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(54) Titre : METHODE DE PRODUCTION DE LENTILLES EN PLASTIQUE ET LENTILLES EN PLASTIQUE
(54) Title: PROCESS FOR PRODUCING PLASTIC LENS AND PLASTIC LENS

(57) Abrégé/Abstract:

The present invention provides a process for producing plastic lenses having higher refractive index and Abbe's number without remarkably deteriorating basic physical properties such as mechanical strength, impact resistance and transparency.



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Abstract

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PROCESS FOR PRODUCING PLASTIC LENS AND PLASTIC LENS

Technical Field to which the Invention Belongs

The present invention relates to a process for producing plastic lenses for spectacles having a high refractive index and a high Abbe's number and having excellent transparency and to plastic lenses obtained by the process.

Prior Art

In the market of plastic lenses, plastic lenses having higher refractive index and Abbe's number without remarkably deteriorating basic physical properties such as mechanical strength and impact resistance are demanded.

As an example of such plastic lenses, JP-A-2001-330701 discloses a plastic lens having a refractive index of about 1.70 and constituted of an epithio group-containing compound, a polythiol compound, and a polyisocyanate compound.

However, plastic lenses having a higher refractive index than that of the plastic lens as disclosed in JP-A-2001-330701 are demanded in the market.

Optical materials having a large refractive index and a large Abbe number are disclosed in EP-A-1 046 931. These

optical materials are obtained from a composition which comprises a mixture of a compound comprising sulfur and an inorganic compound comprising at least one atom of sulfur atom and selenium atom. However, plastic lenses comprising sulfur often exhibit insufficient transparency.

Problems that the Invention is to solve

The invention has been made in order to solve the above-described problems, and its object is to provide plastic lenses having high refractive index and Abbe's number without remarkably deteriorating basic physical properties such as mechanical strength, impact resistance and transparency.

Means for Solving the Problems

In order to achieve the above-described object, the present inventor made extensive and intensive investigations. As a result, it has been found that the problems are solved by the following means. The means is a process for producing a plastic lens, which comprises mixing a) a prepolymer with b) a mixture comprising sulfur and an epithio group-containing compound and c) a catalyst.

A preferred embodiment 1 is a process for producing a plastic lens, which comprises a step of preparing three kinds of starting materials of the lens, (1) a prepolymer obtainable

by reacting a polyisocyanate compound and a polythiol compound in an epithio group-containing compound, (2) a mixed solution (mixture X) obtained by mixing an epithio group-containing compound and sulfur, and (3) a mixed solution (mixture Y) obtained by mixing an epithio group-containing compound and/or a polythiol compound and a catalyst; and a step of mixing the three kinds of starting materials of the lens and polymerizing the mixture.

Further preferred embodiments are:

Embodiment 2 The process for producing a plastic lens according to embodiment 1, wherein the ratio of the polythiol compound to the polyisocyanate compound in the prepolymer is 1.75 or more in terms of -SH/-NCO molar ratio.

Embodiment 3 The process for producing a plastic lens according to embodiment 1, wherein a weight of the epithio group-containing compound in the prepolymer is 50% by weight or more of the whole amount of the starting materials of the prepolymer.

Embodiment 4 The process for producing a plastic lens according to any one of embodiments 1 to 3, wherein the content of sulfur is in the range of from 5 to 30% by weight of the whole amount of the starting materials (1) to (3) of lens.

Embodiment 5 The process for producing a plastic lens according to any one of embodiments 1 to 4, wherein the whole of the polyisocyanate and the polythiol compounds used for the starting materials (1) and (3) of lens is 15% by weight or less of the whole amount of the starting materials (1) to (3) of lens.

Embodiment 6 The process for producing a plastic lens according to embodiment 1, wherein the viscosity of the prepolymer is 5,000 mPa·s (25°C) or less.

Embodiment 7 The process for producing a plastic lens according to claim 1, wherein the polyisocyanate compound is one or more of the group consisting of bis(isocyanatomethyl)bicyclo[2,2,1]heptane, cyclohexane diisocyanate, and bis(isocyanatomethyl)-1,4-dithiane.

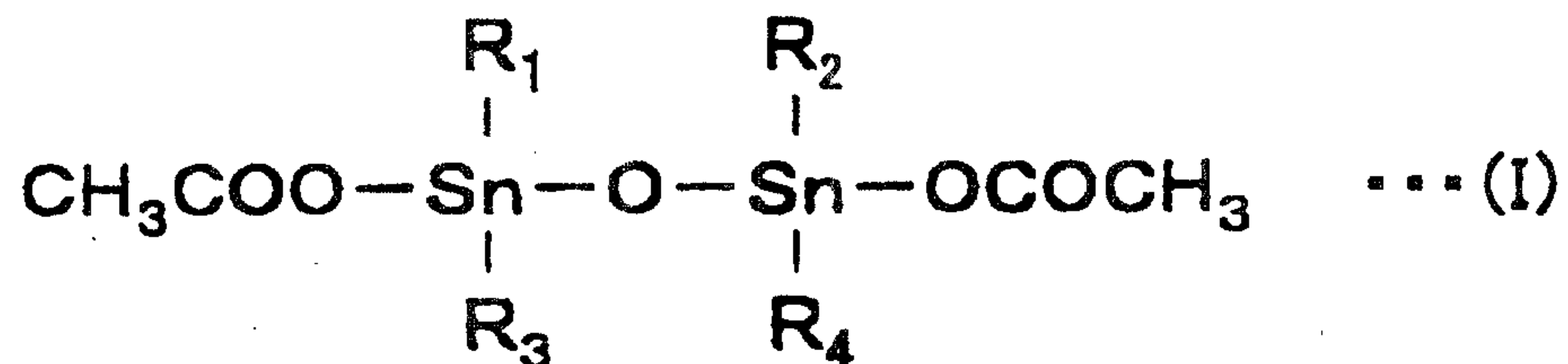
Embodiment 8 The process for producing a plastic lens according to embodiment 1, wherein the polythiol compound is at least one of the group consisting of bis(mercapto-methyl)-1,4-dithiane, bis(mercaptoethyl) sulfide, bis-(mercaptoethyl) disulfide, and 1,2-bis(mercaptoethyl)-thio-3-mercaptopropane.

