly crosslinked polymer networks from thiol-yne reactions, thanks to specifically designed homo-polymerizable starting materials that can be cured through photochemical processes. A same monomer molecule bears two different reactive functions that usually are introduced in a polymerizable composition through different molecules. In the present case, the starting materials feature both alkyne and thiol functions.

Another advantage of the present invention is that the starting monomers can be finely tuned by adapting the substitution pattern to control their mechanical properties and refractive indexes.

DETAILED DESCRIPTION OF THE INVENTION

The terms "comprise" (and any grammatical variation thereof, such as "comprises" and "comprising"), "have" (and any grammatical variation thereof, such as "has" and "having"), "contain" (and any grammatical variation thereof, such as "contains" and "containing"), and "include" (and any grammatical variation thereof, such as "includes" and "including") are open-ended linking verbs. They are used to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof. As a result, a method, or a step in a method, that "comprises," "has," "contains," or "includes" one or more steps or elements possesses those one or more steps or elements, but is not limited to possessing only those one or more steps or elements.

Unless otherwise indicated, all numbers or expressions referring to quantities of ingredients, ranges, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about."

In the present description, unless otherwise specified, an optical article/material is understood to be transparent when the observation of an image through said optical article is

perceived with no significant loss of contrast, that is, when the formation of an image through said optical article is obtained without adversely affecting the quality of the image. This definition of the term “transparent” can be applied to all objects qualified as such in the description, unless otherwise specified.

5 The optical material of the invention is an organic glass, made from a thermosetting resin. The polymer matrix of said material is obtained by polymerization of a polymerizable composition comprising at least one polymerizable compound having at least two mercapto -SH groups, and at least one alkynylene -C≡C- group connected on each side to a carbon atom.

10 The optical material of the invention can be used as the substrate of an optical article, preferably an optical lens or lens blank, more preferably an ophthalmic lens or lens blank, such as a plastic eyeglass lens. It can also be used as a coating.

15 The term “ophthalmic lens” is used to mean a lens adapted to a spectacle frame to protect the eye and/or correct the sight. Said lens can be chosen from afocal, unifocal, bifocal, trifocal, progressive, plano, solar and Fresnel lenses or any other kind of lenses having a discontinuous surface.

20 Although ophthalmic optics is a preferred field of the invention, it will be understood that this invention can be applied to optical articles of other types, such as, for example, lenses for optical instruments, in photography or astronomy, optical sighting lenses, ocular visors, optics of lighting systems, screens, glazing, windshields, sport masks, face shields, goggles, optical coatings or adhesives, etc.

25 If the optical article is an optical lens, it may be coated on its front main surface, rear main side, or both sides with one or more functional coatings. As used herein, the rear face of the substrate is intended to mean the face which, when using the article, is the nearest from the wearer's eye. It is generally a concave face. On the contrary, the front face of the substrate is the face which, when using the article, is the most distant from the wearer's eye. It is generally a convex face. The optical article can also be a plano article.

30 A substrate, in the sense of the present invention, should be understood to mean an uncoated substrate, and generally has two main faces. The substrate may in particular be made of the present optical material having the shape of an optical article, for example an ophthalmic lens destined to be mounted in glasses. In this context, the term “substrate” is understood to mean the base constituent material of the optical article and more particularly of the optical lens. This material may act as support for a stack of one or more coatings or layers.

35 From the viewpoint of reducing the thickness of a lens, a plastic material having a high refractive index is desired. The refractive index of the optical material according to the invention is higher than or equal to 1.50, preferably 1.52 or greater, more preferably 1.54 or greater, more preferably 1.56 or greater, more preferably 1.58 or greater, more preferably 1.60 or greater, and still more preferably 1.65 or greater, 1.67 or greater, 1.70 or greater, 1.72 or greater, or 1.74 or greater, and it is preferably 1.80 or less, more preferably 1.75 or less. Unless otherwise specified, the refractive indexes referred to in the present application are expressed at 25°C at a wavelength
40 of 550 nm.

The refractive index of the optical material can be tuned by adapting the structure of the polymerizable precursor, in particular the weight amount represented by sulfur atoms in the monomer. The refractive index of the material can also be increased by the presence of one or more aromatic groups in the structure of the polymerizable precursor.

5 In one embodiment, the optical material according to the invention is thin, i.e., it preferably has a center thickness of 2 mm or less, more preferably 1.5 mm or less and even better 1.2 or 1.1 mm or less.

The optical material according to the invention preferably has a glass transition temperature higher than or equal to 70, 75, 80 or 85°C. It is preferably lower than or equal to
10 200°C. The glass transition temperature can be measured by DMA (dynamic mechanical analysis). The glass transition temperature of the present optical material is advantageously higher than that of most optical materials obtained by thiol-ene reactions due to a higher crosslinking density provided by the present polymerizable compounds.

The modulus of elasticity E (or Young's modulus, or storage modulus, or tensile modulus
15 of elasticity) of the optical material according to the invention is preferably higher than or equal to 2.5, 3 or 3.5 GPa. The modulus of elasticity E of a material evaluates the ability of the material to deform under the effect of a force applied. It can be measured by DMA (dynamic mechanical analysis).

The sulfur content of the optical material according to the invention preferably ranges from
20 20 to 70 % by weight, relative to the optical material total weight. In one embodiment, said sulfur weight content of the optical material ranges from 30 to 70 % or 50 to 65 %. It can be adapted by changing the nature of the polymerizable precursor.

The optical material according to the invention preferably has a relative light transmission factor in the visible spectrum T_v higher than or equal to 70 %, preferably higher than or equal to
25 75 %, more preferably higher than or equal to 80 %, and better higher than or equal to 85 %.

The T_v factor, also called "luminous transmission" of the system, is such as defined in ISO standard 13666:1998 and is measured according to the standard ISO 8980-3. It is defined as the average transmission in the 380-780 nm wavelength range that is weighted according to the sensitivity of the eye at each wavelength of the range and measured under D65 illumination
30 conditions (daylight). Transmissions are expressed for 2 mm thick optical articles, measured at the center of the optical article and at a normal incidence of the light beam (0° from the normal).

The polymerizable composition leading to the optical material is composed of one main component containing at least two different reactive (polymerizable) functions, namely the polymerizable compound having at least two mercapto -SH groups, and at least one alkynylene
35 -C≡C- group connected on each side to a carbon atom. It will be referred to as "compound A" in the present application. In other words, the optical material is obtained by homo-polymerization of compounds A (forming thioether bonds), which are heterodifunctional compounds, with or without the presence of optional comonomers.

The compound A is generally referred to as a heterodifunctional compound by convention, but may in fact comprise more than two kinds of reactive functions, e.g., when at least one of its substituents (R^1 , R^2 Z, etc.) comprises another kind of reactive function.

5 The polymerizable composition can comprise only one type of compound A, or a mixture of compounds A having different structures.

The polymerizable composition can comprise additional polymerizable compounds that are not compounds A according to the invention. In one embodiment, such additional polymerizable compounds are copolymerizable with compounds A according to the invention.

10 The monomer compounds A according to the invention preferably represent at least 50 % by weight relative to the total weight of polymerizable compounds present in said polymerizable composition, more preferably at least 60 %, 70 %, 80 %, 90 %, 95 %, 99 %, or 100 % by weight relative to the total weight of polymerizable compounds present in said polymerizable composition.

15 Examples of polymerizable compounds that are not compounds A according to the invention include polyols, polyamines, polythiols other than compounds A, polyisocyanates, polyisothiocyanates, epoxy-containing compounds.

20 Generally, the polymerizable composition contains polymerizable compounds in amounts adapted so that the molar ratio of SH groups to alkyne groups present in said polymerizable compounds is from 1.6 to 2.4, more preferably from 1.8 to 2.2, even more preferably 2. Those polymerizable compounds are compounds A, which may be identical or different, and optional polymerizable compounds that are not compounds A.

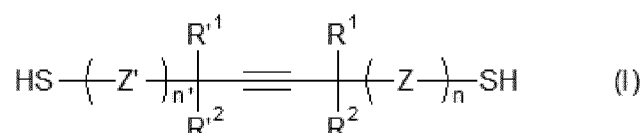
The compound A is defined as a compound comprising at least two sulfhydryl (mercapto) groups. It preferably comprises 2, 3 or 4 mercapto groups, more preferably 2.

25 The compound A is defined as a compound comprising at least one alkyne bond. It preferably comprises one or two alkyne bonds, more preferably one.

30 A stoichiometric reaction requires the use of two equivalents of thiol functions for one equivalent of alkyne functions in the polymerizable composition, when no other functions are present. The compound A does not necessarily contain a molecular ratio of polymerizable functions thiol and alkyne that provides stoichiometry in homopolymerization, i.e., a ratio of thiol groups / alkyne groups of 2:1. However, in one embodiment, the compound A is such that the ratio of thiol groups / alkyne groups per molecule of compound A is equal to 2:1.

In one embodiment, the compound A comprises at least one thioether function, preferably two. In another embodiment, the compound A comprises at least one ester function ($C(O)O$), preferably two.

