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(54) **Title**: LIQUID THIOETHER CARBOXYLIC ACID ESTERS

(57) **Abstract**: The present invention relates to a liquid thioether carboxylic acid ester, a process for the preparation of the liquid thioether carboxylic acid ester, an article comprising the liquid thioether carboxylic acid ester as well as a use of the liquid thioether carboxylic acid ester as a component or substantial part of an optical system, tunable lens, adaptive optical module and materials thereof, actuator, electro-active polymer, laser and all related products, optical liquid, cover glass, lens or container material, tiltable prism or optical calibration liquid or optical refractive index matching liquid and a use of the liquid thioether carboxylic acid ester as a component or substantial part of a color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material or ingredient or additive in a polymer.

Liquid thioether carboxylic acid esters

Field of the invention

The present invention relates to a liquid thioether carboxylic acid esters, a process for the preparation of the liquid thioether carboxylic acid esters, an article comprising the liquid thioether carboxylic acid ester as an ingredient in at least one of its parts or as part of the article itself as well as a use of the liquid thioether carboxylic acid ester as a component or substantial part of an optical system, tunable lens, adaptive optical module and materials thereof, actuator, electro-active polymer, laser and all related products, optical liquid, cover glass, lens or container material, tiltable prism or optical calibration liquid or optical refractive index matching liquid and a use of the liquid thioether carboxylic acid ester as a component or substantial part of a color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material or ingredient or additive in a polymer.

Background of the invention

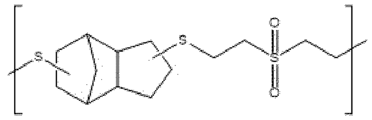
The current development towards ever smaller and lighter optical systems demands novel approaches for the technical realization of optical devices for these intended applications. Especially heavy and slow optical devices based on glass and/or solid lens systems which are moved back and forward for focusing or zooming are sought to be replaced by so called liquid tuneable lens systems. The main part of such lens systens is a liquid-filled core element comprising a rigid container and a deformable membrane, which encloses a so-called “optical liquid”. The lens is typically formed by a lens shaper, which defines the optically clear aperture of the lens and the initial deformation of the lens. In case of manually tuneable lenses (ML), the shaper is pushed directly into the membrane by hand/manually, whereas in case of electrically tuneable lenses (EL), an electromagnetically actuated bobbin is pushed into the membrane, deforming the liquid filled volume and therefore changing the curvature of the lens as a function of the applied force to the actuated bobbin.

The optical liquid is enclosed by a soft membrane and a rigid container. The initial shape of the lens is defined by the lens shaper and the amount of optical liquid in the volume. When a bobbin is pushed into the deformable membrane, fluid is pumped from the surrounding of the lens into the centre, resulting in a deformation of the central part of the lens and therefore in a change of the focal length of the lens.

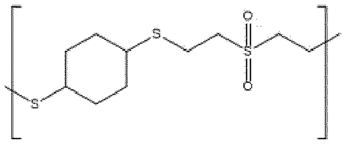
The optical liquid is a crucial component of the liquid tuneable lens system. In particular, it is desirable that the optical liquids have high refractive index (≥1.5), Abbe´s number ≥40, transparency in the visible range (400 – 800 nm) of at least 90 %, low volatility, wide operational range of temperature from desirably about -20 °C to +100 °C and chemical compatibility with other components of the lens system (e. g. membranes, container materials, glues). Further, the viscosity of the optical liquids should be preferably not higher than 5000 mPas.

However, materials having high Abbe´s numbers υ ($\upsilon_d = (n_d - 1)/(n_F - n_C)$ with refractive indices n_d at 587.56 nm, n_F at 486.1 nm, n_C at 656.3 nm or $\upsilon_D = (n_D - 1)/(n_F - n_C)$ with refractive indices n_D at 589.3 nm, n_F at 486.1 nm, n_C at 656.3 nm) as well as high refractive indices n ($n = \sin\alpha_i/\sin\alpha_r$), *i* meaning angle of incident light and *r* angle of reflective light) are not easy to obtain because said features normally cannot be enhanced in parallel. Thus, the materials presently available and which are used as optical liquids represent a compromise between those features.

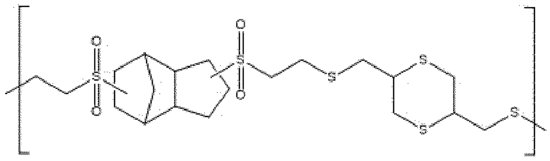
In the art, several attempts for providing materials fulfilling at least some of these requirements have been proposed. For example, commercially available fluorocarbon/perfluoropolyether fluids (DuPont, Nye, Solvay Specialty Polymers) show Abbe´s numbers of $\upsilon > 100$ but have refractive indices of $n \approx 1.3$. Recently, a new class of polythio ether sulfones based compounds exhibiting high Abbe´s numbers and high refractive indices have been reported by Y. Suzuki et al. Macromolecules, 2012, *45*, 3402. The polythio ether sulfones based compounds are of the following formula:



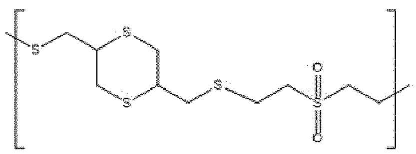
n_D: 1.605 ; Abbe's Number: 48.0



n_D: 1.602 ; Abbe's Number: 50.6



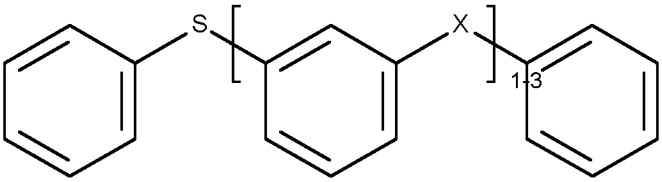
n_D: 1.623 ; Abbe's Number: 45.8



n_D: 1.651 ; Abbe's Number: 42.6

However, the afore-mentioned materials are solids at room temperature including their monomeric building blocks and are therefore not suitable as optical liquids in liquid tuneable lens systems.

Another class of materials has been disclosed by T. Okubo et al. J. Appl. Polmer Sci., 1998, *68*, 1791 and T. Okubo et al. J. Mater Sci., 1999, *34*, 337. Further, materials based on the thio phenol ether motif (n > 1.6) are proposed as ingredients. The thio phenol ether motif of the materials is as follows:



X = O or S

However, these compounds have Abbe's number of 23 and are only available as mixtures and are very costly. In addition the quality is variable and available amounts are low. Other materials containing an oligo-sulfide motif and additionally reactive acrylic residues are used to produce polymers with high n_D and υ (see e.g. DE 4011868, EP 0 284 374 A2).

Thus, there is a need in the art for providing liquids which are suitable as optical liquids, especially in liquid tuneable lens systems. In particular, it is desirable to provide a liquid having high Abbe´s number υ as well as high refractive index n. A high refractive index is needed for a high optical power whereas a high Abbe number is beneficial for low chromatic aberration/ dispersion (dependency of the wave length on the refractive index).

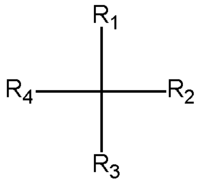
Accordingly, it is an object of the present invention to provide a liquid which is suitable as optical liquid. Furthermore, it is an object of the present invention to provide a liquid which is suitable as optical liquid in liquid tuneable lens systems. It is an even further object of the present invention to provide a liquid having an improved balance of (high) Abbe´s number υ and (high) refractive index n (refractive index ≈ 1.27 and higher, Abbe´s number ≈ 35 and higher). A still further object of the present invention is to provide a liquid having high transmittance in the visible range. An even further object of the present invention is to provide a liquid having good compatibility with the membrane materials. Further objects can be gathered from the following description of the invention.

Summary of the invention

The foregoing and other objects are solved by the subject-matter of the present invention. According to a first aspect of the present invention, a liquid thioether carboxylic acid ester is provided. The liquid thioether carboxylic acid ester is a reaction product of

A) a compound of the formula

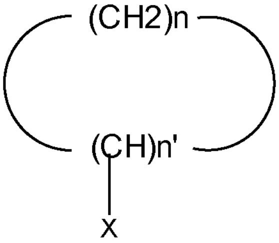
a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

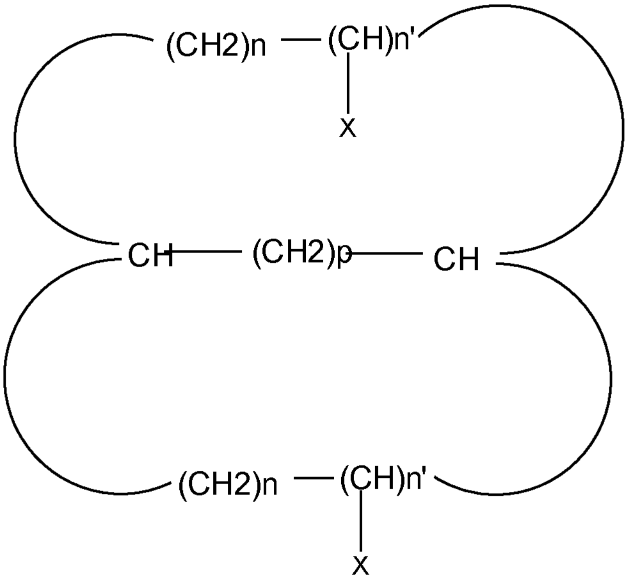
b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

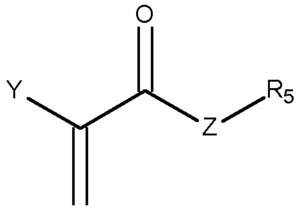
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3; and

B) a compound of the formula (B)

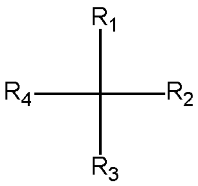


(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl

According to a further aspect of the present invention, a process for the preparation of a liquid thioether carboxylic acid ester, as defined herein, is provided. The process comprising the steps of

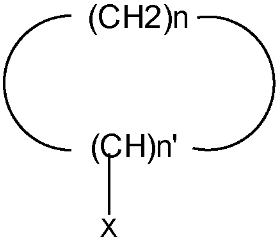
A) providing a compound of the formula
   a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

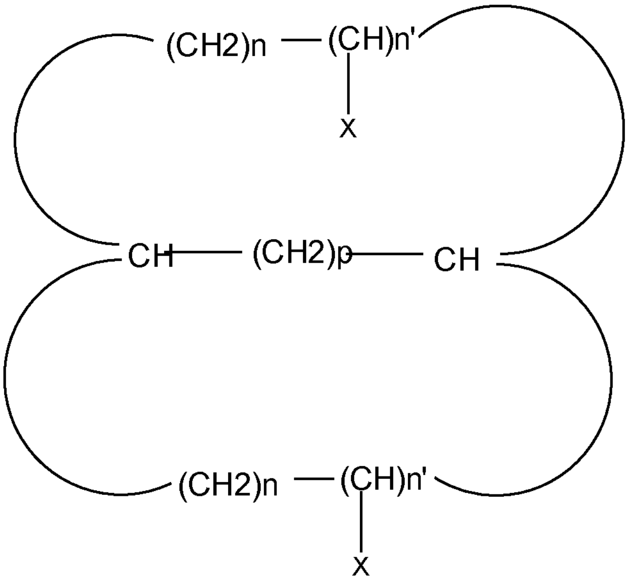
b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and /or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

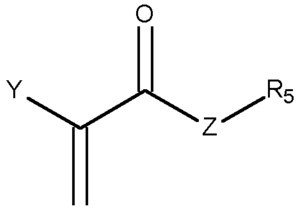
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3;

B) providing a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl, and

C) reacting the compound of step A) with the compound of step B) such as to obtain the liquid thioether carboxylic acid ester.

According to an even further aspect of the present invention, an article, preferably an optical lens such as a tunable focus lens, optical liquid, tiltable prism or calibration liquid or refractive index matching liquid, comprising the liquid thioether carboxylic acid ester, as defined herein, as an ingredient in at least one of its parts or as part of the article itself is provided. According to another aspect of the present invention, an article, preferably an optical lens such as a tunable focus lens, optical liquid, tiltable prism or calibration liquid or refractive index matching liquid, comprising the liquid thioether carboxylic acid ester, as defined herein, as an ingredient in at least one of its parts or as a part of the article itself is provided.

According to a still further aspect, a use of the liquid thioether carboxylic acid ester, as defined herein, as a component or substantial part of an optical system, tunable lens, adaptive optical module and materials thereof, actuator, electro-active polymer, laser and all related products, optical liquid, cover glass, lens or container material, tiltable prism or optical calibration liquid or optical refractive index matching liquid is provided. According to still another aspect, a use of the liquid thioether carboxylic acid ester, as defined herein, as a component or substantial part of a color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material or ingredient or additive in a polymer is provided.

