

POLYMERIZABLE COMPOSITION FOR OPTICAL MATERIALS AND APPLICATION OF SAME

BACKGROUND

Technical Field

[0001]

The present disclosure relates to a polymerizable composition for optical materials including a photochromic compound, and an optical material and a plastic lens obtained from the composition.

[0002]

Since plastic lenses are light, not easily cracked, and can be stained, plastic lenses have been rapidly distributed as optical materials such as eyeglass lenses and camera lenses, and hitherto, molded bodies for lenses using a variety of plastic materials have been developed and used. Representative examples include an allyl resin obtained from diethylene glycol bisallyl carbonate and diallyl isophthalate, a (meth)acrylic resin obtained from (meth)acrylate, and a polythiourethane resin obtained from isocyanate and thiol.

[0003]

In addition, in recent years, high-performance plastic lenses to which various functions were imparted have been developed, and for example, a lens in which light having a harmful wavelength is blocked, a lens in which scratches on the surface are suppressed, and a lens in which cloudiness on the lens surface caused by a temperature difference is suppressed have been known. Plastic lenses having photochromic performance also is one of such high-performance plastic lenses, and development thereof has been progressing. By using the plastic lenses having such photochromic performance, it is possible to obtain eyeglasses which functions as typical eyeglasses having a transparent color indoors, and by the lenses being colored gray or brown in response to sunlight (ultraviolet rays) outdoors, exhibits a function to protect the eyes from glare. The eyeglasses are high-performance eyeglasses which do not need to be worn outdoors and taken off indoors as sunglasses are worn outdoors and taken off indoors and capable of being used both

indoors and outdoors, and in recent years, the demand therefor has been expanding globally.

[0004]

The plastic lens having such photochromic performance is required to be fast responsive for coloring and decoloring and exhibit good coloring performance. For example, by using a specific aliphatic isocyanate or a specific alicyclic isocyanate, it is possible to obtain a urethane resin-based optical material or a thiourethane resin-based optical material and a plastic lens including a photochromic compound without causing deterioration in performance of the photochromic compound (Patent Document 1).

[0005]

According to the polymerizable composition for optical materials including a specific polyol compound, it is possible to obtain a polyurethane-based optical material or a polythiourethane-based optical material including a photochromic compound, which exhibits excellent photochromic performance without causing deterioration in performance of the photochromic compound and is also excellent in physical properties such as mechanical strength (Patent Document 2).

[0006]

In addition, by improving dispersibility by suppressing aggregation of a photochromic compound in a polymerizable composition for optical materials or a resin for optical materials, a technology for improving the photochromic performance of a resin has been proposed. As such a technique, for example, polymer fine particles containing a photochromic compound in a polymer has been proposed (Patent Documents 3 to 7). In addition, a resin for optical materials including nanoparticles containing a photochromic compound and having a refractive index of 1.595 to 1.695 has been also proposed (Patent Document 8).

[0007]

[Patent Document 1] WO 2014/002844

[Patent Document 2] WO 2015/115648

[Patent Document 3] WO 2014/007154

[Patent Document 4] JP2008-506031
[Patent Document 5] JPS64-29489
[Patent Document 6] JPH1-152182
[Patent Document 7] DE102009052986
[Patent Document 8] WO 2004/011506

[0008]

In Patent Document 3, a method of producing a photochromic pigment-containing polythiourethane resin from a polymerizable composition including a polyolefin-based terminal branched copolymer, a naphthopyran-based photochromic pigment, and as a polymerizable monomer, 1,2-bis(2-mercaptoethyl)thio-3-mercaptopropane, pentaerythritoltetra(3-mercaptopropionate), and norbornene diisocyanate is disclosed. However, it is necessary that after polymer particles containing a photochromic pigment are prepared from a polyolefin-based terminal branched copolymer and a naphthopyran-based photochromic pigment in advance, a resin is produced by mixing the polymer particles with a polymerizable monomer, and thus, there are problems that the production process becomes long, and the production efficiency of the resin is significantly reduced.

[0009]

In addition, since in a case where the polymer particles and the polymerizable monomer are mixed, the reactivity between the polymer particles and the polymerizable monomer is high, the viscosity of the polymerizable composition is easily increased, and due to this, the pot life of the polymerizable composition is shortened, and a resin molded body cannot be efficiently produced in some cases, and therefore, there is room for improvement.

[0010]

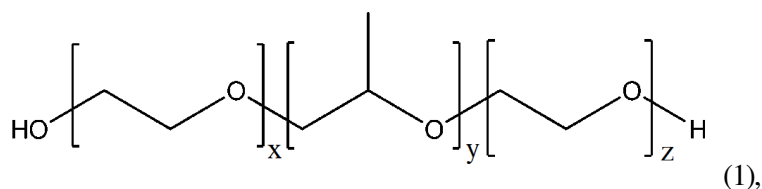
As a result of thorough studies, the present inventors found that by using a specific polymer, it is possible to obtain a polymerizable composition which has excellent handling properties by suppression of viscosity increase, and it is possible to provide an optical material which has excellent photochromic characteristics, excellent clarity, excellent heat resistance, and

excellent mechanical properties, and completed the present invention.

That is, the present invention can be described as follows.

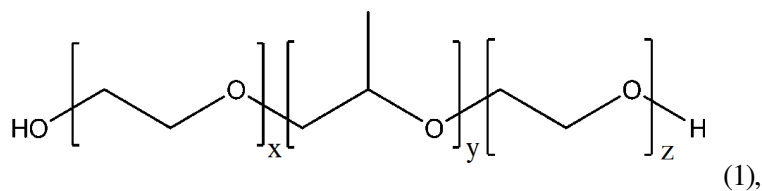
[0011]

[1] A polymerizable composition for optical materials including a polymer composition (a) including a tri-block copolymer of formula (1):



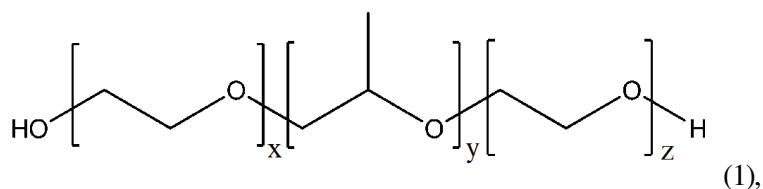
x represents an integer of 3 or more and 300 or less, y represents an integer of 3 or more and 300 or less, and z represents an integer of 3 or more and 300 or less; a photochromic compound (b); and a polymerization reactive compound (c) other than the polymer composition (a). The polymer composition (a) can include an impurity comprising di-block copolymer and mono polymer; and a weight percent of the impurity in the polymer composition (a) is less than 25%.

[2] A polymerizable composition for optical materials including a polymer composition (a) comprising a tri-block copolymer of formula (1):



x represents an integer of 3 or more and 300 or less, y represents an integer of 3 or more and 300 or less, and z represents an integer of 3 or more and 300 or less; a photochromic compound (b); and a polymerization reactive compound (c) comprising at least one selected from the group consisting of metaxylylene diisocyanate, 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, and 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane. The polymer composition (a) has a weight average molecular weight of 4,000 g/mol to 7,000 g/mol.

- [3] A cured body obtained by curing the polymerizable composition of [2].
- [4] The polymerizable composition of [2]. The polymer composition (a) has a weight average molecular weight of about 4,600 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.852.
- [5] A cured body obtained by curing the polymerizable composition of [4].
- [6] The cured body of [5]. A haze value of the cured body is less than 0.27, an yellow index of the cured body is less than 2.71, Initial T% at 550 nm is more than 83.7, and $\Delta T\%$ at 550 nm is more than 69.8.
- [7] The polymerizable composition of [2]. The polymer composition (a) has a weight average molecular weight of about 5,800 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.473.
- [8] A cured body obtained by curing the polymerizable composition of [7].
- [9] The cured body of [8]. A haze value of the cured body is less than 0.61, an yellow index of the cured body is less than 3.48, Initial T% at 550 nm is more than 86.3, and $\Delta T\%$ at 550 nm is more than 73.8.
- [10] The polymerizable composition of [2]. The polymer composition (a) has a weight average molecular weight of about 6,500 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.953.
- [11] A cured body obtained by curing the polymerizable composition of [10].
- [12] The cured body of [11]. A haze value of the cured body is less than 0.37, an yellow index of the cured body is less than 2.93, Initial T% at 550 nm is more than 83.7, and $\Delta T\%$ at 550 nm is more than 70.8.
- [13] A polymerizable composition for optical materials including a polymer composition (a) comprising a tri-block copolymer of formula (1):



x represents an integer of 3 or more and 300 or less, y represents an integer of 3 or more and 300 or less, and z represents an integer of 3 or more and 300 or less; a photochromic compound (b); and a polymerization reactive compound (c) comprising at least one selected from the group consisting of 2,5-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane and 2,6-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, pentaerythritol tetrakis 3-mercaptopropionate, and 4-mercaptopomethyl-1,8-dimercapto-3,6-dithiaoctane. The polymer composition (a) has a weight average molecular weight of 4,000 g/mol to 7,000 g/mol.

[14] A cured body obtained by curing the polymerizable composition of [13].

[15] The polymerizable composition of [13]. The polymer composition (a) has a weight average molecular weight of about 4,600 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.852.

[16] A cured body obtained by curing the polymerizable composition of [15].

[17] The cured body of [16]. An yellow index of the cured body is less than 2.87, Initial T% at 550 nm is more than 85.5, and $\Delta T\%$ at 550 nm is more than 70.5.

[18] The polymerizable composition of [13]. The polymer composition (a) has a weight average molecular weight of about 5,800 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.473.

[19] A cured body obtained by curing the polymerizable composition of [18].

[20] The cured body of [19]. A haze value of the cured body is less than 0.75, an yellow index of the cured body is less than 4.14, Initial T% at 550 nm is more than 82.2, and $\Delta T\%$ at 550 nm is more than 69.

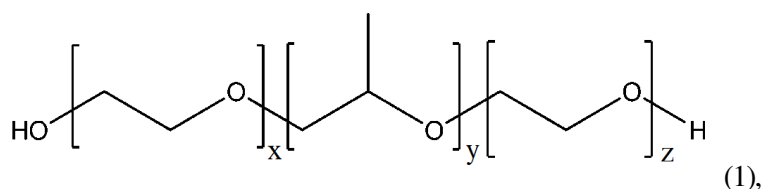
[21] The polymerizable composition for optical materials according to any one of [1] to [20]. The photochromic compound (b) is a naphthopyran derivative.

[22] A molded body obtained by curing the polymerizable composition in a mold for optical materials according to any one of [1] to [21].

[23] An optical material formed of the molded body according to [22].

[24] A plastic lens formed of the molded body according to [23].

[25] A method of removing an impurity from a polymer composition (a) including a tri-block copolymer, the method including dissolving 5-15 parts of the polymer composition (a) in 20-45 parts of acetone to prepare a first mixture; adding 20-45 parts of hexane to the first mixture to prepare a second mixture and stirring the second mixture; separating a hexane phase from the second mixture and removing the hexane phase from the second mixture to prepare a third mixture; and removing volatiles from the third mixture to prepare a purified polymer composition (a). The polymer composition (a) includes a tri-block copolymer of formula (1):



x represents an integer of 3 or more and 300 or less, y represents an integer of 3 or more and 300 or less, and z represents an integer of 3 or more and 300 or less; the impurity can include di-block copolymer and mono polymer; the purified polymer composition (a) can include the impurity less than 25 % weight percent in the purified polymer composition (a).

[Advantage of the Invention]

[0012]

The polymerizable composition for optical materials of the present invention can provide an optical material which has excellent handling properties by suppression of viscosity increase, and excellent photochromic characteristics, excellent heat resistance, and excellent mechanical properties. The method of removing impurities from a polymer composition can provide an optical material which has excellent handling properties by suppression of viscosity increase, excellent photochromic characteristics, excellent heat resistance, and excellent mechanical

properties.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0013]

The above-described purpose and the other purposes, features and advantages become apparent with the suitable embodiments and drawings accompanied therewith described below.