Embodiment 9 The process for producing a plastic lens according to embodiment 1, wherein the epithio group-containing compound is bis(β -epithiopropyl) sulfide and/or bis(β -epithiopropyl) disulfide.

Embodiment 10 The process for producing a plastic

lens according to any one of embodiments 1 to 9, wherein a catalyst is added to a liquid for preparing the prepolymer.

Embodiment 11 The process for producing a plastic lens according to embodiment 10, wherein the catalyst is represented by the following general formula (I):



wherein R₁ to R₄, which may be the same or different, each represents an alkyl group having from 1 to 4 carbon atoms.

Embodiment 12 The process for producing a plastic lens according to embodiment 11, wherein the catalyst represented by the general formula (I) is at least one of the group consisting of tetramethyl-diacetoxy-distannoxane, tetraethyl-diacetoxy-distannoxane, tetrapropyl-diacetoxy-distannoxane, and tetrabutyl-diacetoxy-distannoxane.

Embodiment 13 The process for producing a plastic lens according to any one of embodiments 1 to 12, further comprising a step of forming a cured film on a plastic lens.

Embodiments 14 The process for producing a plastic lens according to any one of embodiments 1 to 13, wherein the cured film is prepared from an organosilicon compound as a starting material.

Embodiment 15 The process for producing a plastic

lens according to embodiment 13 or 14, further comprising a step of forming an antireflection film made of an inorganic substance on the cured film.

Embodiment 16 The process for producing a plastic lens according to embodiment 15, further comprising a step of forming a water repellent film made of a fluorine atom-containing organosilicon compound on the antireflection film.

Embodiment 17 A plastic lens obtained by the process according to any one of embodiments 1 to 16.

Mode for Carrying Out the Invention

The result of the invention is a plastic lens preferably containing an epithio group-containing compound, a polythiol compound, a polyisocyanate compound, and sulfur.

Hitherto, there have been proposals to prepare plastic lenses by adding sulfur to lens monomers in JP-A-2001-2783 and JP-A-2001-2933. However, even when the technique of JP-A-2001-330701 as cited above is combined with those of JP-A-2001-2783 and JP-A-2001-2933, it was impossible to obtain a transparent plastic lens containing an epithio group-containing compound, a polythiol compound, a polyisocyanate compound, and sulfur. As disclosed in the invention, it is possible to obtain a transparent plastic lens containing an epithio group-containing compound, a polythiol

compound, a polyisocyanate compound, and sulfur by previously preparing the above three kinds of starting materials of the lens, mixing these three kinds of starting materials of the lens, and polymerizing the mixture.

The prepolymer that is one of the three kinds of starting materials of the lens may be a polythiourethane prepolymer which is obtainable by reacting a polyisocyanate compound and a polythiol compound, preferably in an epithio group-containing compound.

Examples of suitable polyisocyanate compounds include xylylene diisocyanate, 3,3'-dichlorodiphenyl-4,4'-diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, 2,5-bis(isocyanatomethyl)-1,4-dithiane, bis(isocyanatomethyl) sulfide, bis(isocyanatoethyl) sulfide, bis(isocyanatomethyl) disulfide, bis(isocyanatoethyl) disulfide, 2,2',5,5'-tetrachlorodiphenyl-4,4'-diisocyanate, and tolylene diisocyanate. Polyisocyanates having one or more alicyclic groups can also be used. Specific examples include bis(isocyanatomethyl)cyclohexane, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatomethylcyclohexyl)methane, cyclohexane diisocyanate, isophorone diisocyanate, 2,5-bis(isocyanatomethyl)bicyclo[2,2,2]octane, 2,5-bis(isocyanatomethyl)bicyclo[2,2,1]heptane, 2-isocyanato-

methyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-2-[3-isocyanatopropyl]-5-isocyanatomethyl-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2,2,1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2,2,1]-heptane, and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2,2,1]-heptane.

Of these, bis(isocyanatomethyl)bicyclo[2,2,1]heptane, cyclohexane diisocyanate, and bis(isocyanatomethyl)-1,4-dithiane are enumerated as the preferred polyisocyanates.