Advantageous embodiments of the inventive liquid thioether carboxylic acid ester are defined in the corresponding sub-claims.

According to one embodiment, in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_1-C_6-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_2-C_6-alkyl containing at least one sulfhydryl moiety (SH), and one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O.

According to another embodiment, in the formula (A1) R_1 is hydrogen; R_2 is a linear C_1-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH), and one CH_2 group of R_2 and/or R_3 and R_4 is replaced by S.

According to yet another embodiment, in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH), and two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O.

According to one embodiment, two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O, and O and C=O are directly linked.

According to another embodiment, in the formula (A2) n’ is 2; the sum of n and n’ is an integer in the range from 5 to 7 and two CH_2-groups are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 1 to 3.

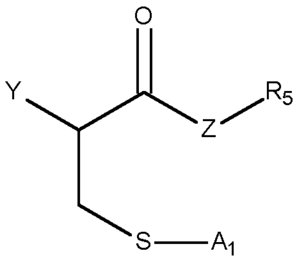
According to yet another embodiment, in the formula (A2) n’ is 2; the sum of n and n’ is 6; two CH_2-groups are replaced with S or O with the proviso that S or O are not directly linked, and X is $(CH_2)_m$-SH with m being 1.

According to one embodiment, Y is hydrogen or methyl; Z is O; R_5 is linear saturated C_1-C_3 alkyl.

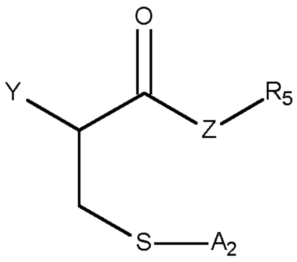
According to another embodiment, Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_4 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

According to yet another embodiment, the reaction product is obtained by a 1,4-addition mechanism of the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) and the compound of the formula (B).

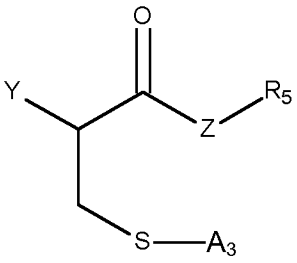
According to one embodiment, the reaction product is of the general formula (C1), (C2) or (C3)



C1



C2



C3

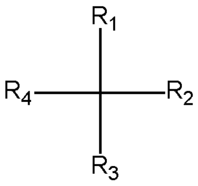
According to one embodiment, the thioether carboxylic acid ester has a refractive index of 1.27 – 1.9 and/or an Abbe’s number of 35 - 110.

In the following, the details and preferred embodiments of the inventive liquid thioether carboxylic acid ester will be described in more detail. It is to be understood that these technical details and embodiments also apply to the inventive process for the preparation of a liquid thioether carboxylic acid ester, the inventive article comprising the liquid thioether carboxylic acid ester and its use.

Detailed description of the invention

The thioether carboxylic acid ester of the present invention is a reaction product of

A) a compound of the formula
   a) (A1)

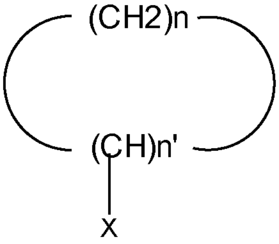


$$R_4 - \overset{R_1}{\underset{R_3}{+}} - R_2$$

(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

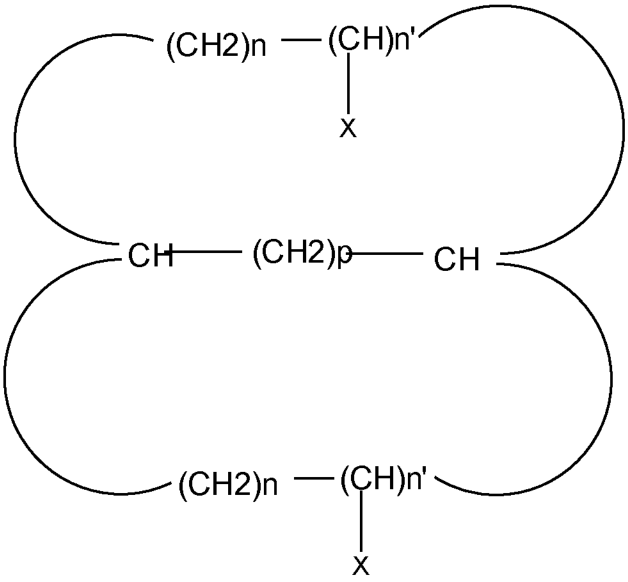
   b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

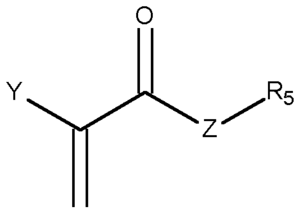
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3; and

B) a compound of the formula (B)



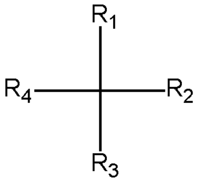
(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

The term “at least one” sulfhydryl moiety (SH) means that the respective compound comprises one or more sulfhydryl moieties (SH).

In one embodiment, the at least one sulfhydryl moiety (SH) is one sulfhydryl moiety (SH). Alternatively, the at least one sulfhydryl moiety (SH) is two or more sulfhydryl moieties (SH). For example, the respective compound comprises two or three or four sulfhydryl moieties (SH). Preferably, the respective compound comprises two or three sulfhydryl moieties (SH).

In one embodiment, the compound of the formula (A1), (A2) or (A3), is the compound of the formula (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O.

In the formula (A1), R_1 is hydrogen, linear or branched C_1-C_7 alkyl, preferably R_1 is hydrogen, linear or branched C_1-C_5 alkyl, more preferably R_1 is hydrogen, linear or branched C_1-C_4 alkyl, even more preferably R_1 is hydrogen, linear or branched C_2-C_4 alkyl and most preferably R_1 is hydrogen or linear C_2-C_3 alkyl. For example, R_1 is hydrogen or ethyl. In one embodiment, R_1 is hydrogen.

Preferably, R_1 is unsubstituted linear or branched C_1-C_7 alkyl.

As used herein, the term "alkyl" is a radical of a saturated aliphatic group, including linear chain alkyl groups and branched chain alkyl groups.

In the formula (A1), R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH). Preferably, R_2 is hydrogen or a linear or branched C_1-C_6-alkyl containing at least one sulfhydryl moiety (SH), more preferably, R_2 is a linear or branched C_1-C_5-alkyl containing at least one sulfhydryl moiety (SH) and most preferably, R_2 is hydrogen or a linear or branched C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH). For example, R_2 is a linear C_1-C_5-alkyl containing at least one sulfhydryl moiety (SH). Alternatively, R_2 is hydrogen or a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH).

In the formula (A1), R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH). Preferably, R_3 and R_4 are independently selected from a linear C_2-C_6-alkyl containing at least one sulfhydryl moiety (SH) and most preferably, R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH).

In formula (A1), one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 can be replaced by O, S and/or C=O.

In one embodiment, one CH_2 group of R_2 and/or R_3 and R_4 is replaced by S. For example, one CH_2 group of R_2 or R_3 and R_4 is replaced by S. Alternatively, one CH_2 group of R_2 and R_3 and R_4 is replaced by S.

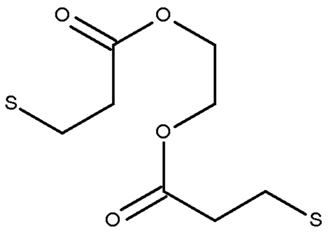
In another embodiment, two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O. For example, two CH_2 groups of R_2 or R_3 and R_4 are replaced by O and C=O. Alternatively, two CH_2 groups of R_2 and R_3 and R_4 are replaced by O and C=O. In one embodiment, two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O, wherein O and C=O are directly linked. For example, two CH_2 groups of R_2 or R_3 and R_4 are replaced by O and C=O, wherein O and C=O are directly linked. Alternatively, two CH_2 groups of R_2 and R_3 and R_4 are replaced by O and C=O, wherein O and C=O are directly linked.

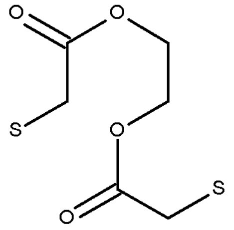
Thus, it is preferred that in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_1-C_6-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_2-C_6-alkyl containing at least one sulfhydryl moiety (SH), and one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O.

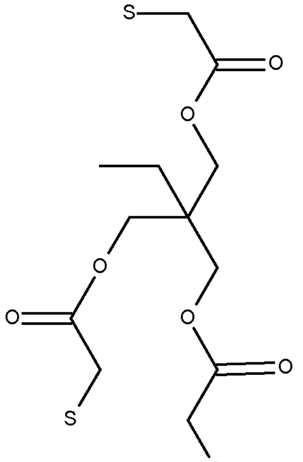
More preferably, in the formula (A1) R_1 is hydrogen; R_2 is a linear C_1-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH), and one CH_2 group of R_2 and/or R_3 and R_4 is replaced by S.

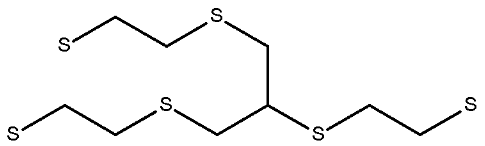
Alternatively, in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH), and two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O. In this embodiment, it is preferred that two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O, and O and C=O are directly linked.

It is appreciated that the compound of the formula (A1) is preferably selected from the group comprising, more preferably consisting of,

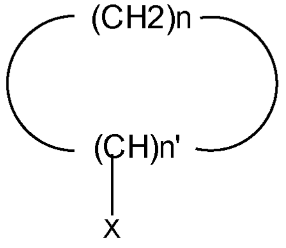








Alternatively, the compound of the formula (A1), (A2) or (A3), is the compound of the formula (A2)



(A2),

wherein n’ is 1 or 2, the sum of n and n’ is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3.

In the formula (A2), n’ is 1 or 2, and preferably n’ is 2.

In the formula (A2), n is preferably an integer in the range from 3 to 6, more preferably n is an integer in the range from 3 to 5, even more preferably, n is 4 or 5, and most preferably n is 4.

It is a further requirement in the formula (A2) that the sum of n and n’ is an integer in the range from 5 to 9, preferably, the sum of n and n’ is an integer in the range from 5 to 7 and most preferably, the sum of n and n’ is 6.

Thus, it is appreciated that in the formula (A2) n’ is 1 or 2 and the sum of n and n’ is an integer in the range from 5 to 9. Preferably, n’ is 1 or 2 and the sum of n and n’ is an integer in the range from 5 to 7. More preferably, n’ is 1 or 2 and the sum of n and n’ is 5 or 6. Most preferably, n’ is 2 and the sum of n and n’ is 6.

In the formula (A2), one or two CH_2-group(s) is/are replaced with S and/or O with the proviso that S and/or O are not directly linked. Preferably, two CH_2-groups are replaced with S and/or O with the proviso that S and/or O are not directly linked. For example, two CH_2-groups are replaced with S and O with the proviso that S and O are not directly linked. Alternatively, two CH_2-groups are replaced with S or O with the proviso that S or O are not directly linked.

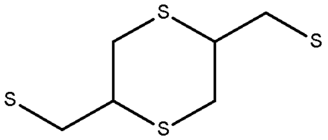
In one embodiment, two CH_2-groups in the formula (A2) are replaced with S with the proviso that the two S are not directly linked.

In the formula (A2), X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3. Preferably, X is $(CH_2)_m$-SH with m being an integer in the range from 1 to 3. More preferably, X is $(CH_2)_m$-SH with m being 1 or 2. Most preferably, X is $(CH_2)_m$-SH with m being 1.

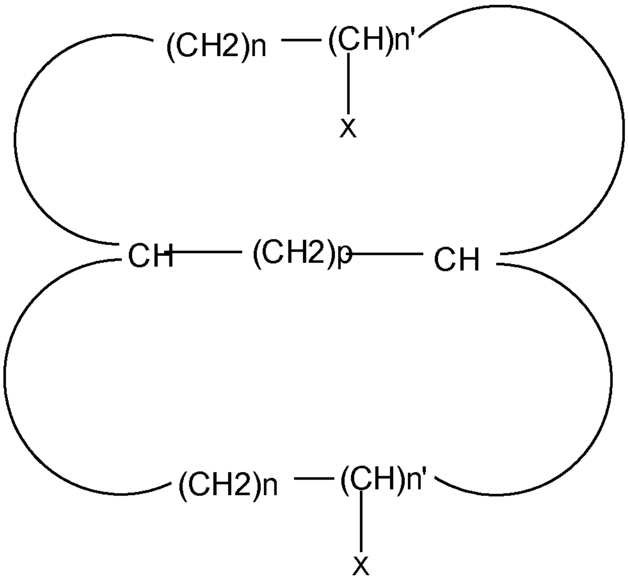
Thus, it is preferred that in the formula (A2) n’ is 2; the sum of n and n’ is an integer in the range from 5 to 7 and two CH_2-groups are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 1 to 3.