35 In one embodiment, the polymerizable compound A is a compound of formula (I):



in which R^1 , R^2 , R'^1 and R'^2 represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, an aryl group, or R^1 and R^2 , taken together, form a divalent group of formula $-R^1-R^2-$, in which $-R^1-R^2-$ represents a substituted or unsubstituted alkylene group, or R'^1 and R'^2 , taken together, form a divalent group of formula $-R'^1-R'^2-$, in which $-R'^1-R'^2-$ represents a substituted or unsubstituted alkylene group,

Z and Z' represent, independently of each other, a divalent group, connected to the adjacent mercapto -SH group through a carbon atom, and $n = 0$ or 1 , $n' = 0$ or 1 .

In the present application, the term "alkyl" denotes a linear or branched, cyclic or acyclic, saturated or unsaturated hydrocarbon-based radical connected to the rest of the molecule via an sp^3 carbon atom, containing preferably from 1 to 25 carbon atoms, especially including acyclic groups containing from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, isopropyl, n-butyl and n-hexyl groups, cycloalkyl groups preferably containing from 3 to 7 carbon atoms, cycloalkylmethyl groups preferably containing from 4 to 8 carbon atoms.

By "substituted alkyl" group is understood an alkyl group as defined above, connected to the rest of the molecule via an sp^3 carbon atom and in which one or more methylene hydrogen atoms are replaced with a substituent. The substituted alkyl group can be substituted by one or a plurality of aryl groups and/or one or a plurality of heteroatoms such as N, S, O or a halogen atom (fluorine, chlorine, bromine or iodine). Mention will be made by way of examples of arylalkyl groups such as the trityl group ($-CPh_3$), the benzyl group or the 4-methoxybenzyl group, alkoxyalkyl groups, particularly dialkoxymethyl groups such as the diethoxymethyl or dimethoxymethyl groups, the groups $CH_2CO_2R^{11}$, wherein R^{11} represents an optionally substituted alkyl or aryl group.

The term "heteroalkyl" denotes an alkyl group as defined above, connected to the rest of the molecule via an sp^3 carbon atom, wherein one or a plurality of carbon atoms of the alkyl chain have been replaced with a heteroatom such as nitrogen (e.g., NH, N-alkyl...), oxygen, phosphorus, or sulfur (e.g., SO, SO_2 ...).

The term "aryl" denotes an aromatic monovalent carbocyclic radical, connected by an sp^2 carbon atom, including a single ring (for example a phenyl group) or multiple condensed rings (for example the naphthyl, terphenyl groups), which may optionally be substituted by one or a plurality of groups such as, without limitation, alkyl (for example methyl), hydroxyalkyl, aminoalkyl, hydroxyl, thiol, amino, halogeno (fluoro, bromo, iodo, chloro), nitro, alkylthio, alkoxy (for example methoxy), aryloxy, mono-alkylamino, dialkylamino, acyl, carboxyl, alkoxycarbonyl, aryloxy carbonyl, hydroxysulphonyl, alkoxysulphonyl, aryloxysulphonyl, alkylsulphonyl, alkylsulphinyl, cyano, trifluoromethyl, tetrazolyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl groups. Alternatively, two adjacent positions of the aromatic ring may be substituted by a methylenedioxy or ethylenedioxy group. The aryl group preferably comprises from 6 to 15 carbon atoms.

The term "heteroaryl" denotes an aryl group as defined above, connected to the rest of the molecule via an sp^2 carbon atom, wherein one or a plurality of carbon atoms of the aromatic ring(s) have been replaced with a heteroatom such as nitrogen, oxygen, phosphorus, or sulfur.

The heteroaryl groups may be structures with a single or a plurality of aromatic rings, or structures with a single or a plurality of aromatic rings coupled with one or a plurality of non-aromatic rings. In the structures having a plurality of rings, the rings may be fused, bonded covalently or bonded together via a divalent common group such as a methylene, ethylene, carbonyl group. Examples of heteroaryl groups are the thiophene (2-thienyl, 3-thienyl), pyridine (2-pyridyl, 3-pyridyl, 4-pyridyl), isoxazole, phthalimide, pyrazole, indole, furan groups and the benzofused analogues thereof, phenyl pyridyl ketone, quinoline, phenothiazine, carbazole, benzopyranone.

The suffix “-ene” is used to describe a divalent group. Thus, any of the terms defined herein can be modified with the suffix “-ene” to describe a divalent version of that moiety. For example, a divalent aryl group is “arylene”, a divalent alkyl group is “alkylene”. Alkylene groups are connected to the rest of the molecule via two sp^3 carbon atoms. Arylene groups are connected to the rest of the molecule via two sp^2 carbon atoms.

A (hetero)alkylene group represents a heteroalkylene or alkylene group. A (hetero)arylene group represents a heteroarylene or arylene group.

Examples of alkylene groups include linear C1-C10 alkylene groups, for example a methylene group $-CH_2-$, an ethylene group $-CH_2-CH_2-$, 1,3-propylene, a butylene or a hexylene group, especially 1,4-butylene and 1,6-hexylene and branched C3-C10 alkylene radicals such as 1,4-(4-methyl pentylene), 1,6-(2,2,4-trimethyl hexylene), 1,5-(5-methyl hexylene), 1,6-(6-methyl heptylene), 1,5-(2,2,5-trimethyl hexylene), 1,7-(3,7-dimethyl octylene), 2,2-(dimethylpropylene), 1,5-pentylene, 1,1-dimethylpentylene and 1,6-(2,4,4-trimethyl hexylene) radicals. Preferred cycloalkylene radicals include cyclopentylene and cyclohexylene radicals, optionally substituted especially by alkyl groups.

Non-limiting examples of heteroalkylene groups include $-CH_2SCH_2-$, $-CH_2CH_2SCH_2CH_2-$, $-CH_2OCH_2-$, $-CH_2CH_2OCH_2CH_2-$, $-CH_2-CH_2-S-CH_2-CH(CH_2SH)-S-CH_2-CH_2-$.

Examples of arylene groups include 2,4-tolylene, 2,6-tolylene, 2,4-naphthylene, 2,6-naphthylene, 1,5-naphthylene, 1,4-phenylene, 1,4-bisphenylene ($-p-C_6H_4-p-C_6H_4-$), 2-methyl-1,3-phenylene, 4-methyl-1,3-phenylene, tetramethylxylylene, 1,4-phenylene-methylene-1,4-phenylene (4,4-biphenylenemethylene).

In the present application, (hetero)alkylene and/or alkyl groups preferably comprise from 1 to 5 carbon atoms, more preferably from 1 to 4 carbon atoms, from 1 to 3 carbon atoms, or from 1 to 2 carbon atoms. It is preferable to have short substituent chains, in particular short alkyl and/or alkylene chains, since long chains tend to decrease the refractive index of the resulting optical material.

In one embodiment, $R^1 = R^2$ and $R'^1 = R'^2$.

The group $-R^1-R^2-$ (and/or the group $-R'^1-R'^2-$) defined in the present application preferably represents a linear alkylene group such as $-(CH_2)_5-$ (thus forming a cyclohexyl group with the carbon atom connected to the alkyne bond) or $-(CH_2)_4-$.

The R^1 , R^2 , R'^1 and R'^2 groups preferably represent, independently of each other, a hydrogen atom or a substituted or unsubstituted alkyl group, the alkyl group being preferably a C1-C5 alkyl group, more preferably a C1-C2 alkyl group and ideally a methyl group.

In preferred embodiments of the invention, $R^1 = R^2 = H$, or $R^{1'} = R^{2'} = H$, or $R^1 = R^2 = R^{1'} = R^{2'} = H$, or $R^1 = R^2 = CH_3$, or $R^{1'} = R^{2'} = CH_3$, or $R^1 = R^2 = R^{1'} = R^{2'} = CH_3$, or $R^1 = H$ and $R^2 = CH_3$, or $R^{1'} = H$ and $R^{2'} = CH_3$, or $R^1 = R^{1'} = H$ and $R^2 = R^{2'} = CH_3$.

In one embodiment, $Z = Z'$. In another embodiment, $n = n'$.

5 In another embodiment, Z and Z' are independently selected from substituted or unsubstituted:

- (hetero)alkylene groups, (hetero)arylene groups,
- carbonyl(hetero)alkylene groups, carbonyl(hetero)arylene groups,
- oxycarbonyl(hetero)alkylene groups, oxycarbonyl(hetero)arylene groups,
- 10 - carbonyloxy(hetero)alkylene groups, carbonyloxy(hetero)arylene groups,
- oxy(hetero)alkylene groups, oxy(hetero)arylene groups,
- thio(hetero)alkylene groups, thio(hetero)arylene groups,
- sulfo(hetero)alkylene groups, sulfo(hetero)arylene groups,
- amino(hetero)alkylene groups, amino(hetero)arylene groups,
- 15 - alkylamino(hetero)alkylene groups, alkylamino(hetero)arylene groups,
- arylamino(hetero)alkylene groups, arylamino(hetero)arylene groups,
- aminocarbonyl(hetero)alkylene groups, aminocarbonyl(hetero)arylene groups,
- alkylaminocarbonyl(hetero)alkylene groups, alkylaminocarbonyl(hetero)arylene groups,
- arylaminocarbonyl(hetero)alkylene groups, arylaminocarbonyl(hetero)arylene groups,
- 20 - carbonylamino(hetero)alkylene groups, carbonylamino(hetero)arylene groups,
- carbonylalkylamino(hetero)alkylene groups, carbonylalkylamino(hetero)arylene groups,
- carbonylarylamino(hetero)alkylene groups, carbonylarylamino(hetero)arylene groups,
- and combinations of the above divalent groups.