Examples of suitable polythiol compounds include compounds having sulfur other than that in a mercapto group, such as methanedithiol, ethanedithiol, propanedithiol, 1,6-hexanedithiol, 1,2,3-propanetrithiol, tetrakis(mercaptomethyl)methane, cyclohexanedithiol, 2,2-dimethylpropane-1,3-dithiol, 3,4-dimethoxybutane-1,2-dithiol, 2-methylcyclo-

hexane-2,3-dithiol, bis(mercaptomethyl)cyclohexane,
 2,3-dimercapto-1-propanol(2-mercaptoacetate), 2,3-di-
 mercapto-1-propanol(3-mercaptoacetate), diethylene glycol
 bis(2-mercaptoacetate), diethylene glycol bis-
 (3-mercaptopropionate), 1,2-dimercaptopropyl methyl ether,
 2,3-dimercaptopropyl methyl ether, 2,2-bis-
 (mercaptomethyl)-1,3-propanedithiol, bis(2-mercaptoethyl)
 ether, ethylene glycol bis(2-mercaptoacetate), ethylene
 glycol bis(3-mercaptopropionate), trimethyloxypropane
 tris(2-mercaptoacetate), trimethylolpropane tris-
 (3-mercaptopropionate), pentaerythritol tetrakis-
 (2-mercaptoacetate), pentaerythritol tetrakis-
 (3-mercaptopropionate), 1,2-bis(2-mercaptoethyl-
 thio)-3-mercapto propane, bis(mercaptomethyl) sulfide,
 bis(mercaptoethyl) sulfide, bis(mercaptopropyl) sulfide,
 bis(mercaptomethylthio)methane, bis(2-mercaptoethylthio)-
 methane, bis(3-mercaptopropyl)methane, 1,2-bis(mercapto-
 methylthio)ethane, 1,2-(2-mercaptoethylthio)ethane,
 1,2-(3-mercaptopropyl)ethane, 1,3-bis(mercaptomethylthio)-
 propane, 1,3-bis(2-mercaptoethylthio)propane, 1,3-bis-
 (3-mercaptopropylthio)propane, 1,2-bis(2-mercaptoethyl-
 thio)-3-mercapto propane, 2-mercaptoethylthio-1,3-propane-
 dithiol, 1,2,3-tris(mercaptomethylthio)propane,
 1,2,3-tris(2-mercaptoethylthio)propane, 1,2,3-tris-
 (3-mercaptopropylthio)propane, tetrakis(mercaptomethyl-

thiomethyl)methane, tetrakis(2-mercaptoethylthiomethyl)-methane, tetrakis(3-mercaptopropylthiomethyl)methane, bis(mercaptomethyl) disulfide, bis(mercaptoethyl) disulfide, bis(mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol, bis(1,3-dimercapto-2-propyl) sulfide, 3,4-thiophenedithiol, tetrahydrothiophene-2,5-dimercaptomethyl, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercapto-1,4-dithiane, 2,5-bis(mercaptomethyl)-1,4-dithiane, and 2,5-bis(mercaptoethyl)-1,4-dithiane.

Of these, bis(mercaptomethyl)-1,4-dithiane, bis(mercaptoethyl) sulfide, bis(mercaptoethyl) disulfide, and 1,2-bis(mercaptoethyl)thio-3-mercaptopropane are preferred as the polythiol compound that is used in the invention.

The epithio group-containing compound is also called an episulfide-based monomer. Examples of suitable monomers include episulfide compounds having an alicyclic skeleton, such as 1,3- and 1,4-bis(β -epithiopropylthio)cyclohexanes, 1,3- and 1,4-bis(β -epithiopropylthiomethyl)cyclohexanes, bis[4-(β -epithiopropylthio)cyclohexyl]methane, 2,2-bis[4-(β -epithiopropylthio)cyclohexyl]propane, and bis[4-(β -epithiopropylthio)cyclohexyl] sulfide; episulfide compounds having an aromatic skeleton, such as 1,3- and 1,4-bis(β -epithiopropylthio)benzenes, 1,3- and 1,4-bis(β -epithiopropylthiomethyl)benzenes, bis[4-(β -epithio-

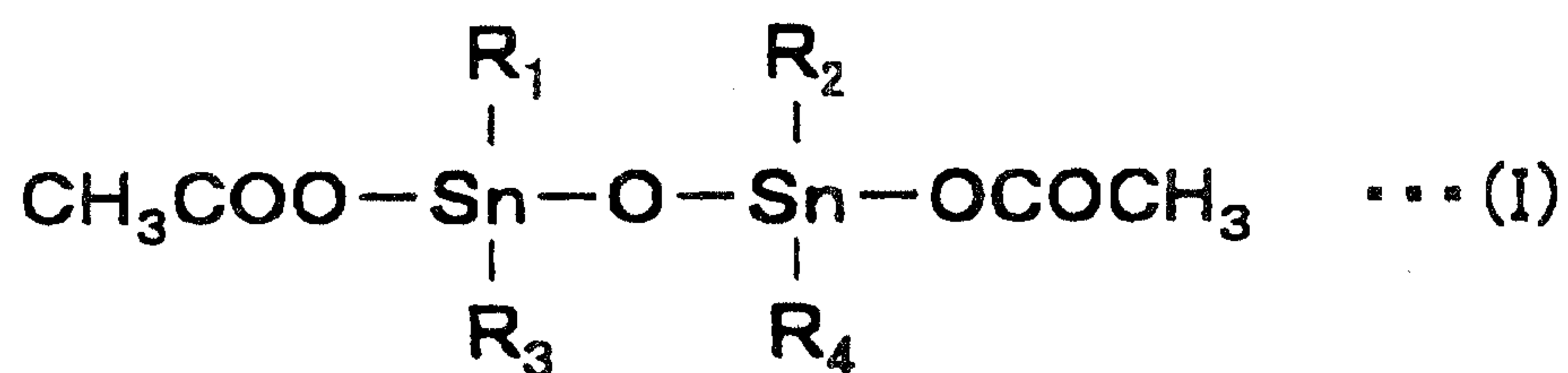
propylthio)phenyl]methane, 2,2-bis[4-(β -epithiopropylthio)phenyl]propane, bis[4-(β -epithiopropylthio)phenyl]sulfide, bis[4-(β -epithiopropylthio)phenyl]sulfine, and 4,4-bis(β -epithiopropylthio)biphenyl; episulfide compounds having a dithiane ring skeleton, such as 2,5-bis(β -epithiopropylthiomethyl)-1,4-dithiane, 2,5-bis(β -epithiopropylthioethylthiomethyl)-1,4-dithiane, 2,5-bis(β -epithiopropylthioethyl)-1,4-dithiane, and 2,3,5-tri(β -epithiopropylthioethyl)-1,4-dithiane; and episulfide compounds having an aliphatic skeleton, such as 2-(2- β -epithiopropylthioethylthio)-1,3-bis(β -epithiopropylthio)propane, 1,2-bis[(2- β -epithiopropylthioethylthio)]-3-(β -epithiopropylthio)propane, tetrakis(β -epithiopropylthiomethyl)methane, 1,1,1-tris(β -epithiopropylthiomethyl)propane, bis(β -epithiopropyl) sulfide, and bis(β -epithiopropyl) disulfide.