In one embodiment, n' is 2; the sum of n and n' is 6; two CH_2-groups are replaced with S or O with the proviso that S or O are not directly linked, and X is $(CH_2)_m$-SH with m being 1 in the formula (A2).

It is appreciated that the compound of the formula (A2) is preferably



Alternatively, the compound of the formula (A1), (A2) or (A3), is the compound of the formula (A3)

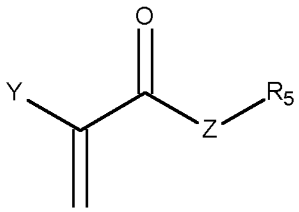


(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3.

It is appreciated that the compound of the formula (A1), (A2) or (A3), is preferably a compound of the formula (A1) or (A2). In one embodiment, the compound of the formula (A1), (A2) or (A3), is a compound of the formula (A1). Alternatively, the compound of the formula (A1), (A2) or (A3), is a compound of the formula (A2). Preferably, the compound of the formula (A1), (A2) or (A3), is a compound of the formula (A1).

It is appreciated that the liquid thioether carboxylic acid ester of the present invention is a reaction product of the compound of the formula (A1), (A2) or (A3), and a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

In the formula (B), Y is hydrogen or methyl. Preferably, Y is methyl. Alternatively, Y is hydrogen.

In the formula (B), R_5 is a linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl. For example, R_5 is a linear or branched saturated C_1-C_8 alkyl, preferably, R_5 is a linear or branched saturated C_1-C_4 alkyl and most preferably R_5 is a linear saturated C_1-C_3 alkyl. For example, R_5 is methyl or ethyl, such as methyl. Alternatively, R_5 is tert-butyl.

In one embodiment, R_5 is a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl. Preferably, R_5 is an aryl system selected from phenyl and benzyl.

In one embodiment, Y is hydrogen or methyl; Z is O and R_5 is linear saturated C_1-C_3 alkyl in the formula (B). Preferably, Y is hydrogen or methyl; Z is O and R_5 is linear saturated C_1 or C_2 alkyl in the formula (B).

Alternatively, Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_4 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl in the formula (B). Preferably, Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_2-C_4 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl in the formula (B). More preferably, Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_3 or C_4 alkyl, such as branched C_4 alkyl like tert-butyl, or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl in the formula (B).

It is appreciated that the compound of the formula (B) is preferably selected from the group comprising, more preferably consisting of, methyl methacrylate, tert-butyl methacrylate, ethyl acrylate, benzyl methacrylate, iso-bornyl acrylate and mixtures thereof.

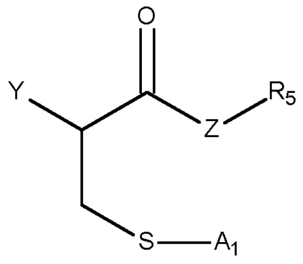
The compound of the formula (B) can be selected depending on the compound of the formula (A1), (A2) or (A3).

For example, if the liquid thioether carboxylic acid ester is a reaction product of the compound of the formula (A1) and the compound of the formula (B), the compound of the formula (B) is preferably selected such that Y is hydrogen or methyl; Z is O and R_5 is linear saturated C_1-C_3 alkyl, such as methyl.

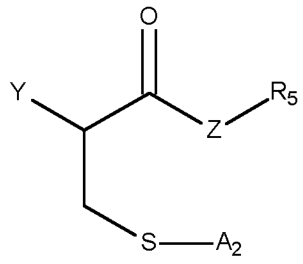
Alternatively, if the liquid thioether carboxylic acid ester is a reaction product of the compound of the formula (A2) and the compound of the formula (B), the compound of the formula (B) is preferably selected such that Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_4 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

It is appreciated that the liquid thioether carboxylic acid ester of the present invention is a reaction product of the compound of the formula (A1), (A2) or (A3), and a compound of the formula (B), wherein the reaction product is preferably obtained by a 1,4-addition mechanism of the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) and the compound of the formula (B). More preferably, the reaction product is obtained by a 1,4-Michael addition mechanism of the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) and the compound of the formula (B).

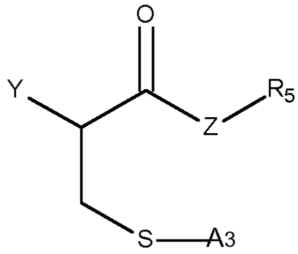
Accordingly, the liquid thioether carboxylic acid ester of the present invention is of the general formula (C1), (C2) or (C3)



C1



C2



C3

It is appreciated that the liquid thioether carboxylic acid ester of the general formula (C1), is a reaction product of the compound of the formula (A1) and the compound of the formula (B), wherein the residue A1 corresponds to the compound of the formula (A1) after its reaction with the compound of the formula (B).

The liquid thioether carboxylic acid ester of the general formula (C2) is a reaction product of the compound of the formula (A2) and the compound of the formula (B), wherein the residue A2 corresponds to the compound of the formula (A2) after its reaction with the compound of the formula (B).

The liquid thioether carboxylic acid ester of the general formula (C3) is a reaction product of the compound of the formula (A3) and the compound of the formula (B), wherein the residue A3 corresponds to the compound of the formula (A3) after its reaction with the compound of the formula (B).

As regards the definition of A1, A2, A3, Y, Z, R_5 and preferred embodiments thereof, reference is thus made to the statements provided above when discussing the technical details of the compounds of the formula (A1), (A2), (A3) and (B) of the present invention.

It is appreciated that the liquid thioether carboxylic acid ester of the present invention has specifically high Abbe´s number υ as well as high refractive index n.

For example, the thioether carboxylic acid ester has a refractive index of 1.27 – 1.9 and/or an Abbe’s number of 35 - 110. Preferably, the thioether carboxylic acid ester has a refractive index of 1.27 – 1.9 or an Abbe’s number of 35 - 110. Alternatively, the thioether carboxylic acid ester has a refractive index of 1.27 – 1.9 and an Abbe’s number of 35 - 110. More preferably, the thioether carboxylic acid ester has a refractive index of 1.29 - 1.67 or an Abbe’s number of 40 - 100. Alternatively, the thioether carboxylic acid ester has a refractive index of 1.29 - 1.67 and an Abbe’s number of 40 - 100.

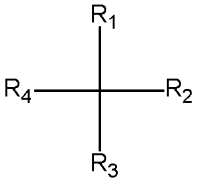
In one embodiment, the thioether carboxylic acid ester has a refractive index in the range of 1.45 and 1.67 and preferably in the range of 1.49 and 1.67.

Additionally or alternatively, the thioether carboxylic acid ester has an Abbe's number in the range of 35 to 100, preferably in the range of 38 to 100 and most preferably in the range of 40 to 100.

The present invention is further directed to a process for the preparation of the liquid thioether carboxylic acid ester.

The process comprising the steps of

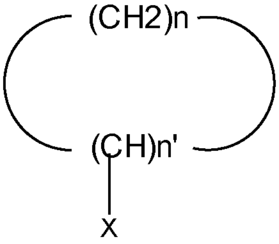
A) providing a compound of the formula
   a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

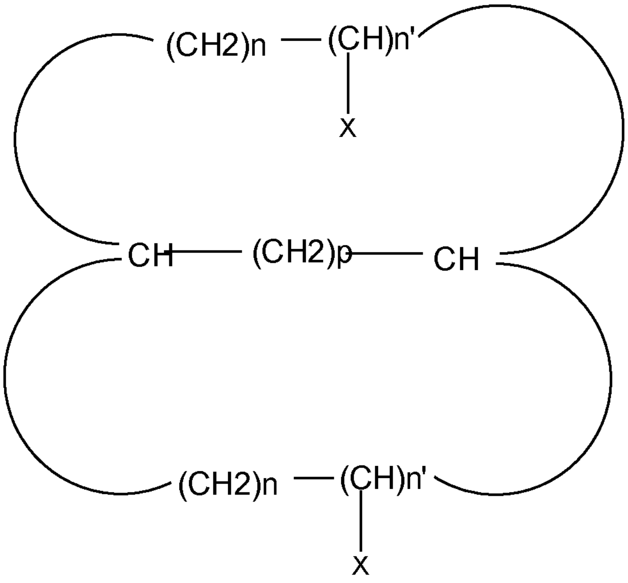
   b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and /or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

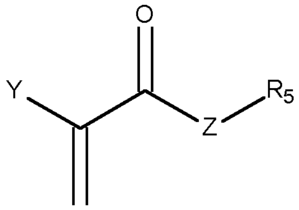
   c) (A3)



(A3),

wherein n’ is 1 or 2, the sum of n and n’ is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3;

B) providing a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl, and

C) reacting the compound of step A) with the compound of step B) such as to obtain the liquid thioether carboxylic acid ester.

As regards the definition of the compound of formula (A1), (A2), (A3), (B), the liquid thioether carboxylic acid ester and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the liquid thioether carboxylic acid ester of the present invention.

In one embodiment, process step C) is carried out such that the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) is reacted with the compound of the formula (B) by a 1,4-addition mechanism. Preferably, process step C) is carried out such that the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) is reacted with the compound of the formula (B) by a 1,4-Michael addition mechanism.

In one embodiment, process step C) is carried out in a suitable solvent. Preferably, process step C) is carried out in an organic solvent. The term “organic solvent” does not exclude that the organic solvent comprises minor amounts of water. If the organic solvent comprises water, the organic solvent comprises water in an amount of from 0.01 to 10.0 wt.-%, preferably from 0.01 to 5.0 wt.-%, more preferably from 0.01 to 2.0 wt.-% and most preferably from 0.01 to 1.0 wt.-%, based on the total weight of the solvent. For example, the organic solvent is free of water. In one embodiment, process step C) is carried out in a mixture of an organic solvent and water. If process step C) is carried out in a mixture of an organic solvent and water, the ratio of organic solvent to water (vol.-%/vol.-%) can be from 10:1 to 1:10, preferably from 5:1 to 1:5, even more preferably from 2:1 to 1:2 and most preferably about 1:1. In an alternative embodiment, process step C) is carried out in water.

Preferably, the solvent is selected such that the compound of the formula (A1), (A2) or (A3) as well as the compound of the formula (B) is soluble in the solvent, such as the organic solvent, mixture of organic solvent and water, or water.

The term “soluble” in the meaning of the present invention refers to systems in which no discrete solid particles of the compound of the formula (A1), (A2) or (A3) as well as the compound of the formula (B) are observed in the solvent, such as organic solvent, mixture of organic solvent and water, or water.

Preferably, the organic solvent is selected from the group comprising dimethylformamide, ethanol, tetrahydrofuran, dimethylformamide, methanol, toluene, xylene, ethyl acetate and mixtures thereof.

In one embodiment, the organic solvent comprises, preferably consists of, a mixture of organic solvents, preferably two or three organic solvents, and most preferably two organic solvents. For example, the organic solvent comprises, preferably consists of, a mixture of dimethylformamide and tetrahydrofuran. Alternatively, the organic solvent comprises, preferably consists of, a mixture of methanol and ethanol.

If the organic solvent comprises, preferably consists of, a mixture of two organic solvents, the organic solvents are preferably present in a ratio (vol:vol) ranging from 10:1 to 1:10, preferably from 5:1 to 1:5, even more preferably from 2:1 to 1:2 and most preferably about 1:1. For example, the organic solvent comprises, preferably consists of, a mixture of dimethylformamide and tetrahydrofuran in a ratio (vol:vol) ranging from 10:1 to 1:10, preferably from 5:1 to 1:5, even more preferably from 2:1 to 1:2 and most preferably about 1:1.

In one embodiment, process step C) is carried out in the presence of a catalyst. The catalyst is preferably a compound having a pK_b-value being suitable for deprotonating a sulfhydride, preferably for deprotonating the compound of formula (A1), (A2) or (A3) of process step A).