The carbonyl function is $-C(O)-$, the oxycarbonyl function is $-O-C(O)-$, the carbonyloxy function is $-C(O)O-$, the sulfo function is $-SO_2-$. An oxycarbonylalkylene group is $-O-C(O)-$ alkylene, while a carbonyloxyalkylene group is $-C(O)O-$ alkylene, etc.

Combinations of the above divalent groups include, without limitation, combinations of groups of the same or a different category, for example cycloalkylene-alkylene groups, bicycloalkylene groups, bicycloalkylene-alkylene groups, arylene-alkylene groups (such as the benzylene group), biarylene groups such as bisphenylene, biarylene-alkylene groups, arylene-oxyalkylene groups, poly[oxyalkylene] groups, poly[oxy(hetero)arylene] groups, poly[thioalkylene] groups, poly[thio(hetero)arylene] groups.

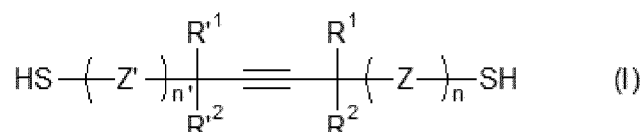
Specific examples of Z and Z' groups include, apart from the alkylene and arylene groups mentioned above, $-S-CH_2-$, $-S-CH_2-CH_2-$, $-S-CH_2-CH_2-S-CH_2-CH_2-$, $-CH_2SCH_2-$, $-S-CH_2-CH_2-S-$, $CH_2-CH(CH_2SH)-S-CH_2-CH_2-$, $-O-C(O)-CH_2-$, $-O-C(O)-CH_2-CH_2-$, $-O-C(O)-CH(CH_3)-$, $-CONH(CH_2)_3-$, $-OCH_2CH(OH)CH_2-$, polyoxyethylene groups such as $-(OCH_2CH_2)_n-$ with n being an integer ranging from 2 to 10, polyoxypropylene groups.

Other useful divalent Z and Z' groups comprise (hetero)alkylene groups or (hetero)arylene groups connected to any one of the following divalent groups: $-OC(O)O-$, $-C(O)C(O)-$, $-OC(O)C(O)O-$, $-C(O)OC(O)-$, $-C(S)-$.

In one embodiment, the groups Z and/or Z' comprise an alkenylene or alkynylene group.

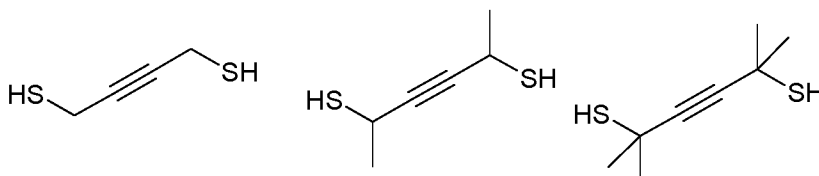
The most preferred Z and Z' groups are thio(hetero)arylene groups, thio(hetero)alkylene groups, and oxycarbonyl(hetero)alkylene groups, the (hetero)alkylene and (hetero)arylene groups being substituted or unsubstituted.

5 In one embodiment, said polymerizable compound A is selected from the compounds of formula (I):

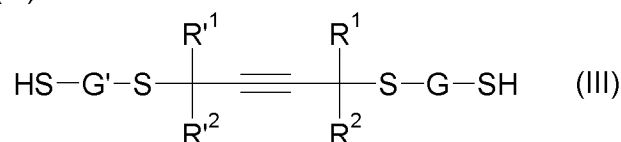


10 in which R¹, R², R^{1'} and R^{2'} are as defined above and preferably represent, independently of each other, a hydrogen atom or a substituted or unsubstituted alkyl group, Z and Z' are as defined above and preferably represent, independently of each other, a thio(hetero)arylene group, a thio(hetero)alkylene group, or a poly[thio(hetero)alkylene] group, the (hetero)alkylene and (hetero)arylene groups being substituted or unsubstituted, and n = 0 or 1, n' = 0 or 1.

Specific examples of such compounds of formula (I) in which n = n' = 0 are shown hereunder:



15 A useful category of compounds of formula (I) in which n = n' = 1 comprises thioether compounds of formula (III):

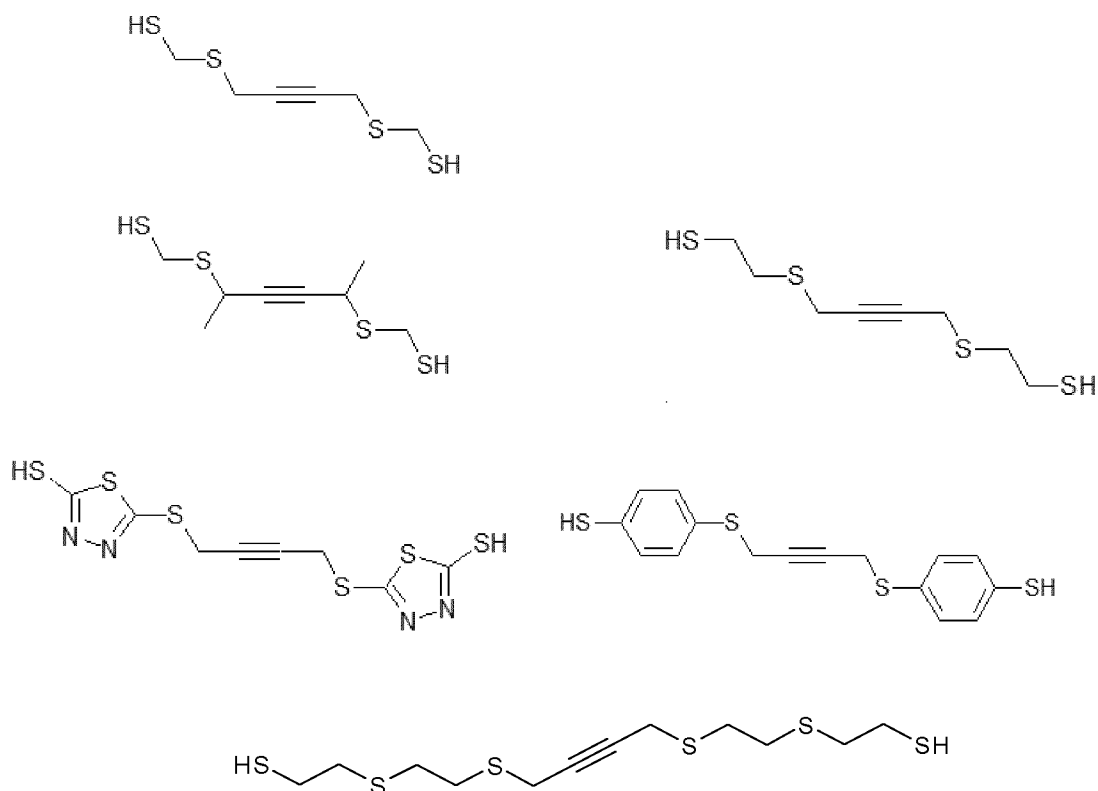


20 in which R¹, R², R^{1'} and R^{2'} are as defined above and preferably represent, independently of each other, a hydrogen atom or a substituted or unsubstituted alkyl group, G and G' represent, independently of each other, a divalent group connected to the adjacent mercapto -SH group through a carbon atom and preferably connected on both sides through a carbon atom.

25 The G and G' groups are preferably independently chosen from substituted or unsubstituted (hetero)alkylene groups, substituted or unsubstituted (hetero)arylene groups. G and G' are preferably independently selected from, substituted or unsubstituted, alkylene, typically a C2-C4 alkylene group, arylene, heteroarylene, or heteroalkylene such as an alkylene-thioalkylene group like the group -(CH₂)₂-S-(CH₂)₂-. In one embodiment, G = G'.