Further, many suitable epithio group-containing compounds are conventionally known, and specific examples thereof are disclosed in, for example, JP-A-09-071580, JP-A-09-110979, JP-A-09-255781, JP-A-03-081320, JP-A-11-140070, JP-A-11-183702, JP-A-11-189592, JP-A-11-180977, and Japanese Domestic Re-Publication No. 01-810575. The episulfide-based monomers disclosed in these patents are also employable in the present invention.

Of these compounds, bis(β -epithiopropyl) sulfide and bis(β -epithiopropyl) disulfide are preferred as the epithio group-containing compound to be used in the invention.

In addition, in order to promote the reaction between the polyisocyanate compound and the polythiol compound, it is preferred to add a catalyst to the liquid of the starting materials for preparing the prepolymer.

As the preferred catalyst is enumerated a tin compound represented by the following general formula (I):



wherein R_1 to R_4 , which may be the same or different, each represents an alkyl group having from 1 to 4 carbon atoms.

Specific examples of the catalyst represented by the general formula (I) include tetramethyl-diacetoxy-distannoxane, tetraethyl-diacetoxy-distannoxane, tetrapropyl-diacetoxy-distannoxane, and tetrabutyl-diacetoxy-distannoxane. An amount of the catalyst to be added is preferably in the range of from 0.0005% by weight to 0.1% by weight of the whole amount of the starting materials of the prepolymer.

In the prepolymer, with respect to the mixing ratio of the polyisocyanate compound and the polythiol compound, it is preferred that there is an excess of polythiol compound so as to have thiols at the end terminals of as many of the molecules of the prepolymer as possible. The -SH/-NCO molar ratio is preferably 1.75 or more.

Further, the epithio group-containing compound may be used as a reactive diluent during the preparation of the prepolymer. Taking into account the viscosity at which the prepolymer can be handled and the amount of the epithio group-containing compound into which sulfur is dissolved, the amount of the epithio group-containing compound to be added during the preparation of the prepolymer is preferably 50% by weight or more of the whole amount of the starting materials of the prepolymer. In the case where the viscosity of the prepolymer is large, an epithio group-containing compound may be added in appropriate amounts in order to regulate the viscosity of the prepolymer. When the epithio group-containing compound is used as the starting material of the prepolymer, it is considered that even when a polythiourethane is formed by the reaction of the polyisocyanate compound and the polythiol compound, the epithio group-containing compound dissolves the formed

polythiourethane therein so that it becomes possible to control increase of viscosity.

Taking into consideration the mixing with other starting materials of the lens and the pouring operation, the viscosity of the prepolymer is preferably 5,000 mPa·s or less at 25°C.

The temperature and reaction time for the preparation of the prepolymer are not particularly limited. However, it is preferred from the standpoint of workability that the reaction is carried out at from 10 to 80°C for from 1 to 48 hours. Further, in order to keep the storage stability of the prepolymer after the preparation, the prepolymer can be cooled to between about -5°C and room temperature.

It is preferred from the standpoints of obtaining good heat resistance and keeping a stable lens shape that a content of the whole of the polyisocyanate compound and the polythiol compounds is 15% by weight or less of the whole amount of the starting materials of the lens.

Next, the second starting material of the three kinds of starting materials of the lens, which is obtained by mixing an epithio group-containing compound and sulfur, will be described.

An object of mixing sulfur and the epithio

group-containing compound is to efficiently dissolve sulfur. In the case where sulfur is added to the polythiol compound and the polyisocyanate compound which are the other starting materials, gases are likely to be generated during the dissolution, or the sulfur is not dissolved so that the obtained lens is inferior in transparency, and hence, this method is not preferred. It is preferred from the standpoints of raising refractive index and reliably obtaining transparency that the amount of sulfur to be added is in the range of from 5 to 30% by weight of the whole amount of the starting materials of the lens.

As the epithio group-containing compound to be mixed with sulfur, compounds the same as or different from the epithio group-containing compounds to be used during the preparation of the prepolymer can be used.