For example, the catalyst is selected from the group comprising alkali hydroxide, such as KOH, NaOH, $Mg(OH)_2$ or $Ca(OH)_2$; earth alkali hydroxide, such as Na_2CO_3, K_2CO_3 or $CaCO_3$; metal hydrogen carbonate, such as $NaHCO_3$, $KHCO_3$ or $Ca(HCO_3)_2$; metal alkoxide, tertiary amines, such as trialkyl amines, e.g. trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, di-isopropyl ethyl amine, or aromatic amines, e.g. pyridine and mixtures thereof. Preferably, the catalyst is a tertiary amine, more preferably, the catalyst is a tertiary amine selected from the group comprising trimethyl amine, triethyl amine, tripropyl amine, tributyl amine, di-isopropyl ethyl amine and mixtures thereof and most preferably the catalyst is triethyl amine or di-isopropyl ethyl amine.

Additionally or alternatively, process step C) is carried out at a temperature ranging from -20 °C to the reflux temperature of the organic solvent, preferably of the organic solvent in which process step C) is carried out. In one embodiment, process step C) is carried out at a temperature ranging from 0 °C to the reflux temperature of the organic solvent, preferably of the organic solvent in which process step C) is carried out. For example, process step C) is carried out at a temperature ranging from room temperature to 40 °C. Most preferably, process step C) is carried out at room temperature.

The term “room temperature” refers to a temperature typically measured in a laboratory, i.e. a temperature ranging from about 16 to 26 °C, preferably from 18 to 25 °C and most preferably from 20 to 24 °C.

The amounts of the compound of formula (A1), (A2) or (A3) and the compound of formula (B) in process step C) in order to reach the liquid thioether carboxylic acid ester can vary in a broad range and can be determined by appropriate calculation.

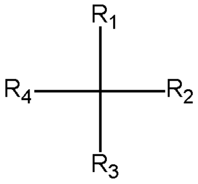
In one embodiment, the process for the preparation of the liquid thioether carboxylic acid ester further comprises a step D) of purifying the liquid thioether carboxylic acid ester obtained in step C).

It is appreciated that step D) of purifying the liquid thioether carboxylic acid ester obtained in step C) can be carried out by every means known to the skilled person for separating a compound from its reaction mixture. For example, process step D) can be carried out by methods selected from the group comprising, methods used for evaporating volatile compounds, such as in vacuum, extraction methods, distillation methods, chromatographic methods and mixtures thereof. Preferably, process step D) is carried out by evaporating volatile compounds, preferably in vacuum, extraction methods, distillation methods and chromatographic methods.

Thus, the process for the preparation of the liquid thioether carboxylic acid ester preferably comprises, more preferably consists of, the steps of

A) providing a compound of the formula

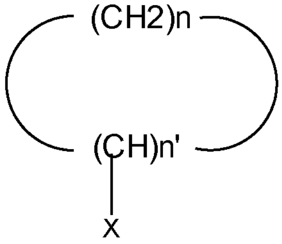
a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

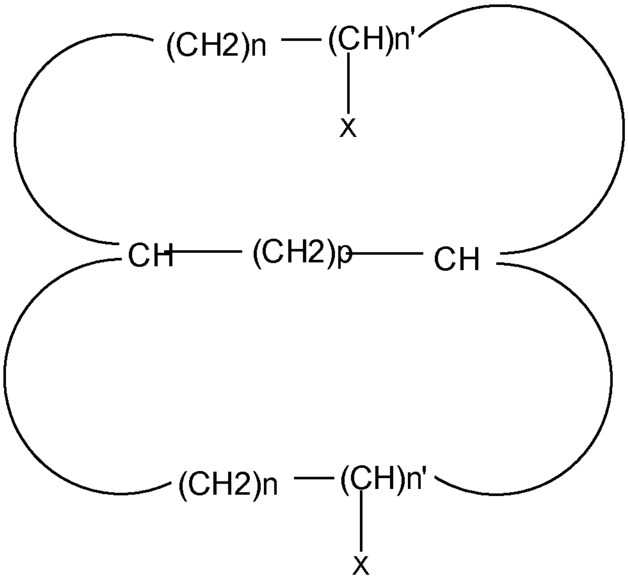
b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and /or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

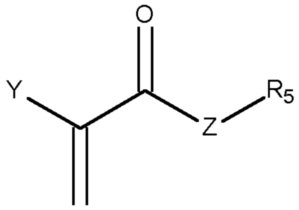
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3;

B) providing a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl;

C) reacting the compound of step A) with the compound of step B) such as to obtain the liquid thioether carboxylic acid ester; and

D) purifying the liquid thioether carboxylic acid ester obtained in step C).

In one embodiment, the liquid thioether carboxylic acid ester is obtainable by the process for the preparation of a liquid thioether carboxylic acid ester as defined herein.

The instant invention is thus further directed to a liquid thioether carboxylic acid ester obtainable by the process for the preparation of a liquid thioether carboxylic acid ester of the instant invention.

With regard to the definition of the liquid thioether carboxylic acid ester and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the liquid thioether carboxylic acid ester of the present invention.

In view of the advantages obtained, the present invention is further directed to an article comprising the liquid thioether carboxylic acid ester as defined herein as an ingredient in at least one of its parts or as part of the article itself.

As regards the definition of the liquid thioether carboxylic acid ester and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the liquid thioether carboxylic acid ester of the present invention.

Preferably, the article comprising the liquid thioether carboxylic acid ester as an ingredient in at least one of its parts or as part of the article itself is an optical lens such as a tunable focus lens, optical liquid, tiltable prism or calibration liquid or refractive index matching liquid.

In one embodiment, the article comprising the liquid thioether carboxylic acid ester as an ingredient in at least one of its parts or as part of the article itself is an optical liquid.

In another embodiment, the article comprising the liquid thioether carboxylic acid ester as an ingredient in at least one of its parts or as part of the article itself is a wave guide material, color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material, ingredient or additive in a polymer.

Furthermore, the present invention is directed to a use of the liquid thioether carboxylic acid ester, as defined herein, as a component or substantial part of an optical system, tunable lens, adaptive optical module and materials thereof, actuator, electro-active polymer, laser and all related products, optical liquid, cover glass, lens or container material, tiltable prism or optical calibration liquid or optical refractive index matching liquid.

For example, the present invention is directed to a use of the liquid thioether carboxylic acid ester, as defined herein, as a component or substantial part of an optical liquid.

Further, the present invention is directed to a use of the liquid thioether carboxylic acid ester, as defined herein, as a component or substantial part of a color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material or ingredient or additive in a polymer.

With regard to the definition of the liquid thioether carboxylic acid ester and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the liquid thioether carboxylic acid ester of the present invention.

The scope and interest of the invention will be better understood based on the following examples which are intended to illustrate certain embodiments of the invention and are non-limitative.

EXAMPLES

1. Methods

NMR-spectroscopy

NMR-data were acquired by using a Bruker Spectroscopin 300 at 300 K. The chemical shifts are given with respect to TMS as an internal standard δ-values (ppm). For the assignment of the signals and multiplicities the following abbreviations have been chosen: s – singulett, d – dublett, t – triplett, q – quartett, m – multiplett, b – broad, virt. – virtuell.

Refractive index n_D and Abbe´s number υ_D

Refractive index and Abbe's number were measured at 25°C with the digital nine-wavelength (approximately 404.7, 435.8, 486.1, 546.1, 587.56, 589.3, 632.8, 656.3 and 706.5 nm) refractometer DSR-λ of Schmidt & Haensch. The refractometer measures the critical angle of total reflection and calculates the refractive index from this value; the Abbe number (υ_D) is calculated by the instrument automatically. For measurements, 300 µL of the corresponding liquid collected by Eppendorf Research® plus 100–1,000 µL pipette were used. The refractive index nis reported at 589.3 nm.

Gravity

Gravity has been defined as a mass of the 1cm^3 (1,000 µL) of liquid being collected by Eppendorf Research® plus 100–1,000 µL pipette and weighed using the Kern Electronic Analytical Balance Type ABS 120-4N with readability of 0.1 mg and reproducibility of 0.2 mg.

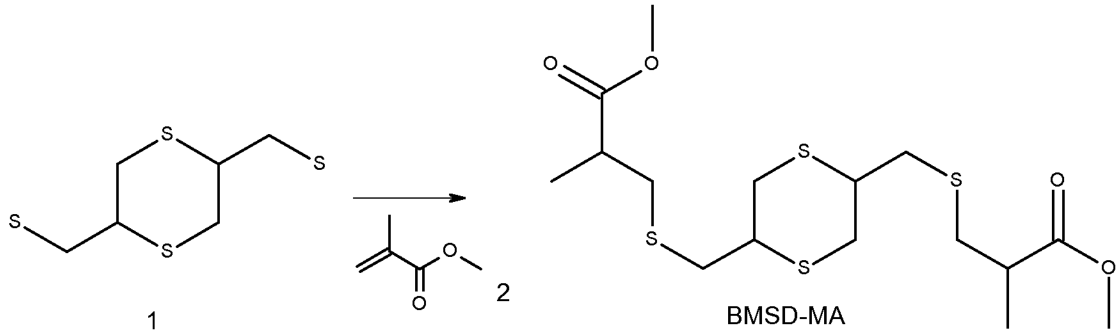
Viscosity

Dynamic shear viscosities of the synthesized liquids were measured in the cone-plate configuration with the Anton Paar MCR 301 rheometer operating in the rotational mode; the fixture CP50-0.5-SN20586 (diameter 50 mm and the angle of 0.5°) has been used as a measuring system; the gap size was set at 0.045 mm. Viscosities were measured as a continuous function of temperature (η - T) - within the temperature range from -20°C to 100°C. The measurements were performed at two different shear rates: at 10 s^{-1} and 100 s^{-1}.

2. Examples

Example 1 (**A2** series) **BMSD-MA**

Dimethyl-,3'-(((1,4-dithiane-2,5-diyl)bis(methylene)) bis(sulfanediyl))bis(2-methylpropanoate) BSMD-MA



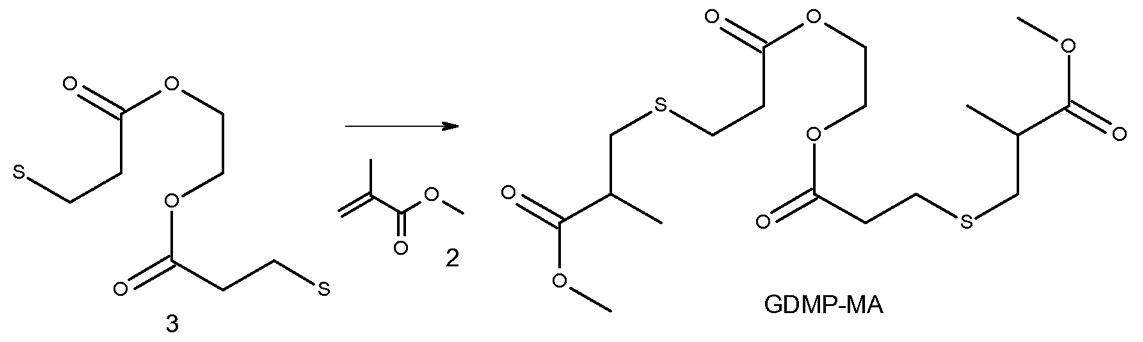
To 5 g (0.02 mol) BSMD **1** (T. Okubo et al. J. Appl. Poly Sci. 1998, *68*, 1791) were added 7.5 g (0.07 mol) methyl methacrylate **2** in a mixture of 10 mL THF and 10 mL DMF. After addition of 1.4 mL (0.01 mol) triethyl amine the obtained solution was stirred for 72 h at room temperature. All volatile components were removed *in vacuum*, the residue was then treated with aqueous 1 N HCl, extracted with dichloromethane (DCM), dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography [*c*-hexane/ ethyl acetate (5:1)] to give a colourless liquid (7.1 g, 73%).