[Fig. 1] Fig. 1 is a flow chart showing a purifying process of Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) of one embodiment of the present disclosure.

[Fig. 2] Fig. 2 is an H-NMR spectrum chart showing PEG/PPG integration of non-purified Pluronic[®] P85 (manufactured by Sigma-Aldrich[®]).

[Fig. 3] Fig. 3 is an H-NMR spectrum chart showing PEG/PPG integration of purified Pluronic[®] P85 (manufactured by Sigma-Aldrich[®]).

[Fig. 4] Fig. 4 is a photograph showing a lens manufactured using non-purified Pluronic[®] P105 (manufactured by Sigma-Aldrich[®]) on the left and a lens manufactured using purified Pluronic[®] P105 (manufactured by Sigma-Aldrich[®]) on the right.

DETAILED DESCRIPTION

[0014]

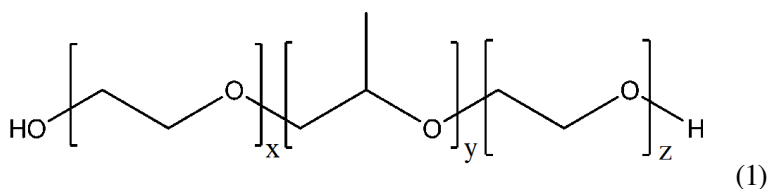
The polymerizable composition for optical materials of the present invention includes a polymer composition (a), a compound (b) of which light absorption characteristics vary by sensing changes in environment, and a polymerization reactive compound (c).

Hereinafter, the present invention will be described with reference to embodiments.

[0015]

[Polymer composition (a)]

In one embodiment, as the polymer composition (a), a compound represented by the following formula (1) can be used.



[0016]

In the present embodiment, as the polymer composition (a), one or two or more kinds selected from the compounds represented by the formula (1) may be used in combination, or one or two or more kinds selected from the compounds represented by any one of the formula (1) can be used in combination. In the present specification, it is preferable to use two compounds selected from the compounds represented by the formula (1) in combination. Although there are no particular limitations on the two kinds of compounds selected in the present embodiment, in a case where a liquid compound of which the length of the hydrophilic block is short and a compound in the form of a solid or a paste of which the hydrophilic block are long are mixed and used, improved photochromic properties are likely to be observed.

[0017]

[Purification of Polymer composition (a)]

The polymer composition (a) may include impurities including smaller molecular weight polymer structures (*e.g.*, mono structure (mono polymers including PPG), di-block structure (di-block copolymers including PEG-PPG), etc.). Such impurities may cause poor clarity to final products, optical materials (*e.g.*, plastic lenses). Especially, high PPG-containing block copolymers may cause lens haziness. In one embodiment, the polymer composition (a) may be purified by organic solvents, such as, acetone and/or hexane.

[0018]

[Compound (b)]

In the present embodiment, a compound (b) of which light absorption characteristics vary by sensing changes in environment is used. Examples of the changes in environment include wavelength changes of light, temperature changes, application of electricity, and types of solvents.

Examples of light absorption characteristics include an absorption spectrum, an intensity change ratio in absorbance at a specific wavelength, and an intensity change rate in absorbance at a specific wavelength. Examples of the compound (b) include a chromic compound (hereinafter, also referred to as a chromic material or a chromic pigment), and the following compounds can be used.

[0019]

(Photochromic Compound)

The molecular structure of the photochromic compound is changed reversibly by irradiation with light having a specific wavelength, and due to this, the light absorption characteristics (absorption spectrum) changes. Examples of the photochromic compound used in the present embodiment include a compound of which the light absorption characteristics (absorption spectrum) changes with respect to light having a specific wavelength. As the photochromic compound, known photochromic compounds can be used, and examples thereof include compounds derived from compounds such as naphthopyran, chromene, spiropyran, spirooxazine and thiospiropyran, benzopyran, stilbene, azobenzene, thioindigo, bisimidazole, spirodihydroindolizine, quinine, perimidinepirocyclohexadienone, viologen, fulgide, fulgimide, diarylethene, hydrazine, aniline, aryl disulfide, arylthioether sulfonate, spiropirimidine, and triarylmethane.

In the present embodiment, as the photochromic compound, a naphthopyran derivative is preferably used.

[0020]

(Thermochromic Compound)

The light absorption characteristics (absorption spectrum) of the thermochromic compound changes depending on the temperature. Examples of the thermochromic compound include leuco compounds, and specific examples include phthalide, phthalan, an acyl-leucomethylene compound, fluoran, spiropyran, and coumarin. Specific examples of the fluoran include 3,3'-dimethoxyfluoran, 3,6-dimethoxyfluoran, 3,6-di-butoxyfluoran, 3-chloro-6-phenylamino-fluoran, 3-diethylamino-6-dimethyl fluoran, 3-diethylamino-6-methyl-7-

chlorofluoran, 3-diethyl-7,8-benzofluoran, 3,3'-bis-(p-dimethyl-aminophenyl)-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-phenylamino-fluoran, 3-diethylamino-7-phenylaminofluoran, and 2-anilino-3-methyl-6-diethylamino-fluoran. Similarly, examples of the phthalide include 3,3',3''-tris(p-dimethylamino-phenyl)phthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3,3-bis(p-diethylamino-phenyl)-6-dimethylamino-phthalide, and 3-(4-diethylamino)phenyl.

[0021]

Since these changes in the absorption spectrum are derived from the molecular structure changes due to an acid-base reaction (protonation-deprotonation) of the molecule, a proton donating agent (also referred to as a "developer") which generates an acid depending on the temperature can also be included.

Examples of the proton donating agent include phenol, azole, organic acids, esters of organic acids, and salts of organic acids.

Examples of the phenol include phenylphenol, bisphenol A, cresol, resorcinol, chlororesorcinol, β -naphthol, 1,5-dihydroxynaphthalene, pyrocatechol, pyrogallol, and a trimer of a p-chlorophenol-formaldehyde condensate. Examples of the azole include benzotriazoles (for example, 5-chlorobenzotriazole, 4-laurylamino-sulfobenzotriazole, 5-butylbenzotriazole, dibenzotriazole, 2-oxybenzotriazole, and 5-ethoxycarbonylbenzotriazole), imidazole (for example, oxybenzimidazole), and tetrazole.

Examples of the organic acid include aromatic carboxylic acids (for example, salicylic acid, resorcylic acid, and benzoic acid) and aliphatic carboxylic acids (for example, stearic acid, 1,2-hydroxystearic acid, tartaric acid, citric acid, oxalic acid, and lauric acid).

To control the reaction by a thermochromic compound and a developer, a proton accepting agent (also referred to as a "desensitizer") which receives an acid depending on the temperature can also be included. Examples of the proton accepting agent include polyhydric alcohols, fatty acid esters, glycol ethers, and polyethylene glycol type nonionic active agents.

[0022]

(Other Chromic Compounds)

Examples of other chromic compounds include an electrochromic compound of which light absorption characteristics vary by electricity (application of a voltage) and a solvatochromic compound of which light absorption characteristics vary depending on the type of solvent which is in contact.

[0023]

The mass ratio of the polymer composition (a) to the chromic compound (b) is not particularly limited but is preferably (b) 0.01 to 100 parts by weight to (a) 100 parts by weight, and more preferably (b) 1 to 10 parts by weight to (a) 100 parts by weight.

[0024]

[Polymerization Reactive Compound (c)]

In the polymerization reactive compound (c), even in the presence or absence of the additives such as an initiator and a catalyst added as necessary, a polymerization reactive compound having at least one or more polymerizable functional groups which are capable of being self-polymerized, copolymerized, or addition-polymerized is included. The polymerization reactive compound (c) does not include the polymer composition (a).

[0025]

Examples of the polymerization reactive compound include a polyiso(thio)cyanate compound having two or more isocyanate groups or isothiocyanate group, a (thio)epoxy compound having one or more epoxy groups or thioepoxy groups, an oxetanyl compound having one or more oxetanyl groups, a thietanyl compound having one or more thietanyl groups or having an oxetanyl group and a thietanyl group, a (meth)acryloyl compound having one or more methacryloyloxy groups, acryloyloxy groups, methacryloylthio groups, acryloylthio groups, methacrylamide groups, or acrylamide groups, a (meth)allyl compound having one or more methallyl groups or allyl groups, an alkene compound having one or more polymerizable carbon-carbon double bond groups other than a methacryloyloxy group, an acryloyloxy group, a methacryloylthio group, an acryloylthio group, a methacrylamide group, or an acrylamide group,

an alkyne compound having one or more polymerizable carbon-carbon triple bond groups, a di- or higher functional active hydrogen compound, and an acid anhydride having one or more acid anhydride groups, and one or two or more compounds selected from these can be used.

[0026]

Examples of the polyiso(thio)cyanate compound include aliphatic polyisocyanate compound such as tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, heptamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, lysinediisocyanato methyl ester, lysine triisocyanate, and xylylene diisocyanate;

alicyclic polyisocyanate compounds such as isophorone diisocyanate, bis(isocyanatomethyl) cyclohexane, bis(isocyanatocyclohexyl) methane, dicyclohexyldimethylmethane isocyanate, 2,5-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, 2,6-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, 3,8-bis(isocyanatomethyl) tricyclodecane, 3,9-bis(isocyanatomethyl) tricyclodecane, 4,8-bis(isocyanatomethyl) tricyclodecane, and 4,9-bis(isocyanatomethyl) tricyclodecane;

aromatic polyisocyanate compounds such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, diphenylsulfide-4,4'-diisocyanate, and phenylene diisocyanate;

heterocyclic polyisocyanate compounds such as 2,5-diisocyanatothiophene, 2,5-bis(isocyanatomethyl) thiophene, 2,5-diisocyanatotetrahydrothiophene, 2,5-bis(isocyanatomethyl) tetrahydrothiophene, 3,4-bis(isocyanatomethyl) tetrahydrothiophene, 2,5-diisocyanato-1,4-dithiane, 2,5-bis(isocyanatomethyl)-1,4-dithiane, 4,5-diisocyanato-1,3-dithiolane, and 4,5-bis(isocyanatomethyl)-1,3-dithiolane;

aliphatic polyisothiocyanate compounds such as hexamethylene diisothiocyanate, lysine diisothiocyanate methyl ester, lysine triisothiocyanate, m-xylylene isothiocyanate, bis(isothiocyanatomethyl) sulfide, bis(isothiocyanatoethyl) sulfide, and bis(isothiocyanatoethyl) disulfide;

alicyclic polyisocyanate compounds such as isophorone diisothiocyanate, bis(isothiocyanatomethyl) cyclohexane, bis(diisothiocyanatocyclohexyl) methane, cyclohexane

diisothiocyanate, methylcyclohexane diisothiocyanate, 2,5-bis(isothiocyanatomethyl) bicyclo-[2.2.1]-heptane, 2,6-bis(isothiocyanatomethyl) bicyclo-[2.2.1]-heptane, 3,8-bis(isothiocyanatomethyl) tricyclodecane, 3,9-bis(isothiocyanatomethyl) tricyclodecane, 4,8-bis(isothiocyanatomethyl) tricyclodecane, and 4,9-bis(isothiocyanatomethyl) tricyclodecane; aromatic polyisothiocyanate compounds such as tolylene diisothiocyanate, 4,4-diphenylmethane diisothiocyanate, and diphenyldisulfide-4,4-diisothiocyanate; and sulfur-containing heterocyclic polyisothiocyanate compounds such as 2,5-diisothiocyanatothiophene, 2,5-bis(isothiocyanatomethyl) thiophene, 2,5-diisothiocyanatotetrahydrothiophene, 2,5-bis(isothiocyanatomethyl) tetrahydrothiophene, 3,4-bis(isothiocyanatomethyl) tetrahydrothiophene, 2,5-diisothiocyanato-1,4-dithiane, 2,5-bis(isothiocyanatomethyl)-1,4-dithiane, 4,5-diisothiocyanato-1,3-dithiolane, and 4,5-bis(isothiocyanatomethyl)-1,3-dithiolane.

