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(54) Title: LIQUID POLYMERIZABLE COMPOSITION COMPRISING MINERAL NANOPARTICLES AND ITS USE TO MANUFACTURE AN OPTICAL ARTICLE

(57) Abstract: The invention concerns a liquid polymerizable composition comprising a phosphine oxide or a phosphine sulphide monomer composition with mineral nanoparticles homogeneously dispersed therein, as well as its use for the preparation of a transparent polymeric material having a high refractive index and its use in the optical field.



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**Liquid polymerizable composition comprising mineral nanoparticles and its  
use to manufacture an optical article**

5     The present invention concerns a liquid polymerizable composition for the preparation of a transparent polymeric material having a high refractive index and its use in the optical field.

The liquid polymerizable composition of the present invention comprises a phosphine oxide or a phosphine sulphide monomer composition with mineral nanoparticles  
10   homogeneously dispersed therein, said mineral nanoparticles being chosen among ZnS, ZrO<sub>2</sub>, TiO<sub>2</sub> or BaTiO<sub>3</sub>.

In the last ten years, it has become more and more difficult to synthesize materials which have a refractive index higher than 1.6 as well as the other properties required in optical field (transparency i.e. high transmission with low haze level, mechanical properties like  
15   chock resistance and abrasion resistance, optical properties including no optic distortion and high contrast, heat resistance, small shrinkage, chemical resistance ...) from pure organic monomers.

One solution to overcome this problem is to introduce mineral nanoparticles into the monomer composition in order to increase its refractive index. Typically, nanoparticles  
20   having a refractive index from 2.1 to 3 may be chosen among ZrO<sub>2</sub>, TiO<sub>2</sub>, BaTiO<sub>3</sub> or ZnS. However, with classical monomers having a refractive index around 1.5-1.6 (such as methylmethacrylate or styrene), the amount of nanoparticles required to achieve a high refractive index can be above 50 % w/w, which may lead to the aggregation of the nanoparticles and adversely affect the transparency of the resulting material.  
25   Furthermore, it renders the material very brittle. To ensure good dispersibility of the nanoparticles into the monomer composition, the nanoparticles may require to be coated with a capping agent (such as hexanoic acid, methacrylic acid or methacryloxy trimethoxysilane). However, the capping agent generally has a refractive index of not more than 1.5 thereby reducing the benefit produced by the nanoparticle itself regarding  
30   the refractive index.

Therefore, the difficulty lies in the selection of the right combination of monomer composition, nanoparticles and capping agent if required that will ensure 1) a good stability over time of nanoparticles in the monomer composition and 2) a good dispersability of the nanoparticles into the monomer composition while leading to a transparent material exhibiting an increased refractive index as well as other advantages such as mechanical properties like for example chock resistance and abrasion resistance. Furthermore, the polymerizable composition obtained after mixing the monomer, nanoparticles and capping agent if required should be compatible with the substrate or support on which it is coated, and therefore display good adhesion properties on said substrate or support.

Lü C. et al. (Advanced material, **2006**, 18, 1188-1192) disclose a polymerizable composition comprising N,N-dimethylacrylamide (DMAA) wherein a high content of mercaptoethanol-capped ZnS nanoparticles are dispersed. However, the refractive index of the poly N, N-DMAA is low ( $n = 1.511$  as measured with Metricon 9010/M Prism coupler  $\lambda=594\text{nm}$ ,  $4\text{ mW.cm}^{-2}$  for 10 min, 3 wt% Irg 184.), which makes it difficult to produce a material with high refractive.

The following discussion of the background to the invention is intended to facilitate an understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge of the person skilled in the art in any jurisdiction as at the priority date of the invention.

Throughout the specification, unless the context requires otherwise, the word “comprise” or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Furthermore, throughout the specification, unless the context requires otherwise, the word “include” or variations such as “includes” or “including”, will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

The inventors have found a new polymerizable composition comprising a monomer having a phosphine oxide function ( $\text{P=O}$ ) or phosphine sulphide function ( $\text{P=S}$ ) whose

structure results in a high refractive index, which is higher than the refractive index of poly N, N-DMAA, and wherein mineral nanoparticles such as ZnS  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and  $\text{BaTiO}_3$  can be homogeneously dispersed in order to increase the refractive index of the material.

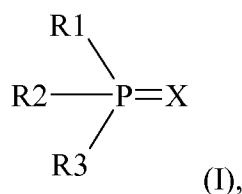
- 5 In one embodiment, the nanoparticles are ZnS nanoparticles coated with one or more thiol-containing compounds which can reach higher refractive index than nanoparticles with typical capping agents. Furthermore, large amounts of such coated ZnS nanoparticles can be introduced into a phosphine oxide function or phosphine sulphide function containing-monomer composition with a very good dispersibility.
- 10 In another embodiment, the nanoparticles are  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and  $\text{BaTiO}_3$  nanoparticles which can be homogeneously dispersed in a phosphine oxide function or phosphine sulphide function containing-monomer composition without any capping agent.

The inventors have thus developed a polymerizable composition based on phosphine oxide monomers or phosphine sulphide monomers within which mineral nanoparticles are homogeneously dispersed. Said nanoparticles have the advantage that they can be added into the composition in large amounts (up to 50% w/w) with a very good dispersibility and stability. The presence of said nanoparticles into the composition allows increasing the refractive index of the material which can be obtained by curing said polymerizable composition. Said material is able to show excellent optical properties, such as a transmission higher than 80%, even higher than 90%.

Therefore, an object of the present invention is a liquid polymerizable composition comprising:

- a liquid monomer composition containing:

- a monomer of formula (I):



wherein:

X is an oxygen atom or a sulphur atom, preferably an oxygen atom, at least one among R1, R2 and R3, identical or different, represents a polymerizable function which is directly linked to P or linked to P via a C1-C20 alkylene, one or several carbon atoms of which may be replaced with:

-O-, -S-, -NH- or -NR- wherein R is a C1-C10 alkyl group, a divalent monocycloalkyl or bicycloalkyl comprising 5 to 9 carbon atoms, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio, or

a phenyl or naphthyl, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio,

and the other(s) among R1, R2 and R3, identical or different, represent(s) an hydrogen atom, a C1-C10alkoxy, C1-C10alkylthio,

phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-C10alkylthio, or

5 - a mixture of two different monomers M1 and M2 which are able to react together and form the monomer of formula (I), wherein M1 or M2 or both M1 and M2 contain the function  $P=X$  and M1 and M2 further contain functions which are able to react together to form a polymer, and

- mineral nanoparticles homogeneously dispersed in said monomer composition.

10 A polymerizable function is a chemical function enabling the monomer of formula (I) to form a solid polymer, for example by thermal and/or UV treatment.

Suitable polymerizable functions include vinyl, allyl, isocyanate, thioisocyanate, acrylate, thioacrylate, methacrylate, thiomethacrylate, ether, thioether, alcohol, epoxy, thiol, and episulfide.

15 Preferably, the polymerizable function is selected from the group consisting of acrylate, thioacrylate, methacrylate, thiomethacrylate, thiol, episulfide, or epoxy, more preferably among acrylate, methacrylate, thiol, or episulfide.

20 C1-C20 alkylene and C1-C6 alkylene respectively mean a linear or branched alkylene group comprising 1 to 20 carbon atoms and a linear or branched alkylene group comprising 1 to 6 carbon atoms, that may be substituted with  $-(CH_2)_n-R'$  wherein n is an integer from 0 to 5 and R' is an aryl, an aryloxy, an arylamine or an arylthio. Preferably, the C1-C20 alkylene is a C1-C6 alkylene, more preferably a C2-C4 alkylene, such as methylene, n-propylene or n-butylene.

25 C1-C6 alkyl and C1-C10 alkyl respectively mean a linear or branched alkyl group comprising from 1 to 6 carbon atoms and a linear or branched alkyl group comprising from 1 to 10 carbon atoms. Alkyl groups include for instance methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, and hexyl.

C1-C6 alkoxy means a C1-C6 alkyl-O- group, wherein C1-C6 alkyl is defined as above. C1-C6 alkoxy groups include for instance methoxy or ethoxy.

C1-C6 alkylthio means C1-C6 alkyl-S- group, wherein C1-C6 alkyl is defined as above. C1-C6 alkylthio include for instance methylthio or ethylthio.

Monocycloalkyl and bicycloalkyl respectively mean a single non-aromatic ring and two fused non-aromatic rings, including saturated rings or partially saturated rings.

- 5 Exemplary monocycloalkyl include cyclopentyl and cyclohexyl. Exemplary bicycloalkyl include norbornyl and adamantyl.

Halogen atom includes fluoro, chloro, bromo or iodo atoms.

- Aryloxy means a phenyl-O- group, wherein phenyl is optionally substituted by 1 to 3 groups chosen independently among C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkylthio or  
10 halogen atom, as defined above. Aryloxy include for instance phenoxy or methylphenoxy.

- Arylthio means a phenyl-S- group, wherein phenyl is optionally substituted by 1 to 3 groups chosen independently among C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkylthio or  
15 halogen atom, as defined above. Arylthio includes for instance phenyl thio or methylphenylthio.