NMR (400 MHZ, $CDCl_3$) δ = 3.67 (s, 6H, OCH_3), 3.22-2.56 (m, 16H), 1.23-1.21 (d, 6H, $CHCH_3$).

n_D: 1.551; Abbe´s numbers υ: 43.76; sp. gravity: 1.968 g/ml; viscosity at 20°C: 980 mPa s

Example 2 (**A1** series) **GDMP-MA**

Dimethyl 3,3'-(((ethane-1,2-diylbis(oxy))bis(3-oxopropane-3,1-diyl)) bis(sulfanediyl))bis(2-methylpropanoate) GDMP-MA



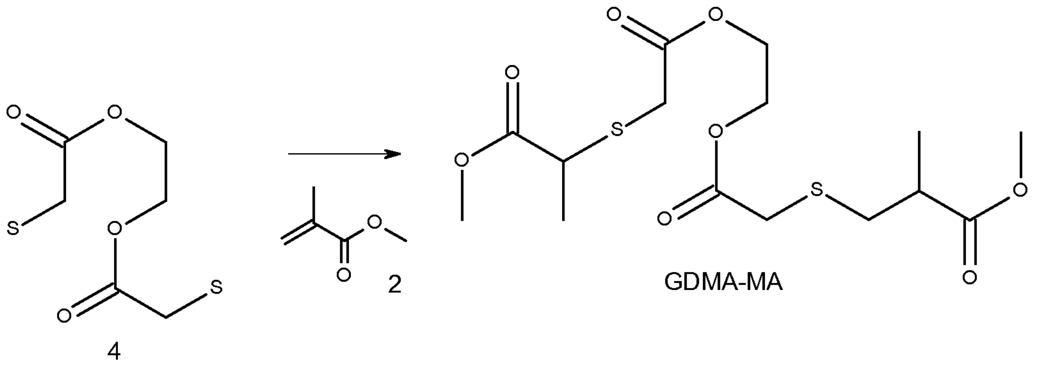
5 g (0.02 mol) of dithiol **3** were treated with 9.5 g (0.08 mol) methyl methacrylate **2** in a mixture of 10 mL THF and 10 mL DMA. 1.4 mL (0.01 mol) triethyl amine were added and the obtained solution was stirred for 72 h at room temperature. All volatile componentswere removed *in vacuum*, the residue was washed with aqueous 1 N HCl, extracted with dichloro methane, washed several times with water, dried over $MgSO_4$, filtered and evaporated to give a colourless liquid (7.1 g, 77%).

NMR (400 MHZ, $CDCl_3$) δ = 4.26 (s, 4H, CH_2CO), 3.65 (s, 6H, OCH_3), 2.88-2.52 (m, 14H), 1.21-1.19 (d, 6H, $CHCH_3$).

n_D: 1.493; Abbe´s numbers υ: 50.56.

Example 3 (<u>A1</u> series) **GDMA-MA**

Dimethyl 3,3'-(((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl)) bis(sulfanediyl))bis(2-methylpropanoate GDMA-MA



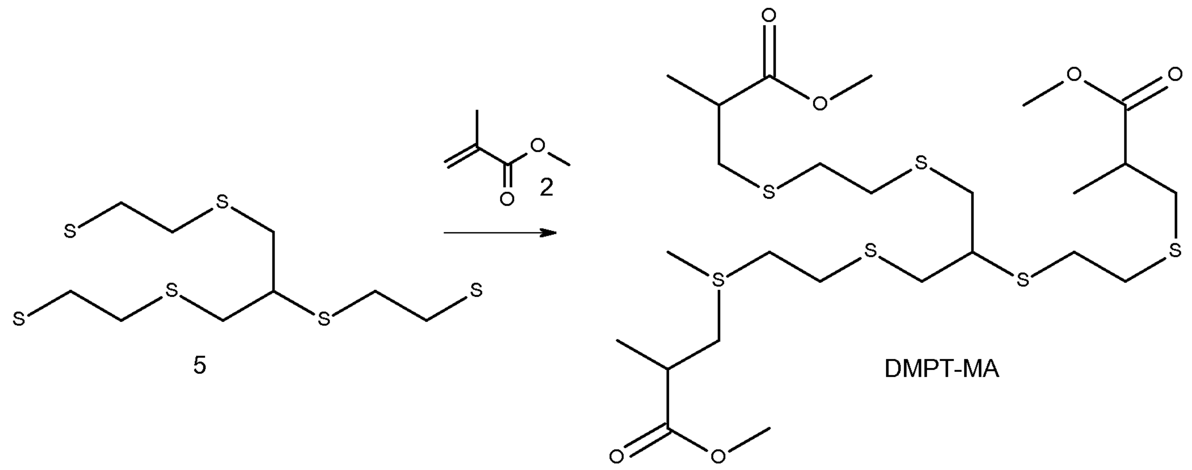
5 g (0.02 mol) dithiol **4** were reacted with 9.5 g (0.08 mol) methyl methacrylate **2** in a mixture of 10 mL THF and 10 mL DMA. 1.4 mL (0.01 mol) triethyl amine were added and the solution stirred for 72 h at room temperature. All volatile components were removed *in vacuum*, the residue was washed with aqueous 1 N HCl, extracted with DCM, washed several times with water, dried over $MgSO_4$, filtered and evaporated to give a colourless liquid (4.1 g, 41%).

NMR (400 MHZ, $CDCl_3$) δ = 4.36 (s,4H, CH_2CO, 3.70 (s, 6H, OCH_3), 3.26 (s, 4H, SCH_2CH), 2.98-2.92 (m, 2H, CH), 2.77-2.70 (m, 4H, OCH_2CH_2O).

n_D: 1.493; Abbe´s numbers ʋ: 49.65.

Example 4 (A1 series) **DMPT-MA**

Dimethyl 8-(((3-methoxy-2-methyl-3-oxopropyl)thio)methyl) -2,15- dimethyl-4,7,10,13-tetrathiahexadecanedioate DMPT-MA



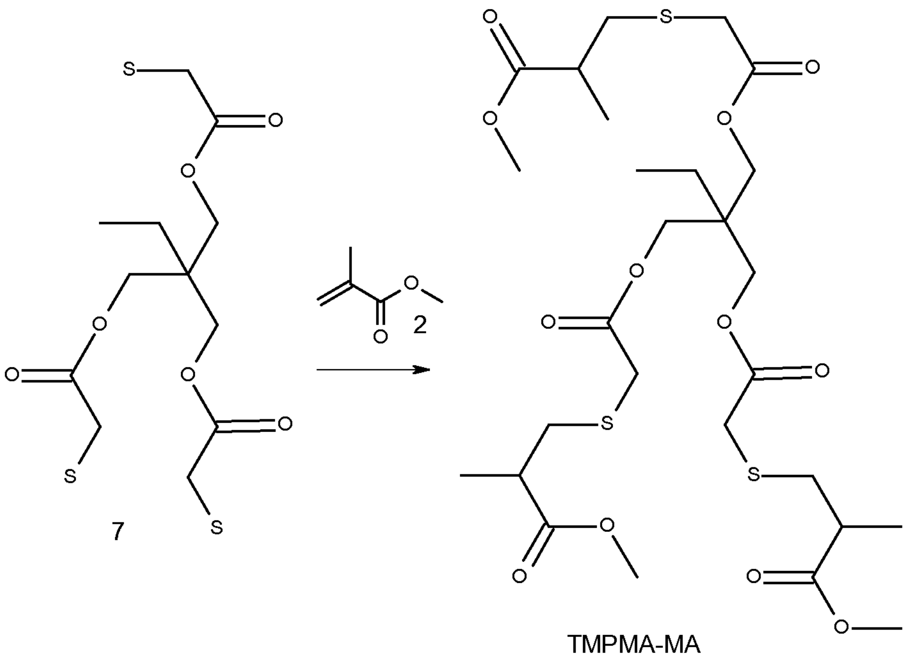
20 mL (0.2 mol) methyl methacrylate **2** and 3 mL (0.014 mol) trithiol **5** were mixed in 15 mL THF/ DMF. 2.5 mL (0.014 mol) di-iso-propyl ethylamine were added and the obtained solution was stirred for 24h at room temperature. All volatile components were removed *in vacuum* and 15 mL DMF was added and stirred for another 24 h. All volatile components were again removed *in vacuum* and the residue was purified by column chromatography [*c*-hexane/ ethyl acetate (4:1)] to yield a pale yellow liquid (1.5 g, 20%).

NMR (400 MHZ, $CDCl_3$) *δ* = 3.72 (s, 9H, OCH_3), 3.00-2.61 (m, 22H), 1.27-1.25 (d, 9H, $CHCH_3$).

n_D: 1.538; Abbe´s numbers ʋ: 44.24

Example 5 (A1 series) **TMPMA-MA**

2-ethyl-2-((2-mercaptoacetoxy)methyl)propane-1,3-diyl-bis (2-mercaptoacetate)-methyl-methacrylate (TMPMA-MA)



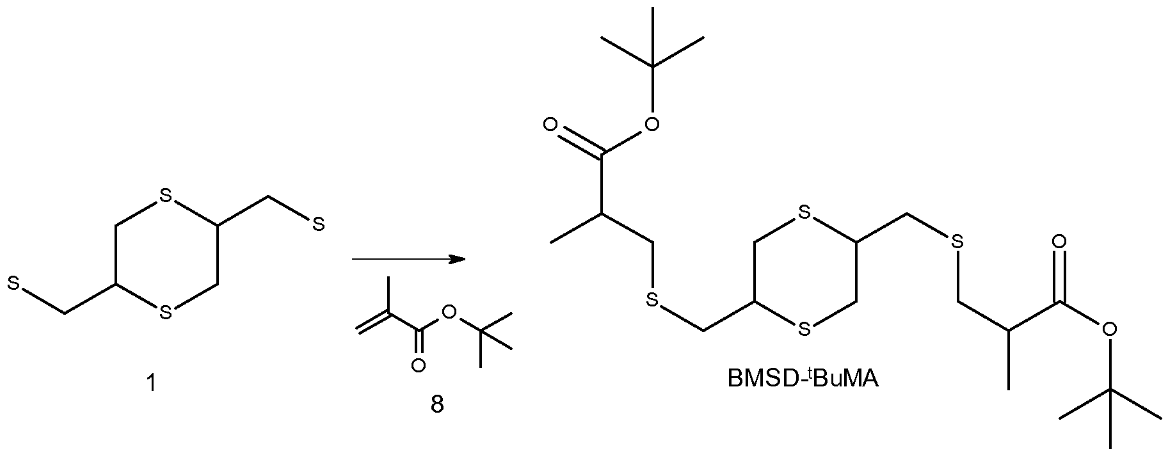
30.0 g (0.084 mol) trimethylolpropan trimercaptoacetate **7** (TMPMA), 29.9 mL (0.27 mol) methyl methacrylate **2**, 450 mL ethanol and 11.6 mL (0.084 mol) triethyl amine were stirred at room temperature for 2h, thereafter an additional amount of 8.40 g triethyl amine was added. After stirring for 24 h at room temperature the solvent was evaporated and the residue was treated with aqueous 1N HCl and then extracted with dichloro methane. The organic phase was dried over $MgSO_4$, filtered and concentrated to give the product as pale yellow liquid. Highly pure material was obtained via silica gel chromatography [hexane/ ethyl acetate (10:4)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (42.8 g, 95 %).

NMR (400 MHZ, $CDCl_3$) δ = 4.09 (s, 6H, CCH_2O), 3.68 (s, 9H, $COOCH_3$), 3.23 (s, 6H, $COCH_2S$), 2.96-2.86 (st, 3H, SCH_2CHCH_3CO), 2.78-2.65 (m, 6H, SCH_2CHCH_3), 1.54-1.48 (q, 2H, CH_3CHC), 1.25-1.23 (d, 9H, $CHCH_3$), 0.92-0.88 (t, 3H, CH_2CH_3).

n_D: 1.502; Abbe´s numbers υ: 49.60

Example 6 (A2 series) **BSMD-^{t} BuMA**

Di ^{t}butyl-,3’-(((1,4-dithiane-2,5-diyl)bis(methylene)) bis(sulfanediyl))bis(2-methylpropanoate) BSMD-^{t}BuMA



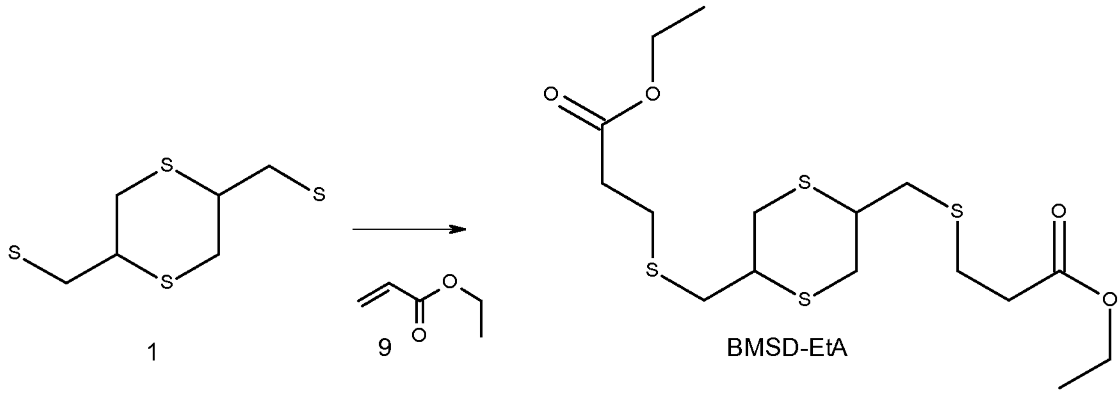
Dithiol **1** (5.0 g, 23.5 mmol) and t-butyl methacrylate **8** (13.4 g, 94.3 mmol) were dissolved in a mixture of 20 ml dimethylformamide and tetrahydrofuran (1:1 (vol:vol)) at room temperature. The reaction was started by the addition of 3.2 ml (23.5 mmol) triethyl amine. After three days at room temperature the mixture was evaporated in high vacuum and the residue was taken up in dichloro methane and successively extracted with 1N hydrogen chloride, water and brine. The organic phase was then filtered over $MgSO_4$ and removed in vacuum giving a yellow oil which was purified via silica gel chromatography [heptane/ ethyl acetate (10:1)] yielding 7.2 g of a clear liquid which consisted of two isomers.

