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(71) Applicant: **ESSILOR INTERNATIONAL** [FR/FR]; 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR).

(72) Inventors: **FROMENTIN, Pierre**; C/O ESSILOR INTERNATIONAL, 147 RUE DE PARIS, 94220 CHARENTON-LE-PONT (FR). **PHOMPAN, Waranya**; C/O ESSILOR INTERNATIONAL, 147 RUE DE PARIS, 94220 CHARENTON-LE-PONT (FR).

(74) Agent: **CHAUVIN, Vincent** et al.; JACOBACCI CORALIS HARLE, 32 rue de l'Arcade, 75008 Paris (FR).

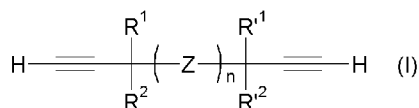
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(54) Title: OPTICAL MATERIAL DERIVED FROM A POLYMERIZABLE COMPOSITION CONTAINING A TERMINAL DIALKYNE COMPOUND



(57) Abstract: The invention relates to a polymerizable composition for an optical material comprising at least one polythiol, at least one polyisocyanate or polyisothiocyanate, and at least one polymerizable compound of formula (I), in which R¹, R², R¹ and R² represent a hydrogen atom, a substituted or unsubstituted alkyl group, an (hetero)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 R¹ and R², taken together, form a divalent group of formula -R¹-R²-, in which -R¹-R²- represents a substituted or unsubstituted alkylene group, Z represents a divalent group and n = 0 or 1.

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Optical material derived from a polymerizable composition containing a terminal dialkyne compound

The present invention relates to optical materials having improved mechanical properties, in particular impact resistance, 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 a polymerizable composition 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, impact resistance, ease of molding and dyeability.

Optical elements prepared from a variety of durable organic polymers have been developed, including polythiourethane obtained by condensation of polyiso(thio)cyanate and polythiol monomers, which are disclosed for example in the applications WO 00/26272, US 2007/098999, WO 2021/182526, EP 3916470 and EP 3919967.

Polythiourethane materials display relatively high refractive indexes and are of major interest since this property allows the manufacture optical articles such as lenses of lower thickness for an equivalent corrective power. However, most resulting polythiourethane polymers display poor mechanical performances, such as low glass transition temperature and low impact resistance.

US 2008/0125570 discloses an optical article comprising a reaction product of (A) a reactive compound comprising a material having functional groups that are reactive with active hydrogens such as isocyanate groups; (B) a thioether-functional, oligomeric polythiol prepared by reacting together a compound having at least two thiol functional groups, a hydroxyl functional compound having triple bond functionality; and a compound having at least two double bonds.

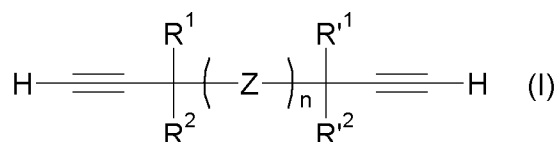
EP 3257876 describes a polymerizable composition comprising 100 parts by weight of a terminal dialkyne compound and 25-75 parts by weight of a polythiol, which is used to obtain materials having a high refractive index. As the dialkyne is used in high quantity, the glass transition temperature of the material is expected to be very low.

EP 2980113 discloses a polymerizable composition for an optical material comprising a polythiol compound and a difunctional compound having a carbon-carbon triple bond and at least one group selected from an isocyanate group and an isothiocyanate group, such as propargyl isocyanate.

JP 2019/026755 and JP 2019/142849 describe an optical material composition that contains a compound having two or more alkyne groups in terminal position, which is polymerizable with a polythiol compound.

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

The present invention relates to a polymerizable composition comprising at least one polythiol, at least one polyisocyanate or polyisothiocyanate, and at least one polymerizable 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 (hetero)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, 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 represents a divalent group and $n = 0$ or 1.

The present inventors have found that alkyne compounds of formula (I) could be used as modifiers in a standard polythiourethane composition containing polythiols and polyiso(thio)cyanates. This addition of alkyne co-monomers allows to make a standard polythiourethane resin, having poor impact resistance, compatible with FDA impact resistance requirements, without the need to use a specific coating or plastifiers providing this property, while at the same time not compromising the glass transition temperature of the material.

The present invention provides polythiourethane polymer networks modified by increased crosslinking from thiol-yne reactions providing thioether functionality, thanks to specifically designed starting materials co-polymerizable with polythiols, and partially curable through photochemical processes. Improving impact resistance of a material by increasing crosslinking with an alkyne modifier is an innovative approach.

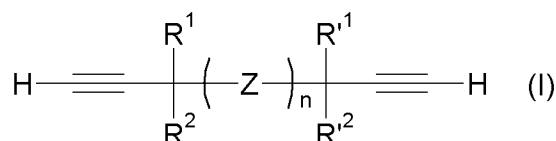
DETAILED DESCRIPTION OF THE INVENTION

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.

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 polythiol, at least one polyisocyanate or polyisothiocyanate, and at least one polymerizable 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 (hetero)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, 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 represents a divalent group and $n = 0$ or 1 .

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.

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.

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.

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.

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.

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 preferably higher than or equal to 1.50, more preferably 1.52 or greater or 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, or 1.72 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 of 550 nm.

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

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, 85, 90 or 92°C. It is preferably lower than or equal to 200°C. The glass transition temperature can be measured by DMA (dynamic mechanical analysis).

The modulus of elasticity E (or Young's modulus, or storage modulus, or tensile modulus of elasticity) of the optical material according to the invention is preferably higher than or equal to 2.5, 3 or 3.2 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).

In one embodiment, the sulfur content of the optical material according to the invention ranges from 6 to 51 % by weight, relative to the optical material total weight, more preferably from 12 to 44 %. In another embodiment, the sulfur content of the optical material according to the invention ranges from 8 to 25 % by weight, relative to the optical material total weight, more preferably from 10 to 20 % or 12 to 17 %. It can be adapted by changing the nature of the polymerizable precursors.

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 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 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 three main components, namely a polythiol, a polyiso(thio)cyanate and a terminal dialkyne compound of formula (I), having at least two terminal alkyne $-C\equiv CH$ groups. This compound is generally referred to as a dialkyne compound by convention, but may in fact comprise more than two alkyne functions, e.g., when its divalent Z group comprises at least one alkyne function.

In one embodiment, the polymerizable compound of formula (I) comprises less than two thiol functions, preferably no thiol function. In one embodiment, the polymerizable compound of formula (I) comprises less than two iso(thio)cyanate functions, preferably no iso(thio)cyanate function.

In a preferred embodiment, the terminal dialkyne compound of formula (I) has (exactly) two terminal alkyne $-C\equiv CH$ groups. Compounds of formula (I) having (exactly) two terminal alkyne $-C\equiv CH$ groups are preferred to those having more than two terminal alkyne $-C\equiv CH$ groups since the latter may cause viscosity issues in the polymerizable composition.

The polymerizable composition can comprise only one type of compound of formula (I), or a mixture of compounds of formula (I) having different structures.

The polymerizable composition can comprise additional polymerizable compounds that are neither compounds of formula (I) according to the invention nor polythiols nor polyiso(thio)cyanates. In one embodiment, such additional polymerizable compounds (comonomers) are copolymerizable with at least one of compounds of formula (I) according to the invention, polyiso(thio)cyanates and polythiols.