In order to obtain the mixture by mixing sulfur with and dissolving it in the epithio group-containing compound, it is preferred that the mixed liquid is heated and dissolved at from 40°C to 70°C and then stirred at from 30 to 50°C for from 1 hour to 24 hours in order to prevent deposition of sulfur. Further, during mixing of the three kinds of starting materials, the mixture can be cooled to from 10 to 25°C.

The mixture which is the preferred third starting

material of the lens, which is obtained by mixing an epithio group-containing compound and/or a polythiol compound and a catalyst, will now be described.

As the epithio group-containing compound, the epithio group-containing compounds that are used during the preparation of the prepolymer and the mixture with sulfur can be used. In this case, the epithio group-containing compounds used for the prepolymer and for the mixture with sulfur and the epithio group containing compound used for the mixture with the catalyst may be the same or may be different.

Similarly, as the polythiol compound, the polythiol compounds used for the prepolymer can be used. In this case, the polythiol compounds used for the prepolymer and, if present, for the mixture with sulfur and the polythiol compound used for the mixture with the catalyst may be the same or may be different.

The catalyst that is used during the preparation of or as the third starting material is added with intent to react the epithio group-containing compound or the polythiol and the epithio group-containing compound. The catalyst can be enumerated amines, phosphines, quaternary ammonium salts, quaternary phosphonium salts, tertiary sulfonium salts, secondary iodonium salts, miral acids, Lewis acids, organic acids, silicates, and tetrafluoroborates.

Particularly preferred examples of the catalyst include aminoethanol, 1-aminopropanol, 2-aminopropanol, amino-butanol, aminopentanol, aminohexanol, tetramethylphosphonium chloride, tetramethylphosphonium bromide, tetraethylphosphonium chloride, tetraethylphosphonium bromide, tetra-n-butylphosphonium chloride, tetra-n-butylphosphonium bromide, tetra-n-butylphosphonium iodide, tetra-n-hexylphosphonium bromide, and tetra-n-octylphosphonium bromide.

Further, with respect to the catalyst to be used as or in the third starting material, it is necessary that the catalyst to be used is selected and that its amount is regulated depending upon the monomers to be used, but the amount is generally from 0.001% by weight to 0.1% by weight of the amount of the whole of the starting materials of the lens.

These three kinds of starting materials are prepared and mixed. The mixing method is not particularly limited. In mixing, the setting temperature, the time required for this, and the like may be basically those conditions under which the respective components are thoroughly mixed. Excessive temperature and time will likely cause an undesirable reaction among the respective starting materials and additives and increase the viscosity, thereby making the casting operation

difficult, and hence, such conditions are not appropriate.

From these viewpoints, the mixing temperature is preferably in the range from -30°C to 50°C , and more preferably in the range from -5°C to 30°C . The mixing time is from about 5 minutes to 2 hours, and preferably from about 5 minutes to 15 minutes.

Further, carrying out degassing operation in vacuo before, during or after mixing the respective starting materials and additives is preferred from the standpoint of preventing the generation of bubbles during cast polymerization curing to be carried out later. At this time, the degree of vacuum is preferably in the range of from about 0.1 mmHg to 50 mmHg, and particularly preferably in the range of from 1 mmHg to 20 mmHg.

Moreover, to purify these mixtures of main and sub-starting materials or to purify the main and sub-starting materials before mixing by filtration of impurities with a filter having a pore diameter of from about 0.05 to 3 μm is preferred from the standpoint of further enhancing the quality of the optical materials of the invention.

The mixed starting materials and the like are poured into a glass or metallic mold and subjected to polymerization curing in an electric furnace or the like. It is preferred

that the curing temperature is from 5°C to 120°C and that the curing time is generally from about 1 to 72 hours. Further, to subject the material after completion of the curing to an annealing processing at a temperature of from 50 to 150°C for from about 10 minutes to 5 hours is preferred for eliminating distortion of the optical materials of the invention.

In the case where after the polymerization, the plastic lens of the invention is hard to peel apart from the mold, using or adding known external and/or internal releasing agents may enhance the release properties. Further, for the purpose of protecting the resin or eyes from ultraviolet rays, UV absorbers may be used; and for the purpose of protecting eyes from infrared rays, IR absorbers may be used. Their amounts vary depending upon the absorptive ability and maximum absorption wavelength of additives to be used, but are in the range between 0.03% by weight and 3% by weight. Also, there is employable a method for impregnating these absorbers in the resin later.

In addition, for the purpose of keeping or enhancing the appearance of the resin, an antioxidant may be added, or bluing with a small amount of a coloring matter may be employed.

The plastic lens obtained in the invention can be subjected to a dyeing processing with a dye. Also, in order

to enhance the resistance to abrasion, a cured film may be formed on the plastic lens using a coating liquid comprising an organosilicon compound or an acrylic compound having fine particles of inorganic materials such as tin oxide, silicon oxide, zirconium oxide, and titanium oxide.

Further, in order to enhance the impact resistance, a primer layer composed mainly of polyurethane may be formed on the plastic lens.

Moreover, in order to impart an antireflection performance, an antireflection film made of an inorganic material such as silicon oxide, titanium dioxide, zirconium oxide, and tantalum oxide may be formed on the cured film. In addition, in order to enhance the water repellence, a water repellent film made of a fluorine atom-containing organosilicon compound may be formed on the antireflection film.

The present invention further relates to a plastic lens obtainable by the above described process as well as to a plastic lens obtainable by reacting a polyisocyanate compound, a polythiol compound, an epithio group-containing compound and sulfur, which is transparent, i.e. which preferably has the same or essentially the same transparency as a plastic lens of the same thickness and being prepared from the same starting materials in the same amounts but without sulfur.