NMR (400 MHZ, $CDCl_3$) δ = 1.2 (d, 6H), 1.48 (s, 18H), 2.5-3.5 (m,16H).

n_D: 1.5227; Abbe´s numbers υ: 44.26

Example 7 (A2 series) **BSMD-EtA**

Diethyl-,3’-(((1,4-dithiane-2,5-diyl)bis(methylene)) bis(sulfanediyl))bis(2-methylpropanoate) BSMD-EtA



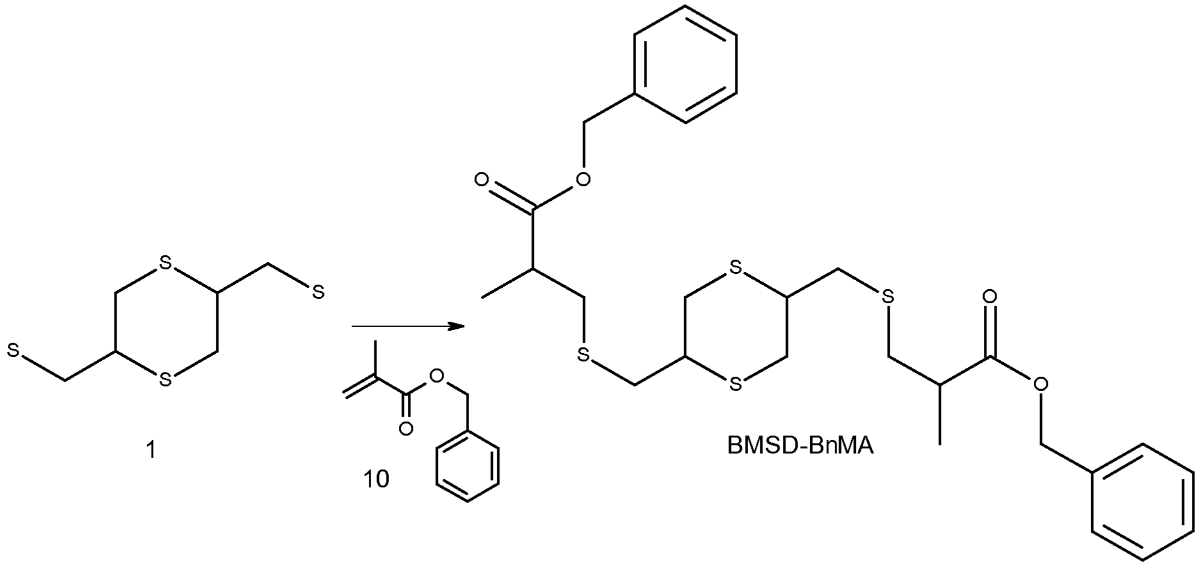
Dithiol **1** (5.0 g, 23.5 mmol) and ethyl acrylate **9** (9.4 g, 94.2 mmol) were dissolved in a mixture of 20 ml dimethylformamide and tetrahydrofuran (1:1 (vol:vol)) at room temperature. The reaction was started by the addition of 3.2 ml (23.5 mmol) triethyl amine. After three days at room temperature the mixture was evaporated in high vacuum and the residue was taken up in dichloro methane and successively extracted with 1N hydrogen chloride, water and brine. The organic phase was then filtered over $MgSO_4$ and removed in vacuum giving a yellow oil which was purified via silica gel chromatography [heptane/ ethyl acetate (3:1)] yielding 8.9 g of a clear liquid.

NMR (400 MHZ, $CDCl_3$) δ = 1.3 (t, 6H), 1.48 (s, 18H), 2.6 (t, 4H), 2.65-3.4 (m, 14H), 4.2 (q, 4H).

n_D: 1.5505; Abbe´s numbers υ: 43.26

Example 8 (**A2** series) **BSMD- BnMA**

Dibenzyl-,3’-(((1,4-dithiane-2,5-diyl)bis(methylene)) bis(sulfanediyl))bis(2-methylpropanoate) BSMD-BnMA

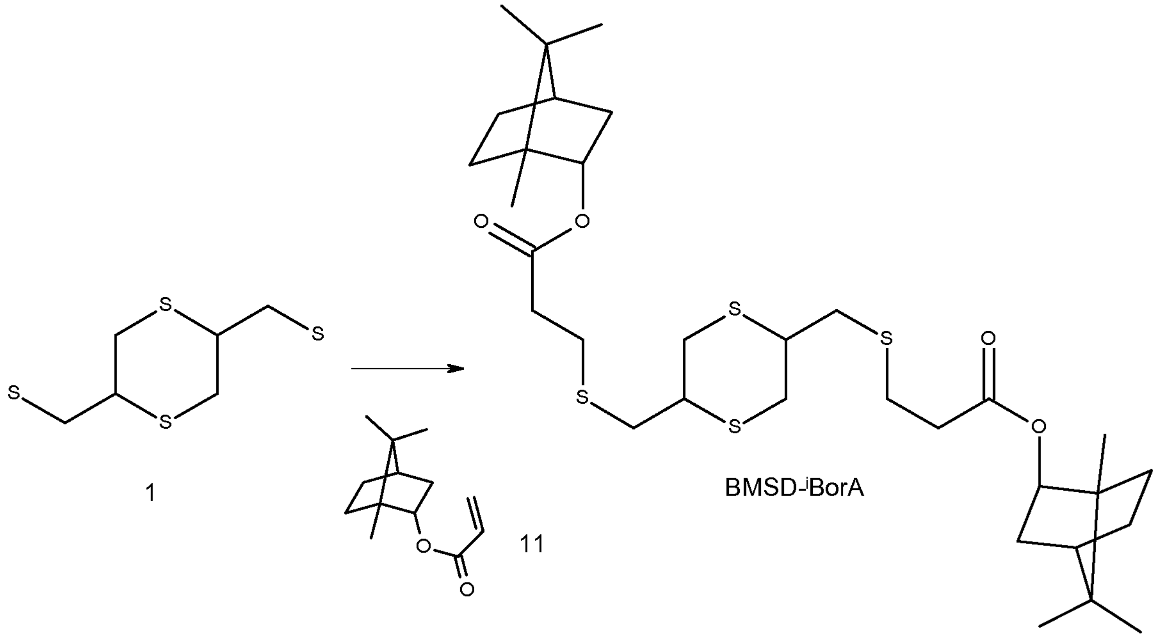


Dithiol **1** (5.0 g, 23.5 mmol) and benzyl methacrylate **10** (16.6 g, 94.2 mmol) were dissolved in a mixture of 20 ml dimethylformamide and tetrahydrofuran (1:1 (vol:vol)) at room temperature. The reaction was started by the addition of 3.2 ml (23.5 mmol) triethyl amine. After three days at room temperature the mixture was evaporated in high vacuum and the residue was taken up in dichloro methane and successively extracted with 1N hydrogen chloride, water and brine. The organic phase was then filtered over $MgSO_4$ and removed in vacuum giving a yellow oil which was purified via silica gel chromatography [heptane/ ethyl acetate (5:1)] yielding 11.0 g of a clear liquid.

NMR (400 MHZ, $CDCl_3$) δ = 1.3 (d, 6H), 2.5-3.4 (m, 16H), 2.6 (t, 4H), 5.2 (s, 4H), 7.33-7.42 (m, 10H).

n_D: 1.5819; Abbe´s numbers υ: 36.51

Example 9 (**A2** series) **BSMD-^{i}BorA**

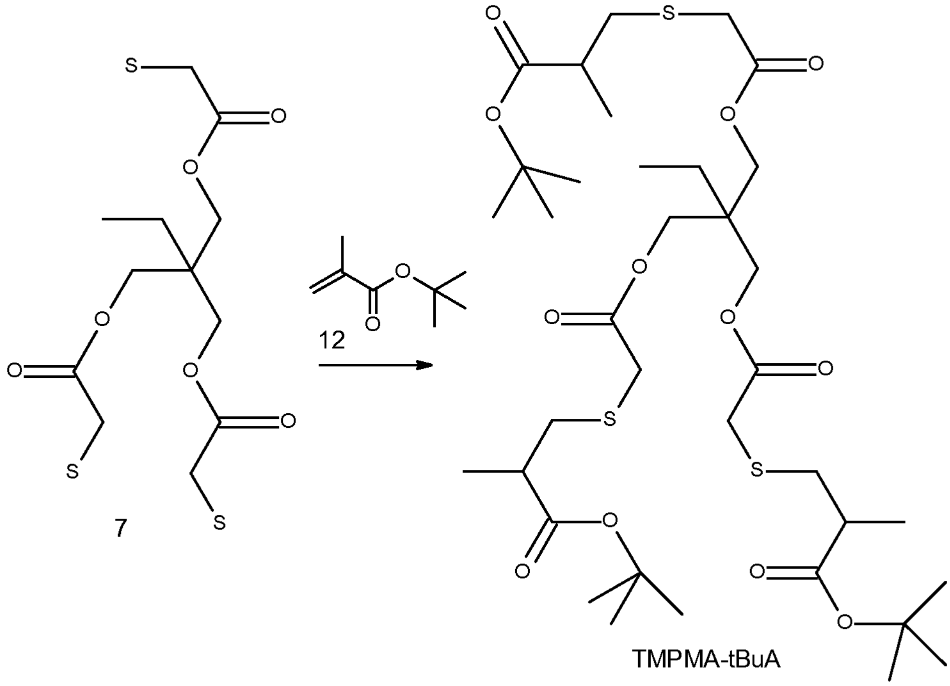


Dithiol **1** (5.0 g, 23.5 mmol) and iso-bornyl acrylate **11** (19.6 g, 94.2 mmol) were dissolved in a mixture of 20 ml dimethylformamide and tetrahydrofuran (1:1 (vol:vol)) at room temperature. The reaction was started by the addition of (3.2 ml , 23.5 mmol) triethyl amine. After three days at room temperature the mixture was evaporated in high vacuum and the residue was taken up in dichloro methane and successively extracted with 1N hydrogen chloride, water and brine. The organic phase was then filtered over $MgSO_4$ and removed in vacuum giving a yellow oil which was purified via silica gel chromatography [heptane/ ethyl acetate (10:1)] yielding 10.3 g of a very viscous clear liquid.

NMR (400 MHZ, $CDCl_3$) δ = 0.95 (s, 12H), 1.0-1.3 (m, 6H), 1.45-1.55 (m, 2H), 1.6-1.85 (m,8H), 2.5-2.6 (dd, 4H), 2.75-2.9 (m, 6H), 2.9-3.0 (m, 4H), 3.1-3.15 (d, 2H) 4.65 (m, 2H).

n_D: 1.5478; Abbe´s numbers υ: 46.84

Example 10 (A1 series) **TMPMA-tBuA**

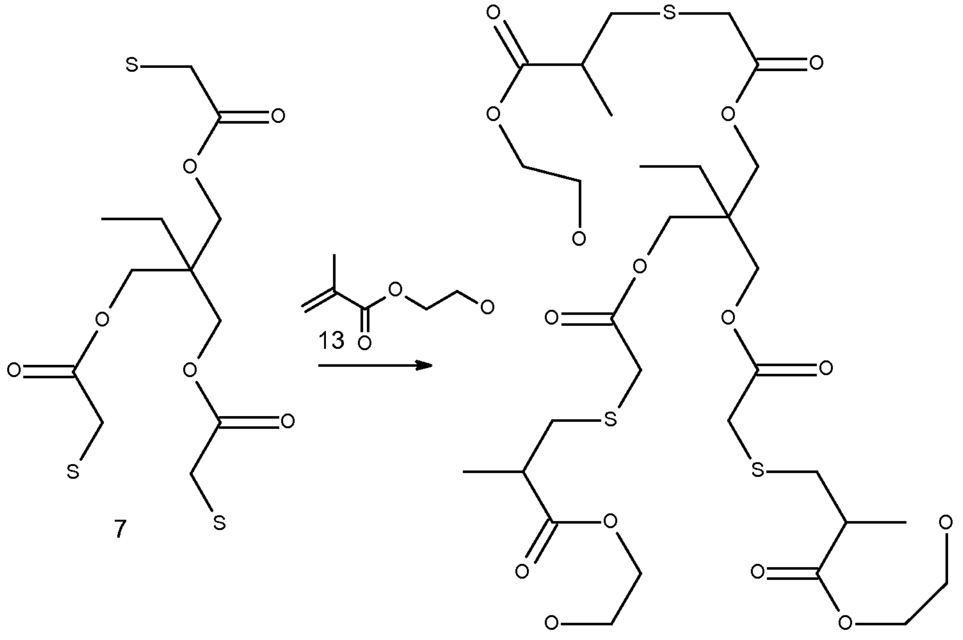


20.0 g (0.056 mol) trimethylolpropan trimercaptoacetate **7** (TMPMA), 31.9 g (0.224 mol) ^{t}butyl methacrylate **12**, 250 mL ethanol and 5.7 mL (0.056 mol) triethyl amine were stirred at room temperature for 48h. Thereafter the solvent was evaporated and a residue was obtained. Highly pure material was obtained via silica gel chromatography [dichloromethane/ methanol (10:0.5)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (29.4 g, 67 %).