[0027]

Examples of the (thio)epoxy compound include polyepoxy compounds such as bisphenol A diglycidyl ether;

Examples of the linear aliphatic 2,3-epoxypropylthio compounds such as bis(2,3-epoxypropyl) sulfide, bis(2,3-epoxypropyl) disulfide, bis(2,3-epoxypropylthio) methane, 1,2-bis(2,3-epoxypropyl) ethane, 1,2-bis(2,3-epoxypropylthio) propane, 1,3-bis(2,3-epoxypropylthio) propane, 1,3-bis(2,3-epoxypropylthio)-2-methyl propane, 1,4-bis(2,3-epoxypropylthio) butane, 1,4-bis(2,3-epoxypropylthio)-2-methyl butane, 1,3-bis(2,3-epoxypropylthio) butane, 1,5-bis(2,3-epoxypropylthio) pentane, 1,5-bis(2,3-epoxypropylthio)-2-methyl pentane, 1,5-bis(2,3-epoxypropylthio)-3-thiapentane, 1,6-bis(2,3-epoxypropylthio) hexane, 1,6-bis(2,3-epoxypropylthio)-2-methyl hexane, 3,8-bis(2,3-epoxypropylthio)-3,6-dithiaoctane, 1,2,3-tris(2,3-epoxypropylthio) propane, 2,2-bis(2,3-epoxypropylthio)-1,3-bis(2,3-epoxypropylthiomethyl) propane, 2,2-bis(2,3-epoxypropylthiomethyl)-1-(2,3-epoxypropylthio) butane, 1,5-bis(2,3-epoxypropylthio)-2-(2,3-epoxypropylthiomethyl)-3-thiapentane, 1,5-bis(2,3-epoxypropylthio)-2,4-bis(2,3-epoxypropylthiomethyl)-3-thiapentane, 1-(2,3-epoxypropylthio)-2,2-bis(2,3-

epoxypropylthiomethyl)-4-thiahexane, 1,5,6-tris(2,3-epoxypropylthio)-4-(2,3-
 epoxypropylthiomethyl)-3-thiahexane, 1,8-bis(2,3-epoxypropylthio)-4-(2,3-
 epoxypropylthiomethyl)-3,6-dithiaoctane, 1,8-bis(2,3-epoxypropylthio)-4,5-bis(2,3-
 epoxypropylthiomethyl)-3,6-dithiaoctane, 1,8-bis(2,3-epoxypropylthio)-4,4-bis(2,3-
 epoxypropylthiomethyl)-3,6-dithiaoctane, 1,8-bis(2,3-epoxypropylthio)-2,5-bis(2,3-
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 epoxypropylthiomethyl)-3,6-dithiaoctane, 1,1,1-tris[[2-(2,3-epoxypropylthio)ethyl]thiomethyl]-2-
 (2,3-epoxypropylthio) ethane, 1,1,2-tetrakis[[2-(2,3-epoxypropylthio)ethyl]thiomethyl] ethane,
 1,11-bis(2,3-epoxypropylthio)-4,8-bis(2,3-epoxypropylthiomethyl)-3,6,9-trithiaundecane, 1,11-
 bis(2,3-epoxypropylthio)-4,7-bis(2,3-epoxypropylthiomethyl)-3,6,9-trithiaundecane, and 1,11-
 bis(2,3-epoxypropylthio)-5,7-bis(2,3-epoxypropylthiomethyl)-3,6,9-trithiaundecane;
 cyclic aliphatic 2,3-epoxypropylthio compounds such as 1,3-bis(2,3-epoxypropylthio) cyclohexane,
 1,4-bis(2,3-epoxypropylthio) cyclohexane, 1,3-bis(2,3-epoxypropylthiomethyl) cyclohexane, 1,4-
 bis(2,3-epoxypropylthiomethyl) cyclohexane, 2,5-bis(2,3-epoxypropylthiomethyl)-1,4-dithiane,
 2,5-bis[[2-(2,3-epoxypropylthio)ethyl]thiomethyl]-1,4-dithiane, and 2,5-bis(2,3-
 epoxypropylthiomethyl)-2,5-dimethyl-1,4-dithiane; and
 aromatic 2,3-epoxypropylthio compounds such as 1,2-bis(2,3-epoxypropylthio) benzene, 1,3-
 bis(2,3-epoxypropylthio) benzene, 1,4-bis(2,3-epoxypropylthio) benzene, 1,2-bis(2,3-
 epoxypropylthiomethyl) benzene, 1,3-bis(2,3-epoxypropylthiomethyl) benzene, 1,4-bis(2,3-
 epoxypropylthiomethyl) benzene, bis[4-(2,3-epoxypropylthio)phenyl] methane, 2,2-bis[4-(2,3-
 epoxypropylthio)phenyl] propane, bis[4-(2,3-epoxypropylthio)phenyl] sulfide, bis[4-(2,3-
 epoxypropylthio)phenyl] sulfone, and 4,4'-bis(2,3-epoxypropylthio) biphenyl.

[0028]

Examples of the oxetanyl compound include 3-ethyl-3-hydroxymethyl oxetane, 1,4-
 bis{[(3-ethyl-3-oxetanyl)methoxy]methyl} benzene, 3-ethyl-3-(phenoxymethyl) oxetane, di[1-
 ethyl-(3-oxetanyl)]methyl ether, 3-ethyl-3-(2-ethylhexyloxymethyl) oxetane, and phenol novolac
 oxetane.

[0029]

Examples of the thietanyl compound include 1-{4-(6-mercaptomethylthio)-1,3-dithianylthio}-3-{2-(1,3-dithietanyl)}methyl-7,9-bis(mercaptomethylthio) 2,4,6,10-tetrathiaundecane, 1,5-bis{4-(6-mercaptomethylthio)-1,3-dithianylthio}-3-{2-(1,3-dithietanyl)}methyl-2,4-dithiapentane, 4,6-bis[3-{2-(1,3-dithietanyl)}methyl-5-mercapto-2,4-dithiapentylthio]-1,3-dithiane, 3-{2-(1,3-dithietanyl)}methyl-7,9-bis(mercaptomethylthio)-1,11-dimercapto-2,4,6,10-tetrathiaundecane, 9-{2-(1,3-dithietanyl)}methyl-3,5,13,15-tetrakis(mercaptomethylthio)-1,17-dimercapto-2,6,8,10,12,16-hexathiaheptadecane, 3-{2-(1,3-dithietanyl)}methyl-7,9,13,15-tetrakis(mercaptomethylthio)-1,17-dimercapto-2,4,6,10,12,16-hexathiaheptadecane, 3,7-bis{2-(1,3-dithietanyl)}methyl-1,9-dimercapto-2,4,6,8-tetrathianonane, 4,5-bis[1-{2-(1,3-dithietanyl)}-3-mercapto-2-thiapropylthio]-1,3-dithiolane, 4-[1-{2-(1,3-dithietanyl)}-3-mercapto-2-thiapropylthio]-5-{1,2-bis(mercaptomethylthio)-4-mercapto-3-thiabutylthio}-1,3-dithiolane, and 4-{4-(5-mercaptomethylthio-1,3-dithiolanyl)thio}-5-[1-{2-(1,3-dithietanyl)}-3-mercapto-2-thiapropylthio]-1,3-dithiolane.

[0030]

Examples of the (meth)acryloyl compound include diacryloyl compounds such as ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, cyclohexanedimethanol diacrylate, alkoxyated hexanediol diacrylate, neopentyl glycol diacrylate, caprolactone modified neopentyl glycol hydroxypivalate diacrylate, cyclohexane dimethanol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, bisphenol A diacrylate, ethoxyated bisphenol A diacrylate, hydroxypivalaldehyde modified trimethylolpropane diacrylate, neopentyl glycol diacrylate, polyethylene glycol diacrylate, propoxyated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecane dimethanol diacrylate, triethylene glycol diacrylate, and tripropylene glycol diacrylate; triacryloyl compounds such as glycerol triacrylate, ethoxyated trimethylolpropane triacrylate, pentaerythritol triacrylate, propoxyated glyceryl triacrylate, propoxyated trimethylolpropane triacrylate, and tris(2-hydroxyethyl) isocyanurate triacrylate; and

tetraacryloyl compounds such as ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated pentaerythritol tetraacrylate, pentaerythritol tetraacrylate, and caprolactone-modified dipentaerythritol hexaacrylate.

[0031]

Examples of the (meth)allyl compound include allyl carbonate compounds such as diethylene glycol bisallyl carbonate, dipropylene glycol bisallyl carbonate, triethylene glycol bisallyl carbonate, tetraethylene glycol bisallyl carbonate, neopentyl glycol bisallyl carbonate, 1,3-propanediol bisallyl carbonate, 1,4-butanediol bisallyl carbonate, 1,5-pentanediol bisallyl carbonate, 1,6-hexanediol bisallyl carbonate, and neopentyl glycol bisallyl carbonate, allyl carbonate bodies such as trimethylolpropane, pentaerythritol, diglycerol, ditrimethylolpropane, and dipentaerythritol, (meth)allyl ether compounds such as trimethylolpropane di(meth)allyl ether, pentaerythritol tri(meth)allyl ether, and glycerine mono(meth)allyl ether, (meth)allyl ester compounds such as (meth)allyl acrylate, di(meth)allyl maleate, di(meth)allyl fumarate, and diallyl phthalate, and triallyl isocyanurate.

[0032]

Examples of the alkene compound include ethylene, propylene, isobutylene, styrene, and divinylbenzene.

[0033]

Examples of the alkyne compound include hydrocarbon-based alkynes such as 2-butyne, 2-pentyne, 2-hexyne, 3-hexyne, 2-heptyne, 3-heptyne, 2-octyne, 3-octyne, 4-octyne, diisopropyl acetylene, 2-nonyne, 3-nonyne, 4-nonyne, 5-nonyne, 2-decyne, 3-decyne, 4-decyne, 5-decyne, di-tert-butyl acetylene, diphenyl acetylene, dibenzyl acetylene, methyl-iso-propyl acetylene, methyl-tert-butyl acetylene, ethyl-iso-propyl acetylene, ethyl-tert-butyl acetylene, n-propyl-iso-propyl acetylene, n-propyl-tert-butyl acetylene, phenyl methyl acetylene, phenyl ethyl acetylene, phenyl-n-propyl acetylene, phenyl-iso-propyl acetylene, phenyl-n-butyl acetylene, and phenyl-tert-butylacetylene; and

alkynyl alcohols such as acetylene diol, propinol, butynol, pentynol, hexynol, hexynediol, heptynol, heptynediol, octynol, and octynediol, and alkynyl amines in which some or all OH groups of the alkynyl alcohols have been substituted with NH₂ groups.

[0034]

Examples of the di- or higher functional active hydrogen compound include a poly(thi)ol compound having two or more hydroxyl groups or mercapto groups, a polyamine compound having two or more amino groups or secondary amino groups, and a polycarboxylic acid compound having two or more carboxyl groups. In addition, a compound having two or more active hydrogen groups selected from a hydroxyl group, a mercapto group, an amino group, a secondary amino group, and a carboxyl group in one molecule can also be exemplified. Two or more active hydrogen groups may be the same as or different from each other.