The polythiols, polyiso(thio)cyanates and compounds of formula (I) 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.

In one embodiment, the polymerizable composition comprises less than 5 % by weight of polymerizable compounds having at least two $C=C$ double bonds, more preferably less than 4, 3, 2 or 1 % by weight, relative to the total weight of polymerizable compounds present in said composition, even more preferably does not comprise any polymerizable compound having at least two $C=C$ double bonds.

Examples of polymerizable compounds that are neither compounds of formula (I) according to the invention nor polythiols nor polyiso(thio)cyanates include polyols, polyamines, epoxy-containing compounds.

In one embodiment, the polymerizable composition comprises from 35 % to 75 % by weight of polythiols relative to the total weight of polymerizable compounds present in said polymerizable composition, more preferably from 40 % to 70 % by weight or 45 to 65 % by weight.

In one embodiment, the polymerizable composition comprises from 15 % to 60 % by weight of polyiso(thio)cyanates relative to the total weight of polymerizable compounds present in said polymerizable composition, more preferably from 20 % to 55 % by weight or 25 to 50 % by weight.

The compound of formula (I) is preferably used as a modifier in the polymerizable composition containing the polythiols and polyiso(thio)cyanates as major components.

In one embodiment, the polymerizable composition comprises from 1 % to 15 % by weight of compounds of formula (I) relative to the total weight of polymerizable compounds present in said polymerizable composition, more preferably from 2 % to 12 % by weight, 2.5 % to 12 % by weight, 2.9 % to 10.5 % by weight or 3 to 8 % by weight. When the amount of alkyne compounds of formula (I) increases, the polymer network becomes richer in thioether bonds resulting from the reaction of alkyne and thiol functions, which creates S-C bonds.

In one embodiment, the polymerizable composition comprises from 85 % to 99 % by weight of polythiols and polyiso(thio)cyanates relative to the total weight of polymerizable compounds present in said polymerizable composition, more preferably from 88 % to 98 % by weight, 89.5 % to 97.1 % or 92 to 97 % by weight.

The inventors surprisingly found that the addition of even a small amount of an alkyne co-monomer compound of formula (I) to a polythiourethane polymerizable composition led to a material having an improved impact resistance, as compared to the pure polythiourethane material that suffers from a low impact resistance.

Without wishing to be bound by any theory, the inventors believe that yet acting as a crosslinking agent in the polymer network, the alkyne compound of formula (I) also introduces thioether bonds imparting more flexibility to the polymer network, as compared to a pure polythiourethane matrix without the alkyne co-monomer.

In one embodiment, the polymerizable composition (initially) contains polymerizable compounds in amounts adapted so that the molar ratio of (NCX groups + 2 alkyne groups) / SH groups present in said polymerizable compounds ranges from 0.9 to 1.1, and is preferably 1, X being O or S. When this ratio is close to 1, the polymerization reaction is generally close to balance, in terms of reactive functions. Indeed, a stoichiometric reaction between polyiso(thio)cyanates, polythiols and compounds of formula (I) requires the use of two equivalents of alkyne functions and one equivalent of NCX functions for three equivalents of thiol functions in the polymerizable composition, when no other function reactive toward these functions is present.

In one embodiment, the polymerizable composition (initially) contains polymerizable compounds in amounts adapted so that the molar ratio of SH groups to alkyne groups present in

said polymerizable compounds ranges from 1.5 to 16, more preferably from 3 to 14. Those polymerizable compounds may be compounds of formula (I), which may be identical or different, polythiols, optional polymerizable compounds of other categories, etc.

In one embodiment, the polymerizable composition (initially) contains polymerizable compounds in amounts adapted so that the molar ratio of NCX groups to alkyne groups present in said polymerizable compounds ranges from 1 to 15, more preferably from 1.5 to 12. Those polymerizable compounds may be compounds of formula (I), which may be identical or different, poly(iso)thiocyanates, optional polymerizable compounds of other categories, etc.

In one embodiment, the polymerizable composition (initially) contains polymerizable compounds in amounts adapted so that the molar ratio of NCX/SH groups present in said polymerizable compounds ranges from 0.3 to 1.2, more preferably from 0.4 to 1, X being O or S.

The compound of formula (I) is defined as a compound comprising at least two alkyne bonds. It preferably comprises two or three alkyne bonds, more preferably two.

In one embodiment, the compound of formula (I) comprises at least one ester function (C(O)O), preferably one or two.

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,

aryloxycarbonyl, 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 monovalent groups 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.

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 is selected from (hetero)alkylene, (hetero)arylene, carbonyl $(-C(O)-)$, carboxy $(-C(O)O-)$, $-OC(O)O-$, $-C(O)C(O)-$, $-OC(O)C(O)O-$, $-C(O)OC(O)-$, $-OC(O)OC(O)-$, $-O-$, $-NH-$, $-NR^5-$ in which R^5 represents a substituted or unsubstituted alkyl group or (hetero)aryl group, $-NHC(O)-$, $-NHS(O)_2-$, $-NHS(O)-$, $-S-C(O)-S-$, $-S-$, $-S-S-$, $-C(S)-$, $-SO-$, $-SO_2-$, alkenylene, alkynylene, and combinations of the above divalent groups, each of the alkylene and arylene groups being substituted or unsubstituted.

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 (such as a polyoxyethylene group of formula $-(CH_2CH_2O)_n-$, n being an integer preferably ranging from 2 to 20, or a polyoxypropylene group), poly[oxy(hetero)arylene] groups, poly[thioalkylene] groups, poly[thio(hetero)arylene] groups, poly(oxyalkylene)-oxy 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 (such as $-OCH_2CH(OH)CH_2-$), oxy(hetero)arylene groups, oxy(hetero)alkylene-oxy groups [(hetero)alkylene dioxy groups], oxy(hetero)arylene-oxy groups [(hetero)arylene dioxy groups], thio(hetero)alkylene-thio groups (such as $-SCH_2CH_2S-$), thio(hetero)arylene-thio groups, (hetero)alkylene dicarboxy, (hetero)arylene dicarboxy, 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, carbonylalkylamino(hetero)alkylene groups, carbonylalkylamino(hetero)arylene groups, carbonylarylamino(hetero)alkylene groups, carbonylarylamino(hetero)arylene groups.

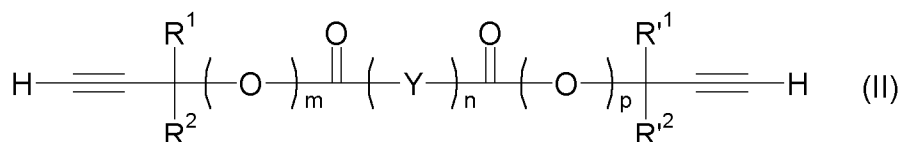
The oxycarbonyl function is $-O-C(O)-$, the carbonyloxy (carboxy) function is $-C(O)O-$, the sulfo function is $-SO_2-$. An oxycarbonylalkylene group is $-O-C(O)-$ alkylene, while a carbonyloxyalkylene group is $-C(O)O-$ alkylene, etc.