The transparency of the lens is defined by its transmission factor $\tau = \Phi_{\text{ex}} / \Phi_{\text{in}}$, wherein Φ_{ex} is the radiation flux of a light beam emerging the lens and Φ_{in} is the radiation flux of the light beam shining into the lens, the light beam being visible (i.e. having a wavelength in the range of 400 to 750 nm).

The value of transparency of a lens depends on the value of refractive index of the lens, without coating of any anti-reflective film, because a lens having a high refractive index shows high reflection.

The transparent lens of the present invention when having a refractive index of 1.55 to 1.65 preferably has a transparency in the range of 0.80-0.92, more preferably in the range of 0.85-0.92 and most preferably in the range of 0.88-0.92, when measured with a lens having a thickness of 1.8 mm at any wavelength in the range of 500 nm to 600 nm.

The transparent lens of the present invention when having a refractive index of 1.66 to 1.76 preferably has a transparency in the range of 0.80-0.91, more preferably in the range of 0.85-0.91 and most preferably in the range of 0.88-0.91, when measured with a lens having a thickness of 1.8 mm at any wavelength in the range of 500 nm to 600 nm.

The invention will be described below in more details

with reference to the Examples, but it should not be construed that the invention is limited to these Examples.

Incidentally, the physical properties of the plastic lenses for spectacles obtained in the Examples and Comparative Examples were evaluated in the following manners.

(1) Refractive index and Abbe's number:

Measured at 20°C using a precision refractometer, Model KPR-200 manufactured by Kalnew Optical Industrial Co., Ltd.

(2) Transparency:

Judgement by naked eye

Example 1:

(a) Preparation of prepolymer (component A):

In a three-necked flask were charged 14.40 parts by weight of bis(isocyanatomethyl)-1,4-dithiane, 33.20 parts by weight of bis(mercaptomethyl)-1,4-dithiane, 0.024 parts by weight of tetra-n-butyl-1,3-diacetoxy-distannoxane, and 47.60 parts by weight of bis(β -epithiopropyl) sulfide, and the mixture was reacted under stirring in a nitrogen atmosphere for 24 hours while keeping at 50°C. Thereafter, the reaction mixture was cooled to a temperature in the vicinity of room temperature.

(b) Preparation of mixture X (component B):

In a three-necked flask were charged 14.29 parts by weight of powdered sulfur and 75.19 parts by weight of

bis(β -epithiopropyl) sulfide, and the mixture was heated at 60°C and dissolved in a nitrogen atmosphere, followed by reacting while stirring at 40°C for about 12 hours. The reaction mixture was cooled to about 25°C before mixing.

(c) Preparation of mixture Y (component C):

Tetrabutylphosphonium bromide (0.04 parts by weight) and bis(β -epithiopropyl) sulfide (2.00 parts by weight) were weighed and dissolved to prepare a solution.

(d) Mixing and polymerization of component A, component B and component C:

In a three-necked flask charged with 89.48 parts by weight of the component B, 9.52 parts by weight of the component A (the whole amount of 4-dithiane the urethane components, namely bis(isocyanatomethyl)-1,4-dithiane and bis(mercaptomethyl)-1, was 4.76 parts by weight) was added and mixed. To this mixed liquid, 1.02 parts by weight of the component C was added and mixed, and the mixture was subjected to degassing. Thereafter, the mixture was poured into lens molds of 0.00D and -3.00D, while filtering through a 1.0-micron filter made of PTFE (polytetrafluoroethylene). Polymerization and curing were carried out by gradually elevating the temperature from 35°C to 95°C over 24 hours. After the curing, the cured products were cooled to a temperature in the vicinity of 70°C and released from the molds, to obtain a 0.00D lens and a -3.00D lens. The evaluation

results are shown in Table 1. The obtained lenses were transparent and had physical properties of a refractive index of 1.73 and an Abbe's number of 33.

Examples 2 to 9:

The same procedures as in Example 1 were followed, except that the types and mixing ratio of the polyisocyanate compound and the polythiol compound and the amount of the epithio group-containing compound to be added were changed as shown in Table 1. The evaluation results are shown in Table 1. Similar to Example 1, there were obtained lenses that were transparent and had characteristics of a high refractive index and a high Abbe's number.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Prepolymer (component A) (parts by weight)	Polyisocyanate compound	BIMD: 1.44	BIMD: 1.44	BIMD: 2.88	DIMB: 1.33	DIMB: 1.66	BIMD: 1.67	BIMD: 1.65	BIMD: 1.44
	Polythiol compound	BMMD: 3.32	BMMD: 3.32	BMMD: 6.64	BMMD: 3.43	DMES: 3.10	BMMD: 3.09	DMTMP: 3.11	BMMD: 3.32
	SH/NCO	2.5	2.5	2.5	2.5	2.5	2.0	2.5	2.5
	Epithio group- containing compound	BEPS: 4.76	BEPS: 4.76	BEPS: 9.52	BEPS: 4.76	BEPS: 4.76	BEPS: 4.76	BEPS: 4.76	BEPS: 4.76
Mixture X (component B) (parts by weight)	Catalyst: TK-1	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
	Epithio group- containing compound	BEPS: 75.19	BEPS: 79.95	BEPS: 72.81	BEPS: 75.19	BEPS: 75.19	BEPS: 75.19	BEPS: 75.19	BEPS: 34.72 BEPDS: 40.48
Mixture Y (component C) (parts by weight)	Sulfur	14.29	9.52	16.67	14.29	14.29	14.29	14.29	14.29
	Epithio group- containing compound	BEPS: 1	BEPS: 1	BEPS: 1	BEPS: 1	BEPS: 1	BEPS: 1	BEPS: 1	BEPS: 1
	Catalyst: TBPB	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	Urethane component	5	5	5	5	5	5	5	5
Composition ratio	Epithio component	85	90	82.5	85	85	85	85	85
	Sulfur component	15	10	17.5	15	15	15	15	15
Appearance		Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent
	D (Refractive index)	1.73	1.72	1.74	1.72	1.72	1.73	1.73	1.74
Optical characteristics	v _D (Abbe's number)	33	34	33	34	34	33	33	32