[0035]

Among the poly(thi)ol compounds (here, alcohol used as a solvent is not included), examples of the polyol compound include aliphatic polyols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, butylene glycol, neopentyl glycol, glycerin, trimethylol ethane, trimethylol propane, ditrimethylol propane, butanetriol, 1,2-methyl glucoside, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, erythritol, threitol, ribitol, arabinitol, xylitol, allitol, mannitol, dulcitol, iditol, glycol, inositol, hexanetriol, triglycerose, diglylperol, triethylene glycol, polyethylene glycol, tris(2-hydroxyethyl) isocyanurate, cyclobutanediol, cyclopentane diol, cyclohexane diol, cycloheptane diol, cyclooctane diol, cyclohexane dimethanol, hydroxypropyl cyclohexanol, tricyclo[5.2.1.0^{2,6}]decane-dimethanol, bicyclo[4.3.0]-nonanediol, dicyclohexanediol, tricyclo[5.3.1.1]dodecanediol, bicyclo[4.3.0]nonanedimethanol, tricyclo[5.3.1.1] dodecane-diethanol, hydroxypropyl tricyclo[5.3.1.1]dodecanol, spiro[3.4]octanediol, butyl cyclohexanediol, 1,1'-bicyclohexylidenediol, cyclohexanetriol, maltitol, and lactose; aromatic polyols such as dihydroxynaphthalene, trihydroxynaphthalene, tetrahydroxynaphthalene, dihydroxybenzene, benzenetriol, biphenyl tetraol, pyrogallol, (hydroxynaphthyl) pyrogallol,

trihydroxyphenanthrene, bisphenol A, bisphenol F, xylylene glycol, di(2-hydroxyethoxy) benzene, bisphenol A-bis-(2-hydroxyethylether), tetrabromobisphenol A, and tetrabromobisphenol A-bis-(2-hydroxyethylether);

halogenated polyols such as dibromoneopentyl glycol; and

polymeric polyols such as an epoxy resin. In the present embodiment, at least one type selected from these can be used in combination.

[0036]

Additionally, examples of the polyol compound include fused reaction products of an organic acid such as oxalic acid, glutamic acid, adipic acid, acetic acid, propionic acid, cyclohexanecarboxylic acid, β -oxocyclohexanepropionic acid, dimer acid, phthalic acid, isophthalic acid, salicylic acid, 3-bromopropionic acid, 2-bromoglycol, dicarboxycyclohexane, pyromellitic acid, butanetetracarboxylic acid, or bromophthalic acid with the above-described polyols;

addition reaction products of the above-described polyols with an alkylene oxide such as ethylene oxide or propylene oxide;

addition reaction product of an alkylenepolyamine with an alkylene oxide such as ethylene oxide or propylene oxide;

bis-[4-(hydroxymethyl)phenyl] sulfide, bis-[4-(2-hydroxypropoxy)phenyl] sulfide, bis-[4-(2,3-dihydroxypropoxy)phenyl] sulfide, bis-[4-(4-hydroxycyclohexyloxy)phenyl] sulfide, bis-[2-methyl-4-(hydroxyethoxy)-6-butylphenyl] sulfide, and compounds obtained by adding three or less molecules on average of ethylene oxide and/or propylene oxide per hydroxyl group to these compounds; and

polyols containing a sulfur atom such as di-(2-hydroxyethyl) sulfide, 1,2-bis-(2-hydroxyethylmercapto) ethane, bis(2-hydroxyethyl) disulfide, 1,4-dithiane-2,5-diol, bis(2,3-dihydroxypropyl) sulfide, tetrakis(4-hydroxy-2-thiabutyl) methane, bis(4-hydroxyphenyl) sulfone (bisphenol S), tetrabromobisphenol S, tetramethyl bisphenol S, 4,4'-thiobis(6-tert-butyl-3-methylphenol), and 1,3-bis(2-hydroxyethylthioethyl)-cyclohexane. In the present embodiment, at

least one type selected from these can be used in combination.

[0037]

Examples of the polythiol compound include aliphatic polythiol compounds such as methanedithiol, 1,2-ethanedithiol, 1,2,3-propanetrithiol, 1,2-cyclohexanedithiol, bis(2-mercaptoethyl) ether, tetrakis(mercaptomethyl) methane, diethylene glycol bis(2-mercaptoacetate), diethylene glycol bis(3-mercaptopropionate), ethylene glycol bis(2-mercaptoacetate), ethylene glycol bis(3-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), trimethylolethane tris(2-mercaptoacetate), trimethylolethane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), bis(mercaptomethyl) sulfide, bis(mercaptomethyl) disulfide, bis(mercaptoethyl) sulfide, bis(mercaptoethyl) disulfide, bis(mercaptopropyl) sulfide, bis(mercaptomethylthio) methane, bis(2-mercaptoethylthio) methane, bis(3-mercaptopropylthio) methane, 1,2-bis(mercaptomethylthio) ethane, 1,2-bis(2-mercaptoethylthio) ethane, 1,2-bis(3-mercaptopropylthio) ethane, 1,2,3-tris(mercaptomethylthio) propane, 1,2,3-tris(2-mercaptoethylthio) propane, 1,2,3-tris(3-mercaptopropylthio) propane, 4-mercaptomethyl-1,8-dimercapto-3,6-dithiaoctane, 5,7-mercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, tetrakis(mercaptomethylthiomethyl) methane, tetrakis(2-mercaptoethylthiomethyl) methane, tetrakis(3-mercaptopropylthiomethyl) methane, bis(2,3-mercaptopropyl) sulfide, 2,5-dimercaptomethyl-1,4-dithiane, 2,5-dimercapto-1,4-dithiane, 2,5-dimercaptomethyl-2,5-dimethyl-1,4-dithiane, and esters of these thioglycolic acid and mercaptopropionic acid, hydroxymethyl sulfide bis(2-mercaptoacetate), hydroxymethyl sulfide bis(3-mercaptopropionate), hydroxyethyl sulfide bis(2-mercaptoacetate), hydroxyethyl sulfide bis(3-mercaptopropionate), hydroxymethyl disulfide bis(2-mercaptoacetate), hydroxymethyl disulfide bis(3-mercaptopropionate), hydroxyethyl disulfide bis(2-mercaptoacetate), hydroxyethyl disulfide bis(3-mercaptopropionate), 2-mercaptoethyl ether bis(2-mercaptoacetate), 2-mercaptoethyl ether bis(3-mercaptopropionate), thiodiglycolic acid bis(2-mercaptoethylester),

thiodipropionic acid bis(2-mercaptoethylester), dithiodiglycolic acid bis(2-mercaptoethyl ester), dithiodipropionic acid bis(2-mercaptoethylester), 1,1,3,3-tetrakis(mercaptomethylthio) propane, 1,1,2,2-tetrakis(mercaptomethylthio) ethane, 4,6-bis(mercaptomethylthio)-1,3-dithiane, tris(mercaptomethylthio) methane, and tris(mercaptoethylthio) methane;

aromatic polythiol compounds such as 1,2-dimercaptobenzene, 1,3-dimercaptobenzene, 1,4-dimercaptobenzene, 1,2-bis(mercaptomethyl) benzene, 1,3-bis(mercaptomethyl) benzene, 1,4-bis(mercaptomethyl) benzene, 1,2-bis(mercaptoethyl) benzene, 1,3-bis(mercaptoethyl) benzene, 1,4-bis(mercaptoethyl) benzene, 1,3,5-trimercaptobenzene, 1,3,5-tris(mercaptomethyl) benzene, 1,3,5-tris(mercaptomethyleneoxy) benzene, 1,3,5-tris(mercaptoethyleneoxy) benzene, 2,5-toluenedithiol, 3,4-toluenedithiol, 1,5-naphthalenedithiol, and 2,6-naphthalenedithiol; and

heterocyclic polythiol compounds such as 2-methylamino-4,6-dithiol-sym-triazine, 3,4-thiophene dithiol, bismuthiol, 4,6-bis(mercaptomethylthio)-1,3-dithiane, and 2-(2,2-bis(mercaptomethylthio)ethyl)-1,3-dithietane.

[0038]

Examples of the polyamine compound include primary polyamine compounds such as ethylene diamine, 1,2-, or 1,3-diaminopropane, 1,2-, 1,3-, or 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-aminooctane, 1,10-diaminodecane, 1,2-, 1,3-, or 1,4-diaminocyclohexane, o-, m- or p-diaminobenzene, 3,4- or 4,4'-diaminobenzophenone, 3,4- or 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfide, 3,3'- or 4,4'-diaminodiphenylsulfone, 2,7-aminofluorene, 1,5-, 1,8-, or 2,3-diaminonaphthalene, 2,3-, 2,6-, or 3,4-diaminopyridine, 2,4- or 2,6-diaminotoluene, m-, or p-xylylenediamine, isophoronediamine, diaminomethylbicycloheptane, 1,3- or 1,4-diaminomethylcyclohexane, 2- or 4-aminopiperidine, 2- or 4-aminomethylpiperidine, 2- or 4-aminoethylpiperidine, N-aminoethylmorpholine, and N-aminopropylmorpholine;

monofunctional secondary amine compounds such as diethylamine, dipropylamine, di-n-butylamine, di-sec-butylamine, diisobutylamine, di-n-pentylamine, di-3-pentylamine, dihexylamine, dioctylamine, di(2-ethylhexyl)amine, methylhexylamine, diallylamine, N-

methylallylamine, piperidine, pyrrolidine, diphenylamine, N-methylamine, N-ethylamine, dibenzylamine, N-methylbenzylamine, N-ethylbenzylamine, dicyclohexylamine, N-methylaniline, N-ethylaniline, dinaphthylamine, 1-methylpiperazine, and morpholine; and

secondary polyamine compounds such as N,N'-dimethylethylenediamine, N,N'-dimethyl-1,2-diaminopropane, N,N'-dimethyl-1,3-diaminopropane, N,N'-dimethyl-1,2-diaminobutane, N,N'-dimethyl-1,3-diaminobutane, N,N'-dimethyl-1,4-diaminobutane, N,N'-dimethyl-1,5-diaminopentane, N,N'-dimethyl-1,6-diaminohexane, N,N'-dimethyl-1,7-diaminoheptane, N,N'-diethylethylenediamine, N,N'-diethyl-1,2-diaminopropane, N,N'-diethyl-1,3-diaminopropane, N,N'-diethyl-1,2-diaminobutane, N,N'-diethyl-1,3-diaminobutane, N,N'-diethyl-1,4-diaminobutane, N,N'-diethyl-1,5-diaminopentane, N,N'-diethyl-1,6-diaminohexane, N,N'-diethyl-1,7-diaminoheptane, piperazine, 2-methylpiperazine, 2,5-dimethylpiperazine, 2,6-dimethylpiperazine, homopiperazine, 1,1-di-(4-piperidyl)methane, 1,2-di-(4-piperidyl)ethane, 1,3-di-(4-piperidyl)propane, 1,4-di-(4-piperidyl)butane, and tetramethylguanidine.

[0039]

Examples of the polycarboxylic acid compound include succinic acid, adipic acid, sebacic acid, azelaic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, orthophthalic acid, phthalic anhydride, tetrahydrophthalic acid, hexahydrophthalic acid, naphthalene dicarboxylic acid, biphenyl dicarboxylic acid, dimer acid, trimellitic acid, pyromellitic acid, and ϵ -caprolactone.

[0040]

Examples of the acid anhydride include succinic anhydride, phthalic anhydride, maleic anhydride, tetrabromophthalic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, and dodecylsuccinic anhydride.

The above polymerization reactive compounds may be used alone or two or more types thereof may be used in combination.

[0041]

The polymerization reactive compound included in the composition of the present embodiment will be described in more detail below. The polymerization reactive compound can

be classified into (Group A) and (Group B) according to reactivity.

[0042]

(Group A): a polyiso(thio)cyanate compound, a (thio)epoxy compound, an oxetanyl compound, a thietanyl compound, a (meth)acryloyl compound, an alkene compound, or an alkyne compound can be classified into (Group A) as a self-polymerizable or copolymerizable compound. Here, the following (Group B) is not included in (Group A).