In one embodiment, Z is selected from (hetero)alkylene, (hetero)arylene, carbonyl ($-C(O)-$), carboxy ($-C(O)O-$), $-OC(O)O-$, $-C(O)C(O)-$, $-OC(O)C(O)O-$, $-C(O)OC(O)-$, $-O-$, $-S-$, $-S-S-$, $-C(S)-$, and combinations of the above divalent groups, each of the alkylene and arylene groups being substituted or unsubstituted, and especially $-OC(O)C(O)O-$, and especially the following groups combinations: alkylene dioxy, (hetero)arylene dioxy, poly(oxyalkylene)-oxy, (hetero)alkylene dicarboxy, (hetero)arylene dicarboxy.

In another embodiment, Z is selected from carbonyl ($-C(O)-$), carboxy ($-C(O)O-$), $-OC(O)O-$, $-C(O)C(O)-$, $-OC(O)C(O)O-$, $-C(O)OC(O)-$, $-O-$, and optionally $-S-$.

Specific examples of 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, methylene dicarboxy, ethylene dioxy.

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

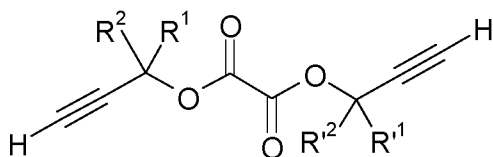


in which R^1 , R^2 , R^1 and R^2 are as defined above and preferably represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, or an aryl group, Y represents an alkylene or arylene group, n, m and p are independently equal to 0 or 1.

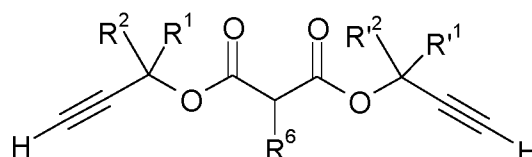
In one embodiment, $m = p$. In another embodiment, $m = p = 1$. In another embodiment, $m = p = 1$ and $n = 0$. In another embodiment, $m = p = n = 1$.

In one embodiment, $n = 1$ and Y is an alkylene group having preferably from 1 to 3 carbon atoms, m and p being preferably 1.

In one embodiment, said polymerizable compound is selected from the oxalyl compounds of formula (VII) and malonic acid diester compounds of formula (VIII):



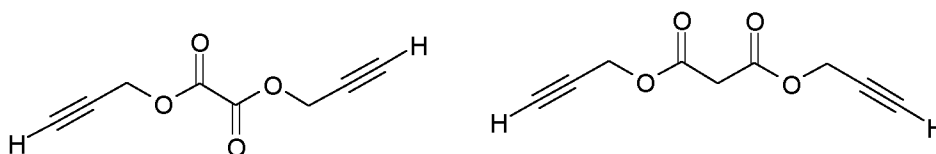
(VII)



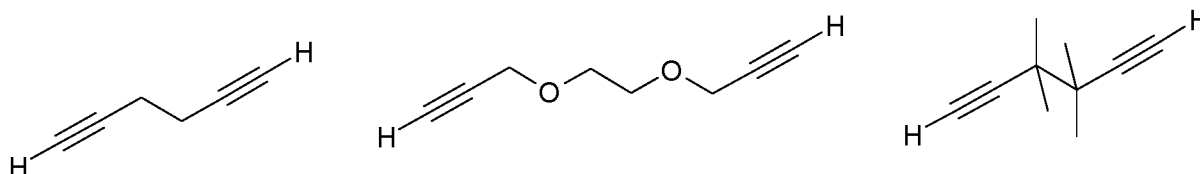
(VIII)

in which R^1 , R^2 , R^1 and R^2 are as defined above and preferably represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, or an aryl group, R^6 represents a hydrogen atom, a substituted or unsubstituted alkyl group, or an aryl group.

Specific examples of such compounds of formula (II), (VII) or (VIII) are shown hereunder:



5 Other examples of useful polymerizable compounds of formula (I) are shown hereunder:

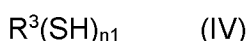


The polymerizable compounds of general formulae (I), (II) (VII) and (VIII) can be easily synthesized from widely available and relatively cheap raw materials, such as propargyl alcohol, propargyl chloride, ethylene glycol, ethane dithiol, malonic acid, 1-ethynyl-1-cyclohexanol, 3-butyn-2-ol, 2-methyl-3-butyn-2-ol, oxalyl chloride, 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.

15 The polythiols that may be used in the present invention are defined as compounds comprising at least two sulfhydryl (mercapto) groups, in other words dithiols, trithiols, tetrathiols etc. Polythiols pre-polymers or oligomers may be used. The polythiol may be any suitable polythiol having two or more, preferably two, three or four thiol functions.

By pre-polymer, it is meant a polymer or oligomer comprising pre-polymer molecules. By pre-polymer molecule, it is meant a macromolecule or oligomer molecule capable of entering, through reactive (polymerizable) groups, into further polymerization, thereby contributing more than one monomeric unit to at least one chain of the final macromolecule. It is generally formed from two or more different monomers.

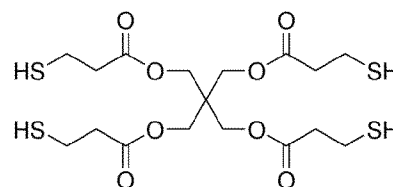
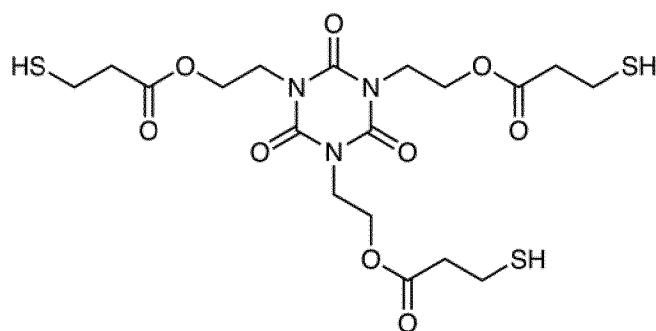
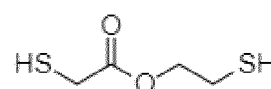
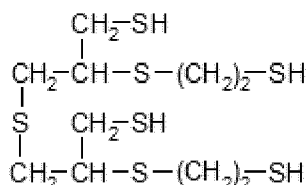
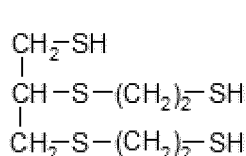
In one embodiment of the invention, said polythiol is a compound of formula:



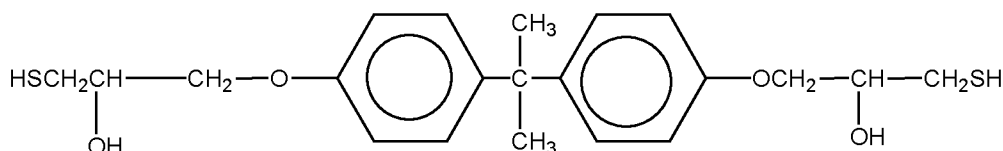
25 wherein $n1$ represents an integer ranging from 2 to 6 and R^3 represents an aliphatic, alicyclic, heterocyclic or aromatic group.