- Arylamine means a phenyl-NH- group, wherein phenyl is optionally substituted by 1 to 3 groups chosen independently among C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkylthio or  
halogen atom, as defined above. Aryloxy include for instance phenoxy or methylphenoxy.

- 20 ArylC1-C10alkyloxy means the radical RR'-O- wherein R is a phenyl optionally substituted with 1 to 3 groups independently chosen among C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkylthio or halogen atom, as defined above, and R' is a C1-C10alkyl as defined above.

- ArylC1-C10alkylthio means the radical RR'-S- wherein R is a phenyl optionally  
25 substituted with 1 to 3 groups independently chosen among C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkylthio or halogen atom and R' is a C1-C10alkyl as defined above.

In the monomer of formula (I), at least one among R1, R2 and R3 comprises a polymerizable function. Hence, the monomer of formula (I) may contain one, two or three polymerizable functions, identical or different, preferably identical.



In one embodiment, R1 and R2 are identical and both bear a polymerizable function, preferably the same polymerizable function.

In one particular embodiment, R1, R2 and R3 are identical and all bear a polymerizable function, preferably the same polymerizable function.

- 5 Preferably, R1, R2 and R3, identical or different, represent a polymerizable function which is directly linked to P or linked to P via a C1-C20 alkylene, one or several carbon atoms of which is replaced with -O-, -S- or -NR-, wherein R is a C1-C6 alkyl group.

Without wishing to be bound by any theory, in formula (I), the phosphine oxide function P=O or phosphine sulphide function P=S is believed to help in dispersing the  
10 nanoparticles, as well as to help in increasing the refractive index of the material which can be obtained by curing the polymerizable composition.

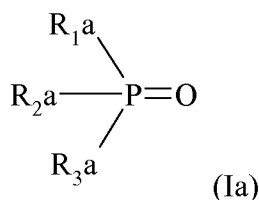
The nanoparticles are homogeneously dispersed in the monomer of formula (I) by solvation. Solvation involves different types of intermolecular interactions, such as hydrogen bonding, ion-dipole, dipole-dipole attractions or Van der Waals forces.

- 15 In a preferred embodiment, the other(s) among R1, R2 and R3, identical or different, bearing no polymerizable function, comprises a high refractive index moiety, which helps in increasing the refractive index of the material which can be obtained by curing the polymerizable composition. Such a high refractive index moiety may be chosen from a phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-C10alkylthio, in particular  
20 arylC1-C6alkyloxy, or aryl C1-C6alkylthio.

Sulfur atoms and aromatic rings have a high polarizability and are easily deformed under the action of external field, which leads to a material having a high refractive index.

- The high refractive index moiety may also be carried by R1, R2 or R3 bearing a polymerizable function. In that case, the high refractive index may be a phenyl or  
25 naphthyl, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio.

In one embodiment, the monomer is a phosphine oxide monomer of formula (Ia):



wherein:

at least one among  $R_{1a}$ ,  $R_{2a}$  and  $R_{3a}$ , identical or different,  
 5 represents:

$-(R_4)_n-X-(R_5-Y)_m-(R_6)_p-Q$  wherein:

$R_4$ ,  $R_5$  and  $R_6$ , identical or different, represent a C1-C6 alkylene group, one or several carbon atoms of which may be replaced with a phenylene group,

10  $X$  and  $Y$ , identical or different, represent O, S, or  $-NR-$ , wherein  $R$  is a C1-C6 alkyl group,

$n$ ,  $m$  and  $p$ , identical or different, represent an integer from 0 to 4, preferably from 0 to 2, more preferably 0 or 1,

15  $Q$  represents a polymerizable function, preferably chosen from acrylate, methacrylate, episulfide, or thiol,

and the other(s) among  $R_{1a}$ ,  $R_{2a}$  and  $R_{3a}$ , identical or different, represent(s) an hydrogen atom, a phenyl, an C1-C6alkoxy, C1-C6alkylthio, aryloxy, arylthio, aryl C1-C6alkoxy, or aryl C1-C6alkylthio.

20 Preferably,  $R_4$ ,  $R_5$  and  $R_6$ , identical or different, represent a C1-C2 alkylene.

In one embodiment,  $n$  and  $m$  are 0,  $p$  is 1,  $R_6$  is  $-C_2H_4-$ ,  $X$  is O, S or  $-NR-$ , wherein  $R$  is a C1-C6 alkyl group and  $Q$  is chosen from acrylate or methacrylate.

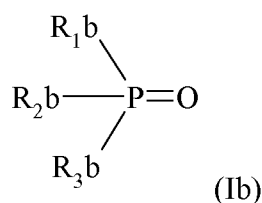
In one embodiment,  $R_{1a}$  and  $R_{2a}$  are identical and both bear a polymerizable function, preferably the same polymerizable function.

25 In one particular embodiment,  $R_{1a}$ ,  $R_{2a}$  and  $R_{3a}$  are identical and all bear a polymerizable function, preferably the same polymerizable function.

In a preferred embodiment, the other(s) among  $R_{1a}$ ,  $R_{2a}$  and  $R_{3a}$ , bearing no polymerizable function, identical or different, comprises a high refractive index moiety,

which helps in increasing the refractive index of the material which can be obtained by curing the polymerizable composition. Such a high refractive index moiety may be chosen from a phenyl, aryloxy, arylthio, arylC1-C10alkoxy, or aryl C1-C10alkylthio, in particular arylC1-C6alkoxy, or aryl C1-C6alkylthio.

- 5 In one embodiment, the monomer is a phosphine oxide monomer of formula (Ib):



wherein:

- 10 at least one among R<sub>1b</sub>, R<sub>2b</sub> and R<sub>3b</sub>, identical or different, represents:

-(CHR')<sub>n</sub>-X-(CHR'')<sub>m</sub>-Q wherein:

X represent O, S, or -NR-, wherein R is a C1-C6 alkyl group,

- 15 n and m, identical or different, represent an integer from 0 to 4, preferably 0, 1 or 2,

R' and R'', identical or different, represent a hydrogen atom, a C1-C6alkyl, a phenyl, arylthio or arylthio-CH<sub>2</sub>-,

Q represents a polymerizable function, preferably chosen from acrylate, methacrylate, episulfide, thiol or thioacrylate,

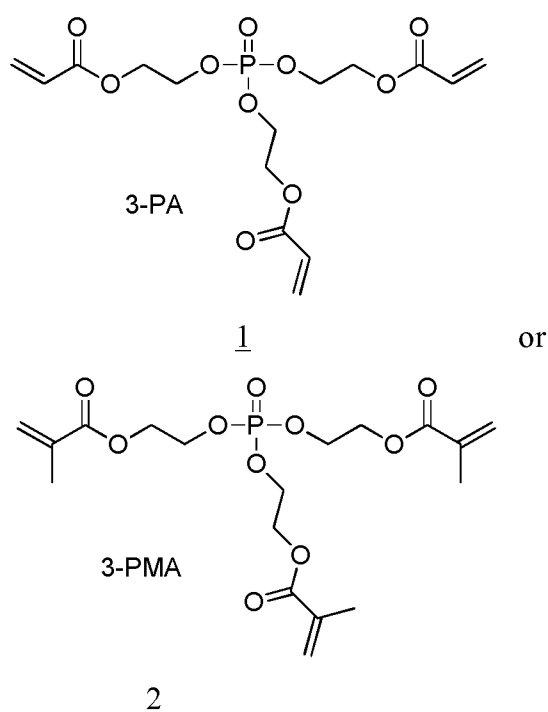
- 20 and the other(s) among R<sub>1a</sub>, R<sub>2a</sub> and R<sub>3a</sub>, identical or different, represent(s) an hydrogen atom, a phenyl, an C1-C6alkoxy, C1-C6alkylthio, aryloxy, arylthio, arylC1-C6alkoxy, or arylC1-C6alkylthio.

- In one embodiment, R<sub>1b</sub> and R<sub>2b</sub> are identical and both bear a polymerizable function,  
25 preferably the same polymerizable function.

In one particular embodiment, R<sub>1b</sub>, R<sub>2b</sub> and R<sub>3b</sub> are identical and all bear a polymerizable function, preferably the same polymerizable function.

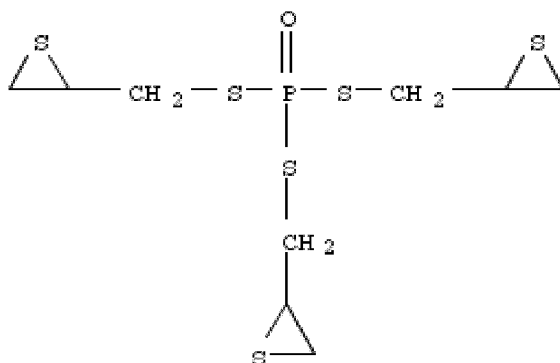
In a preferred embodiment, the other(s) among R<sub>1b</sub>, R<sub>2b</sub> and R<sub>3b</sub>, bearing no polymerizable function, identical or different, comprises a high refractive index moiety, which helps in increasing the refractive index of the material which can be obtained by curing the polymerizable composition. Such a high refractive index moiety may be  
 5 chosen from a phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-C10alkylthio, in particular arylC1-C6alkyloxy, or aryl C1-C6alkylthio.