[0043]

(Group B): a di- or higher functional active hydrogen compound which is a poly(thi)ol compound, a polyamine compound, or a polycarboxylic acid compound, or an acid anhydride can be classified into (Group B) as an addition-polymerizable compound. Here, the above (Group A) is not included in (Group B).

[0044]

In a case where the polymerization reactive compound is used alone, any one type selected from (Group A) or (Group B) is selected. In a case where the polymerization reactive compound is used alone (one type), one type selected from (Group A) which is a self-polymerizable or copolymerizable compound is more easily cured than one type selected from (Group B) which is an addition-polymerizable compound, and thus this is preferable.

[0045]

In a case where two or more polymerization reactive compounds are used, a method of mixing two or more types selected from only (Group A), two or more types selected from only (Group B), or one or more types selected from (Group A) and one or more types selected from (Group B) can be exemplified.

[0046]

In the present embodiment, as a polymerization reactive compound, a polyiso(thio)cyanate compound in (Group A), and a di- or higher functional active hydrogen compound in (Group B) can be used.

[0047]

The polyiso(thio)cyanate compound classified into a self-polymerizable or copolymerizable compound tends to have lower self-polymerizability than other compounds classified into (Group A) or lower reactivity of copolymerization with (Group A) compounds, and if selecting conditions, a self-polymerization reaction type polymer such as a 1-nylon type polymer or an isocyanurate type polymer is obtained in some cases. Also, in the copolymerization with a (thio)epoxy compound, an ethylene carbonate type copolymerization polymer is obtained in some cases.

[0048]

Even in the case of selecting two or more types from only the addition-polymerizable (Group B), in general, polymerization is difficult, but in a case where an acid anhydride and a poly(thi)ol compound are used in combination, in a case where an acid anhydride and a polyamine compound are used in combination, or in a case where three types of acid anhydride, poly(thi)ol compound, and polyamine compound are used in combination, there is a tendency that polymerization reaction is likely to proceed, and a curable resin is obtained. The blending ratio between acid anhydride and poly(thi)ol or polyamine is within a range of about 8/2 to 2/8, preferably within a range of 6/4 to 4/6, and more preferably within a range of range of 55/45 to 45/55, in the functional group molar ratio of the acid anhydride group of an acid anhydride/the mercapto group of poly(thi)ol (or amino group of polyamine).

[0049]

The blending ratio in a case where both (Group A) and (Group B) are used is within a range of about 999/1 to 1/9, preferably within a range of 99/1 to 10/90, more preferably within a range of 9/1 to 3/7, and most preferably within a range of 7/3 to 4/6, when expressed in the functional group molar ratio of the polymerizable functional group of (Group A)/the polymerizable functional group of (Group B).

[0050]

With respect to 100 parts by weight of the polymerization reactive compound (c), the polymerizable composition for optical materials of the present embodiment may contain 0.01 to 50

parts by weight of the polymer composition (a), preferably 0.05 to 20 parts by weight, and more preferably 0.1 to 10 parts by weight of the polymer composition (a), and may contain 0.0001 to 5 parts by weight of the compound (b), preferably 0.001 to 1 part by weight, and more preferably 0.005 to 0.5 parts by weight. These numerical ranges may be appropriately combined.

[0051]

[Other Components such as Additives]

The polymerizable composition of the present embodiment may include components other than the polymerization reactive compound described above. Examples thereof include a monofunctional iso(thio)cyanate compound, a monofunctional (thio)epoxy compound, a monofunctional oxetanyl compound, a monofunctional thietanyl compound, a monofunctional (meth)acryloyl compound having one functional group arbitrarily selected from a methacryloyloxy group, an acryloyloxy group, a methacryloylthio group, an acryloylthio group, a methacrylamide group, and an acrylamide group, a monofunctional alkene compound having one polymerizable carbon-carbon double bond other than a methacryloyloxy group, an acryloyloxy group, a methacryloyloxythio group, an acryloylthio group, a methacrylamide group, and an acrylamide group, a monofunctional alcohol compound other than alcohols used as a solvent, a monofunctional thiol compound, a monofunctional amine compound having one functional group arbitrarily selected from an amino group and a secondary amino group, a monofunctional carboxylic acid compound having one carboxyl group, a solvent, and water.

[0052]

In the process for producing a molded body by cast-polymerizing the composition of the present embodiment, as necessary, in the case of being cured by heat, a polymerization catalyst or a thermal polymerization initiator is added, and in the case of being cured by radiation other than infrared rays (heat), such as ultraviolet rays, a photopolymerization initiator is added.

[0053]

Examples of the polymerization catalyst include Lewis acid, amine, a tertiary amine compound and an inorganic acid salt or an organic acid salt thereof, a metal compound, a

quaternary ammonium salt, and an organic sulfonic acid.

[0054]

The amount of polymerization catalyst used is preferably within a range of 5 ppm to 15% by weight, more preferably within a range of 10 ppm to 10% by weight, and still more preferably within a range of 50 ppm to 3% by weight, with respect to the polymerizable composition.

Examples of the metal compound used as a polymerization catalyst include dimethyl tin chloride, dibutyl tin chloride, and dibutyl tin laurate.

Examples of the thermal polymerization initiator used include ketone peroxide compounds such as methyl isobutyl ketone peroxide and cyclohexanone peroxide; diacyl peroxide compounds such as isobutyryl peroxide, o-chlorobenzoyl peroxide, and benzoyl peroxide;

dialkyl peroxide compounds such as tris(t-butylperoxy) triazine and t-butyl cumyl peroxide;

peroxyketal compounds such as 1,1-di(t-hexylperoxy) cyclohexane, 2,2-bis(4,4-di-t-butylperoxycyclohexyl) propane, and 2,2-di(t-butylperoxy) butane;

alkyl perester compounds such as α -cumylperoxyneodecanoate, t-butylperoxypivalate, 2,4,4-trimethylphenylperoxy-2-ethyl hexanoate, t-butylperoxy-2-ethyl hexanoate, and t-butylperoxy-3,5,5-trimethyl hexanoate; and

peroxycarbonate compounds such as di-3-methoxybutyl peroxydicarbonate, bis(4-t-butylcyclohexyl) peroxydicarbonate, t-butyl peroxyisopropyl carbonate, and diethylene glycol bis(t-butylperoxycarbonate).

[0055]

Examples of the photopolymerization initiator used include a photoradical polymerization initiator, a photocationic polymerization initiator, and a photoanionic polymerization initiator, and among these photopolymerization initiators, a photoradical polymerization initiator is preferable.

[0056]

Examples of the photoradical polymerization initiator include Irgacure 127 (manufactured by BASF Corp.), Irgacure 651 (manufactured by BASF Corp.), Irgacure 184 (manufactured by BASF Corp.), Darocure 1173 (manufactured by BASF Corp.), benzophenone, 4-phenyl benzophenone, Irgacure 500 (manufactured by BASF Corp.), Irgacure 2959 (manufactured by BASF Corp.), Irgacure 907 (manufactured by BASF Corp.), Irgacure 369 (manufactured by BASF Corp.), Irgacure 1300 (manufactured by BASF Corp.), Irgacure 819 (manufactured by BASF Corp.), Irgacure 1800 (manufactured by BASF Corp.), Darocure TPO (manufactured by BASF Corp.), Darocure 4265 (manufactured by BASF Corp.), Irgacure OXE01 (manufactured by BASF Corp.), Irgacure OXE02 (manufactured by BASF Corp.), Esacure KT55 (manufactured by Lamberti S.p.A.), Esacure ONE (manufactured by Lamberti S.p.A.), Esacure KIP150 (manufactured by Lamberti S.p.A.), Esacure KIP100F (manufactured by Lamberti S.p.A.), Esacure KT37 (manufactured by Lamberti S.p.A.), Esacure KTO46 (manufactured by Lamberti S.p.A.), Esacure 1001M (manufactured by Lamberti S.p.A.), Esacure KIP/EM (manufactured by Lamberti S.p.A.), Esacure DP250 (manufactured by Lamberti S.p.A.), Esacure KB1 (manufactured by Lamberti S.p.A.), and 2,4-diethyl thioxanthone.

[0057]

Among these photoradical polymerization initiators, Irgacure 127 (manufactured by BASF Corp.), Irgacure 184 (manufactured by BASF Corp.), Darocur 1173 (manufactured by BASF Corp.), Irgacure 500 (manufactured by BASF Corp.), Irgacure 819 (manufactured by BASF Corp.), Darocur TPO (manufactured by BASF Corp.), Esacure ONE (manufactured by Lamberti S.p.A.), Esacure KIP100F (manufactured by Lamberti S.p.A.), Esacure KT37 (manufactured by Lamberti S.p.A.), or Esacure KTO46 (manufactured by Lamberti S.p.A.) is preferable.

[0058]

Examples of the photocationic polymerization initiator include Irgacure 250 (manufactured by BASF Corp.), Irgacure 784 (manufactured by BASF Corp.), Esacure 1064 (manufactured by Lamberti S.p.A.), CYRAURE UVI6990 (manufactured by Union Carbide Corporation Japan), ADEKA OPTOMER SP-172 (manufactured by ADEKA CORPORATION),

ADEKA OPTOMER SP-170 (manufactured by ADEKA CORPORATION), ADEKA OPTOMER SP-152 (manufactured by ADEKA CORPORATION), and ADEKA OPTOMER SP-150 (manufactured by ADEKA CORPORATION).

[0059]

In a case where the above-described photopolymerization initiator is used, a photopolymerization accelerator may be used in combination. Examples of the photopolymerization accelerator include 2,2-bis(2-chlorophenyl)-4,5'-tetraphenyl-2'H-<1,2'>biimidazolyl, tris(4-dimethylaminophenyl) methane, 4,4'-bis(dimethylamino) benzophenone, 2-ethylanthraquinone, and camphorquinone.

[0060]

The amount of the photopolymerization initiator and the thermal polymerization initiator used is preferably within a range of 0.1% to 20% by weight, more preferably within a range of 0.5% to 10% by weight, and still more preferably within a range of 1% to 5% by weight, in the polymerizable composition.

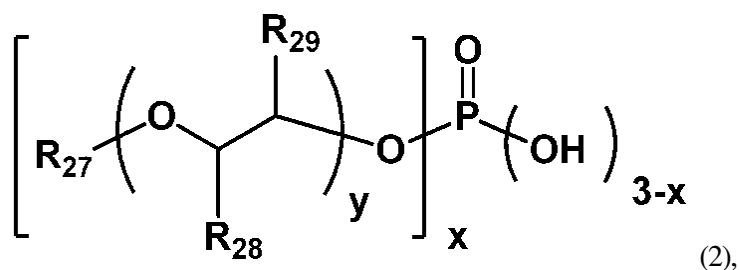
In the process for producing a molded body by cast-polymerizing the composition of the present embodiment, as necessary, an internal mold release agent may be added.

[0061]

An acidic phosphoric ester can be used as the internal mold release agent. Examples of the acidic phosphoric ester include a phosphoric monoester and a phosphoric diester, and the acidic phosphoric ester can be used alone or in a mixture of two or more types thereof.

The acidic phosphoric ester used as the internal mold release agent can be represented by General Formula (2).

[0062]



[0063]

In the formula (2), x represents an integer of 1 or 2, y represents an integer of 0 to 18, R₂₇ represents an alkyl group having 1 to 20 carbon atoms, and R₂₈ and R₂₉ each independently represent a hydrogen atom, a methyl group, or an ethyl group. The number of carbon atoms in x is preferably 4 to 20. A plurality of R₂₇'s may be the same as or different from each other, a plurality of R₂₈'s may be the same as or different from each other, or a plurality of R₂₉'s may be the same as or different from each other.