The preferred polythiol monomers and/or oligomers suitable in accordance with the present invention, there may be cited aliphatic polythiols such as trimethylolpropanetris(2-mercaptoacetate), trimethylolpropanetris(3-mercaptopropionate), trimethylethanoltris(2-mercaptoacetate), trimethylethanoltris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), bis(mercaptomethyl)sulfide, bis(mercaptomethyl)disulfide, bis(mercaptoethyl)sulfide, bis(mercaptoethyl)disulfide, bis(mercaptopropyl)sulfide, bis(mercaptopropyl)disulfide, 2,3-bis((2-mercaptoethyl)thio)-1-propanethiol of formula (VIa), 4,8-

dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane of formula (VIIa), 4,7-dimercaptoethyl-1,11-dimercapto-3,6,9-trithiaundecane, 5,7-dimercaptoethyl-1,11-dimercapto-3,6,9-trithiaundecane, 2,5-bis (mercaptomethyl)-1,4-dithiane, and 2,5-bis[(2-mercaptoethyl)thiomethyl]-1,4-dithiane, 1-(1'-mercaptoethylthio)-2,3-dimercaptopropane, 1-(2'-mercapropylthio)-2,3-dimercaptopropane, 1-(3'-mercapropylthio)-2,3-dimercaptopropane, 1-(4'-mercaptobutylthio)-2,3-dimercaptopropane, 1-(5'-mercapentylthio)-2,3-dimercaptopropane, 1-(6'-mercapohexylthio)-2,3-dimercaptopropane, 1,2-bis-(4'-mercaptobutylthio)-3-mercaptopropane, 1,2-bis-(5'-mercaptopentylthio)-3-mercaptopropane, 1,2-bis-(6'-mercaptohexylthio)-3-mercaptopropane, 1,2,3-tris(mercaptomethylthio)propane, 1,2,3-tris-(3'-mercaptopropylthio)propane, 1,2,3-tris-(2'-mercaptoethylthio)propane, 1,2,3-tris-(4'-mercaptobutylthio)propane, 1,2,3-tris-(6'-mercaptohexylthio)propane, methanedithiol, 1,2-ethanedithiol, 1,1-propanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 2,2-propanedithiol, 1,6-hexanedithiol, 1,2,3-propanetrithiol, 1,2-bis(2'-mercaptoethylthio)-3-mercaptopropane, tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate of formula (VIIIa), 2-mercaptoethyl 2-mercaptoacetate of formula (IX), 2-mercaptoethyl 3-mercaptopropionate, 1,1,3,3-tetrakis (mercaptomethylthio)propane, 4,6-bis (mercaptomethylthio)-1,3-dithiane, 1,1,2,2-tetrakis (mercaptomethylthio)ethane, 3-mercaptomethyl-1,5-dimercapto-2,4-dithiapentane, tris (mercaptomethylthio) methane, ethylene glycol bis (3-mercaptopropionate), butylene glycol bis (3-mercaptopropionate), 2-(2,2-bis (mercaptomethylthio) ethyl)-1,3-dithietane.



Further examples of polythiols are shown in the formulae below or can be found in WO 25 2014/133111, EP 394495, US 4775733 or EP 1877839:





In one embodiment of the invention, said polythiol is selected from the group consisting of

5 pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), tris(3-mercaptopropionate) trimethylolpropane, tris(2-mercaptoacetate) trimethylolpropane, 2,3-bis((2-mercaptopropionate) thio)-1-propanethiol, ethylene glycol bis (3-mercaptopropionate), butylene glycol bis (3-mercaptopropionate), 2-mercaptoethyl 2-mercaptoacetate, 2-mercaptoethyl 3-mercaptopropionate, 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-

10 dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 2,5-bis (mercaptomethyl)-1,4-dithiane, bis (mercaptoethyl) sulfide, 1,1,3,3-tetrakis (mercaptomethylthio) propane, 4,6-bis (mercaptomethylthio)-1,3-dithiane, 2-(2,2-bis (mercaptomethylthio) ethyl)-1,3-dithietane, 1,1,2,2-tetrakis (mercaptomethylthio) ethane, 3-mercaptomethyl-1,5-dimercapto-2,4-dithiapentane, tris (mercaptomethylthio) methane,

15 dipentaerythritol hexakis(3-mercaptopropionate), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate, and ethanedithiol.

The most preferred polythiols are 2-mercaptoethyl 2-mercaptoacetate of formula (IX), pentaerythritol tetrakis (3-mercaptopropionate) of formula (X) and 2,3-bis((2-mercaptoethyl)thio)-1-propanethiol of formula (VIa). Especially, a mixture of 2-mercaptoethyl 2-mercaptoacetate and

20 2,3-bis((2-mercaptoethyl)thio)-1-propanethiol can be used.

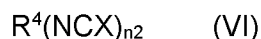
By polyisocyanate, it is meant any compound comprising at least two isocyanate groups, in other words diisocyanates, triisocyanates, etc. Polyisocyanate pre-polymers may be used. The polyisocyanate may be any suitable polyisocyanate having two or more, preferably two or three isocyanate functions.

25 The polyisocyanates may be selected from aliphatic, aromatic, cycloaliphatic or heterocyclic polyisocyanates and mixtures thereof.

Polyisothiocyanates are defined in the same manner as polyisocyanates above, by replacing the "isocyanate" group by the "isothiocyanate" group.

In one embodiment of the invention, said polyisocyanate or polyisothiocyanate is a

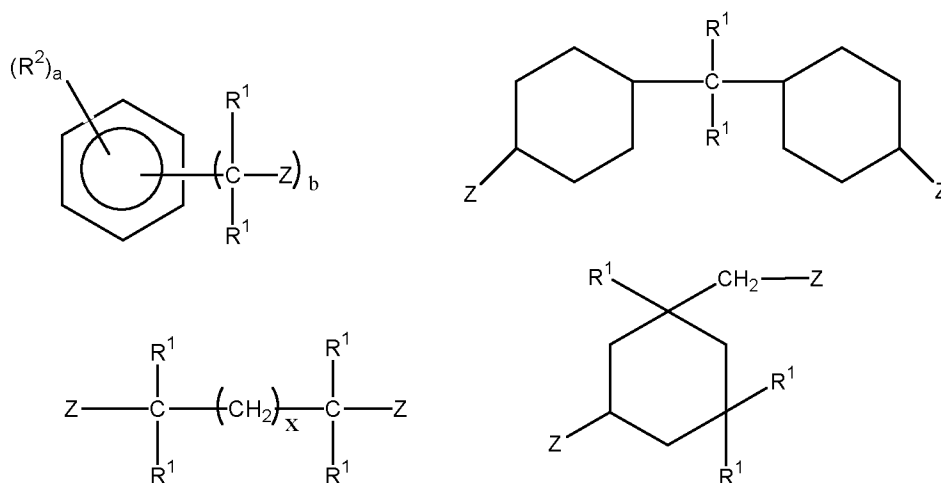
30 compound of formula (VI):



wherein X represents O or S, $n2$ represents an integer ranging from 2 to 6 and R^4 represents an aliphatic, alicyclic, heterocyclic or aromatic group.

The preferred polyisocyanate or polyisothiocyanate compounds are those having the

35 formulae:



wherein R^1 is independently H or a C_1 - C_5 alkyl group, preferably CH_3 or C_2H_5 ;

R^2 is H, a halogen, preferably Cl or Br, or a C_1 - C_5 alkyl group, preferably CH_3 or C_2H_5 ;

5 Z is $-N=C=X$, with X being O or S, preferably O;

a is an integer ranging from 1 to 4, b is an integer ranging from 2 to 4 and $a + b \leq 6$; and

x is an integer from 1 to 10, preferably 1 to 6.