Monomers of formula (Ia) or (Ib) include the following compounds:



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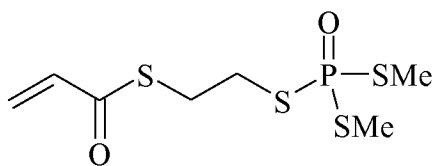
Monomers of formula (Ia) or (Ib) also include the following compounds:



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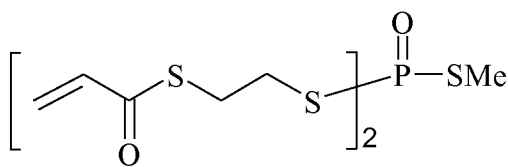
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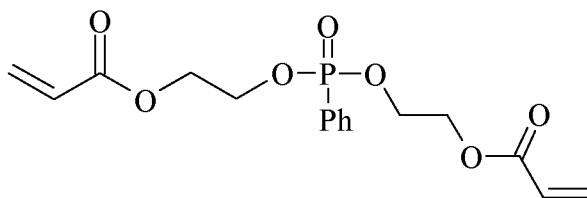
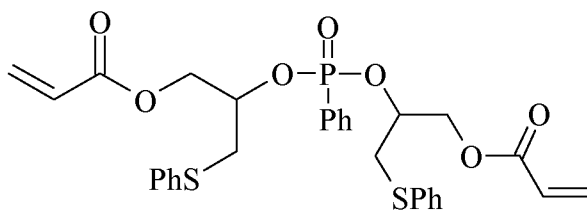
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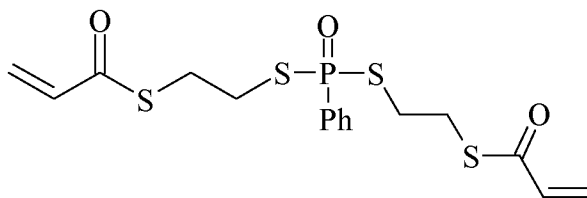
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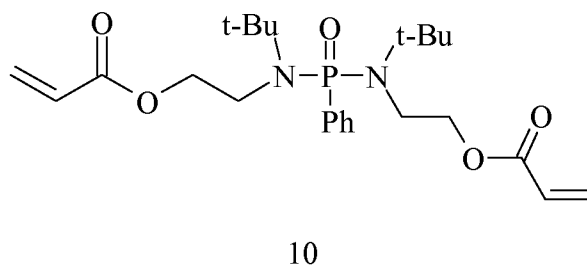
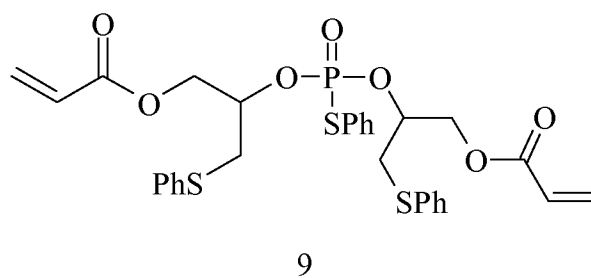
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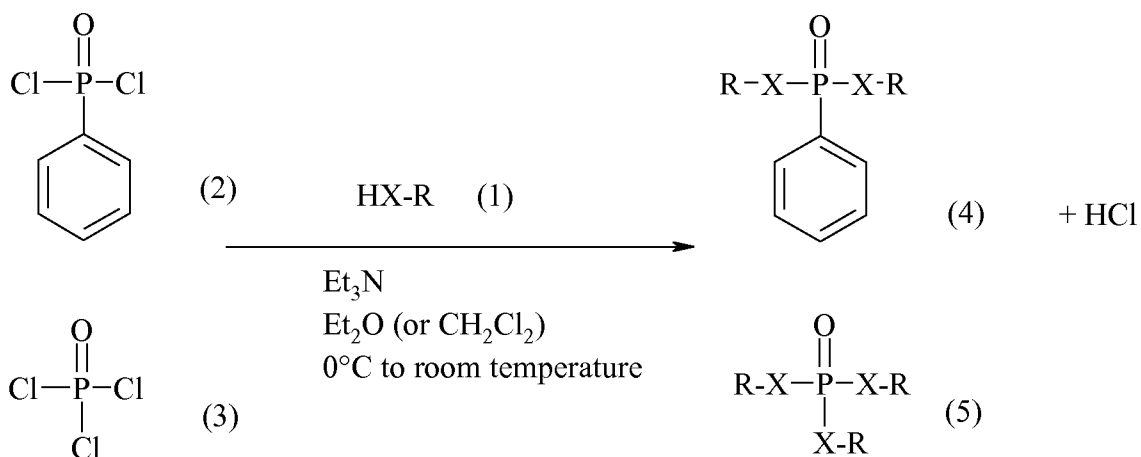
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10 The monomer of formula (I) may be synthesized via a nucleophilic addition reaction by reacting a halide compound containing a P=O or a P=S function with a nucleophilic compound, such as an organometallic compound, a hydroxyl compound, a thiol

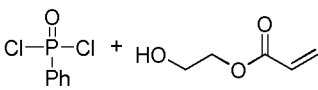
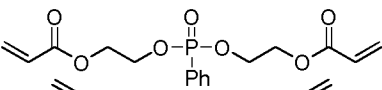
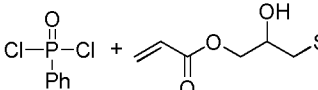
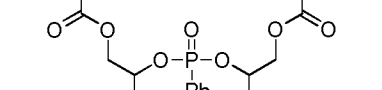
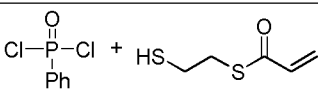
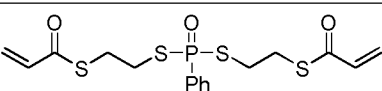
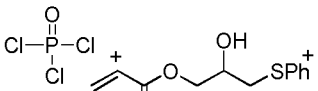
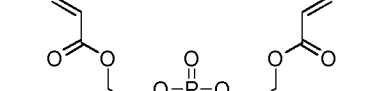
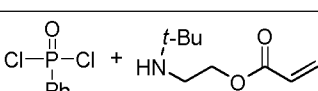
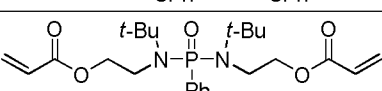
For instance, acrylate or methacrylate monomers (4) and (5) bearing a phosphine oxide function may be synthesized by a nucleophilic addition of a compound H-XR of formula (1) which is a thiol (X=S), an alcohol (X=O) or a secondary amine (X=N-alkyl), wherein  
 15 R is an alkyl or an aryl bearing an acrylate or methacrylate function, respectively on a phenyl phosphonic dichloride (2) and a phosphoric trichloride (3) as represented below in scheme 1:



Scheme 1

In table 1, some examples of nucleophilic compounds HX-R (X = O, S, N-alkyl) that can be used and the corresponding acrylate monomers, are listed. The corresponding methacrylate precursors may be used for synthesizing the corresponding methacrylate monomers.

Table 1

| HX-R       | Precursors                                                                          | Monomers                                                                             | Simulated Refractive Index |
|------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------|
| X= O       |    |    | n = 1.51                   |
|            |    |    | n = 1.60                   |
| X= S       |   |   | n = 1.61                   |
| X= O and S |  |  | n = 1.62                   |
| X= NR      |  |  | n = 1.52                   |

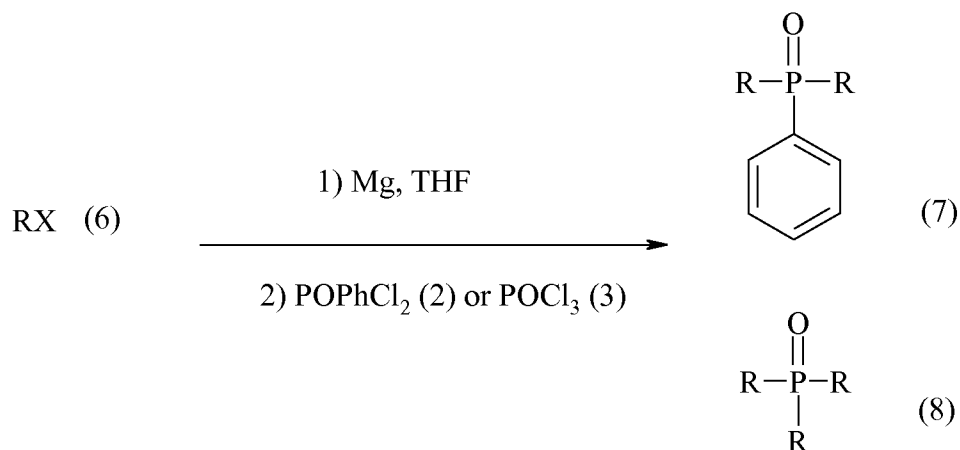
Refractive indexes indicated in Table 1 were simulated by using ChemSketch software.

The precursor commercial availability or references for synthesis are indicated in table 2a.