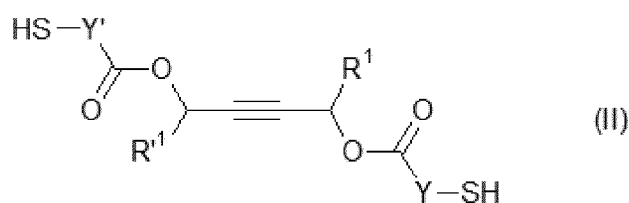
Specific examples of such compounds of formula (III) are shown hereunder:

30



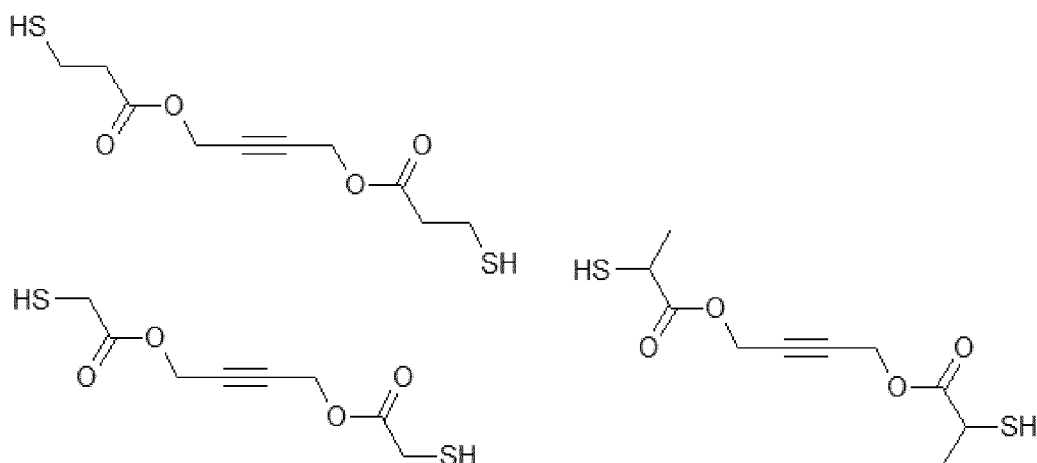
5

Another useful category of polymerizable compounds A comprises compounds of formula (II) having an ester function (C(O)O):



10 in which R¹ and R'¹ are as defined above and preferably represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group or an aryl group, Y and Y' represent, independently of each other, a substituted or unsubstituted (hetero)alkylene group.

Specific examples of such compounds are mercaptocarboxylic acid esters such as the compounds shown hereunder:



15

Compounds A can be easily synthesized from widely available and relatively cheap raw materials, such as 1,4-butyne-3-diol, 3-hexyne-2,5-diol, 2,5-dimethyl-3-hexyne-2,5-diol, 1,4-dichloro-2-butyne, thiolactic acid, mercaptopropionic acid, thioglycolic acid, ethane dithiol, etc., through chemical reactions well known to those skilled in the art. The widespread use of these raw materials used to synthesize the monomers of the present invention enables very competitive cost in regard of the refractive index achieved.

Compounds A can be stored in the presence of an antioxidant such as BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol) to prevent addition of thiol groups on the alkyne bond.

The polymerizable composition according to the invention may also include additives which are conventionally employed in polymerizable compositions intended for molding optical articles, in particular ophthalmic lenses, in conventional proportions, namely catalysts/polymerization initiators, photochromic agents, UV absorbers, perfumes, deodorants, resin modifiers, color balancing agents, chain extenders, crosslinking agents, free radical scavengers such as antioxidants or hindered amine light stabilizers (HALS), dyes, pigments, fillers, adhesion accelerators, inhibitors, anti-yellowing agents and mold release agents.

UV absorbers are frequently incorporated into optical materials in order to reduce or prevent UV light from reaching the retina (in particular in ophthalmic lens materials). The UV absorber that may be used in the present invention preferably have the ability to at least partially block light having a wavelength shorter than 400 nm, but can also have an absorption spectrum extending to the visible blue light range of the electromagnetic spectrum (400-450 nm), in particular 420-450 nm.

Said UV absorbers both protect the user's eye from UV light and the optical material itself, thus preventing it from weathering and becoming brittle and/or yellow. The UV absorber according to the invention can be, without limitation, a benzophenone-based compound, a benzotriazole-based compound or a dibenzoylmethane-based compound, preferably a benzotriazole compound. Suitable UV absorbers include without limitation 2-(2-hydroxyphenyl)-benzotriazoles such as 2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole (Seesorb® 703 / Tinuvin® 326), or other allyl hydroxymethylphenyl chlorobenzotriazoles, 2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methylphenol (Viosorb® 550), n-octyl-3-[3-tert-butyl-4-hydroxy-5-(5-chloro-2H-benzotriazol-2-yl)phenyl] propionate (Eversorb® 109), 2-(2-hydroxy-5-methoxyphenyl)benzotriazole, 2-(2-hydroxy-5-butoxyphenyl)benzotriazole and also Tinuvin® CarboProtect® from BASF. Preferred absorbers are of the benzotriazole family. Other examples of benzotriazole UV absorbers protecting from blue light can be found in WO 2017/137372.

The amount of UV absorber compounds according to the invention used herein is an amount sufficient to provide a satisfactory protection from UV light but not excessive so as to prevent precipitation. The UV absorber compounds are generally present in an amount ranging from 0.05 to 4 % by weight relative to the optical material total weight (or per 100 parts by weight of the polymerizable compounds present in the composition or relative to the weight of the optical material composition), preferably from 0.1 to 3 % by weight, more preferably from 0.1 to 2 % by weight.

Among the release agents that may be used in the invention, there may be cited mono and dialkyl phosphates, alkyl ester phosphates, silicones, fluorinated hydrocarbon, fatty acids and ammonium salts. The preferred release agents are mono and dialkyl phosphates, alkyl ester phosphates and mixtures thereof. Such release agents are disclosed inter alia in US 4975328 and EP 271839. The release agent is preferably used in an amount lower than or equal to 1 % by weight based on the total weight of the polymerizable compounds present in the polymerizable composition.

The optical material composition is photopolymerizable and can contain at least one system for initiating the polymerization (initiator), preferably a photoinitiator. A photoinitiator represents a molecule that absorbs light and generates reactive species (ions or radicals) that initiate a chemical reaction or transformation.

Photoinitiators can be selected for example from haloalkylated aromatic ketones such as chloromethylbenzophenones, benzoin and benzoin alkyl ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin, dialkoxyacetophenones such as diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone, benzylideneacetophenone, hydroxy ketones such as (1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one) (Irgacure® 2959 from CIBA), 2,2-di-sec-butoxyacetophenone, 2,2-diethoxy-2-phenyl-acetophenone, 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure® 184 from CIBA) and 2-hydroxy-2-methyl-1-phenylpropan-1-one (such as Darocur® 1173 sold by CIBA), alpha amino ketones, particularly those containing a benzoyl moiety, otherwise called alpha-amino acetophenones, for example 2-methyl 1-[4-phenyl]-2-morpholinopropan-1-one (Irgacure® 907 from CIBA), (2-benzyl-2-dimethyl amino-1-(4-morpholinophenyl)-butan-1-one (Irgacure® 369 from CIBA), monoacyl and bisacyl phosphine oxides and sulphides, such as phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure® 819 sold by CIBA, and Irgacure® 2022, which is a blend containing Irgacure® 819 and Darocur® 1173), 2,4,6,-trimethylbenzoylthoxydiphenyl phosphine oxide, triacyl phosphine oxides, 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole and mixtures thereof.

Free radical initiators such as peroxides and azo compounds, either thermally or photocatalyzed, can also be used, as well as Lewis acids, such as triarylsulfonium hexafluoroantimonate salts or diaryliodonium salts.

Initiators shall be used in the polymerizable composition in an amount sufficient to promote the polymerization reaction. They are generally present in an amount ranging from 0.05 to 10% by weight, preferably from 0.2 % to 5 %, and more preferably from 0.25 to 2 % by weight, relative to the total weight of polymerizable compounds present in the polymerization composition.

The polymerizable composition of the present invention can comprise a solvent for promoting the dissolution of additives. Any polar organic solvent can be used such as acetonitrile, tetrahydrofuran, dioxane, ethanol, 2-mercaptoethanol, acetone, or 3-methyl-2-butene-1-ol. The amount of solvent is generally kept below 2% by weight, based on the total weight of the polymerizable compounds present in the composition and preferably from 0 to 0.5% by weight, to avoid haze and bubbling.

The invention also relates to a process for the preparation of an optical material as described above, comprising polymerization of the polymerizable composition in the presence of at least one initiator, preferably a photoinitiator, followed by a thermal post-cure. The process preferably involves casting polymerization.

5 The mixing of the different constituents of the polymerizable composition can be performed by any known mixing technique such as those mentioned in US 5973098, preferably by introducing the constituents in a small reactor chamber and then mixing with a screw mixer.

A molding cavity of a casting mold assembly having any desirable shape can then be filled with the mixture of reactants.

10 The casting mold assembly generally comprises two mold parts defining two molding surfaces that cooperate to form a molding cavity when moved from an open position to a closed position. Each of the molding surfaces can be concave, convex, or planar, depending on the desired article shape. The molding surface can be convex, e.g., to form a concave substrate surface, or concave, e.g., to form a convex substrate surface.

15 More specifically, the optical material composition can be poured into the cavity of two mold parts held together using an annular closure such as a gasket or an adhesive tape.

An annular closure member can be disposed around the periphery of the two mold pieces and attached to them. The conventional way to fill such a two-piece mold is by causing the (liquid) optical material composition to flow into the molding cavity through a casting opening provided for
20 this purpose in the closure member. In at least a partly automated process, the molding cavity to be filled is vertically aligned with a filling device that is adapted to deliver a particular quantity of molding material through a nozzle.

Depending on the desired characteristics of the resulting optical material, degassing can be performed under reduced pressure and/or filtration can be performed under increased
25 pressure or reduced pressure before pouring the optical material composition in the mold assembly.

After pouring the composition in the casting mold assembly, preferably a lens casting mold assembly, polymerization, preferably photopolymerization of the polymerizable composition is generally performed by irradiating the composition, preferably with ultraviolet light. Preferably, UV
30 light wavelength ranges from 320 to 390 nm. UV light intensity typically ranges from 40 to 90 mW/cm² and the total exposure time to UV light, either in one shot or several shots, preferably ranges from 200 to 1650 seconds, more preferably from 200 to 600 seconds.