Comparative Example 1:

It was attempted to prepare lenses in the same composition ratio as in Example 1, without preparing the urethane prepolymer.

(a) Preparation of component D:

Bis(β -epithiopropyl) sulfide (80.95 parts by weight) and powdered sulfur (14.29 parts by weight) were mixed, and the mixture was heated and dissolved at 60°C in a nitrogen atmosphere, followed by reacting under stirring at 40°C for about 12 hours. The reaction mixture was cooled to about 25°C before mixing.

(b) Mixing and polymerization of starting materials of lens:

To the component D, 1.44 parts by weight of bis(isocyanatomethyl)-1,4-dithiane, 3.32 parts by weight of bis(mercaptomethyl)-1,4-dithiane, 0.0024 parts by weight of tetra-n-butyl-1,3-diacetoxy-distannoxane, and 0.02 parts by weight of tetrabutylphosphonium bromide were added and mixed, and the mixture was subjected to degassing. Thereafter, the mixture was poured into lens molds of 0.00D and -3.00D, while filtering through a 1.0-micron PTFE-made filter. Polymerization and curing were carried out by gradually elevating the temperature from 35°C to 95°C over 24 hours. After the curing, the cured products were cooled to a temperature in the vicinity of 70°C and released from the molds. The obtained lenses were cloudy.

Comparative Example 2:

It was attempted to prepare lenses by following the same procedures as in Comparative Example 1, except that the ratio of the urethane component was decreased.

The same procedures as in Comparative Example 1 were followed, except that the amounts of the urethane components bis(isocyanatomethyl)-1,4-dithiane and bis(mercaptomethyl)-1,4-dithiane were changed to 0.58 parts by weight and 1.33 parts by weight respectively and the amount of bis(β -epithiopropyl) sulfide was changed to 83.81 parts by weight. The obtained lenses were cloudy.

Comparative Example 3:

It was attempted to prepare lenses with the same composition as in Example 2, except that sulfur was mixed and dissolved in the epithio group-containing compound containing the urethane prepolymer.

In a flask, 79.95 parts by weight of bis(β -epithiopropyl) sulfide, 1.44 parts by weight of bis(isocyanatomethyl)-1,4-dithiane, 3.32 parts by weight of bis(mercaptomethyl)-1,4-dithiane, and 0.0024 parts by weight of tetra-n-butyl-1,3-diacetoxy-distannoxane were weighed, and the mixture was stirred and reacted for 24 hours in a nitrogen atmosphere while keeping at 50°C. After the reaction, 9.52

parts by weight of powdered sulfur was added, and the mixture was heated at 60°C in a nitrogen atmosphere. During the dissolution step, the solution became reddish and became a tar while generating heat and a yellow gas.

Comparative Example 4:

It was attempted to prepare lenses in the same composition ratio as in Example 1, except that the reactive diluent (epitho compound) was not used during the preparation of the urethane prepolymer.

Bis(isocyanatomethyl)-1,4-dithiane (1.44 parts by weight), bis(mercaptomethyl)-1,4-dithiane (3.32 parts by weight), and tetra-n-butyl-1,3-diacetoxy-distannoxane (0.0024 parts by weight) used as the catalyst were weighed, and the mixture was reacted for 24 hours in a nitrogen atmosphere while keeping at 50°C. The solution solidified, and even by adding bis(β -epithiopropyl) sulfide, mixing could not be done.

Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Polyisocyanate compound		BIMD: 1.44	BIMD: 0.58	BIMD: 1.44	BIMD: 1.44
Polythiol compound		BMMD: 3.32	BMMD: 1.33	BMMD: 3.32	BMMD: 3.32
SH/NCO		2.5	2.5	2.5	2.5
Epithio group-containing compound		-	-	BEPS: 79.95	-
Catalyst: TK-1		0.0024	0.0024	0.0024	0.0024
Catalyst: TBPB		0.02	0.02	0.02	0.02
Powdered sulfur		-	-	9.52	-
Component D (parts by weight)	Epithio group- containing compound	BEPS: 80.95	BEPS: 83.81	-	BEPS: 80.95
	Sulfur	14.29	14.29	-	14.29
Composition ratio	Urethane component	5	2	5	5
	Epithio component	85	88	90	85
	Sulfur component	15	15	10	15
Appearance		Cloudy	Cloudy	Sulfur runaway during reaction	Hardened while mixing

BIMD: Bis(isocyanatomethyl)-1,4-dithiane
 DIMB: Bis(isocyanatomethyl)bicyclo[2,2,1]heptane
 BMMD: Bis(mercaptomethyl)-1,4-dithiane
 DMES: Bis(mercaptoethyl) sulfide
 DMTMP: 1,2-Bis(mercaptoethylthio)-3-mercapto propane
 BEPS: Bis(β -epithiopropyl) sulfide
 BEPDS: Bis(β -epithiopropyl) disulfide
 TBPB: Tetrabutylphosphonium bromide
 TK-1: Tetrabutyl-diacetoxy-distannoxane

According to the production process of the invention, plastic lenses for spectacles, having a high refractive index and a high Abbe's number and having excellent transparency can be obtained.