Table 2a

| Precursors | CAS          | Company / reference                                                    |
|------------|--------------|------------------------------------------------------------------------|
|            | 824-72-6     | Aldrich                                                                |
|            | 10025-87-3   | Aldrich                                                                |
|            | 818-61-1     | TCI                                                                    |
|            | 1159203-53-8 | Repub. Korean Kongkae Taeho Kongbo (2009),<br>KR 2009045836 A 20090508 |
|            | 52135-50-9   | U.S.S.R (1974), SU 246511 A1 19740325                                  |
|            | 14206-21-4   | Journal of Organic Chemistry (1957), 22, 787-9.                        |
| PhSH       | 108-98-5     | Aldrich                                                                |

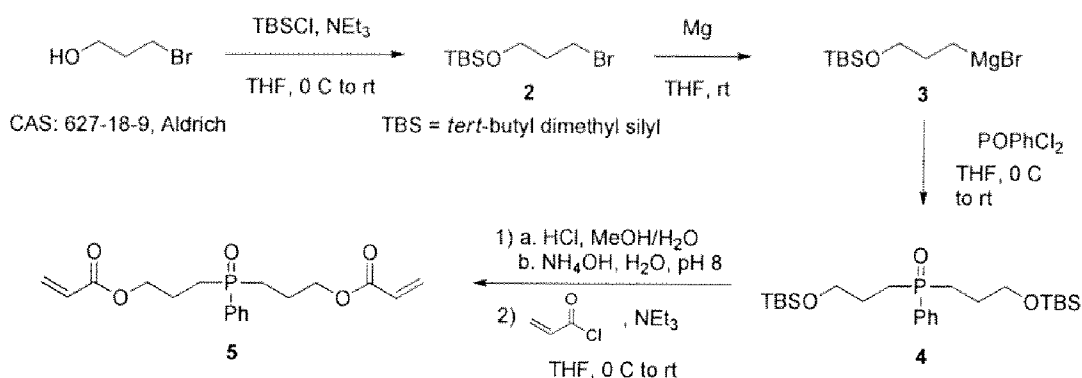
The synthesis as described above can be extended to organometallic nucleophiles. One of the synthetic pathways is shown below in scheme 2. First Grignard reagent is prepared by oxidative addition of Mg into the carbon-halogen bond of a compound R-X (6) wherein R is alkyl or aryl and X is an halogen, then after nucleophilic addition of this organometallic compound onto the halide, the corresponding phosphine oxide (7) or (8) is obtained.





Since organometallic reagents are very reactive, the polymerizable unit should be added after the nucleophilic addition.

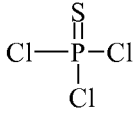
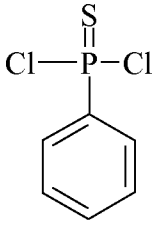
In the following example (scheme 3), bromo-1-propanol is chosen as the starting material. In a first step the alcohol is protected as a silyl ether **2** by treatment with tert-butyltrimethyl silyl chloride in the presence of triethylamine. Then Grignard reagent **3** is formed by additive oxidation of magnesium into the carbon-bromide bond (if this step is difficult, organometallic specie can be made by halogen-metal exchange by treatment with t-BuLi for example). Condensation of **3** with phenyl phosphonic dichloride gives compound **4**. After deprotection of silyl ethers under acidic treatment (Journal of Organic Chemistry, 68 (19), 7249-7253, 2003), regular acrylation reaction gives target compound **5**.



Scheme 3

Phosphine sulphides may be synthesized by similar routes, for instance from the precursors indicated in table 2b:

Table 2b

| Precursors                                                                                                                 | CAS       | Company |
|----------------------------------------------------------------------------------------------------------------------------|-----------|---------|
|  <p>Thiophosphoryl chloride</p>           | 3982-91-0 | Aldrich |
|  <p>Phenylphosphonothioic dichloride</p> |           | Aldrich |

Treatment of **4** with H<sub>2</sub>S should also give the corresponding phosphine sulphide.

Similar routes may be used to synthesize monomers with other polymerizable functions, such as alcohol, thiol or epoxy function. For instance, a thiol function may be added to the monomer by treatment of an halide with NaSH through nucleophilic substitution. An epoxy can be added to the monomer by condensing glycidol with a phosphoryl chloride compound. An alcohol function may be added to the monomer after deprotection of di-silylether functions (of compound **4** for instance) under acidic conditions to form a diol.

Compounds of formula (I) wherein R<sub>1</sub> ≠ R<sub>2</sub> ≠ R<sub>3</sub> may be synthesized according to the above mentioned routes, in mixture with the corresponding compounds wherein R<sub>1</sub> = R<sub>2</sub> or R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub>, then be isolated according to techniques well known by the person skilled in the art.

The liquid monomer composition may also comprise a mixture of two different monomers M1 and M2 which are able to react together and form the monomer of formula (I), wherein M1 or M2 or both M1 and M2 contain a phosphine oxide or sulphide oxide function P=X and M1 and M2 further contain functions which are able to

react together to form a polymer, such as isocyanate/alcohol, thiocyanate/alcohol, ene/thiol or thiol/episulfide.

Some monomers of formula (I) may be commercially available, such as 3PA (tris(2-acryloyloxyethyl) phosphate, CAS :35057-49-9, marketed by Osaka Organic Chemicals under the commercial name Viscoat 3PA®) and 3PMA (tris(2-methacryloyloxyethyl) phosphate, CAS :15458-75-0, marketed by Osaka Organic Chemicals under the commercial name Viscoat 3PMA®).

The liquid polymerizable composition of the invention may comprise only one monomer of formula (I) or a mixture of monomers of formula (I). If the monomer of formula (I) is solid, it may be solubilized in another monomer of formula (I) which is liquid in order to form a liquid polymerizable composition.

According to the invention, the mineral nanoparticles are homogeneously dispersed in the monomer of formula (I), i.e. do not form aggregates having a size higher than 100 nm, as measured by transmission electronical microscopy. A homogeneous dispersion of nanoparticles allows obtaining a composite material whose haze after curing is below 5 % as measured according to Japanese Industrial Standard No. K 7136-2000. Furthermore, the material composite is transparent.

The mineral nanoparticles may be chosen among ZnS, ZrO<sub>2</sub>, TiO<sub>2</sub> or BaTiO<sub>3</sub>.

The nanoparticles can be synthesized according to methods well known by the person skilled in the art, or be commercially available in the form of powder or a suspension in a solvent, such as methanol.

For instance, TiO<sub>2</sub> nanoparticles in suspension in methanol with a particle size of 60 nm are marketed by Sakai chemical under the commercial name SRD-2M.

For instance, ZrO<sub>2</sub> nanoparticles in suspension in methanol with a particle size of 35 nm are marketed by Sakai chemical under the commercial name SZR-M.

For instance, BaTiO<sub>3</sub> nanoparticles in the form of powder (cubic crystalline phase) with a particle size of less than 100 nm (BET) are marketed by Aldrich under the commercial name Barium Titanate (IV) (No. Cas: 12047-27-7).

According to the invention, the “particle size” is the diameter of the highest population of particles as measured with dynamic light scattering (DLS).

The particle size of the mineral nanoparticles is preferably less than 50 nm, more preferably between 30 and 5 nm. This size range allows limiting haze in the final polymerized material. It can be measured by dynamic light scattering (DLS), for instance by using Horiba SZ-100 size measurement instrument.

The nanoparticles of ZnS are preferably coated with one or more thiol-containing compounds. Preferentially, nanoparticles of ZnS are coated with mercaptoethanol, thiophenol, mercaptophenol, or a mixture thereof.

- Typically, the refractive index of the nanoparticles is as follows:
- ZnS, spharelite, cubic,  $n(589\text{ nm}) = 2.3691$  (Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, III/30A, High Frequency Properties of Dielectric - Crystals. Piezooptic and Electrooptic Constants, Springer-Verlag, Berlin 1996);
  - BaTiO<sub>3</sub>, tetragonal, ordinary ray:  $n(589\text{ nm}) = 2.4405$  (Shannon, R.D., Shannon, R.C., Medenbach, O., and Fischer, R. X., “Refractive Index and Dispersion of Fluorides and Oxides”, J. Phys. Chem. Ref. Data 31, 931, 2002.);
  - TiO<sub>2</sub>, rutile, tetragonal, ordinary ray:  $n(589\text{ nm}) = 2.562$  (Shannon, R.D., Shannon, R.C., Medenbach, O., and Fischer, R. X., “Refractive Index and Dispersion of Fluorides and Oxides”, J. Phys. Chem. Ref. Data 31, 931, 2002.);
  - ZrO<sub>2</sub>, tetragonal, ordinary ray:  $n(589\text{ nm}) = 2.20$  (Polymer Journal, 2008, 40, 1157-1163);

The particle size of the ZnS nanoparticles is less than 10 nm, preferably between 3 and 6 nm. This size range allows limiting haze in the final polymerized material.

- Methods for preparing ZnS nanoparticles with capping agent(s), such as thiol-containing compound(s), are well known to the person skilled in the art.