The final thermal post-cure can be performed in an oven or a heating device immersed in water according to a predetermined temperature program to cure the resin in the mold assembly.
35 The curing temperature generally ranges from 60°C to 140°C. The curing time is preferably lower than 5 hours, more preferably lower than 4, 3 or 2 hours. As used herein, curing refers to a chemical process of converting monomers or oligomers into a polymer of higher molar mass and then into a network.

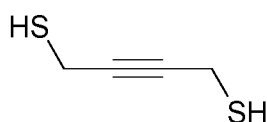
The resin molded product may then be annealed if necessary, at a temperature preferably
40 ranging from 100°C to 150°C.

Thereafter, the mold assembly is withdrawn from the heating source, the annular closure member is removed and the polymerized optical material can be recovered after disassembly of the mold parts.

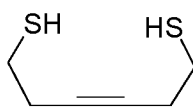
The present process can be used to manufacture a finished lens, having both sides at the required geometries, or a semi-finished lens, having one face that still needs to be surfaced at the required geometry.

In some applications, it is preferred that the main surface of the optical material be coated with one or more functional coating(s) to improve the optical and/or mechanical properties. The term "coating" is understood to mean any layer, layer stack or film which may be in contact with the substrate and/or with another coating, for example a sol-gel coating or a coating made of an organic resin. A coating may be deposited or formed through various methods, including wet processing, gaseous processing, and film transfer. These functional coatings classically used in optics may be, without limitation, an impact-resistant and/or adhesion primer, an abrasion-resistant and/or scratch-resistant coating, an antireflection coating, a polarized coating, a photochromic coating, or an antistatic coating, or a stack made of two or more such coatings, especially an impact-resistant primer coating coated with an abrasion and/or scratch-resistant coating.

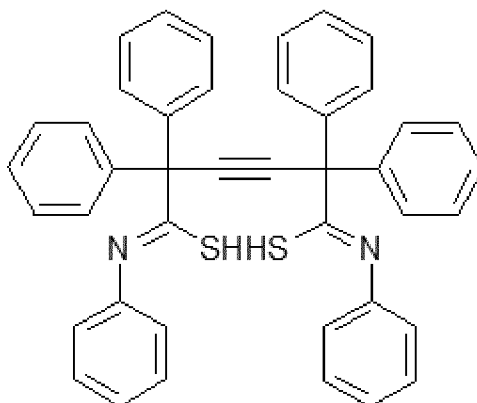
The invention also relates to a polymerizable compound of formula (I), (II) or (III), in which R^1 , R^2 , R'^1 , R'^2 , Z , Z' , n , n' , G , G' , Y , Y' have been defined previously, with the proviso that the polymerizable compound is not:



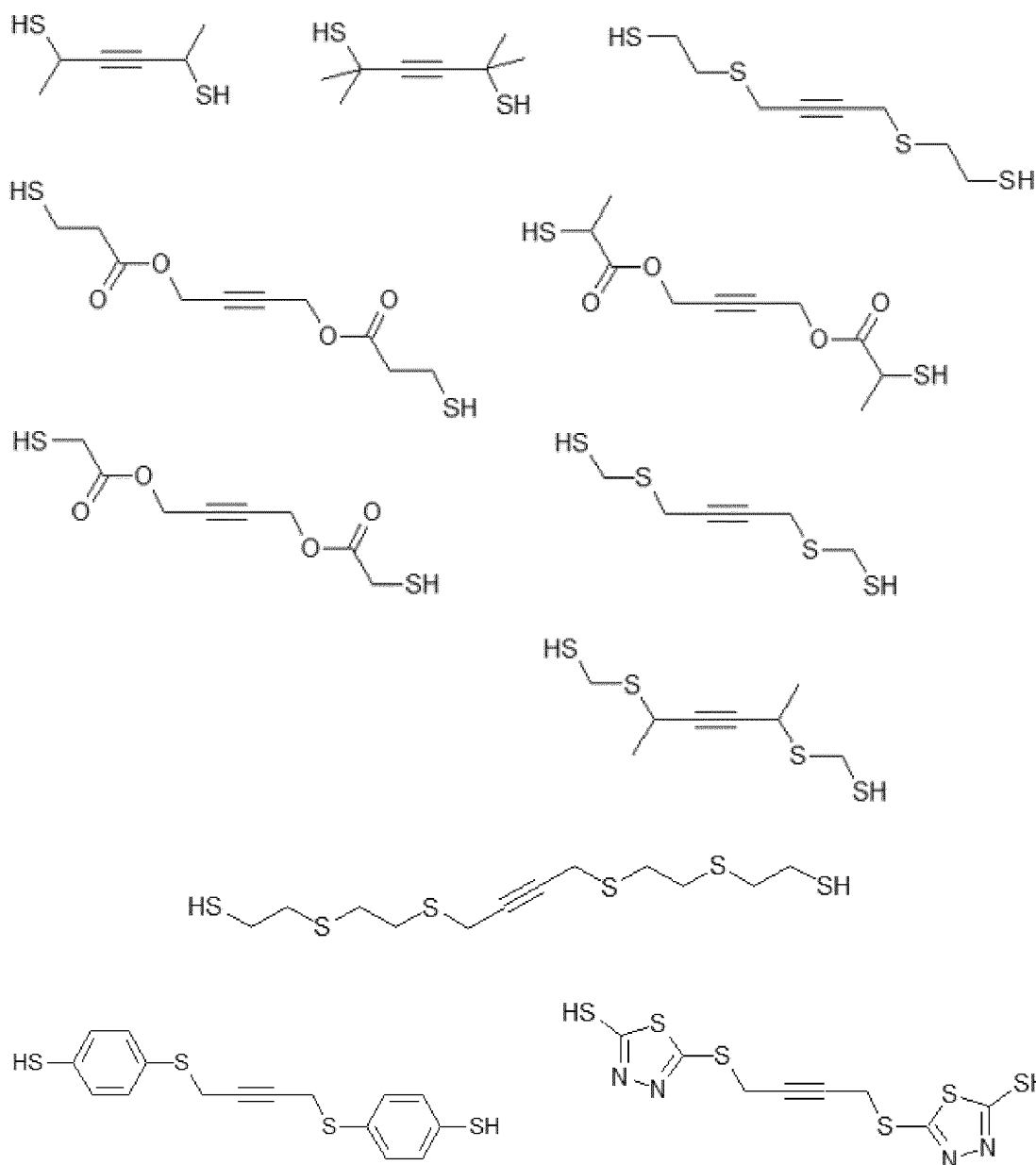
In one embodiment, said polymerizable compound is not:



In another embodiment, said polymerizable compound is not:



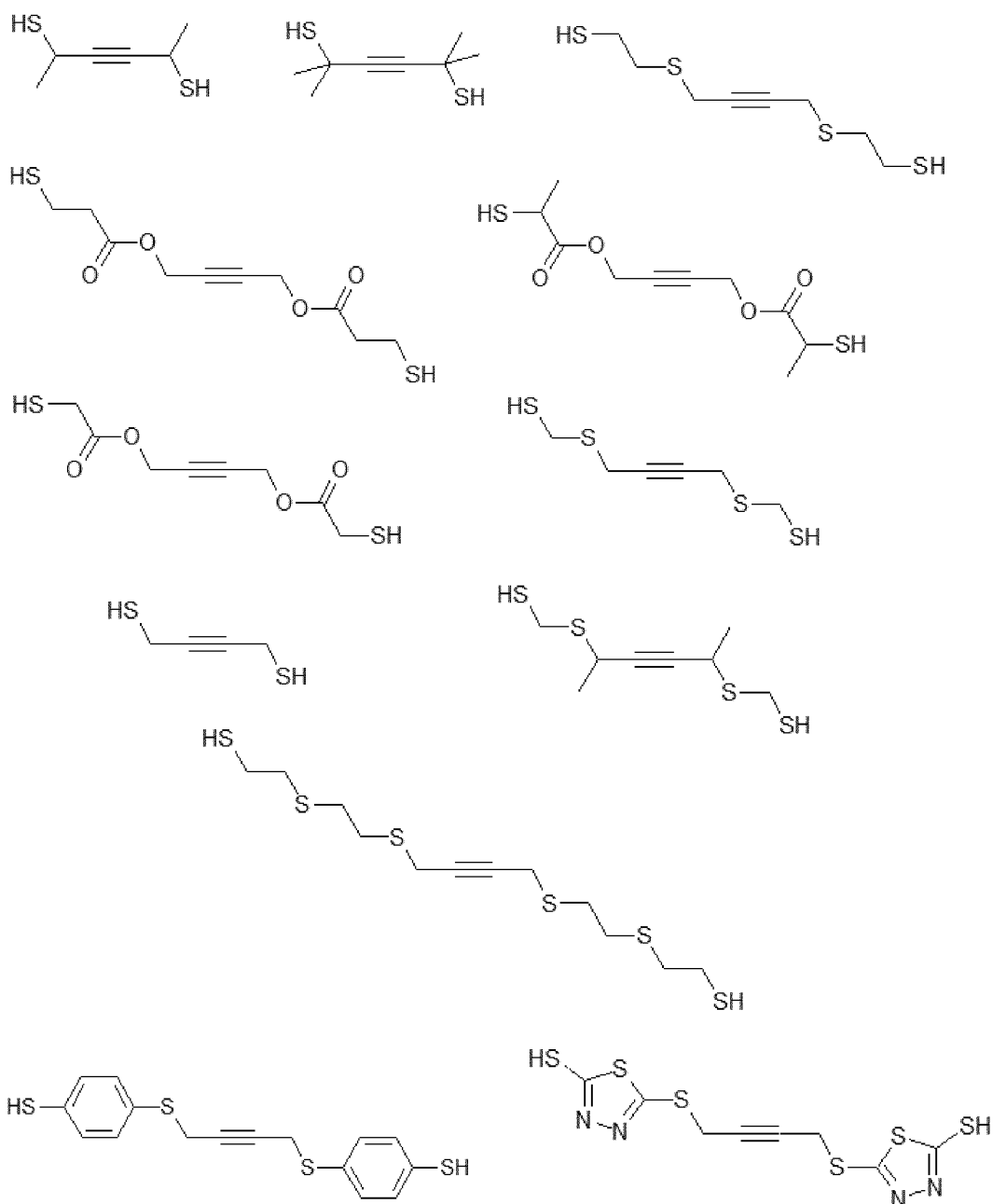
The polymerizable compound is preferably selected from the compounds of formulae:



5 The following examples illustrate the present invention in a more detailed, but non-limiting manner. Unless stated otherwise, all thicknesses disclosed in the present application relate to physical thicknesses. The percentages given in the tables are weight percentages.

Examples

The polymerizable compound A can be selected, without limitation, from the compounds of formulae:



1. Chemicals used and polymerization conditions

5 Optical substrates were prepared by homopolymerization of alkyne dithiol monomers in the presence of a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 1 % by weight). The polymerizable composition also contained Zelec UN[®] as a mold release agent.

10 The following alkyne dithiol monomers were used: 2-butyne-1,4-diol bis(2-mercaptopropanoate) (example 1), 2-butyne-1,4-dithiol (example 2), 3-hexyne-2,5-dithiol (example 3), 2,5-dimethyl-3-hexyne-2,5-dithiol (example 4), 2-butyne-1,4-diyl bis(2-mercaptopropanoate) (example 5), but-2-yne-1,4-diyl bis(3-mercaptopropanoate) (example 6), bis(ethane-1,2-dithiol)but-2-yne (example 7), 5,5'-(but-2-yne-1,4-diyl)bis(1,3,4-thiadiazole-2-thiol) (example 8),

bis(mercaptomethylthio)but-2-yne (example 9) and bis(mercaptomethylthio)hex-3-yne (example 10).

4,4'-(but-2-yne-1,4-diylbis(sulfanediyl)) dibenzenethiol (compound of formula (III) in which $G = G' = p$ -phenylene and $R^1 = R^2 = R'^1 = R'^2 = H$) can be used similarly (data not shown).

5 In a Duran bottle with a magnetic stirrer, the alkynylene dithiol monomer of formula (I) was mixed with the photoinitiator and the mold release agent. The composition was stirred at room temperature for 30 minutes and allowed to degas for 10 minutes to avoid bubbles in the final material.

10 Cleaned convex and concave plano glass molds of high refractive index having 65-80 mm diameter were assembled with a tape. A center thickness adjustment was made to obtain 2 mm thick samples.

The assembled molds were filled with the above monomer formulation using a cleaned syringe, and the polymerization reaction was carried out by UV-irradiation for 4 minutes (365 nm), followed by a thermal post-cure (80°C, 1h) in an oven from ShenZhen Height-LED Technology
15 Company Limited. The molds were then disassembled to obtain lenses comprising a body of a thermoset material.

2. Synthesis of alkynylene dithiol monomers

20 Preparation of 2-butyne-1,4-diol bisthioglycolate (example 1)

2-butyne-1,4-diol (0.05 mol, 4.305 g), BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol, 0.1 g), thioglycolic acid (0.105 mol, 9.673 g) and p-toluene sulfonic acid (0.2 g) were introduced in a flask, and the mixture was heated at 60°C under reduced pressure (7 mbar) until completion of
25 the reaction as shown by FTIR. Ethyl acetate (40 mL) was added, and the organic phase cleaned 3 times with NaHCO₃ 10 %, one time with deionized water), dried over CaCl₂, filtered and stripped under vacuum. The isolated compound was decolorized using charcoal in dichloromethane, then filtered and solvent stripped. It is stable enough to be stored over antioxidant (BHT, 300 ppm) at 4°C for at least 2 months.

30 The monomers of example 5 (2-butyne-1,4-diol bis(2-mercaptopropanoate) and example 6 (but-2-yne-1,4-diyl bis(3-mercaptopropanoate)) can be prepared similarly. 2-butyne-1,4-dithiol (example 2) can be synthesized according to a known method by thiolation of 1,4-dichloro-2-butyne with sodium thioacetate. 3-hexyne-2,5-dithiol (example 3) and 2,5-dimethyl-3-hexyne-2,5-dithiol (example 4) can be prepared similarly. Bis(ethane-1,2-dithiol)but-2-yne (example 7) can
35 be prepared from butyne-1,4-dichloride and ethane dithiol. Bis(mercaptomethylthio)but-2-yne (example 9) and bis(mercaptomethylthio)hex-3-yne (example 10) can be prepared from butyne-1,4-dichloride and acetylthiomethylthiol following a procedure described in US 6770734, followed by alcoholysis.

Preparation of 5,5'-(but-2-yne-1,4-diylbis(sulfaneydiyl)) bis(1,3,4-thiadiazole-2-thiol)
(example 8)

In a 500 mL round-bottom flask equipped with a condenser and an addition funnel, 15.025 g of 2,5-dimercapto-3,4-thiadiazole (bismuthiol, 0.1 mol) were dissolved in 200 mL of ethanol, and a solution of 4 g NaOH in 20mL deionized water was slowly added over ~10 minutes. The mixture was heated to reflux. In a beaker, 6.419 g of 1,4-dichloro-2-butyne (0.05 mol) were dissolved in 50 mL of ethanol. The solution was charged in the addition funnel and slowly added in the bismuthiol hemi-salt solution. The mixture was heated to reflux for 2 hours. The mixture was allowed to cool to room temperature and the precipitate was filtered under vacuum. The isolated compound had a melting point of 170°C. It needed to be molten prior to photopolymerization.

3. Testing methods

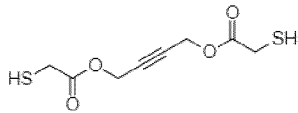
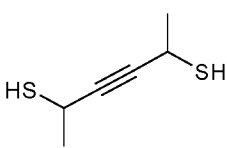
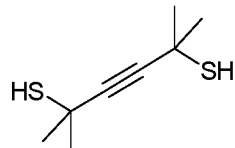
The following test procedures were used to evaluate the optical articles prepared according to the present invention.

The measurements of refractive index and Abbe number were carried out by ellipsometry at the wavelength of 550 nm in the manner disclosed in WO 2015/166144.

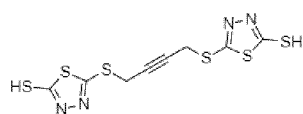
The thermal and mechanical properties of the lenses (glass transition temperature T_g and modulus of elasticity E) have been evaluated by DMA (dynamic mechanical analysis) using a dynamic mechanical analyzer Q800 module supplied by TA Instruments. Measurements were conducted in the multi-frequency strain mode. A sample was in rectangular shape with dimensions of 50x8x2 mm. The operating was performed at a heating rate of 2°C/min from 25-130°C at a 30 µm amplitude, pre-load force 0.5 N with force track 150 %.

4. Optical articles prepared and characterizations

The tables hereunder indicate the structure of the monomer used, the refractive index of the resulting polymer and its theoretical sulfur content, by weight.

Example	1	2	3	4
Monomer				
% sulfur	27.3	54.2	43.7	36.7
Refractive index	1.61	1.71	1.67	1.65

Example	5	6	7
Monomer			
% sulfur	24.4	24.4	53.7
Refractive index	1.60	1.60	1.71

Example	8	9	10
Monomer			
% sulfur	54.7	60.8	53.7
Refractive index	1.72	1.74	1.71

The resulting new polymers had high refractive indexes, ranging from 1.60 to 1.74, depending on the structure of the starting monomer.

- 5 The optical material of example 1 had an Abbe number of 39, a glass transition temperature T_g of 89°C and a modulus of elasticity E of 3.7 GPa. As a comparison, a material obtained by classic thiol-ene polymerization of a stoichiometric mixture of pentaerythritol tetrakis (mercaptopropionate) and pentaerythritol tetraacrylate has a much lower glass transition temperature ($T_g = 13^\circ\text{C}$) and refractive index (1.545).