NMR (400 MHZ, $CDCl_3$) δ = 4.09 (s, 6H, CCH_2O), 3.24 (s, 6H, $COCH_2S$), 2.90-2.83 (dd, 3H, SCH_2C), 2.68-2.62 (dd, 2H, SCH_2C), 2.56 (m, 3H, CCHC), 1.53-1.47 (q, 2H, CH_3CH_2C), 1.43 (s, 27 H, $C(CH_3)_3$), 1.20-1.18 (d, 9H, $CHCH_3$), 0.93-0.88 (t, 3H, CH_2CH_3).

n_D: 1.4838; Abbe´s numbers υ: 50.80

Example 11 (A1 series) **TMPMA-hydroxy ethylA**



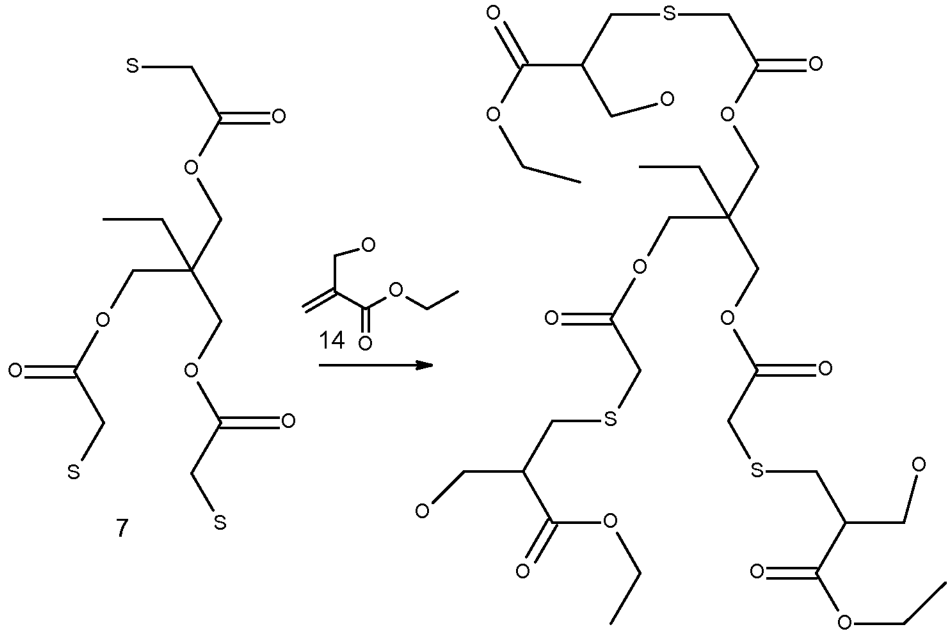
TMPMA-ethoxyethylA

10.0 g (0.028 mol) trimethylolpropan trimercaptoacetate **7** (TMPMA), 14.5 g (0.111 mol) 2-hydroxyethyl methacrylate **13**, 150 mL ethanol and 2.8 g (0.028 mol) triethyl amine were stirred at room temperature for 24h. Thereafter the solvent was evaporated and a residue was obtained. Highly pure material was obtained via silica gel chromatography [dichloromethane/ methanol (10:0.6)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (18.3 g, 88 %).

NMR (400 MHZ, $CDCl_3$) δ = 4.31-4.22 (m, 3H, $(O)COCH_2$), 4.19-4.14 (m, 3H, $(O)COCH_2$), 4.09 (s, 6H, CCH_2O), 3.84-3.80 (t, 6H, CH_2OH), 3.23 (s, 6H, $COCH_2S$), 2.96-2.89 (m, 3H, CCHC), 2.88-2.71 (m, 6H, SCH_2CH), 2.04 (s, 3H, OH), 1.55-1.49 (q, 2H, CH_3CH_2C), 1.20-1.18 (d, 9H, $CHCH_3$), 0.93-0.88 (t, 3H, CH_2CH_3).

n_D: 1.5111; Abbe´s numbers υ: 50.30

Example 12 (A1 series) **TMPMA-2 hydroxymethyl ethylA**



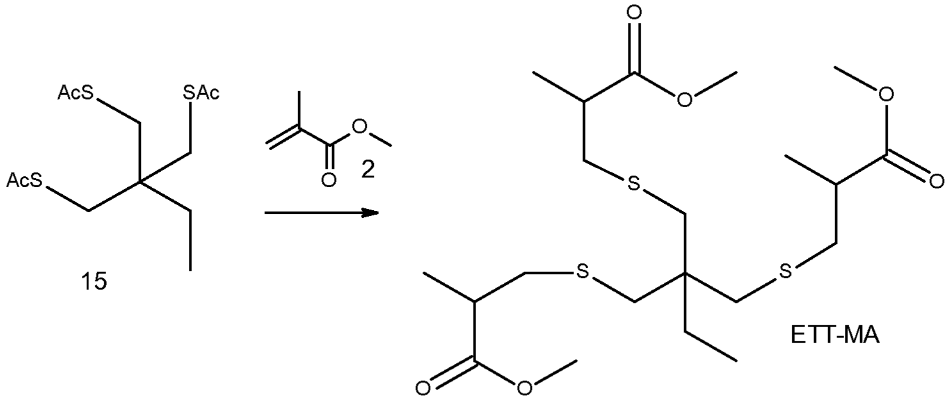
TMPMA-ethoxy hydroxymethylA

7.6 g (0.021 mol) trimethylolpropan trimercaptoacetate **7** (TMPMA), 10.0 g (0.077 mol) 2-hydroxymethyl ethylacrylate **14**, 100 mL ethanol and 2.2 g (0.022 mol) triethyl amine were stirred at room temperature for 48h. The mixture has then been taken up in ethylacetate and subsequently been extracted with 1 N HCl, water and brined and stored over sodium sulfate and then filtered. Thereafter the solvent was evaporated and a residue was obtained. Highly pure material was obtained via silica gel chromatography [dichloromethane/ methanol (50:1.0)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (7.1 g, 45 %).

NMR (400 MHZ, $CDCl_3$) δ = 4.23-4.18 (q, 6H, $(O)COCH_2CH_3$), 4.14 (s, 6H, CCH_2O), 3.89-3.85 (d, 6H, CH_2OH), 3.30 (s, 6H, $COCH_2S$), 3.02-2.93 (m, 6H, SCH_2CH), 2.84-2.78 (m, 6H, OH, CCHC), 1.57-1.51 (q, 2H, CH_3CH_2C), 1.31-1.28 (t, 9H, OCH_2CH_3), 0.95-0.91 (t, 3H, CH_2CH_3).

n_D: 1.5100; Abbe´s numbers υ: 50.40

Example 13 (A1 series) **2 ethyl, 2-(2thio-methylmethyacrylate) 1,3 di(thiomethylmethacrylate) ETT**

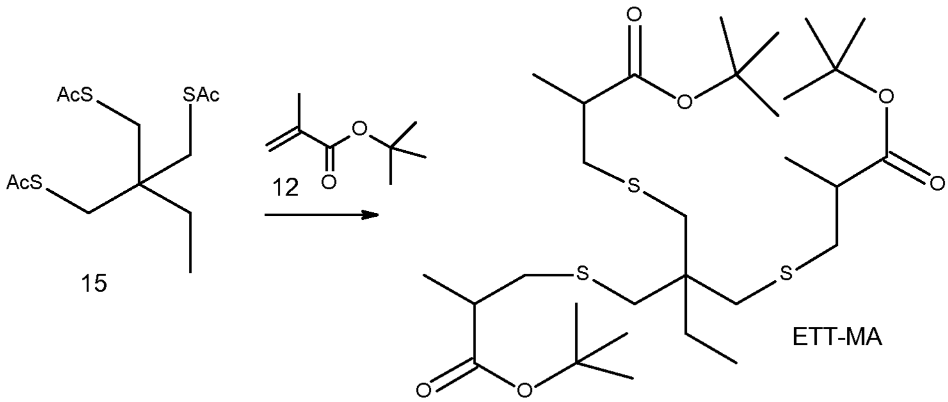


13.25 g (0.043 mol) of triacetate **15** are dissolved at room temperature in a mixture of 70 ml methanol containing 351 mg of sodium methanolate and 15.5 g (0.155 mol) methyl methacrylate **2** and stirred for 24 h. The mixture is evaporated, the resulting residue dissolved in diethylether and filtered over char coal. Evaporation gives an oil which is purified by silica gel chromatography [hexane/ ethylacetate (10:2)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (18.3 g, 88 %).

NMR (400 MHZ, $CDCl_3$) δ = 3.66 (s, 9H, CH_3O), 2.84-2.70 (m, 3H, SCH), 2.70-2.65 (m, 3 H, SCH), 2.64-2.54 (m, 9 H, CH_2S, CCHC), 1.41-1.35 (q, 2H, CH_3CH_2C), 1.22-1.20 (d, 9H, CCH_3), 0.81-0.77 (t, 3H, CH_2CH_3).

n_D: 1.5088; Abbe´s numbers υ: 48.40

Example 14 (A1 series) **2 ethyl, 2-(2thio-^{t}butylmethyacrylate) 1,3 di(thio^{t}butylmethacrylate) ETT**



4.50 g (0.014 mol) of triacetate **15** are dissolved at room temperature in a mixture of 25 ml methanol containing 110 mg of sodium methanolate and 8.3 g (0.058 mol) ^{t}butyl methacrylate and stirred for 48 h. The mixture is evaporated, the resulting residue dissolved in dichloromethane and subsequently extracted with 1 N HCl, water and brine, filtered over sodium sulfate and evaporated. The oily residue is purified by silica gel chromatography [hexane/ ethylacetate (10:0.5)] and high vacuum treatment (80°C for 10 h) to remove traces of solvent (7.2 g, 82 %).

NMR (400 MHZ, $CDCl_3$) δ = 2.83-2.78 (dd, 3H, SCH), 2.63 (s, 6 H, SCH_2), 2.59-2.52 (m, 6 H, CH_2S, CCHC), 1.45-1.42 (m, 29H, CH_3CH_2C, CCH_3), 0.88-0.81 (t, 3H, CH_2CH_3).

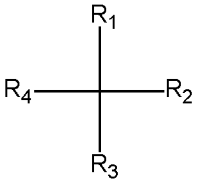
n_D: 1.4842; Abbe´s numbers υ: 50.20

CLAIMS

1. Liquid thioether carboxylic acid ester, wherein the thioether carboxylic acid ester is a reaction product of

A) a compound of the formula

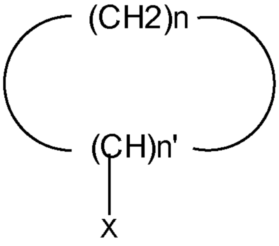
a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

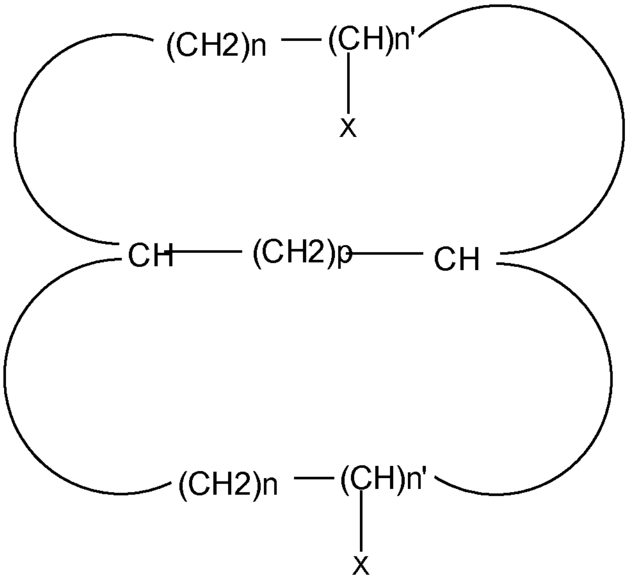
b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

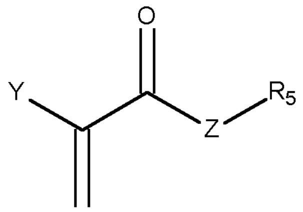
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3; and

B) a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

2. The liquid thioether carboxylic acid ester according to claim 1, wherein in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_1-C_6-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_2-C_6-alkyl containing at least one sulfhydryl moiety (SH), and one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O.