Hoya Corporation

Ref.: 2002P32001

Claims

1. Process for producing a plastic lens, which comprises mixing a) a prepolymer with b) a mixture comprising sulfur in an epithio group-containing compound and c) a catalyst.
2. Process according to claim 1, wherein the prepolymer comprises an epithio group-containing compound.
3. Process according to any of the preceding claims, wherein the prepolymer is obtainable by reacting a polyisocyanate compound and a polythiol compound in an epithio group-containing compound.
4. Process according to any of the preceding claims, wherein the catalyst c) is added as mixture of the catalyst with an epithio group-containing compound and/or a polythiol compound.
5. Process according to any of the preceding claims, wherein the ratio of the polythiol compound to the polyisocyanate compound in the prepolymer is 1.75 or more in terms of -SH/-NCO molar ratio.

6. Process according to any of the preceding claims, wherein the weight of the epithio group-containing compound in the prepolymer is 50% by weight or more of the whole amount of the starting materials of the prepolymer.

7. Process according to any of the preceding claims, wherein the content of sulfur is in the range of from 5 to 30% by weight of the whole amount of the starting materials a), b) and c).

8. Process according to any of the preceding claims, wherein the whole of the polyisocyanate and the polythiol compounds used for the starting materials a) and c) of the lens is 15% by weight or less of the whole amount of the starting materials a), b) and c).

9. Process according to any of the preceding claims, wherein the polyisocyanate compound is one or more of the group consisting of bis(isocyanatomethyl)bicyclo[2,2,1]heptane, cyclohexane diisocyanate, and bis-(isocyanatomethyl)-1,4-dithiane.

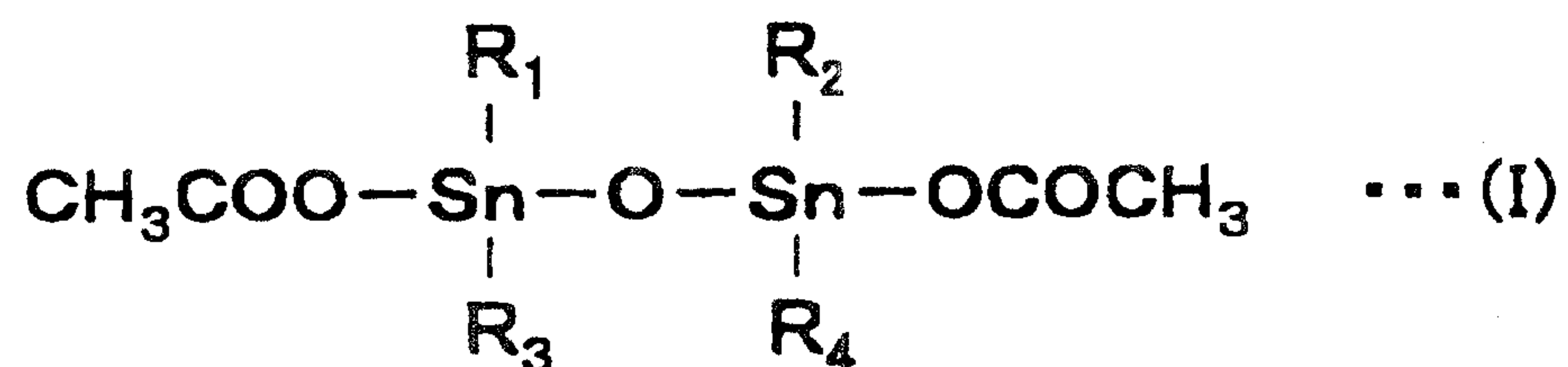
10. Process according to any of the preceding claims, wherein the polythiol compound is at least one of the group

consisting of bis(mercaptomethyl)-1,4-dithiane, bis(mercaptoethyl) sulfide, bis(mercaptoethyl) disulfide, and 1,2-bis(mercaptoethyl)thio-3-mercaptopropane.

11. Process according to any of the preceding claims, wherein the epithio group-containing compound is bis(β -epithiopropyl) sulfide and/or bis(β -epithiopropyl) disulfide.

12. Process according to any one of claims 3 to 11, wherein a catalyst is added to the reaction mixture for preparing the prepolymer.

13. Process according to claim 12, wherein the catalyst is represented by the following general formula (I):



wherein R_1 to R_4 , which may be the same or different, each represents an alkyl group having from 1 to 4 carbon atoms.

14. Process according to claim 13, wherein the catalyst represented by the general formula (I) is at least one of the group consisting of tetramethyl-diacetoxy-distannoxane,

tetraethyl-diacetoxy-distannoxane, tetrapropyl-diacetoxy-distannoxane, and tetrabutyl-diacetoxy-distannoxane.

15. Plastic lens obtainable by the process according to any one of claims 1 to 14.

16. Plastic lens obtainable by reacting a polyisocyanate compound, a polythiol compound, an epithio group-containing compound, and sulfur, characterized in that the plastic lens is transparent.