For instance, Zn(OAc)<sub>2</sub> (a Zn source), the capping agent (s) and thiourea (a sulphur source) are dissolved in a solvent, such as DMF (dimethylformaldehyde), N,N

Diméthylacetamide, or DMSO (dimethylsulfoxide) (for instance 2.5g of  $\text{Zn}(\text{OAc})_2$  in 30ml of DMF). The glassware set-up is purged with nitrogen during 10 minutes in order to prevent the formation of ZnO and reduce the amount of water. Then the solution is heated under reflux. At the end of the heating process, a transparent solution is obtained.

5 A solvent such as ethanol, acetone, acetonitrile, toluene or water, is added to the solution to induce precipitation of the coated ZnS nanoparticles, depending on the particles properties. The precipitation allows the separation of the particles from the solvent and the capping agent which has not reacted. The solvent is chosen depending on the coupling agent. Typically, when thiophenol is used as a coupling agent, water is used to

10 precipitate the coated particles. Particles may be separated from the solution by centrifugation and washed with methanol, acetonitrile or toluene. See for instance the method described in Changli Lü, Yuanrong Cheng, Yifei Liu, Feng Liu, and Bai Yang ("A Facile Route to ZnS-Polymer Nanocomposite Optical Materials with High Nanophase Content via Gamma-Ray Irradiation Initiated Bulk Polymerization", Adv.

15 Mater., 2006, 18, 1188-1192.).

The above method advantageously allows the dispersion of the nanoparticle in powder form in the monomer composition, as opposed to other methods which require the dispersion of the nanoparticles into a solvent before the introduction into the monomer composition.

20 Suitable thiol-containing compounds include small molecules, such as those having a molar mass lower than 250g/mol, containing one thiol function and having a high refractive index higher than 1.5 (at 594 nm).

The thiol-containing compound of the invention is preferably chosen among mercaptoethanol, thiophenol, mercaptophenol, or a mixture thereof.

25 When preparing the coated nanoparticles of ZnS, the relative molar amounts of the Zn source, the thiol-containing compound and the S source is chosen so that during the process of preparation, no self precipitation occurs. Typically, the molar ratio of the thiol-containing compound over Zn is comprised between 0.5 and 3, preferably between 0.8 and 2. The molar ratio is number of moles of thiol-containing compound for one

30 mole of zinc acetate.

Preferably, the nanoparticles of ZnS are coated with a mixture of mercaptoethanol (ME) and thiophenol (PhS). The molar ratio of ME and PhS over Zn is comprised between 2.0 and 0.1, more preferably between 0.4 and 0.2. When the ZnS nanoparticles are coated with only with ME, the molar ratio of ME over Zn is comprised between 1.3 and 1.6.

- 5 The nanoparticles of ZnS have a crystal size comprised between 3 and 10 nm, more preferably between 3 and 6 nm. The crystal size can be determined by XR diffraction according to the Williamson-Hall method.

The nanoparticles of ZnS coated with said thiol-containing compound(s) have a particle size of comprised between 4 and 80 nm. The particle size of the coated nanoparticles can  
10 be determined by measurement with a Dynamic Light Scattering instrument (SZ-100 from Horiba) and correspond to size of highest population determine with this tool.

The amount of the mineral nanoparticles (coated if required or uncoated if not required) in the polymerizable composition is comprised between 5 and 50% w/w, preferably between 10 and 40% w/w, more preferably between 30 and 35% w/w based on the total  
15 weight of the liquid polymerizable composition.

The liquid polymerizable composition of the invention may comprise other ingredients typically used in polymerizable compositions, such as a mold release agent, photostabilizer, antioxidant, dye anti-coloring agent, fillers, UV light absorber or optical brightener.

- 20 Another object of the present invention is an optical substrate coated with the liquid polymerizable composition as previously defined.

In this invention “coating” or “coat” should be construed to cover not only regular coatings but also a resin layer having aspherical shape provided on a spheric or aspheric glass lens to obtain aspheric effect. The typical such resin layer is disclosed in US  
25 7,070,862.

The optical substrate may be any organic glass commonly known and used in the optical field. It may be a thermoplastic resin such as a thermoplastic polycarbonate, or a thermoset or photo-cured resin such as CR®, polyurethane or polythiourethane.

The thickness of the liquid polymerizable coating can be comprised between 1  $\mu\text{m}$  and 1 mm.

Another object of the present invention is an optical article comprising:

- (a) an optical substrate, and
- 5 (b) a coating obtained by thermal and/or UV curing of the liquid polymerizable composition as previously defined.

Another object of the present invention is to cure the liquid polymerizable as bulk material for optical article. The thickness of cured liquid polymerizable as bulk material can be comprised between 1 mm and 2 cm.

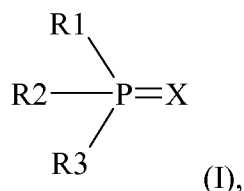
- 10 The optical article is preferably an optical lens, such as an ophthalmic lens, sunglass lens or other optical lens for optical instrument, and most preferably an ophthalmic lens. It may contain functional layers such as polarizing layers, anti-reflecting coatings, visible light and UV absorbing coatings, anti-choc coatings, abrasion-resistant-coating, anti-smudge-coating, anti-fog coating, anti-dust coating, photochromic coatings, all of which
- 15 are familiar to the skilled person.

The liquid polymerizable composition coating may be applied onto the optical substrate by any suitable coating method such as dip-coating, bar coating, spray coating, or spin coating.

- 20 The curing of the resulting layer is done by subjecting the coated substrate to UV light and/or heat. The refractive index of the cured layer can be increased between 0.01 and 0.15 for example.

- Another object of the present invention is the use of mineral nanoparticles having a refractive index which is higher than the refractive index of the monomer of formula (I), preferably higher than 2, for increasing the refractive index of a polymeric material
- 25 obtained by thermal and/or UV curing of a liquid monomer composition containing:

- a liquid monomer composition containing:
  - a monomer of formula (I):



wherein:

X is an oxygen atom or a sulphur atom, preferably an oxygen atom,  
 at least one among R1, R2 and R3, identical or different, represents  
 a polymerizable function which is directly linked to P or linked to P  
 via a C1-C20 alkylene, one or several carbon atoms of which may be  
 replaced with :

–O–, –S–, –NH– or –NR– wherein R is a C1-C10 alkyl group,

a divalent monocycloalkyl or bicycloalkyl comprising 5 to 9  
 carbon atoms, optionally substituted with 1 to 4 groups independently  
 chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6  
 alkylthio, or

a phenyl or naphthyl, optionally substituted with 1 to 4 groups  
 independently chosen among an halogen atom, C1-C6 alkyl, C1-C6  
 alkoxy, or C1-C6 alkylthio,

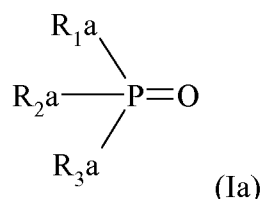
and the other(s) among R1, R2 and R3, identical or different,  
 represent(s) an hydrogen atom, a C1-C10alkoxy, C1-C10alkylthio,  
 phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-  
 C10alkylthio , or

- a mixture of two different monomers M1 and M2 which are able  
 to react together and form the monomer of formula (I), wherein M1 or  
 M2 or both M1 and M2 contain the function P=X and M1 and M2  
 further contain functions which are able to react together to form a  
 polymer, and

wherein said mineral nanoparticles are homogeneously dispersed in said  
 monomer composition.



In one embodiment, said use of mineral nanoparticles is for increasing the refractive index of a polymeric material obtained by thermal and/or UV curing of a phosphine oxide monomer of formula (Ia):



5                    wherein:

at least one among R<sub>1a</sub>, R<sub>2a</sub> and R<sub>3a</sub>, identical or different, represents:

-(R<sub>4</sub>)<sub>n</sub>-X-(R<sub>5</sub>-Y)<sub>m</sub>-(R<sub>6</sub>)<sub>p</sub>-Q wherein:

10                    R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>, identical or different, represent a C1-C6 alkylene group, one or several carbon atoms of which may be replaced with a phenylene group,

X and Y, identical or different, represent O, S, or -NR-, wherein R is a C1-C6 alkyl group,

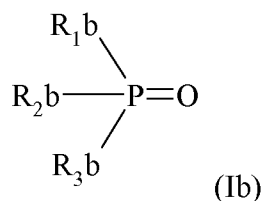
15                    n, m and p, identical or different, represent an integer from 0 to 4, preferably from 0 to 2, more preferably 0 or 1,

Q represents a polymerizable function, preferably chosen from acrylate, methacrylate, episulfide, or thiol,

20                    and the other(s) among R<sub>1a</sub>, R<sub>2a</sub> and R<sub>3a</sub>, identical or different, represent(s) an hydrogen atom, a phenyl, an C1-C6alkoxy, C1-C6alkylthio, aryloxy, arylthio, aryl C1-C6alkoxy, or aryl C1-C6alkylthio.