3. The liquid thioether carboxylic acid ester according to any one of claims 1 or 2, wherein in the formula (A1) R_1 is hydrogen; R_2 is a linear C_1-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl

containing at least one sulfhydryl moiety (SH), and one CH_2 group of R_2 and/or R_3 and R_4 is replaced by S.

4. The liquid thioether carboxylic acid ester according to any one of claims 1 or 2, wherein in the formula (A1) R_1 is hydrogen or ethyl; R_2 is hydrogen or a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear C_3-C_5-alkyl containing at least one sulfhydryl moiety (SH), and two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O.

5. The liquid thioether carboxylic acid ester according to claim 4, wherein two CH_2 groups of R_2 and/or R_3 and R_4 are replaced by O and C=O, and O and C=O are directly linked.

6. The liquid thioether carboxylic acid ester according to claim 1, wherein in the formula (A2) n' is 2; the sum of n and n' is an integer in the range from 5 to 7 and two CH_2-groups are replaced with S and/or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 1 to 3.

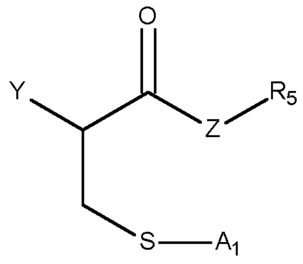
7. The liquid thioether carboxylic acid ester according to any one of claims 1 or 6, wherein in the formula (A2) n' is 2; the sum of n and n' is 6; two CH_2-groups are replaced with S or O with the proviso that S or O are not directly linked, and X is $(CH_2)_m$-SH with m being 1.

8. The liquid thioether carboxylic acid ester according to any one of claims 1 to 5, wherein Y is hydrogen or methyl; Z is O; R_5 is linear saturated C_1-C_3 alkyl.

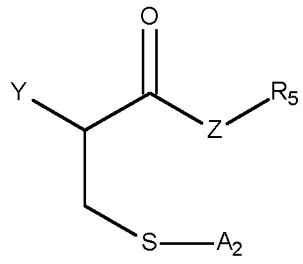
9. The liquid thioether carboxylic acid ester according to any one of claims 1 or 6 or 7, wherein Y is hydrogen or methyl; Z is O; R_5 is a linear or branched saturated C_1-C_4 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl- menthyl-, camphyl- or an aryl system selected from phenyl and benzyl.

10. The liquid thioether carboxylic acid ester according to any one of claims 1 to 9, wherein the reaction product is obtained by a 1,4-addition mechanism of the at least one sulfhydryl group of the compound of the formula (A1), (A2) or (A3) and the compound of the formula (B).

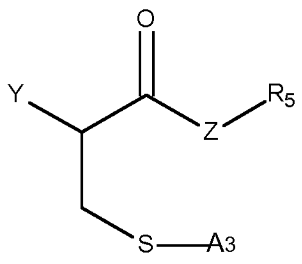
11. The liquid thioether carboxylic acid ester according to any one of claims 1 to 10, wherein the reaction product is of the general formula (C1), (C2) or (C3)



C1



C2



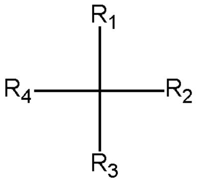
C3 ,

12. The thioether carboxylic acid ester according to any one of claims 1 to 11, wherein the thioether carboxylic acid ester has a refractive index of 1.27 – 1.9, and/or an Abbe's number of 35 - 110.

13. Process for the preparation of a liquid thioether carboxylic acid ester as defined in any one of claims 1 to 12, the process comprising the steps of

A) providing a compound of the formula

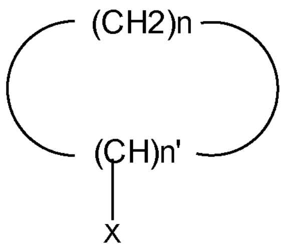
a) (A1)



(A1),

wherein R_1 is hydrogen, linear or branched C_1-C_7 alkyl; R_2 is hydrogen or a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH); R_3 and R_4 are independently selected from a linear or branched C_1-C_8-alkyl containing at least one sulfhydryl moiety (SH), and optionally one or two CH_2 group(s) of R_2 and/or R_3 and/or R_4 is/are replaced by O, S and/or C=O; or

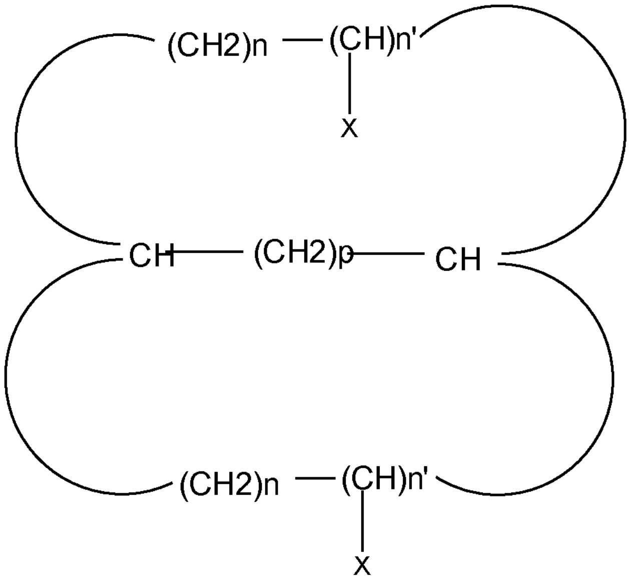
b) (A2)



(A2),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9 and one or two CH_2-group(s) is/are replaced with S and /or O with the proviso that S and/or O are not directly linked, and X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3; or

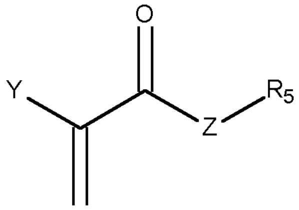
c) (A3)



(A3),

wherein n' is 1 or 2, the sum of n and n' is an integer in the range from 5 to 9; X is $(CH_2)_m$-SH with m being an integer in the range from 0 to 3 and p is an integer in the range from 0 to 3;

B) providing a compound of the formula (B)



(B),

wherein Y is hydrogen or methyl; Z is O; R_5 is linear or branched saturated C_1-C_8 alkyl or a saturated bicyclic aliphatic system selected from the group consisting of norbornyl-, isonorbornyl-, pinenyl-, menthyl-, camphyl- or an aryl system selected from phenyl and benzyl, and

C) reacting the compound of step A) with the compound of step B) such as to obtain the liquid thioether carboxylic acid ester.

14. Article, preferably an optical lens such as a tunable focus lens, optical liquid, tiltable prism or calibration liquid or refractive index matching liquid, comprising the liquid thioether carboxylic acid ester according to any one of claims 1 to 12 as an ingredient in at least one of its parts or as part of the article itself.

15. Article, preferably a wave guide material, color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material, ingredient or additive in a polymer, comprising the liquid thioether carboxylic acid ester according to any one of claims 1 to 12 as an ingredient in at least one of its parts or as part of the article itself.

16. Use of the liquid thioether carboxylic acid ester according to any one of claims 1 to 12 as a component or substantial part of an optical system, tunable lens, adaptive optical module and materials thereof, actuator, electro-active polymer, laser and all related products, optical liquid, cover glass, lens or container material, tiltable prism or optical calibration liquid or optical refractive index matching liquid.

17. Use of the liquid thioether carboxylic acid ester according to any one of claims 1 to 12 as a component or substantial part of a color filter, window material, coating, varnish, lacquer, dye or pigment formulation, immersion liquid, ingredient or additive in a plastic material or ingredient or additive in a polymer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/071926

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D339/08 C07C323/52
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NAOYA OGATA: "Active condensation of dicarboxylic acid derivatives having beta-hetero atoms", POLYMER JOURNAL, vol. 5, no. 2, 1 January 1973 (1973-01-01), pages 186-194, XP055174091,	1,2,8-17
A	compound III	3-5

X	US 2 640 848 A (DENHAM HARMAN ET AL) 2 June 1953 (1953-06-02)	1,2,8-17
A	example VI	3-5

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 17 November 2015	Date of mailing of the international search report 19/01/2016
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 Hacking, Michiel

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ROBERTO SOLARO ET AL: "An investigation of the condensation kinetics in poly(ester-amide) and poly(ester-sulphide) preparation", MACROMOLECULAR SYMPOSIA, vol. 197, no. 1, 1 July 2003 (2003-07-01), pages 315-330, XP055174080, ISSN: 1022-1360, DOI: 10.1002/masy.200350728	1,2,8-17
A	Scheme 4	3-5

X	US 2 530 872 A (GREGORY JAMES T ET AL) 21 November 1950 (1950-11-21)	1,2, 8-12, 14-17
A	Compounds second page	3-5,13

X	GB 1 603 651 A (LAFON LABOR) 25 November 1981 (1981-11-25)	1,2,8-12
A	examples 1-3, 5-7	3-5, 13-17

X	US 3 699 152 A (HECHENBLEIKNER INGENUIN A ET AL) 17 October 1972 (1972-10-17)	1,2,4,5, 8-12
A	Intermediate B in column 13	3,13-17

A	JP 48 005780 A (SHOWA DENKO) 20 February 1973 (1973-02-20) Compounds page 2; compound III	1-5,8-17

A	YASUO SUZUKI ET AL: "Synthesis and Characterization of High Refractive Index and High Abbe's Number Poly(thioether sulfone)s based on Tricyclo[5.2.1.0 2,6]decane Moiety", MACROMOLECULES, vol. 45, no. 8, 24 April 2012 (2012-04-24), pages 3402-3408, XP055172709, ISSN: 0024-9297, DOI: 10.1021/ma300379w cited in the application the whole document	1-5,8-17

A	TSUYOSHI OKUBO ET AL: "Synthesis, characterization, and optical properties of polymers comprising 1,4-dithiane-2,5-bis(thiomethyl) group", JOURNAL OF APPLIED POLYMER SCIENCE, vol. 68, no. 11, 13 June 1998 (1998-06-13), pages 1791-1799, XP055172715, ISSN: 0021-8995, DOI: 10.1002/(SICI)1097-4628(19980613)68:11<1791::AID-APP10>3.0.CO;2-Y cited in the application the whole document	1-5,8-17

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International application No
PCT/EP2015/071926

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 40 11 868 A1 (BAYER AG [DE]) 17 October 1991 (1991-10-17) cited in the application the whole document -----	1-5,8-17

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2015/071926

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

2-5(completely); 1, 8-17(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 2-5(completely); 1, 8-17(partially)

   Compounds resulting from reaction between a compound according to formula (A1) and (B) and uses thereof.

   ---

2. claims: 6, 7(completely); 1, 8-17(partially)

   Compounds resulting from reaction between a compound according to formula (A2) and (B) and uses thereof.

   ---

3. claims: 1, 8-17(all partially)

   Compounds resulting from reaction between a compound according to formula (A3) and (B) and uses thereof.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/071926

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2640848 A	02-06-1953	NONE	
US 2530872 A	21-11-1950	NONE	
GB 1603651 A	25-11-1981	BE 864998 A1	17-07-1978
		CH 627368 A5	15-01-1982
		DE 2810521 A1	05-10-1978
		ES 468330 A1	01-10-1979
		FR 2395027 A2	19-01-1979
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		IT 1111621 B	13-01-1986
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		DE 2059916 A1	16-06-1971
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		US 3699152 A	17-10-1972
		ZA 7007508 A	25-08-1971
JP 48005780 A	20-02-1973	------------------------------------	
DE 4011868 A1	17-10-1991	NONE	