[0064]

As R₂₇ in the formula (2), an organic residue derived from a linear aliphatic compound such as methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tetradecane, or hexadecane, an organic residue derived from a branched aliphatic compound such as 2-methylpropane, 2-methylbutane, 2-methylpentane, 3-methylpentane, 3-ethylpentane, 2-methylhexane, 3-methylhexane, 3-ethylhexane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylheptane, 4-ethylheptane, 4-propylheptane, 2-methyloctane, 3-methyloctane, 4-methyloctane, 3-ethyloctane, 4-ethyloctane, or 4-propyloctane, and an organic residue derived from an alicyclic compound such as cyclopentane, cyclohexane, 1,2-dimethyl cyclohexane, 1,3-dimethyl cyclohexane, and 1,4-dimethyl cyclohexane can be exemplified, and at least one type selected from these can be used. Moreover, the present invention is not limited to these exemplary compounds. As the acidic phosphoric ester, at least one type or a mixture of two or more types can be used.

In the formula (2), y is preferably 0 or 1.

In a case where y is 0, R₂₇ is preferably a linear or branched alkyl group having 4 to 12

carbon atoms, and more preferably a linear alkyl group having 4 to 12 carbon atoms.

In a case where y is 1, R₂₇ is preferably a linear or branched alkyl group having 1 to 20 carbon atoms, and preferably a linear or branched alkyl group having 3 to 12 carbon atoms.

The acidic phosphoric ester can be used as one type or a mixture of two or more types selected from these.

[0065]

As the acidic phosphoric ester, ZelecUN (manufactured by STEPAN Company), an internal mold release agent for MR (manufactured by Mitsui Chemicals, Inc.), JP series manufactured by JOHOKU CHEMICAL CO., LTD., Phosphanol series manufactured by TOHO Chemical Industry Co., Ltd., or AP and DP Series manufactured by DAIHACHI CHEMICAL INDUSTRY CO., LTD. can be used, and ZelecUN (manufactured by Stepan Company) or an internal mold release agent for MR (manufactured by Mitsui Chemicals, Inc.) is more preferable.

[0066]

To prevent changing in quality even in a case where a molded body formed of the curable resin of the present embodiment is exposed to the outside for a long period of time, it is desirable that by further adding an ultraviolet absorbent and a hindered amine-based stabilizer to the composition of the present embodiment, a composition at which weather resistance is imparted is obtained.

[0067]

The ultraviolet absorbent is not particularly limited, and for example, various ultraviolet absorbents such as a benzotriazole-based ultraviolet absorbent, a triazine-based ultraviolet absorbent, a benzophenone-based ultraviolet absorbent, a benzoate-based ultraviolet absorbent, a propanedioic acid ester-based ultraviolet absorbent, and an oxanilide-based ultraviolet absorbent can be used.

[0068]

Specific examples thereof include benzotriazole-based ultraviolet absorbents such as 2-(2H-benzotriazol-2-yl)-4-methyl-6-(3,4,5,6-tetrahydrophthalibizylmethyl)phenol, 2-(2H-

benzotriazol-2-yl)-p-cresol, 2-(2H-benzotriazol-2-yl)-4-tert-butylphenol, 2-(2H-benzotriazol-2-yl)-4,6-di-tert-butylphenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-6-(1-methyl-1-phenylethyl)phenol, 2-(2H-benzotriazol-2-yl)-4-(3-one-4-oxa-dodecyl)-6-tert-butyl-phenol, 2-{5-chloro(2H)-benzotriazol-2-yl}-4-(3-one-4-oxa-dodecyl)-6-tert-butyl-phenol, 2-{5-chloro (2H)-benzotriazol-2-yl}-4-methyl-6-tert-butyl-phenol, 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentyl phenol, 2-{5-chloro(2H)-benzotriazol-2-yl}-4,6-di-tert-butylphenol, 2-(2H-benzotriazol-2-yl)-4-tert-octylphenol, 2-(2H-benzotriazole-2-yl)-4-methyl-6-n-dodecylphenol, octyl 3-[3-tert-butyl-5-(5-chloro-2H-benzotriazol-2-yl)-4-hydroxyphenyl] propionate, 2-ethylhexyl 3-[3-tert-butyl-5-(5-chloro-2H-benzotriazol-2-yl)-4-hydroxyphenyl] propionate, methyl-3-{3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl}propionate, a reaction product of polyethylene glycol 300, product name Viosorb583 (manufactured by KYODO CHEMICAL CO.,LTD.), product name Tinuvin 326 (manufactured by BASF Corp.), product name Tinuvin 384-2 (manufactured by BASF Corp.), product name Tinuvin PS (manufactured by BASF Corp.), product name Seesorb706 (manufactured by SHIPRO KASE KAISHA LTD.), and product name EVERSORB109 (manufactured by Everlight Chemical Industrial Corp.); triazine-based ultraviolet absorbents such as 2-(4-phenoxy-2-hydroxy-phenyl)-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-oxa-hexadesiloxy)-4,6-di(2,4-dimethyl-phenyl)-1,3,5-triazine, 2-(2-hydroxy-4-oxa-heptadesiloxy)-4,6-di(2,4-dimethyl-phenyl)-1,3,5-triazine, 2-(2-hydroxy-4-iso-octyloxy-phenyl)-4,6-di(2,4-dimethyl-phenyl)-1,3,5-triazine, product name Tinuvin 400 (manufactured by BASF Corp.), product name Tinuvin 405 (manufactured by BASF Corp.), product name Tinuvin 460 (manufactured by BASF Corp.), and product name Tinuvin 479 (manufactured by BASF Corp.); benzophenone-based ultraviolet absorbents such as 2-hydroxy-4-n-methoxybenzophenone and 2-hydroxy-4-n-octoxybenzophenone; benzoate-based ultraviolet absorbents such as 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate; propanedioic acid ester-based ultraviolet absorbents such as propanedioic acid-[(4-methoxyphenyl)-methylene]-dimethyl ester, product name Hostavin PR-25 (manufactured by Clariant Japan K.K.), and product Name Hostavin B-CAP (manufactured by

Clariant Japan K.K.); and oxanilide-based ultraviolet absorbents such as 2-ethyl-2'-ethoxy-oxanilide and product Name Sanduvor VSU (manufactured by Clariant Japan K.K.). Among these ultraviolet absorbents, benzotriazole-based ultraviolet absorbents or triazole-based ultraviolet absorbents are preferable.

[0069]

In addition to the compound (b) that will be described below, materials contained inside a microphase separation structural body constituted from the polymer composition (a) may be added to the composition of the present embodiment. Examples of such materials include metal fine particles.

The microphase separation structural body can also act as a dispersant for a substance which is likely to be aggregated in a composition.

[0070]

In some cases, the polymerizable composition for optical materials of the present embodiment includes a partially formed microphase separation structural body of the polymer composition (a) depending on the preparation condition.

[0071]

<Purifying Method of Polymer Composition (a)>

The polymerizable composition for optical materials of the present embodiment can be produced by preparing a purified polymer composition (a). The polymer composition (a) can be purified by dissolving the polymer composition (a) in acetone to prepare a first mixture, adding hexane to the first mixture to prepare a second mixture, stirring the second mixture, separating a hexane phase from the second mixture and removing the hexane phase from the second mixture to prepare a third mixture, and removing volatiles from the third mixture to prepare a purified polymer composition (a). In one embodiment, the polymer composition (a) can be purified by dissolving 5-15 parts of the polymer composition (a) in 20-45 parts of acetone to prepare a first mixture by *e.g.*, stirring/mixing, adding 20-45 parts of hexane to the first mixture to prepare a second mixture, stirring/mixing the second mixture, separating a hexane phase from the second mixture and

removing the hexane phase from the second mixture to prepare a third mixture, and removing volatiles from the third mixture to prepare a purified polymer composition (a). Each of the above steps of the purification process can be performed at any suitable temperature, for example, at 1-30 °C, preferably at 1-25 °C, or more preferably at 15-25 °C.

[0072]

The hexane extraction process can be repeated two or more times to further remove the impurity. Processes of adding fresh hexane to the purified polymer composition (a), stirring the mixture, and separating the hexane phase can be repeated two or more times to ensure the purity of the purified polymer composition (a). In one embodiment, the processes of adding parts of fresh hexane to the purified polymer composition (a), stirring the mixture, and separating the hexane phase can be repeated two times to ensure the purity of the purified polymer composition (a). In one embodiment, the processes of adding parts of fresh hexane to the purified polymer composition (a), stirring the mixture, and separating the hexane phase can be repeated three times to ensure the purity of the purified polymer composition (a).

[0073]

<Production Method of Polymerizable Composition for Optical Materials>

The polymerizable composition for optical materials of the present embodiment can be produced by mixing and stirring the purified polymer composition (a), the compound (b) of which light absorption characteristics vary by sensing changes in environment, the polymerization reactive compound (c) other than the polymer composition (a), and a catalyst, an internal mold release agent, and other additives used as necessary. Depressurization and defoaming may be performed as necessary. The temperature at the time of mixing is typically 25 °C or lower. There are cases in which the temperature is preferably a lower temperature from the viewpoint of a pot life of the polymerizable composition for optical materials. Here, in a case where the solubility of the catalyst, the internal mold release agent, and the additives in the polymerization reactive compound (c) is not good, it is also possible to dissolve by heating in advance.

[0074]

Polymer particles containing the compound (b) are prepared from the polymer composition (a) in a predetermined solvent and the compound (b) of which light absorption characteristics vary by sensing changes in specific environment factors in advance, and after the polymerization reactive compound (c) is mixed therewith, by distilling off the solvent under reduced pressure, a polymerizable composition for optical materials may be prepared.

[0075]

In addition, it is also possible that two or more compounds are used as the polymerization reactive compound (c), some of the polymer composition (a), the compound (b), and the polymerization reactive compound (c) is mixed, and then, the remaining polymerization reactive compound (c) is mixed with the obtained mixture.

In some cases, the polymerizable composition for optical materials of the present embodiment includes a partially formed microphase separation structural body of the polymer composition (a) depending on the preparation condition.

[0076]

<Cured Body>

A cured body can be obtained by polymerizing and curing the polymerizable composition for optical materials of the present embodiment. The cured body of the present embodiment includes a microphase separation structural body of the polymer composition (a) comprised of one or more compounds selected from compounds represented by the formula (1) or (2), the compound (b) of which light absorption characteristics vary by sensing changes in environment; and the resin formed by polymerization of the polymerization reactive compound (c). As the microphase separation structural body, polymer particles (micelle-like particles) having a microphase separation structure configured of the component (a) are exemplified. A cured body including a microphase separation structural body can provide an optical material which is excellent in photochromic characteristics, heat resistance, and mechanical properties.

[0077]

At least some of the compound (b) may be contained inside the microphase separation

structural body configured of the polymer composition (a), and in this case, the above-described effects are particularly excellent. The volume 50% average particle diameter of the polymer particles which are microphase separation structural bodies 1 nm to 1000 nm. The structure can be confirmed by a transmission electron microscope.

[0078]

(Microphase Separation Structure)

The microphase separation structure is described as follows. A block copolymer is a polymer formed of a plurality of different homopolymer subunits linked through a covalent bond. This copolymer portions have physical properties and affinities different with each other. For example, for amphiphilic block copolymers, the copolymer portions tend to separate respectively, due to strong repulsive force, and the copolymers are not mixed as water and oil, and as a result, phase separation occurs. However, since respective copolymer portions are chemically bonded, as in a case where simply two homopolymers are mixed, macroscopic phase separation does not completely occur. On the other hand, in the microphase separation of a block copolymer formed of portions of different copolymers A and B, a microaggregate having a portion in which the copolymer A is rich and a portion in which the copolymer B is rich is formed. As a result, depending on the structure of the block copolymer, some of morphology such as a nano-size spherical polymer micelle can be observed. Details of the microphase separation of such a block copolymer, for example, are described in reference (Chem. Soc. Rev., 2012, 41, 5969-5985). By including the microphase separation structural body such as polymer particles having a microphase separation structure, it is possible to obtain a transparent cured body with low turbidity.