Claims

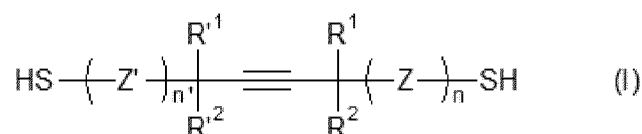
1. An optical material having a refractive index higher than or equal to 1.50 obtained by polymerization of a polymerizable composition comprising at least one polymerizable compound A having at least two mercapto -SH groups, and at least one alkynylene -C≡C- group connected on each side to a carbon atom, wherein:

a) the polymerizable compounds A having at least two mercapto -SH groups and at least one alkynylene -C≡C- group connected on each side to a carbon atom represent at least 70 % by weight relative to the total weight of polymerizable compounds present in said polymerizable composition, or

b) the sulfur content of said optical material ranges from 20 to 70 % by weight, relative to the optical material total weight, or

c) the polymerizable composition contains polymerizable compounds in amounts adapted so that the molar ratio of SH groups to alkyne groups present in said polymerizable compounds ranges from 1.6 to 2.4.

2. The optical material of claim 1, wherein said polymerizable compound A is a compound of formula (I):



in which R¹, R², R^{1'} and R^{2'} represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, an aryl group, or R¹ and R², taken together, form a divalent group of formula -R¹-R²-, in which -R¹-R²- represents a substituted or unsubstituted alkylene group, or R^{1'} and R^{2'}, taken together, form a divalent group of formula -R^{1'}-R^{2'}-, in which -R^{1'}-R^{2'}- represents a substituted or unsubstituted alkylene group,

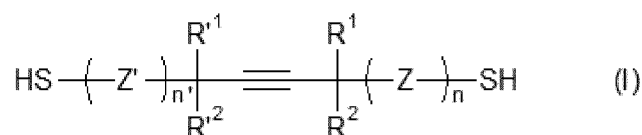
Z and Z' represent, independently of each other, a divalent group, connected to the adjacent mercapto -SH group through a carbon atom, and n = 0 or 1, n' = 0 or 1.

3. The optical material of any one of the preceding claims, wherein Z and Z' are independently selected from substituted or unsubstituted:

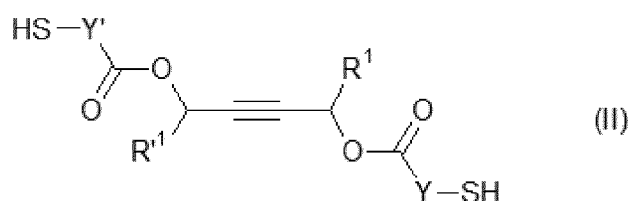
- (hetero)alkylene groups, (hetero)arylene groups,
- carbonyl(hetero)alkylene groups, carbonyl(hetero)arylene groups,
- oxycarbonyl(hetero)alkylene groups, oxycarbonyl(hetero)arylene groups,
- carbonyloxy(hetero)alkylene groups, carbonyloxy(hetero)arylene groups,
- oxy(hetero)alkylene groups, oxy(hetero)arylene groups,
- thio(hetero)alkylene groups, thio(hetero)arylene groups,
- sulfo(hetero)alkylene groups, sulfo(hetero)arylene groups,
- amino(hetero)alkylene groups, amino(hetero)arylene groups,
- alkylamino(hetero)alkylene groups, alkylamino(hetero)arylene groups,
- arylamino(hetero)alkylene groups, arylamino(hetero)arylene groups,

- aminocarbonyl(hetero)alkylene groups, aminocarbonyl(hetero)arylene groups,
 - alkylaminocarbonyl(hetero)alkylene groups, alkylaminocarbonyl(hetero)arylene groups,
 - arylaminocarbonyl(hetero)alkylene groups, arylaminocarbonyl(hetero)arylene groups,
 - carbonylamino(hetero)alkylene groups, carbonylamino(hetero)arylene groups,
 - 5 - carbonylalkylamino(hetero)alkylene groups, carbonylalkylamino(hetero)arylene groups,
 - carbonylarylamino(hetero)alkylene groups, carbonylarylamino(hetero)arylene groups,
- and combinations of the above divalent groups.

4. The optical material of any one of the preceding claims, wherein Z and Z' are independently selected from thio(hetero)arylene groups, thio(hetero)alkylene groups, and
 10 oxycarbonyl(hetero)alkylene groups, the (hetero)alkylene and (hetero)arylene groups being substituted or unsubstituted.
5. The optical material of any one of the preceding claims, wherein said polymerizable compound A is selected from the compounds of formula (I):



- 15 in which R¹, R², R'¹ and R'² represent, independently of each other, a hydrogen atom or a substituted or unsubstituted alkyl group, Z and Z' represent, independently of each other, a thio(hetero)arylene group, a thio(hetero)alkylene group, or a poly[thio(hetero)alkylene] group, the (hetero)alkylene and (hetero)arylene groups being substituted or unsubstituted, and n = 0 or 1, n' = 0 or 1.
- 20 6. The optical material of any one of claims 1 to 4, wherein said polymerizable compound A is selected from the compounds of formula (II):



- in which R¹ and R'¹ represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group or an aryl group, Y and Y' represent, independently of each other, a
 25 substituted or unsubstituted (hetero)alkylene group.
7. The optical material of any one of claims 2 to 6, wherein the (hetero)alkylene and/or alkyl groups comprise from 1 to 5 carbon atoms.
8. The optical material of any one of the preceding claims, wherein:
- a) the polymerizable compounds A having at least two mercapto -SH groups and at least one
 30 alkynylene -C≡C- group connected on each side to a carbon atom represent at least 70 % by weight relative to the total weight of polymerizable compounds present in said polymerizable composition, or

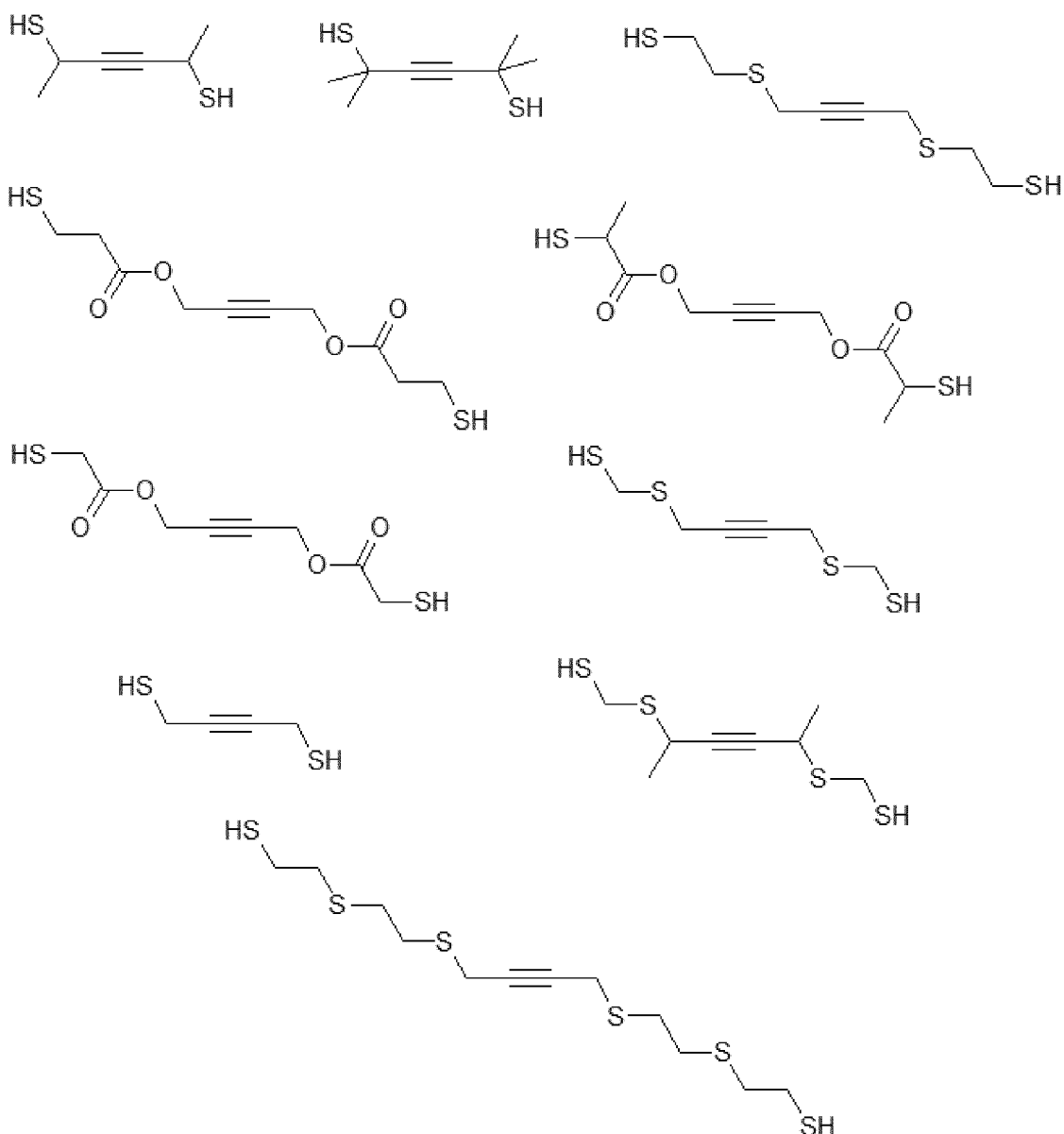
b) the sulfur content of said optical material ranges from 20 to 70 % by weight, relative to the optical material total weight.