The polyisocyanates of the invention are preferably diisocyanates, such as arylene diisocyanates. Among the available diisocyanates may be cited toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, paraphenylene diisocyanate, xylylene diisocyanate, biphenyl-diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, 2,2,4-trimethyl hexane-1,6-diisocyanate, lysine methyl ester diisocyanate, bis(isocyanatoethyl) fumarate, isophorone diisocyanate, ethylene diisocyanate, dodecane-1,12-diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene-2,4-diisocyanate, tetramethylxylylene diisocyanate, hexahydrotoluene-2,6-diisocyanate, perhydro diphenylmethane-2,4'-diisocyanate, 4,4'-dicyclohexylmethanediisocyanate, bis(isocyanatomethyl)cyclohexane, dicyclohexylmethane diisocyanate, 2,5-bis(isocyanatomethyl)bicyclo-[2.2.1]-heptane 2,6-bis(isocyanatomethyl)bicyclo-[2.2.1]-heptane, 1,5-naphtalene diisocyanate, pentamethylene diisocyanate, isophorone diisocyanate trimer, 1,6-hexamethylene diisocyanate trimer, and mixtures thereof.

Further polyiso(thio)cyanates suitable for the present invention are described in detail in WO 98/37115, WO 2014/133111 or EP 1877839.

25 Preferred embodiments are combination of xylylene diisocyanate and pentaerythritol tetrakis(3-mercaptopropionate); combination of xylylene diisocyanate and 2,3-bis((2-mercaptopropyl)thio)-1-propanethiol; combination of 2,5 (or 2,6)-bis(isocyanatomethyl)bicyclo-[2.2.1]-heptane, pentaerythritol tetrakis(3-mercaptopropionate) and 2,3-bis((2-mercaptopropyl)thio)-1-propanethiol; combination of xylylene diisocyanate and 4,8(or 4,7 or 5,7)-

dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane; combination of dicyclohexylmethane diisocyanate and 4,8(or 4,7 or 5,7)-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane.

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 a dual cure system in the sense that it is both thermally polymerizable and photopolymerizable.

5 In one embodiment, the optical material polymerizable composition contains at least one system for initiating and/or accelerating the polymerization reaction (initiator). The polymerization initiating system can comprise at least one (thermal) catalyst or at least one photochemical polymerization initiating agent (photoinitiator) or alternatively, a mixture of (thermal) and photochemical polymerization initiating agents. In a preferred embodiment, the polymerizable
10 composition contains both a photoinitiator and a (thermal) catalyst.

A photoinitiator represents a molecule that absorbs light and generates reactive species (ions or radicals) that initiate a chemical reaction or transformation. In the present invention, a photoinitiator is preferably used to promote the reaction between thiol groups and alkyne groups (thiol-yne reaction).

15 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-
20 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-phenylketone (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-
25 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,-trimethylbenzoyl ethoxydiphenyl phosphine oxide, triacyl phosphine oxides, 2,2'-bis(2-
30 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.

Photoinitiators shall be used in the polymerizable composition in an amount sufficient to
35 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.

In the present invention, a thermal catalyst promotes the reaction between thiol groups and iso(thio)cyanate groups (thiourethanization reaction). This condensation reaction is favored by heat.

In one embodiment, the (thermal) catalyst is selected from tin compounds such as alkyltins, alkyltin oxides, metal coordination complexes such as cobalt naphthenate and amines or nitrogen-containing basic compounds. Several catalysts can be combined in the present polymerizable composition.

Tin catalysts may be chosen from the group consisting of tin octylate, stannous octoate (tin 2-ethylhexanoate), dibutyltin diacetate, dibutyltin dichloride, dimethyltin dichloride, dibutyltin dilaurate, dibutyltin mercaptide, dibutyltin dimaleate, dimethyltin diacetate, dimethyltin dilaurate, dimethyltin mercaptide, dimethyltin dimaleate, triphenyltin acetate, triphenyltin hydroxide.

Amine or nitrogen-containing basic catalysts may be chosen from aliphatic or aromatic tertiary amines preferably containing a supplemental heteroatom in the ring or functional groups having a positive inductive and/or positive mesomeric effect (for example, alkyl groups or amino groups). Examples include 1,4-diazabicyclo[2.2.2]octane (DABCO), triethylamine, quinuclidine, 2,2'-dimorpholinodiethylether, N,N-dimethylpiperazine, 1-methylimidazole, 2-methyl-1-vinylimidazole, 1-allylimidazole, 1-phenylimidazole, 1,2,4,5-tetramethylimidazole, 1(3-aminopropyl)imidazole, 4-dimethylaminopyridine, 4-pyrrolidino-pyridine, 4-morpholinopyridine, 4-methylpyridine, 3,5-lutidine, N-dodecyl-2-methylimidazole, triazines such as tris(dimethylaminopropyl) hexahydrotriazine, dimethylbenzylamine, N,N-dimethylcyclohexyl amine, bis-dimethylamino-ethylether and pentamethyl diethylenetriamine.

In another embodiment, the catalyst is a salt compound of formula $M_m^{p+} Y_n^{-}$, wherein M^{p+} is a cation of valence p selected from the group consisting of alkaline metal cations, alkaline earth metal cations, transition metal cations and ammonium groups of formula NR_4^+ in which R is an alkyl group having preferably from 1 to 10 carbon atoms, Y^- is an anion such that the corresponding acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 14$, m, n and p being integers such that $n = m \times p$.

The preferred metallic cations of the salts are Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Ag^+ , Ba^{2+} and Al^{3+} . The particularly preferred metallic cations are Li^+ , Na^+ and K^+ due to their absence of color and solubility in the composition. Transition metals are less preferred because their salts can lead to colored compositions and therefore colored polymerized resins. In one embodiment, the method according to the invention does not use a catalyst containing tin.

The preferred NR_4^+ groups are those in which R is a C_1 - C_8 alkyl group and more preferably, a methyl, ethyl, propyl, butyl or hexyl group.

Preferably, Y^- is an anion such that the corresponding acid YH which fulfills the condition $0.5 \leq pKa \leq 10$ and more preferably $0.5 \leq pKa \leq 8$. In the present application, pKa is preferably expressed at 25°C. pKa can be measured in water at standard pressure by potentiometric (pH) titration, using a glass electrode and a pH meter.

Preferably, the anion Y^- is selected from the group consisting of thiocyanate, carboxylate anions, thiocarboxylate anions, acetylacetonate, diketone anions, acetoacetic ester, malonic

ester anions, cyanoacetic ester anions, ketonitrile anions, malononitrile anion and anions of formula RS^- wherein R is a substituted or non-substituted alkyl group having preferably from 1 to 10 carbon atoms or an aryl group having preferably from 6 to 12 carbon atoms.

The preferred anions Y^- are SCN^- , acetylacetonate, acetate, thioacetate, formate and benzoate. The preferred salt catalyst is potassium thiocyanate KSCN.

Such salt catalysts are described in more detail in the application US 2007/202265. They are preferably used in combination with electron-donor compounds also described in US 2007/202265, such as crown ethers, typically 18-crown-6.

The (thermal) catalyst shall be used in the polymerizable composition in an amount sufficient to promote the polymerization of the mixture, i.e., in an amount ranging from 0.01 % to 5 % by weight with respect to the total weight of polymerizable compounds present in the composition, more preferably from 0.02 to 2% by weight. A too high amount of catalyst should also be avoided to prevent premature gelation of the polymerizable mixture before it is introduced in the mold.