[0079]

(Nanodomain Separation Structure)

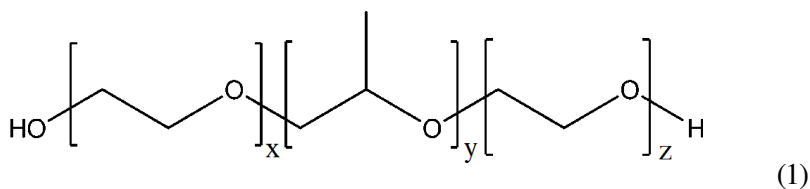
The microphase separation structures as the aggregation of polymers, form nanodomain separation structure, such as Pluronic[®], to make nano-sized particles. By including the nanodomain separation structural body, it is possible to obtain a transparent cured body with low turbidity. Due to the effect obtained by the presence of the nanodomain separation structure on

the functionality of the compound (b), it is supposed that the compound (b) is preferentially, or at least partially, located inside the nanodomain separation structure. The compound (b) expresses better performance (*e.g.*, good coloration and faster fading speed) in the nanodomain separation structures.

[0080]

[Pluronic[®]]

Pluronics[®] are nonionic tri-block copolymers with a central hydrophobic segment of polypropylene oxide (PPG) flanked by two hydrophilic segments of polyethylene oxide (PEG) represented by the following formula (1). They can function as antifoaming agents, wetting agents, dispersants, thickeners, and emulsifiers.



[0081]

One of the characteristics of Pluronic[®] solutions is their temperature dependent selfassembling behavior. At low temperatures and concentrations (below the critical micelle temperature and critical micelle concentration), individual block copolymers (unimers) are present in solution. Above these values, aggregation of individual unimers occurs in a process called micellization. In a hydrophilic environment, the core of the polymeric micelles is made from the insoluble blocks (PPG) while the soluble portion (PEG) forms the shell of the micelles.

[0082]

(Impurity)

The polymer composition (a) may include impurities. The impurities may include polymer structures that have a molecular weight smaller than the molecular weight of the tri-block copolymer. The polymer structures may include, for example, block copolymers with less than three distinct blocks (*e.g.*, mono structure, di-block structure). Examples of the mono structure

include polypropylene oxide (PPG) mono polymer. Examples of the di-block structure include polypropylene oxide/polypropylene oxide (PEG-PPG) di-block copolymers.

[0083]

The production method of the cured body of the present embodiment includes a step of polymerizing and curing the above-described polymerizable composition for optical materials. By the step, specifically, a resin is formed by polymerization of the polymerization reactive compound (c), the polymer composition (a) forms a microphase separation structural body, and a cured body formed of the resin, the microphase separation structural body, and the compound (b) is formed. In the step, by heating or irradiating with radiation such as ultraviolet rays or the like other than infrared rays, the polymerizable composition for optical materials is polymerized and cured, whereby a cured body can be obtained. The polymerization conditions are suitably selected.

[0084]

<Molded Body>

The resin obtained by heat-polymerizing the composition of the present embodiment and the molded body formed of the resin are produced by adding a polymerization reactive compound and as necessary, various additives described above. In addition, a polymerization reactive compound and an additive which are not described in the present disclosure may be added to the composition of the present embodiment may be added within a range not impairing the effects of the present embodiment. The molded body of the present embodiment includes the microphase separation structural body of the polymer composition (a), similarly to the cured body.

[0085]

As the resin configuring the molded body of one embodiment, resins obtained from a liquid polymerizable composition of which casting work is easy are preferable, and among these resins, resins described as the following (a) to (z) are preferable.

(a) a poly(thio)urethane resin obtained by polymerization of a polyiso(thio)cyanate compound and a poly(thi)ol compound, in the present application, a poly(thio)urethane resin means a polyurethane

resin, a polythiourethane resin, or a polydithiourethane resin;

(b) a poly(thio)urea resin obtained by polymerization of a polyisocyanate compound or a polyisothiocyanate compound and a polyamine compound, in the present application, a poly(thio)urea resin means a polyurea resin or a polythiourea resin;

(c) a poly(thio)epoxy resin obtained by polymerization of a (thio)epoxy compound;

(d) a poly(thio)epoxy-poly(thi)ol resin obtained by polymerization of a (thio)epoxy compound and a poly(thi)ol compound;

(e) a poly(thio)epoxy-polyamine resin obtained by polymerization of a (thio)epoxy compound and a polyamine compound;

(f) a poly(thio)epoxy-acid anhydride resin obtained by polymerization of a (thio)epoxy compound and an acid anhydride;

(g) a poly(meth)acryloyl resin obtained by polymerization of a (meth)acryloyl compound;

(h) a poly(meth)acryloyl-poly(thi)ol resin obtained by polymerization of a (meth)acryloyl compound and a poly(thi)ol compound;

(i) a poly(meth)acryl-polyalkene resin obtained by polymerization of a (meth)acryloyl compound and an alkene compound;

(j) a poly(meth)acryl-polyalkyne resin obtained by polymerization of a (meth)acryloyl compound and an alkyne compound;

(k) a poly(meth)acryl-polyamine resin obtained by polymerization of a (meth)acryloyl compound and a polyamine compound;

(l) a polyalkene resin obtained by polymerization of an alkene compound;

(m) a polyalkene-poly(thi)ol resin obtained by polymerization of an alkene compound and a poly(thi)ol compound;

(n) a polyalkene-polyamine resin obtained by polymerization of an alkene compound and a polyamine compound;

(o) a polyalkyne resin obtained by polymerization of an alkyne compound;

(p) a polyalkyne-poly(thi)ol resin obtained by polymerization of an alkyne compound and a

- poly(thi)ol compound;
- (q) a polyalkyne-polyamine resin obtained by polymerization of an alkyne compound and a polyamine compound;
- (r) a polyalkyne-polyalkene resin obtained by polymerization of an alkyne compound and an alkene compound;
- (s) a polyoxetanyl resin obtained by polymerization of an oxetanyl compound;
- (t) a polyoxetanyl-poly(thi)ol resin obtained by polymerization of an oxetanyl compound and a poly(thi)ol compound;
- (u) a polyoxetanyl-polyamine resin obtained by polymerization of an oxetanyl compound and a polyamine compound;
- (v) a polyoxetanyl-acid anhydride resin obtained by polymerization of an oxetanyl compound and an acid anhydride;
- (w) a polythietanyl-poly(thi)ol resin obtained by polymerization of a thietanyl compound and a poly(thi)ol compound;
- (x) a polythietanyl-polyamine resin obtained by polymerization of a thietanyl compound and a polyamine compound;
- (y) a polythietanyl-acid anhydride resin obtained by polymerization of a thietanyl compound and an acid anhydride; and
- (z) mixed resins obtained by copolymerization of two or more selected from (a) to (y).

[0086]

Among the resins of the above-described (a) to (z), as more preferable resins, the resins described in (a) to (i) and (s) to (z) and mixed resins thereof (a mixture of a copolymer and a resin) are exemplified, and as still more preferable resins, the resins described in (a) to (f), (s) to (v), and (z) and mixed resins thereof are exemplified.

[0087]

<Molded Body and Application thereof>

In the present embodiment, by changing the mold shape when polymerizing the

polymerizable composition for optical materials as described above, molded bodies having various shapes and optical materials formed of the molded bodies can be obtained. The molded body of the present embodiment can be molded in a desired shape and can be used as various optical materials by providing a coating layer formed as necessary, other members, or the like.

[0088]

Examples of the optical materials include a plastic lens, a light emitting diode (LED), a prism, an optical fiber, an information recording substrate, and a filter. A plastic lens is particularly suitable. The plastic lens formed of the molded body of the present embodiment will be described below. The plastic lens can be produced in the following manner.

[0089]

<Production Method of Plastic Lens>

The plastic lens of the present embodiment is typically produced by a cast polymerization method using the polymerizable composition for optical materials described above. The production method of the plastic lens of the present embodiment includes, specifically, a step of forming a lens substrate by cast-polymerizing the polymerizable composition for optical materials.

[0090]

In the step, by injecting the obtained composition of the present embodiment into a cavity formed of a glass mold and a gasket or a tape and by heating or irradiating with radiation such as ultraviolet rays or the like other than infrared rays to polymerize and cure the composition, a resin of the present embodiment and a plastic lens substrate formed of the resin are produced. By the step, a resin is formed by polymerization of the polymerization reactive compound (c), the polymer composition (a) forms a microphase separation structural body, and it is possible to obtain a plastic lens substrate formed of the resin, the microphase separation structural body, and the compound (b).

[0091]

In a case where a curable resin of the present embodiment and a plastic lens formed of the resin are produced by heating, for the purpose of preventing polymerization uniformity (striae) by convection, typically, polymerization is conducted by slowly heating from a low temperature.

Since polymerization conditions significantly vary depending on the types and amounts of polymerizable composition for optical materials and the catalyst used, the shape of the mold, and the like, the polymerization conditions are not limited, but, approximately, polymerization is performed at a temperature of -50 °C to 150 °C for 1 hour to 50 hours. Depending on cases, the polymerizable composition is preferably held in a temperature range of 10 °C to 150 °C or slowly heated and cured for 1 to 25 hours.

[0092]

Similarly, even in a case where polymerization is performed by radiation such as UV, to prevent polymerization uniformity (striae) by convection, typically, polymerization is slowly conducted by dividing irradiation of radiation or reducing illuminance. For the purpose of making convection not further occur, a dual cure system in which by cooling overnight after a uniform polymerizable reactive composition is injected into a cavity, a state in which convection is less likely to occur is formed, and the semi-cured composition which has become a uniform gel state by irradiation with a weak radiation is completely cured by heating is taken in some cases.

[0093]

For the purpose of removing the distortion due to polymerization completion or residual stress, the plastic lens obtained by releasing from the mold may be subjected to a re-heat treatment (annealing) as required. Typically, the heat treatment is performed within a range of 1 to 24 hours at T_g of the obtained plastic lens to $T_g \times 2$ times the temperature. A heat treatment condition of 1 to 16 hours at T_g to $T_g \times 1.5$ times the temperature is more preferable, and a heat treatment condition of 1 to 4 hours at T_g to $T_g \times 1.2$ times the temperature is still more preferable.

[0094]

In a case where a curable resin of the present embodiment and a plastic lens formed of the resin are produced by radiation, as the radiation used, energy rays having a wavelength range within a range of 0.0001 to 800 nm are typically used. The radiation is classified into α rays, β rays, γ rays, X-rays, electron beams, ultraviolet rays, visible light, and the like, and can be suitably selected according to the composition of the mixture and used. Among the radiation, ultraviolet

rays is preferable, and the output peak of ultraviolet rays is preferably within a range of 200 to 450 nm, more preferably within a range of 230 to 445 nm, still more preferably within a range of 240 to 430 nm, and still more preferably within a range of 250 to 400 nm. By using ultraviolet rays within the range of the output peak, defects such as yellowing and thermal deformation at the time of polymerization are small, and it is possible to complete the polymerization in a relatively short period of time even in a case where an ultraviolet absorbent is added.

[0095]

In addition, in a case where an ultraviolet absorbent and a hindered amine-based stabilizer are added in the composition, there is a tendency that ultraviolet rays having an energy output peak of ultraviolet rays within a range of 250 to 280 nm or within a range 370 to 430 nm is preferably used.

[0096]

The curable resin of the present embodiment and the plastic lens formed of the resin obtained in the above manner may be subjected to processing of imparting various functionalities by providing a functional coat layer such as a hard coat, an anti-reflection coat, a dimming coat, a slipperiness-imparting coat or a slipperiness-imparting treatment, or an antistatic coat to the surface, by performing a dyeing treatment for imparting fashionability, by performing a treatment of the surface, the edge, or the like, and by putting a polarizing film in the interior for the purpose of imparting polarizability or attaching a polarizing film to the surface.