In one particular embodiment, said use of mineral nanoparticles is for increasing the refractive index of a polymeric material obtained by thermal and/or UV curing of a phosphine oxide monomer of formula (Ib):

25



wherein:

at least one among  $R_{1b}$ ,  $R_{2b}$  and  $R_{3b}$ , identical or different, represents:

$-(CHR')_n-X-(CHR'')_m-Q$  wherein:

5 X represent O, S, or  $-NR-$ , wherein R is a C1-C6 alkyl group,  
n and m, identical or different, represent an integer from 0 to 4,  
preferably 0, 1 or 2,

R' and R'', identical or different, represent a hydrogen atom, a C1-C6alkyl, a phenyl, arylthio or arylthio- $CH_2-$ ,

10 Q represents a polymerizable function, preferably chosen from  
acrylate, methacrylate, episulfide, thiol or thioacrylate,

and the other(s) among  $R_{1a}$ ,  $R_{2a}$  and  $R_{3a}$ , identical or different,  
represent(s) an hydrogen atom, a phenyl, an C1-C6alkoxy, C1-  
C6alkylthio, aryloxy, arylthio, arylC1-C6alkoxy, or arylC1-  
15 C6alkylthio.

Preferably, the mineral nanoparticles are chosen among ZnS,  $ZrO_2$ ,  $TiO_2$  or  $BaTiO_3$ .

The invention will now be further described in the following examples. These examples  
are offered to illustrate the invention and should in no way be viewed as limiting the  
20 invention.

### Examples

#### 1) Preparation of ZnS nanoparticles coated with a thiol-containing compound.

$Zn(OAc)_2$ , the capping agent and thiourea (TUA) are dissolved in DMF. The glassware  
25 set-up is purge with nitrogen during 10 min. Then the solution is heated under reflux at  
160 °C under small nitrogen flow. At the end of the heating process, a transparent  
solution is obtained. The solution is poured in methanol, acetonitrile or water to induce  
the precipitation of the ZnS nanoparticles. Nanoarticles of ZnS are separated from the  
solution by centrifugation and washed with methanol or acetonitrile twice. The powder is  
30 dried under vacuum for 10 hours.

The capping agents used in this set of experiments are mercaptoethanol (ME) (60-24-2), thiophenol (PhS) (108-98-5), and mercaptophenol (MPhO) (637-89-8).

The relative molar amounts of  $\text{Zn}(\text{OAc})_2$ , the capping agent and thiourea are indicated in table 3.

- 5 The amount of capping agent is chosen so that during reflux and after cooling of the mixture, no self-precipitation occurs. Examples of relative molar amounts leading to a stable dispersion are indicated in table 3. A mixture of 2 different capping agents allows the use of a lower amounts of capping agent.

Tableau 3

| Compound                  | Relative molar amounts |              |              |              |
|---------------------------|------------------------|--------------|--------------|--------------|
|                           | Experiment 1           | Experiment 2 | Experiment 3 | Experiment 4 |
| ME                        | 2.18                   | 0.6          | 0.44         | 0            |
| PhS                       | 0                      | 0.3          | 0.44         | 0            |
| MPhO                      | 0                      | 0            | 0            | 2.78         |
| $\text{Zn}(\text{OAc})_2$ | 1                      | 1            | 1            | 1            |
| TUA                       | 1.65                   | 1.65         | 1.65         | 1.65         |

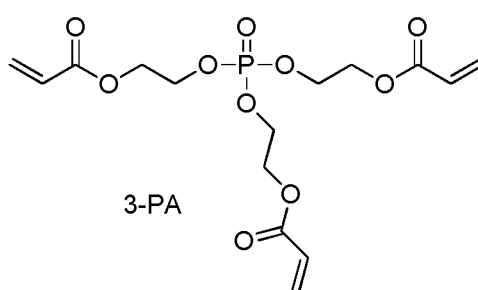
- 10 An XRD analysis was performed on the powder of ZnS-ME from experiment 1. The results show that the ZnS particles have a sphalerite structure.

- The mean crystal size of the ZnS nanoparticles (without coating) was determined according to the Williamson-Hall method. The mean crystal size of the ZnS nanoparticles was evaluated at 3.58 nm with a relative dispersion of 4.5% (measured by  
15 XR diffraction).

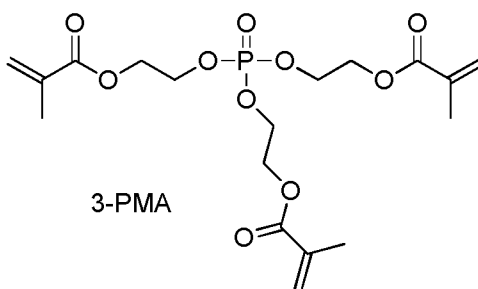
- The particle size of the coated ZnS nanoparticles obtained from experiment 3 was measured using Horiba SZ-100 size measurement instrument after cooling of the dispersion in DMF. The results show a particle size of around 7 nm with a narrow distribution size going from 4 to 14 nm. This small particle size and narrow distribution  
20 size allow the limitation of light scattering in the final composite.

2) Preparation of liquid polymerizable composition comprising ZnS nanoparticles coated with a thiol-containing compound dispersed in a phosphine oxide containing monomer.

ZnS nanoparticles coated with PhS, ME and/or MPhO were introduced into the following phosphine oxide monomer 1 and 2 (marketed by Osaka Organic Chemicals respectively under the commercial name Viscoat 3-PA® and 3-PMA®) at 60 °C under ultrasonic waves. Table 4 gives the maximum amount of particles that can be homogeneously dispersed in the monomers 1 and 2.



1 (3PA)



2 (3PMA)

Table 4

| Molar amount of the capping agent relative to ZnS |      |      | 3PA          | 3PMA         |
|---------------------------------------------------|------|------|--------------|--------------|
| PhS                                               | ME   | MPhO |              |              |
| 0.3                                               | 0.6  | -    | Up to 20 wt% | N/A          |
| 0.88                                              | -    | -    | Up to 20 wt% | Up to 20 wt% |
| -                                                 | 2.18 | -    | 6 wt%        | 4 wt%        |
| -                                                 | -    | 2.78 | Up to 17 wt% | N/A          |

The data of table 4 shows that ZnS particles capped with MPhO, PhS, Me or a mixture of PhS and Me can be homogeneously dispersed in relatively high amounts (up to 20 wt%) in 3PA or 3PMA monomer composition.

The polymerizable composition was applied between two glass plates separated by a spacer of 200 $\mu$ m. Photopolymerization was performed after addition of a radical photoinitiator (Irgacure184, BASF) and illumination with a Hg lamp during 10 min (4 mW.cm<sup>-2</sup>). Photopolymerization was induced between two glass substrates to avoid the inhibition by oxygen. A Teflon spacer of 200 $\mu$ m was used between the two glass substrates. The resulting thickness of the cured material was 220  $\mu$ m.

Haze was measured after demolding with a spectrophotometer UV-Vis (Hitachi U-4100) according to Japanese Industrial Standard No 7136-2000.

The refractive index (n) of the cured material was measured after demolding using a Metricon 2010M (prism coupling method). The results are indicated in table 5.

Table 5

|                    | Wavelength  | Refractive index of 3PA (180 $\mu$ m) | Refractive index of 3PA + coated particles ZnS (220 $\mu$ m) [20 wt% of particles] | $\delta$ n |
|--------------------|-------------|---------------------------------------|------------------------------------------------------------------------------------|------------|
| ZnS PhS ME 0.3:0.6 | 654 nm      | 1.505                                 | 1.551                                                                              | 0.046      |
|                    | 594 nm      | 1.508                                 | 1.554                                                                              | 0.046      |
|                    | 473 nm      | 1.516                                 | 1.566                                                                              | 0.05       |
|                    | Abbe number | 52                                    | 41                                                                                 |            |
|                    | T (400nm)   | 86%                                   | 80%                                                                                |            |
|                    | Haze        |                                       |                                                                                    |            |
|                    | 392 nm      | 0.31%                                 | 4.5%                                                                               |            |
|                    | 436 nm      | 0.27%                                 | 4.2%                                                                               |            |
|                    | 544 nm      | 0.25%                                 | 4.0%                                                                               |            |
|                    | 653 nm      | 0.25%                                 | 3.8%                                                                               |            |

The data of table 5 shows that the refractive index of the polymer containing 20 wt% of coated ZnS particles is increased by 0.05 at 473 nm compared with the same polymer without particles.

Furthermore, the data of table 5 shows that the composite material is suitable for optical materials (haze below 5%).

3) Preparation of liquid polymerizable composition comprising ZrO<sub>2</sub> nanoparticles dispersed in a phosphine oxide containing monomer.

- Five compositions were prepared by adding to the phosphine oxide monomer 1 (marketed by Osaka Organic Chemicals under the commercial name Viscoat 3-PA®) respectively 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% of ZrO<sub>2</sub> from a suspension of ZrO<sub>2</sub>/MeOH (30 wt% in MeOH, commercially available from Sakai chemical), and then adding to this mixture 3 wt% of Irgacure 184 (a radical photoinitiator marketed by BASF). The methanol of the resulting composition was evaporated under reduced pressure.
- Then, each composition was applied between two glass plates separated by a spacer of 500µm. Photopolymerization was performed by illumination with a Hg lamp during 10 min (4 mW.cm<sup>-2</sup>). Photopolymerization was induced between two glass substrates to avoid the inhibition by oxygen. A Silicon spacer of 500µm was used between the two glass substrates.
- The refractive index and Haze were measured as for example 2.