The polymerizable composition of the present invention can comprise a solvent for promoting the dissolution of additives, such as a catalyst. 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 an optical material obtained by polymerization of a polymerizable composition as described above. The optical material combines at least thioether and thiourethane functionalities. Thioether bonds result from the reaction of alkyne groups with thiols, while thiourethane bonds result from the reaction of iso(thio)cyanate groups with thiols.

The optical material according to the invention is distinguishable from related polythiourethane-based optical materials obtained in the prior art by means of its improved mechanical properties (impact resistance), as demonstrated in the experimental part.

The invention further 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 polymerization in the presence of at least one catalyst. The process preferably involves casting polymerization.

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.

The optical material is obtained by a one-pot process in which the polythiol, the poly(iso)thiocyanate and the compound of formula (I) are simultaneously present in the polymerizable composition.

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

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.

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 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 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 is triggered.

Photopolymerization of the polymerizable composition is generally performed by irradiating the composition with radiation, preferably ultraviolet light. Preferably, UV 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 120 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. Thermal polymerization includes induction and infrared heating. The curing temperature generally ranges from 60°C to 140°C. The curing time is preferably lower than or equal to 5 hours, more preferably lower than or equal to 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 ranging from 100°C to 150°C.

Without wishing to be bound by any theory, the inventors believe that the sequence of polymerization reactions follows the order in which the polymerization initiating are triggered, i.e., the thiol-yne reaction occurs first when irradiation is employed, then the thiourethanization reaction occurs upon heating or heat release from the photopolymerization reaction. Thiol-iso(thio)cyanate and thiol-yne condensations can proceed orthogonally, especially when a combination of a thermal catalyst and a photoinitiator to polymerize the polymerizable composition.

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.

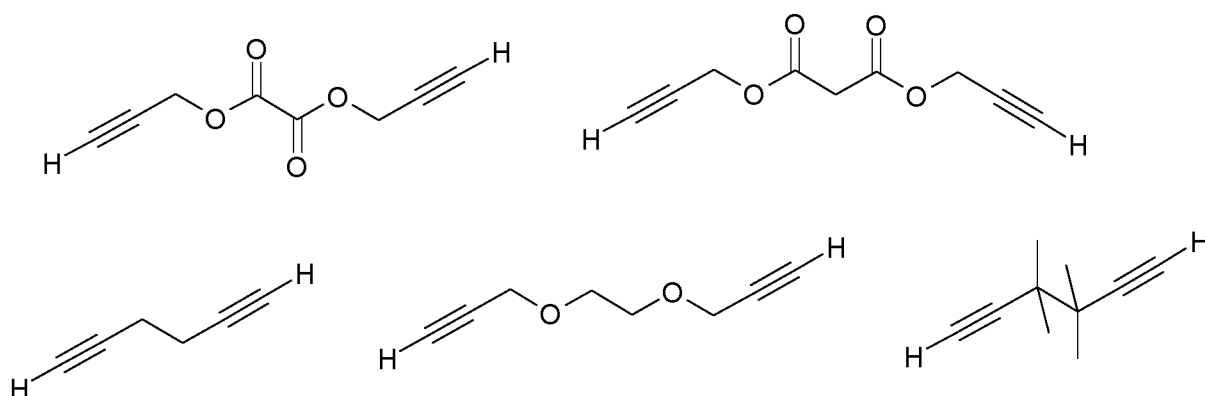
The present process can be used to manufacture a finished lens, having both sides at the required geometries, or a semi-finished lens, having one face that still needs to be surfaced at the required geometry.

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 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 terminal dialkyne compounds according to the invention can be selected, without limitation, from the compounds of formulae:



1. Chemicals used and polymerization conditions

Optical substrates were prepared by polymerization of a terminal dialkyne monomer (1,2-di-2-propyn-1-yl ethanedioate, CAS No. 71573-77-8), a polythiol monomer (pentaerythritol tetrakis (3-mercaptopropionate), CAS No. 7575-23-7) and a polyisocyanate monomer

(isophorone diisocyanate, CAS No. 4098-71-9 in the presence of a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, CAS No. 24650-42-8, 0.25 % by weight) and a thermal catalyst (dimethyl tin dichloride, CAS No. 753-73-1, 0.2 % by weight). The polymerizable composition also contained Zelec UN® as a mold release agent.

5 Cleaned convex and concave plano glass molds of high refractive index having 75 mm diameter were assembled with a tape. A center thickness adjustment was made to obtain 1.1 mm thick samples.

 The dialkyne monomer was dissolved in the polythiol monomer at 50°C for 40 minutes. The polyisocyanate monomer was added to the mixture, which was degassed for 20 minutes, the
10 thermal catalyst, the photoinitiator and the mold release agent were then added, and degassing was continued for 5 minutes, to avoid bubbles in the final material.

 The assembled molds were filled with the above prepared polymerizable composition using a cleaned syringe, and the polymerization reaction was carried out by UV-irradiation for 2 minutes (365 nm), followed by a thermal curing (100°C, 2h) to complete polymerization, by placing
15 the assembled molds in a convection oven from ShenZhen Height-LED Technology Company Limited. The molds were removed from the oven and allowed to cool at room temperature for 10 minutes, and then disassembled when the surface temperature of the molds was < 50°C, to obtain lenses comprising a body of a thermoset material.

 In comparative example 1 (noted C1), no terminal dialkyne monomer was used.
20 Isophorone diisocyanate being difunctional and pentaerythritol tetrakis (3-mercaptopropionate) tetrafunctional, the NCO/SH molar ratio of 1:1 used indicates that 0.5 mol of the latter was used for 1 mol of the former (see § 4).

25 2. Synthesis of the 1,2-di-2-propyn-1-yl ethanedioate monomer

 In a 2-neck 500 mL flask equipped with an addition funnel and a condenser (calcium chloride guard), 200 mL of tetrahydrofuran were introduced, followed by 12.21 g (0.2 mol) of propargyl alcohol and 20.25 g (0.2 mol) of trimethylamine. A solution of 12.69 g (0.1mol) of oxalyl
30 chloride in 50 mL of tetrahydrofuran was then added dropwise under stirring and reflux. Reflux was maintained for 3h, then the mixture is cooled down to room temperature, and filtered. The trimethylamine hydrochloride precipitate was washed twice with 20 mL of tetrahydrofuran. The filtrate was evaporated to c.a. 20 % its volume, and one volume of hexane was added. 13 g of crude product were obtained by filtration. Recrystallization in absolute ethanol yielded 9.5 g of
35 white crystals, having a melting point of 96-97°C.

3. Testing methods

 The following test procedures were used to evaluate the optical articles prepared
40 according to the present invention. They were obtained from consolidation of 5 different casting runs.

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 μ m amplitude, pre-load force 0.5 N with force track 150 %.

The impact resistance of the 75 mm diameter plano lenses (center thickness: 1.1 mm) was evaluated according to the FDA drop ball test for ophthalmic glasses (ANSI Z87.1-1989 standard). This test consists in dropping a steel ball of 16 g from a height of 127 cm on the center of the convex face of the lens, which corresponds to an energy of 200 mJ. The lens successfully passed the test when the lens is neither broken nor presents star-shaped cracks. Impact tests were performed on at least four independent casting runs to ensure reproducibility.