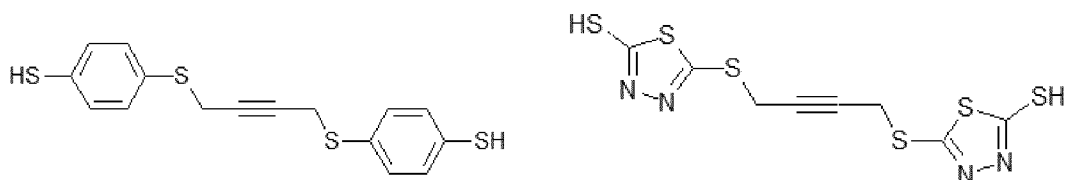
9. The optical material of any one of the preceding claims, further defined as having a refractive index higher than or equal to 1.60, more preferably higher than or equal to 1.65, even more preferably higher than or equal to 1.70.

10. The optical material of any one of the preceding claims, further defined as having a glass transition temperature higher than or equal to 85°C.

11. The optical material of any one of the preceding claims, further defined as the substrate of an optical lens.

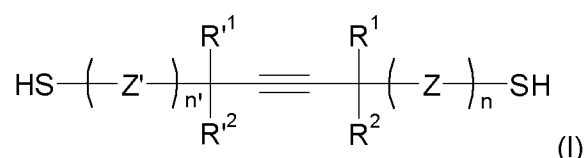
10 12. The optical material of any one of the preceding claims, wherein said polymerizable
compound A is selected from the compounds of formulae:





13. A process for the preparation of an optical material according to any one of the preceding claims, comprising polymerization of said polymerizable composition in the presence of at least one initiator, followed by a thermal post-cure.

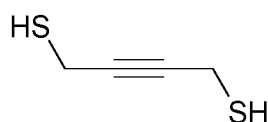
5 14. A polymerizable compound of formula (I):



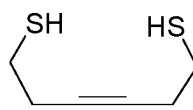
10 in which R^1 , R^2 , $\text{R}^{1'}$ and $\text{R}^{2'}$ represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, an aryl group, or R^1 and R^2 , taken together, form a divalent group of formula $-\text{R}^1-\text{R}^2-$, in which $-\text{R}^1-\text{R}^2-$ represents a substituted or unsubstituted alkylene group,

Z and Z' represent, independently of each other, a divalent group, connected to the adjacent mercapto $-\text{SH}$ group through a carbon atom,

15 and $n = 0$ or 1 , $n' = 0$ or 1 , with the proviso that the compound of formula (I) is not:

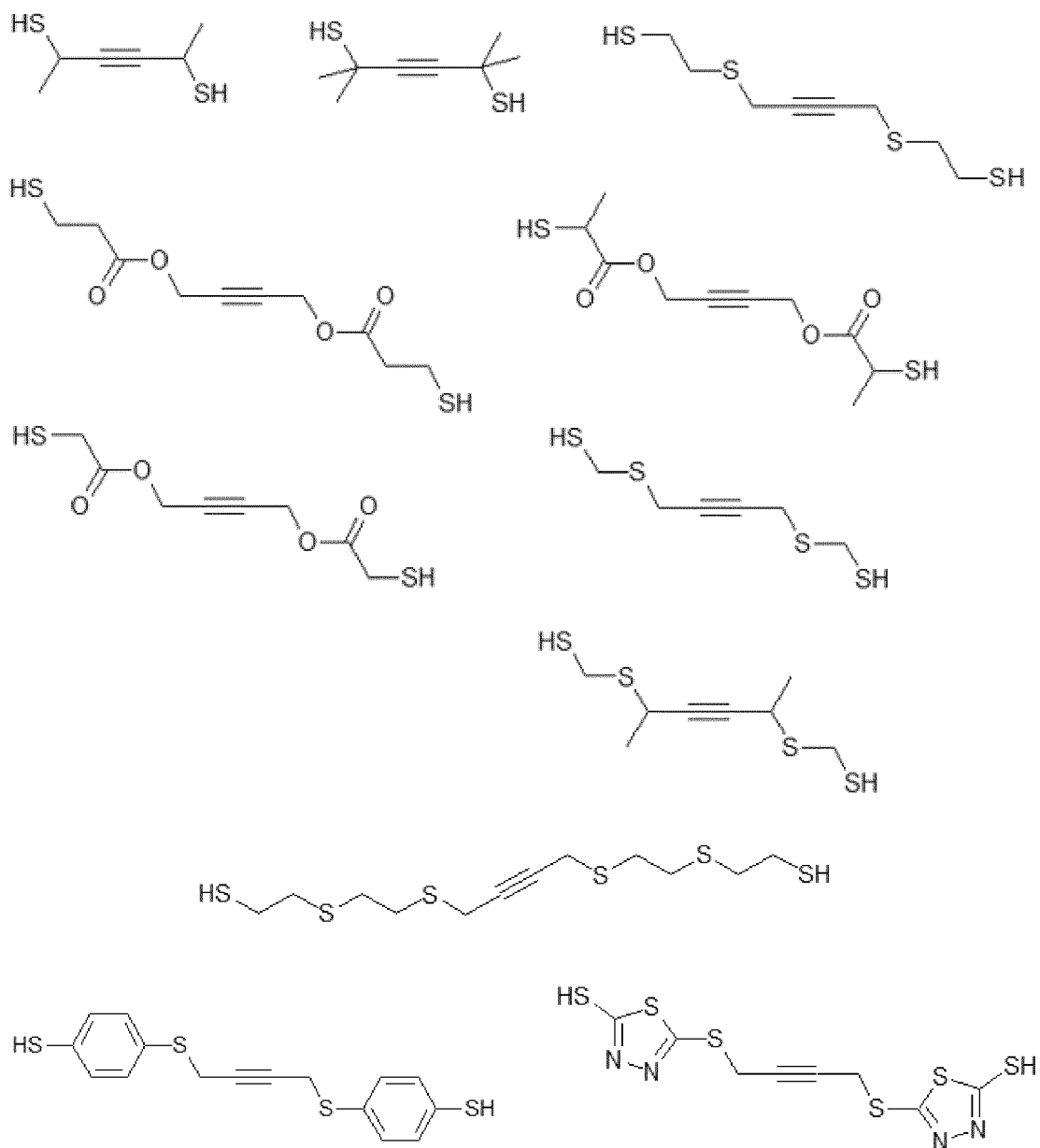


and with the proviso that the compound of formula (I) is not:



20

15. The polymerizable compound of claim 14, wherein said polymerizable compound is selected from the compounds of formulae:



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/070623

A. CLASSIFICATION OF SUBJECT MATTER		
INV. G02B1/04 C07C321/00 C07C321/08 C07C321/18 C07C321/28 C07C323/52		
ADD. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) G02B C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/009293 A1 (YAO HUIRONG [US] ET AL) 14 January 2010 (2010-01-14) paragraph [0038]; claims 1, 9 ----- - / - -	1 - 15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 25 September 2024		Date of mailing of the international search report 08/10/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Le Masson, Nicolas

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/070623

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BERGMANN ERNST: "Einige alkaliorganische Versuche. (Zugleich eine Bemerkung zu der Arbeit von Wittig und Leo über die Polarisierbarkeit der Äthylen-Bindung.)", BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT ABTEILUNG B:ABHANDLUNGEN , vol. 63, no. 9 15 October 1930 (1930-10-15), pages 2593-2597, XP093119736, DE ISSN: 0365-9488, DOI: 10.1002/cber.19300630935 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/pdf/10.1002/cber.19300630935 page 2597; compound XIII -----	14
A	BRUDERMÜLLER MARTIN ET AL: "Eliminierung statt umlagerung bei schwefelhaltigen, ungesättigten C 12 -ringen", CHEMISCHE BERICHTE , vol. 121, no. 12 1 December 1988 (1988-12-01), pages 2239-2244, XP093119703, DE ISSN: 0009-2940, DOI: 10.1002/cber.19881211224 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/pdf/10.1002/cber.19881211224 page 2239; compound 12 -----	1-15
A	HSU LIANG-YAN ET AL: "Light-driven electron transport through a molecular junction based on cross-conjugated systems", THE JOURNAL OF CHEMICAL PHYSICS , vol. 141, no. 12 28 September 2014 (2014-09-28), XP093119681, US ISSN: 0021-9606, DOI: 10.1063/1.4895963 Retrieved from the Internet: URL:https://pubs.aip.org/aip/jcp/article/141/12/124703/74655/Light-driven-electron-transport-through-a-figure-1(a) -----	1-15
1 A	US 2003/149230 A1 (TANAKA MAMORU [JP] ET AL) 7 August 2003 (2003-08-07) the whole document -----	1-15
1		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/070623

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010009293	A1	14-01-2010	CN 102056969 A 11-05-2011
			EP 2300518 A1 30-03-2011
			JP 5568791 B2 13-08-2014
			JP 2011527460 A 27-10-2011
			KR 20110042262 A 26-04-2011
			MY 155242 A 30-09-2015
			TW 201002793 A 16-01-2010
			US 2010009293 A1 14-01-2010
			WO 2010004377 A1 14-01-2010
US 2003149230	A1	07-08-2003	NONE