The refractive indexes at 594 nm, Abbe numbers and haze of the resulting materials are indicated in 6.

Table 6

| Optical properties | 0wt%  | 10wt% | 20wt% | 30wt% | 40□wt% | 50□wt% |
|--------------------|-------|-------|-------|-------|--------|--------|
| 594 nm             | 1.506 | 1.520 | 1.539 | 1.555 | 1.569  | 1.592  |
| δn                 | -     | 0.014 | 0.033 | 0.049 | 0.063  | 0.086  |
| Abbe Number        | 57    | 51    | 48    | 52    | 46     | 45     |
| T (400 nm)         | 86%   | 85%   | 75%   | 75%   | 71%    | 77%    |
| Haze               | 0wt%  | 10wt% | 20wt% | 30wt% | 40wt%  | 50wt%  |
| 392 nm             | 0.31% | 0.95% | 1.3%  | 1.3%  | 2.1%   | 3.8%   |
| 436 nm             | 0.27% | 0.86% | 1.2%  | 1.2%  | 1.9%   | 3.5%   |
| 544 nm             | 0.25% | 0.75% | 1.0%  | 1.0%  | 1.5%   | 3.1%   |
| 653 nm             | 0.25% | 0.70% | 0.92% | 0.94% | 1.3%   | 2.8%   |

The data of table 6 shows that the refractive index of the polymer may be increased by 0.086 at 594 nm with the addition of 50 wt % of ZrO<sub>2</sub> nanoparticles compared with the same polymer without nanoparticles.

Furthermore, the data of table 6 shows that the composite material is suitable for optical materials (haze below 5%).

In table 7 below, materials obtained according to the above described method from a composition containing 3-PA and 20 wt% of ZrO<sub>2</sub> nanoparticles or 20 wt% of ZnS nanoparticles coated with 0.3:0.6 PhS:ME are compared.

Table 7

| Optical properties | 3-PA   | 20 wt%<br>coated ZnS | 20 wt % ZrO <sub>2</sub> |
|--------------------|--------|----------------------|--------------------------|
| thickness          | 500 μm | 220 μm               | 500 μm                   |
| 594 nm             | 1.506  | 1.554                | 1.539                    |
| δn                 | -      | 0.046                | 0.033                    |
| Abbe Number        | 57     | 41                   | 48                       |
| T (400 nm)         | 91%    | 80%                  | 75%                      |
| Haze               | 3-PA   | 20 wt%<br>coated ZnS | 20 wt % ZrO <sub>2</sub> |
| Thickness          | 500 μm | 220 μm               | 500 μm                   |
| 392 nm             | 0.31%  | 4.5%                 | 1.3%                     |
| 436 nm             | 0.27%  | 4.2%                 | 1.2%                     |
| 544 nm             | 0.25%  | 4.0%                 | 1.0%                     |
| 653 nm             | 0.25%  | 3.8%                 | 0.92%                    |

The data of table 7 shows that the increase of the refractive index of the polymer is higher with ZnS nanoparticles than with ZrO<sub>2</sub> nanoparticles.

4) Preparation of liquid polymerizable composition comprising TiO<sub>2</sub> nanoparticles dispersed in a phosphine oxide containing monomer.

Three compositions were prepared by adding to the phosphine oxide monomer 1 (marketed by Osaka Organic Chemicals under the commercial name Viscoat 3-PA®)

respectively 10 wt%, 20 wt% and 30 wt% of TiO<sub>2</sub> from a suspension of TiO<sub>2</sub>/MeOH (15 wt% in MeOH, commercially available from Sakai chemical), and then adding to this mixture 1 wt% of Irgacure 184 (a radical photoinitiator marketed by BASF). The methanol of the resulting composition was evaporated under reduced pressure.

- 5 Then, each composition was applied between two glass plates separated by a spacer of 500µm. Photopolymerization was performed by illumination with a Hg lamp during 10 min (1.7 J.cm<sup>-2</sup>). A silicon spacer of 500µm was used between the two glass substrates.

The refractive index and Haze were measured as for example 2.

- The refractive indexes at 594 nm, Abbe numbers and front scattering of the resulting  
10 materials are indicated in 6.

Table 8

| Optical properties | 0 wt% | 10 wt% | 20 wt% | 30 wt% |
|--------------------|-------|--------|--------|--------|
| 594 nm             | 1.506 | 1.524  | 1.566  | 1.617  |
| δn                 | -     | 0.018  | 0.006  | 0.111  |
| Abbe Number        | 57    | 44     | 33     | 27     |
| T (400 nm)         | 86%   | 23%    | 1%     | 1%     |

- In table 9 below, materials obtained according to the above described method from a composition containing 3-PA and 30 wt% of ZrO<sub>2</sub> nanoparticles or 30 wt% of TiO<sub>2</sub>  
15 nanoparticles are compared.

Table 9

| 30 wt%      | ZrO2  | TiO2  |
|-------------|-------|-------|
| 594 nm      | 1.555 | 1.617 |
| δn          | 0.049 | 0.111 |
| Abbe Number | 52    | 27    |
| T (400 nm)  | 75%   | 1%    |

- The data of table 9 show that the transmission of a 3PA material containing TiO<sub>2</sub> nanoparticles is much lower than the transmission of the same material comprising ZrO<sub>2</sub> nanoparticles. However, it is to be noted that the particle size of TiO<sub>2</sub> used to prepare this material is higher than the particle size of ZrO<sub>2</sub>. Thus, the transmission of a 3-PA composition containing TiO<sub>2</sub> nanoparticles should be increased by using TiO<sub>2</sub> nanoparticles of lower particle size and by choosing a monomer having a higher refractive index than 3-PA.

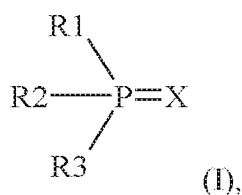


**Claims**

1. A liquid polymerizable composition comprising :

- a liquid monomer composition containing:

- a monomer of formula (I):



wherein:

X is an oxygen atom or a sulphur atom, preferably an oxygen atom,

at least one among R1, R2 and R3, identical or different, represents a polymerizable function which is directly linked to P or linked to P via a C1-C20alkylene, one or several carbon atoms of which may be replaced with :

–O–, –S–, –NH– or –NR– wherein R is a C1-C10 alkyl group,

a divalent monocycloalkyl or bicycloalkyl comprising 5 to 9 carbon atoms, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio, or

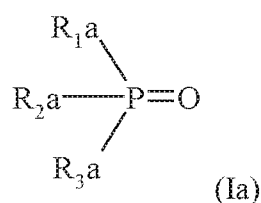
a phenyl or naphthyl, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio,

and the other(s) among R1, R2 and R3, identical or different, represent(s) an hydrogen atom, a C1-C10alkoxy, C1-C10alkylthio, phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-C10alkylthio, or

- a mixture of two different monomers M1 and M2 which are able to react together and form the monomer of formula (I), wherein M1 or M2 or both M1 and M2 contain the function P=X and M1 and M2 further contain functions which are able to react together to form a polymer, and

- mineral nanoparticles homogeneously dispersed in said monomer composition.

2. The liquid polymerizable composition of claim 1, wherein said mineral nanoparticles are chosen among ZnS, ZrO<sub>2</sub>, TiO<sub>2</sub> or BaTiO<sub>3</sub>.
3. The liquid polymerizable composition of claim 1 or 2, wherein said polymerizable function is selected from the group consisting of vinyl, allyl, isocyanate, thioisocyanate, acrylate, thioacrylate, methacrylate, thiomethacrylate, ether, thioether, alcohol, epoxy, thiol, and episulfide, preferably acrylate, methacrylate, episulfide or thiol.
4. The liquid polymerizable composition of any one of claims 1 to 3, wherein the other(s) among R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> bearing no polymerizable function, identical or different, represent(s) a phenyl, aryloxy, arylthio, arylC<sub>1</sub>-C<sub>10</sub>alkyloxy, or aryl C<sub>1</sub>-C<sub>10</sub>alkylthio.
5. The liquid polymerizable composition of any one of claims 1 to 4, wherein said monomer of formula (I) is a phosphine oxide of formula (Ia):



wherein:

at least one among R<sub>1</sub>a, R<sub>2</sub>a and R<sub>3</sub>a, identical or different, represents:

-(R<sub>4</sub>)<sub>n</sub>-X-(R<sub>5</sub>-Y)<sub>m</sub>-(R<sub>6</sub>)<sub>p</sub>-Q wherein:

R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>, identical or different, represent a C<sub>1</sub>-C<sub>6</sub> alkylene group, one or several carbon atoms of which may be replaced with a phenylene group,