4. Optical articles prepared and characterizations

The table hereunder indicates the different monomer formulations prepared and the thermomechanical properties and theoretical sulfur content, by weight, of the resulting polymer. NCO/SH, NCO/alkyne and SH/alkyne are molar ratios of reactive functions introduced in the polymerizable composition. Polyisocyanate / Alkyne compound (I) and Polythiol / Alkyne compound (I) are molar ratios of monomers introduced in the polymerizable composition. The polythiol was added in order to balance the polyisocyanate / dialkyne compound (I) in terms of reactive functions.

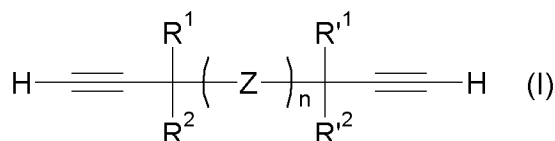
Example	C1	1	2	3
Polyisocyanate (wt %)	47.64	42.02	38.22	28.69
Alkyne compound (I) (wt %)	0	2.99	5.02	10.09
Polythiol (wt %)	52.36	54.99	56.77	61.23
Total	100	100	100	100
NCO/SH	1:1	0.84:1	0.74:1	0.51:1
NCO/alkyne	1:0	10.5:1	5.7:1	2.12:1
SH/alkyne	1:0	12.5:1	7.7:1	4.12:1
Polyisocyanate / Alkyne compound (I)	1:0	10.5:1	5.7:1	2.12:1
Polythiol / Alkyne compound (I)	1:0	6.25:1	3.85:1	2.06:1
% sulfur	13.72	14.43	14.92	14.92
Impact test	Fail	Pass	Pass	Pass
E (GPa)	3.44	3.01	3.41	3.22
T_g (°C)	97	89	100	94

The optical materials according to the invention successfully passed the FDA impact resistance test at an amount of dialkyne component as low as 3 % by weight, while keeping very good optical qualities such as low visual haze or no visual haze. As a comparison, the optical material of comparative example 1 (devoid of dialkyne component) did not pass the impact test.

The presence of such dialkyne component was not detrimental to the glass transition temperature of the resulting polymer, which maintained a high modulus of elasticity, although slightly decreased.

Claims

1. A polymerizable composition comprising at least one polythiol, at least one polyisocyanate or polyisothiocyanate, and at least one polymerizable compound of formula (I):

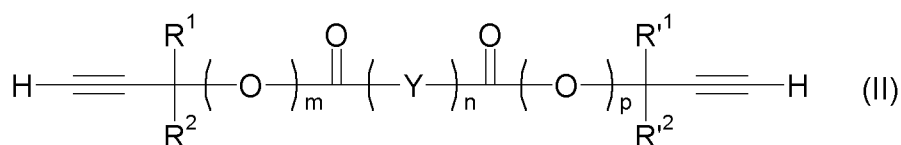


in which R^1 , R^2 , R'^1 and R'^2 represent, independently of each other, a hydrogen atom, a substituted or unsubstituted alkyl group, an (hetero)aryl group, or R^1 and R^2 , taken together, form a divalent group of formula $-\text{R}^1-\text{R}^2-$, in which $-\text{R}^1-\text{R}^2-$ represents a substituted or unsubstituted alkylene group, 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 represents a divalent group and $n = 0$ or 1 .

2. The polymerizable composition of claim 1, wherein Z is selected from:

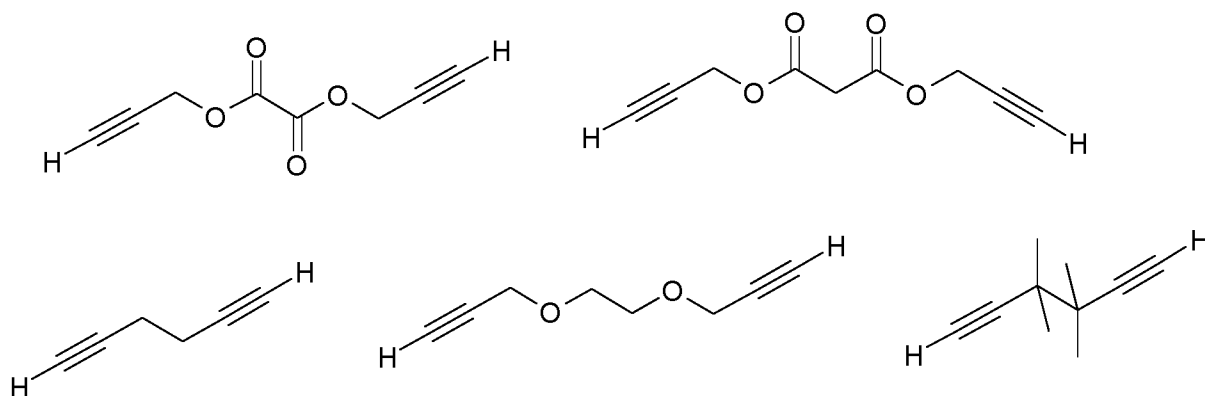
-(hetero)alkylene, (hetero)arylene, carbonyl ($-\text{C}(\text{O})-$), carboxy ($-\text{C}(\text{O})\text{O}-$), $-\text{OC}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{C}(\text{O})-$, $-\text{OC}(\text{O})\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{OC}(\text{O})-$, $-\text{O}-$, $-\text{S}-$, $-\text{S}-\text{S}-$, $-\text{C}(\text{S})-$, and combinations of the above divalent groups, each of the alkylene and arylene groups being substituted or unsubstituted.

3. The polymerizable composition of any one of the preceding claims, wherein said polymerizable compound is selected from the compounds of formula (II):



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, or an aryl group, Y represents an alkylene or arylene group, n , m and p are independently equal to 0 or 1 .

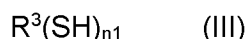
4. The polymerizable composition of any one of claims 1 to 2, wherein said polymerizable compound is selected from the compounds of formulae:



5. The polymerizable composition of any one of the preceding claims, wherein the polymerizable composition comprises from 1% to 15% by weight of compounds of formula (I),

relative to the total weight of polymerizable compounds present in said polymerizable composition.

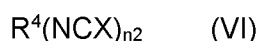
6. The polymerizable composition of any one of the preceding claims, wherein said polythiol is a compound of formula:



wherein $n1$ represents an integer ranging from 2 to 6 and R^3 represents an aliphatic, alicyclic, heterocyclic or aromatic group.

7. The polymerizable composition of any one of the preceding claims, wherein said polythiol is selected from the group consisting of pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), tris(3-mercaptopropionate) trimethylolpropane, tris(2-mercaptoacetate) trimethylolpropane, 2,3-bis((2-mercaptoethyl)thio)-1-propanethiol, ethylene glycol bis (3-mercaptopropionate), butylene glycol bis (3-mercaptopropionate), 2-mercaptoethyl 2-mercaptoacetate, 2-mercaptoethyl 3-mercaptopropionate, 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 2,5-bis (mercaptomethyl)-1,4-dithiane, bis (mercaptoethyl) sulfide, 1,1,3,3-tetrakis (mercaptomethylthio) propane, 4,6-bis (mercaptomethylthio)-1,3-dithiane, 2-(2,2-bis (mercaptomethylthio) ethyl)-1,3-dithietane, 1,1,2,2-tetrakis (mercaptomethylthio) ethane, 3-mercaptomethyl-1,5-dimercapto-2,4-dithiapentane, tris (mercaptomethylthio) methane, dipentaerythritol hexakis(3-mercaptopropionate), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate, and ethanedithiol.

8. The polymerizable composition of any one of the preceding claims, wherein said polyisocyanate or polyisothiocyanate is a compound of formula (VI):



wherein X represents O or S, $n2$ represents an integer ranging from 2 to 6 and R^4 represents an aliphatic, alicyclic, heterocyclic or aromatic group.

9. The polymerizable composition of any one of the preceding claims, wherein said polyisocyanate or polyisothiocyanate is selected from the group consisting of toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, paraphenylene diisocyanate, xylylene diisocyanate, biphenyl-diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, 2,2,4-trimethyl hexane-1,6-diisocyanate, lysine methyl ester diisocyanate, bis(isocyanatoethyl) fumarate, isophorone diisocyanate, ethylene diisocyanate, dodecane-1,12-diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene-2,4-diisocyanate, tetramethylxylylene diisocyanate, hexahydrotoluene-2,6-diisocyanate, perhydro diphenylmethane-2,4'-diisocyanate, 4,4'-dicyclohexylmethanediisocyanate, bis(isocyanatomethyl)cyclohexane, dicyclohexylmethane diisocyanate, 2,5-bis(isocyanatomethyl)bicyclo-[2.2.1]-heptane, 2,6-bis(isocyanatomethyl)bicyclo-[2.2.1]-heptane, 1,5-naphtalene diisocyanate, pentamethylene diisocyanate, isophorone diisocyanate trimer and 1,6-hexamethylene diisocyanate trimer.

10. The polymerizable composition of any one of the preceding claims, wherein the polymerizable composition contains polymerizable compounds in amounts adapted so that the molar ratio of (NCX groups + 2 alkyne groups) / SH groups present in said polymerizable compounds ranges from 0.9 to 1.1, X being O or S.
- 5 11. The polymerizable composition of any one of the preceding claims, wherein the polymerizable composition contains polymerizable compounds in amounts adapted so that the molar ratio of NCX/alkyne groups present in said polymerizable compounds ranges from 1 to 15, X being O or S.
12. The polymerizable composition of any one of the preceding claims, wherein the
10 polymerizable composition contains polymerizable compounds in amounts adapted so that the molar ratio of SH/alkyne groups present in said polymerizable compounds ranges from 1.5 to 16.
13. An optical material obtained by polymerization of a polymerizable composition according to any one of the preceding claims.
14. The optical material of claim 13, further defined as the substrate of an optical lens.
- 15 15. A process for the preparation of an optical material, comprising polymerization of a polymerizable composition according to any one of claims 1 to 12 in the presence of at least one initiator, followed by a thermal polymerization in the presence of at least one catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/070624

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08G18/24	C08F290/06
	C08G18/38	C08G18/67
	C08G18/75	C08G75/045
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)		
C08G C09J C08F		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2019 142849 A (MITSUBISHI GAS CHEMICAL CO) 29 August 2019 (2019-08-29)	1, 2, 6, 7, 12-14
Y	paragraphs [0001], [0048] - [0053]; claims; examples 6-9; tables; compounds 1, t1, Poly-1	1-15
Y	EP 3 257 876 A1 (MITSUI CHEMICALS INC [JP]) 20 December 2017 (2017-12-20) formula (1), formulas (1a) - (1g); paragraphs [0001], [0008], [0009], [0056] - [0063], [0067], [0085] - [0086]; claims; examples	1-15
A	EP 2 980 113 A1 (MITSUI CHEMICALS INC [JP]) 3 February 2016 (2016-02-03) paragraphs [0001], [0011] - [0012], [0018] - [0035], [0038], [0043], [0073]; claims; examples 8-14; tables 3, 5	1-15
- / - -		
☒	Further documents are listed in the continuation of Box C.	☒ See patent family annex.
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"A" document defining the general state of the art which is not considered to be of particular relevance		
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"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		Date of mailing of the international search report
24 September 2024		09/10/2024
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 Eigner, Markus

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/070624

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/224139 A1 (RETSCH JR WILLIAM H [US]) 6 September 2012 (2012-09-06) paragraphs [0002], [0006] - [0011], [0076] - [0079], [0130]; claims; examples; tables 3,4 -----	1 - 15
A	WO 2007/131145 A1 (PPG IND OHIO INC [US]) 15 November 2007 (2007-11-15) paragraphs [0002], [0005], [0006], [0035], [0097], [0103], [0107]; claims; examples; tables 3, 4 -----	1 - 15
A	WO 2013/069965 A1 (KOC SOLUTION CO LTD [KR]) 16 May 2013 (2013-05-16) paragraphs [0001], [0010], [0014] - [0033], [0052]; claims; examples; table 1 -----	1 - 15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/070624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2019142849 A	29-08-2019	JP 7234677 B2 JP 2019142849 A	08-03-2023 29-08-2019
EP 3257876 A1	20-12-2017	CN 107207656 A EP 3257876 A1 JP 6034997 B1 JP WO2016129563 A1 KR 20170101296 A US 2018066082 A1 WO 2016129563 A1	26-09-2017 20-12-2017 30-11-2016 27-04-2017 05-09-2017 08-03-2018 18-08-2016
EP 2980113 A1	03-02-2016	BR 112015024306 A2 CN 105143300 A EP 2980113 A1 JP 5859709 B2 JP WO2014157664 A1 KR 20150119030 A US 2016280840 A1 WO 2014157664 A1	18-07-2017 09-12-2015 03-02-2016 10-02-2016 16-02-2017 23-10-2015 29-09-2016 02-10-2014
US 2012224139 A1	06-09-2012	US 2012224139 A1 WO 2012121997 A1	06-09-2012 13-09-2012
WO 2007131145 A1	15-11-2007	AR 062250 A1 CN 101437873 A CN 101437874 A CN 101437875 A CN 102030880 A CN 102030902 A DK 2027186 T3 EP 2016115 A1 EP 2016116 A1 EP 2024420 A2 EP 2027186 A2 EP 2559721 A1 ES 2447035 T3 HK 1128707 A1 HK 1128708 A1 HK 1129410 A1 HK 1153765 A1 JP 4838882 B2 JP 4944193 B2 JP 5123934 B2 JP 2009536255 A JP 2009536256 A JP 2009536257 A KR 20080108155 A KR 20090014344 A KR 20090018041 A US 2007270548 A1 US 2007270549 A1 US 2008125525 A1 US 2008125570 A1 US 2008160318 A1 WO 2007131145 A1 WO 2007131148 A1 WO 2007131149 A1 WO 2007131150 A2	29-10-2008 20-05-2009 20-05-2009 20-05-2009 27-04-2011 27-04-2011 14-04-2014 21-01-2009 21-01-2009 18-02-2009 25-02-2009 20-02-2013 11-03-2014 06-11-2009 06-11-2009 27-11-2009 05-04-2012 14-12-2011 30-05-2012 23-01-2013 08-10-2009 08-10-2009 08-10-2009 11-12-2008 10-02-2009 19-02-2009 22-11-2007 22-11-2007 29-05-2008 29-05-2008 03-07-2008 15-11-2007 15-11-2007 15-11-2007 15-11-2007

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/070624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		WO 2007131155 A2	15-11-2007

WO 2013069965 A1	16-05-2013	KR 20130050263 A	15-05-2013
		WO 2013069965 A1	16-05-2013