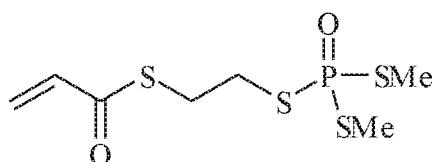
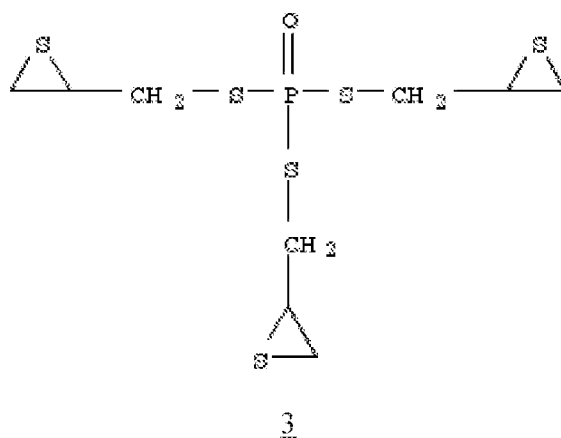
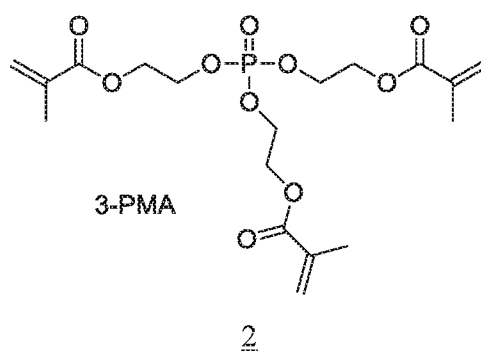
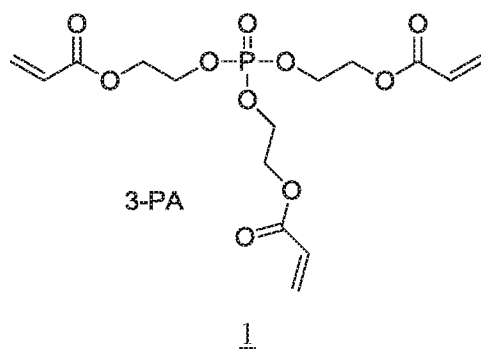
X and Y, identical or different, represent O, S, or -NR-, wherein R is a C<sub>1</sub>-C<sub>6</sub> alkyl group,

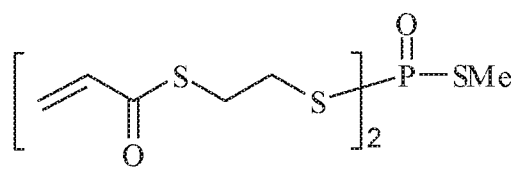
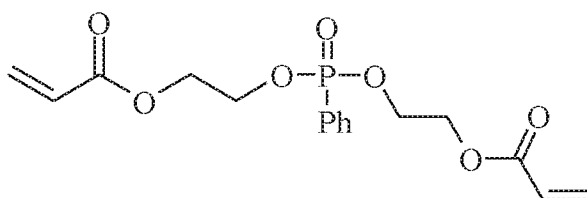
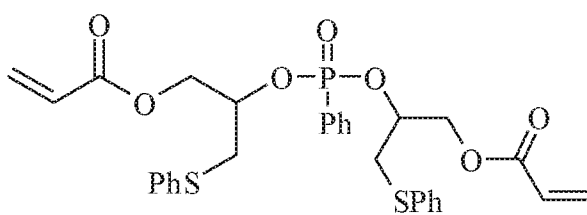
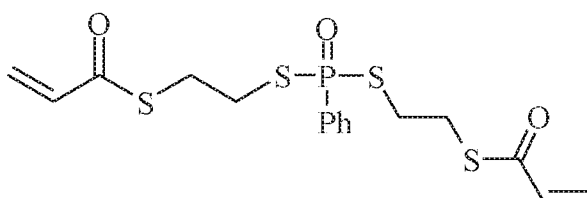
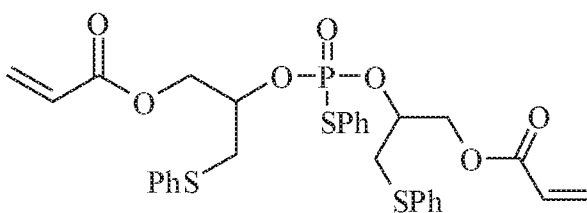
n, m and p, identical or different, represent an integer from 0 to 4, preferably from 0 to 2, more preferably 0 or 1,

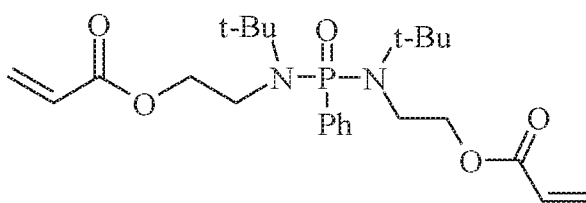
Q represents a polymerizable function, preferably chosen from acrylate, methacrylate, episulfide, or thiol,

and the other(s) among R<sub>1</sub>a, R<sub>2</sub>a and R<sub>3</sub>a, identical or different, represent(s) an hydrogen atom, a phenyl, an C<sub>1</sub>-C<sub>6</sub>alkoxy, C<sub>1</sub>-C<sub>6</sub>alkylthio, aryloxy, arylthio, aryl C<sub>1</sub>-C<sub>6</sub>alkoxy, or aryl C<sub>1</sub>-C<sub>6</sub>alkylthio.

6. The liquid polymerizable composition of any one of claims 1 to 5, wherein said phosphine oxide of formula (Ia) is selected from the group consisting of:



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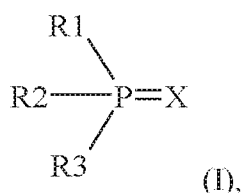
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7. The liquid polymerizable composition of any one claims 1 to 6, wherein said nanoparticles have a particle size less than 50 nm, preferably between 30 and 5 nm.
8. The liquid polymerizable composition of any one of claims 1 to 7, wherein said nanoparticles are chosen among of ZnS nanoparticles coated with one or more thiol-containing compounds.
9. The liquid polymerizable composition of claim 8, wherein said ZnS nanoparticles are coated with mercaptoethanol, thiophenol, mercaptophenol, or a mixture thereof.
10. The liquid polymerizable composition of claims 8 or 9, wherein said nanoparticles of ZnS are coated with a mixture of mercaptoethanol and thiophenol, preferably with a molar ratio of mercaptoethanol and thiophenol over Zn comprised between 2.0 and 0.1, preferably between 0.4 and 0.2.
11. The liquid polymerizable composition of any one of claims 8 to 10, wherein said nanoparticles of ZnS are coated with mercaptoethanol preferably with a molar ratio of mercaptoethanol over ZnS is comprised between 1.3 and 1.6.
12. The liquid polymerizable composition of any one claims 8 to 11, wherein said nanoparticles of ZnS have crystal size comprised between 3 and 10 nm, and the particle size of the nanoparticles of ZnS coated with said thiol-containing compound(s) is comprised between 4 and 80 nm.
13. The liquid polymerizable composition of any one of claims 1 to 12, wherein the amount of said mineral nanoparticles in the polymerizable composition is comprised between 5 and 50% w/w, preferably between 10 and 40% w/w, more preferably

between 30 and 35% w/w based on the total weight of the liquid polymerizable composition.

14. An optical substrate coated with the liquid polymerizable composition according to any one of claims 1 to 13.
15. An optical article cured of the liquid polymerizable composition according to any one of claims 1 to 13.
16. An optical article comprising :
  - (c) an optical substrate, and
  - (d) a coating obtained by thermal and/or UV curing of the liquid polymerizable composition according to any one of claims 1 to 13.
17. The optical substrate according to claim 15, wherein the article is an ophthalmic lens or an optical lens for optical instrument.
18. The optical article according to claim 16, wherein the article is an ophthalmic lens or an optical lens for optical instrument.
19. Use of mineral nanoparticles for increasing the refractive index of a polymeric material obtained by thermal and/or UV curing of a liquid monomer composition containing :

- a monomer of formula (I):



wherein:

X is an oxygen atom or a sulphur atom, preferably an oxygen atom,

at least one among R1, R2 and R3, identical or different, , represents a polymerizable function which is directly linked to P or linked to P via a C1-C20 alkylene, one or several carbon atoms of which may be replaced with:

–O–, –S–, –NH– or –NR– wherein R is a C1-C10 alkyl group,

a divalent monocycloalkyl or bicycloalkyl comprising 5 to 9 carbon atoms, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio, or

a phenyl or naphthyl, optionally substituted with 1 to 4 groups independently chosen among an halogen atom, C1-C6 alkyl, C1-C6 alkoxy, or C1-C6 alkylthio,

and the other(s) among R1, R2 and R3, identical or different, represent(s) an hydrogen atom, a C1-C10alkoxy, C1-C10alkylthio, phenyl, aryloxy, arylthio, arylC1-C10alkyloxy, or aryl C1-C10alkylthio, or

- a mixture of two different monomers M1 and M2 which are able to react together and form the monomer of formula (I), wherein M1 or M2 or both M1 and M2 contain the function  $P=X$  and M1 and M2 further contain functions which are able to react together to form a polymer, and

wherein said mineral nanoparticles are homogeneously dispersed in said monomer composition.

20. Use according to claim 19, wherein said mineral nanoparticles are chosen among ZnS,  $ZrO_2$ ,  $TiO_2$  or  $BaTiO_3$ .