[0097]

For the purpose of improving adhesion between the functional coat layer and the substrate, the surface of the obtained curable resin of the present embodiment or the plastic lens formed of the resin can also be subjected to a corona treatment, an ozone treatment, a low-temperature plasma treatment using oxygen gas or nitrogen gas, a glow discharge treatment, an oxidation treatment by chemicals, or a physical or chemical treatment such as a flame treatment.

[0098]

Instead of these treatments or in addition to these treatments, a primer layer formed by a

primer treatment, an undercoat treatment, or an anchor coat treatment may be provided between the surface of the curable resin of the present embodiment or the plastic lens formed of the resin and the outermost layer (air contact surface) formed by the physical or chemical treatment.

[0099]

As the coating agent used in the primer layer, for example, a coating agent which has a resin such as a polyester-based resin, a polyamide-based resin, a polyurethane-based resin, an epoxy-based resin, a phenol-based resin, a (meth)acrylic resin, a polyvinyl acetate resin, a polyolefin-based resin of polyethylene or polypropylene or a copolymer thereof or a modified resin, or a cellulose-based resin as the main component of vehicle can be used. The coating agent may be any one of a solvent type coating agent and an aqueous type coating agent.

[0100]

Among these coating agents, a modified polyolefin-based coating agent, an ethyl vinyl alcohol-based coating agent, a polyethylene imine-based coating agent, a polybutadiene-based coating agent, or a polyurethane-based coating agent;
a polyester-based polyurethane emulsion coating agent, a polyvinyl chloride emulsion coating agent, a urethane acryl emulsion coating agent, a silicon acryl emulsion coating agent, a vinyl acetate acryl emulsion coating agent, or an acryl emulsion coating agent; or
a styrene-butadiene copolymer latex coating agent, an acrylonitrile-butadiene copolymer latex coating agent, a methyl methacrylate-butadiene copolymer latex coating agent, a chloroprene latex coating agent, a rubber-based latex coating agent of polybutadiene latex, a polyacrylic acid ester latex coating agent, a polyvinylidene chloride latex coating agent, a polybutadiene latex coating agent, or a coating agent formed of carboxylic acid-modified product latex or dispersion of a resin included in these latex coating agents is preferable.

[0101]

These coating agents can be applied, for example, by a dip coating method, a spin coating method, or a spray coating method, and the coating amount to a substrate is typically 0.05 g/m^2 to 10 g/m^2 in the dry state.

[0102]

Among these coating agents, a polyurethane-based coating agent is more preferable. The polyurethane-based coating agent is a coating agent having a urethane bond in the main chain or the side chain of the resin included in the coating agent. The polyurethane-based coating agent is, for example, a coating agent including polyurethane obtained by reacting polyol such as polyester polyol, polyether polyol, or acrylic polyol with an isocyanate compound.

[0103]

Among these polyurethane-based coating agents, a polyurethane-based coating agent obtained by mixing polyester polyol such as condensed polyester polyol or lactone-based polyester polyol and an isocyanate compound such as tolylene diisocyanate, hexamethylene diisocyanate, or xylylene diisocyanate is preferable from the viewpoint of excellent adhesion.

[0104]

The method of mixing a polyol compound and an isocyanate compound is not particularly limited. In addition, the blending ratio is also not particularly limited, but if the isocyanate compound is too small, curing defects occur in some cases, and thus, the OH groups of the polyol compound and the NCO groups of the isocyanate compound are preferably within a range of 2/1 to 1.40 in terms of equivalent.

[0105]

The curable resin of the present embodiment may be applied to those other than plastic lenses, and as applications other than plastic lenses, a sheet, a film, and the like produced in the same manner as in plastic lenses using a flat mold are exemplified. The surface of the sheet, the film, or the like formed of the curable resin of the present embodiment may be physically or chemically treated in the same manner as in plastic lenses, and the primer layer described above and the functional outermost layer (air contact surface) formed by a physical or chemical treatment may be laminated.

[0106]

The plastic lens formed of the curable resin of the present embodiment may be a laminate

including the primer layer between the functional outermost layer (air contact surface) formed by a physical or chemical treatment described above and the curable resin surface.

[0107]

The plastic lens of the present embodiment obtained in the above manner can be used in various lens applications such as an eyeglass lens, a camera lens, a pickup lens, a Fresnel lens, a prism lens, and a lenticular lens. Examples of a particularly preferable application among these include an eyeglass lens, a camera lens, and a pickup lens, having a smooth surface.

[0108]

The sheet and the film of the present embodiment obtained in the same manner can be used in various planar member applications requiring high transparency, such as display members including a flat panel and a smart phone panel, film members including a scatter proof film, a specific wavelength-cutting film, and a decorative film, and glass alternative members including building window glass, vehicle window glass, and a mirror.

Examples

[0109]

Hereinafter, the present disclosure will be described in more detail based on Examples, but the disclosure is not intended to be limited to these.

[0110]

[Photochromic Characteristics Test 1]

A molded lens with a thickness of 2.0 mm was colored by a metal halide lamp (180W) as the light source for 15 minutes, providing an ultraviolet intensity of 1.2 mW/cm². The amount of change in light transmittance ($\Delta T\%$ at 550 nm) before and after coloration was measured by an accumulated light quantity meter at a temperature of 23 °C.

Light source: a metal halide lamp light source device "LA-i 80ME" manufactured by HAYASHI WATCH-WORKS

Accumulated light quantity meter: an accumulated light quantity meter "UIT-102 photodetector UVD36SPD)" manufactured by USHIO Inc

Transmission measurement system: "MV-3 150" manufactured by JASCO Corporation

The amount of change in light transmittance $\Delta T\%$ at 550 nm corresponds to the difference in the light transmittance before and after coloration at the wavelength of 550 nm. The half-life fading time ($t_{1/2}$) is defined as the time to recover 50% of the light transmittance $\Delta T\%$ at 550 nm.

[0111]

(Comparative Examples 1, 2, 3)

Preparation Method of Comparative Examples 1, 2, and 3

30.8 mg (684 ppm) of Reversacol Wembley Grey (manufactured by Vivimed) and 16.7 mg (376 ppm) of Reversacol Heath Green (manufactured by Vivimed) as photochromic compounds, 1.0 g (2 parts by weight) of non-purified Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), and 150 mg (3000 ppm) of butoxyethyl acid phosphate were added to 20.35 g (40.7 parts by weight) of metaxylylene diisocyanate, followed by stirring for dissolution using a stirring apparatus. Subsequently, 24.65 g of (49.3 parts by weight) a composition containing 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, and 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane was added thereto and mixed, followed by continuous stirring. 5.0 g (10 parts by weight) of metaxylylene diisocyanate in which 4 mg (80 ppm) of dimethyltin dichloride (manufactured by Sigma-Aldrich Co. LLC.) had been dissolved was added thereto, followed by stirring for 1 hour. After decompressing and degassing was performed in a degree of decompression of 133 to 400 Pa for 40 minutes using a vacuum pump, filtration through a 1 μ m membrane filter was performed, and while stirring, a decompressing and degassing operation was performed for 2 hours until foams disappeared using a vacuum pump. The prepared monomer was charged in a glass mold having a thickness of 2 mm, and resinification was performed by raising the temperature from room temperature to 120°C in an oven to prepare a molded body.

[0112]

(Examples 1, 2, 3)

Preparation Method of Example 1

(Purifying Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic®))(1) A first mixture was prepared by dissolving 8.0 g of Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) in 30 ml of acetone (manufactured by Avantor Performance Materials, LLC) in a separating funnel at room temperature. (2) A second mixture was prepared by adding 30 ml of hexane (manufactured by Avantor Performance Materials, LLC) to the first mixture and agitating the immiscible second mixture for five minutes. (3) A third mixture was prepared by separating a hexane phase from the second mixture and removing the separated hexane phase from the second mixture. (4) Repeated the process (2) using fresh hexane and the process (3) two more times. (5) A purified polymer composition (a) was prepared by removing volatiles from the third mixture using EYELA vacuum oven (manufactured by Tokyo Rikakikai Co., Ltd.) from the third mixture.

[0113]

30.8 mg (684 ppm) of Reversacol Wembley Grey (manufactured by Vivimed) and 16.7 mg (376 ppm) of Reversacol Heath Green (manufactured by Vivimed) as photochromic compounds, 1.0 g (2 parts by weight) of the purified Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), and 150 mg (3000 ppm) of butoxyethyl acid phosphate were added to 20.35 g (40.7 parts by weight) of metaxylylene diisocyanate, followed by stirring for dissolution using a stirring apparatus. Subsequently, 24.65 g of (49.3 parts by weight) a composition containing 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, and 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane was added thereto and mixed, followed by continuous stirring. 5.0 g (10 parts by weight) of metaxylylene diisocyanate in which 4 mg (80 ppm) of dimethyltin dichloride (manufactured by Sigma-Aldrich Co. LLC.) had been dissolved was added thereto, followed by stirring for 1 hour. After decompressing and degassing was performed in a degree of decompression of 133 to 400 Pa for 40 minutes using a vacuum pump, filtration through a 1 µm membrane filter was performed, and while stirring, a decompressing and degassing operation was

performed for 2 hours until foams disappeared using a vacuum pump. The prepared monomer was charged in a glass mold having a thickness of 2 mm, and resinification was performed by raising the temperature from room temperature to 120 °C in an oven to prepare a molded body. This block copolymer-added composition was able to be cast into a mold without having a rapid increase in viscosity in the middle of the process. The measurement results of the photochromic characteristics are shown in Table 3.

[0114]

As the Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), Example 1 includes 1.0 g (2 parts by weight) of Pluronic[®] P85 (manufactured by Sigma-Aldrich[®]), Example 2 includes 1.0 g (2 parts by weight) of Pluronic[®] PE10500 (manufactured by BASF[®] Corp.), and Example 3 includes 1.0 g (2 parts by weight) of Pluronic[®] P123 (manufactured by Sigma-Aldrich[®]).

[0115]

The Pluronics[®] used for one embodiment have the following characteristics shown in Table 1.

[Table 1]

Pluronic [®]	Average MW	PEO%	Structure
P85	4600	50%	(PEG)23-(PPG)43-(PEG)23
PE10500	6500	50%	(PEG)37-(PPG)56-(PEG)37
P123	5800	30%	(PEG)20-(PPG)69-(PEG)20

[0116]

Ratio of PEG/PPG before and after purification calculated from H-NMR is shown in Table 2. The PEG/PPG integration ratio was calculated as follows using the H-NMR spectrums. Figs. 2 and 3 show difference between the H-NMR spectrum before and after the purification of the present disclosure. As shown in Fig. 2, integration of PEG before purification of Pluronic[®]

P85 was calculated as follows:

$$\text{Integration of PEG} = 8.11 - 3 = 5.11$$

$$\text{Integration ratio PEG/PPG} = 5.11/6 = 0.852$$

As shown in Fig. 3, integration of PEG after purification of Pluronic[®] P85 was calculated as follows:

$$\text{Integration of PEG} = 8.38 - 3 = 5.38$$

$$\text{Integration ratio PEG/PPG} = 5.38/6 = 0.897$$

Integrations of PEG before and after purification were calculated similarly for Pluronic[®] P123 (manufactured by Sigma-Aldrich[®]) and Pluronic[®] PE10500 (manufactured by BASF[®]). As shown in Table 2, PEG/PPG ratio increased in all the three Pluronics[®] after purification, indicating high PPG-containing block copolymers which caused lens haziness were removed.

[Table 2]

PEG/PPG ratio (manufacturer)	Before purification	After purification
P85 (Aldrich)	0.852	0.857-0.937 (0.897)
PE10500 (BASF)	0.953	0.958-0.985 (0.972)
P123 (Aldrich)	0.473	0.478-0.584 (0.531)

[0117]

[Table 3]

	Polymer additive			Photochromic Dye				Photochromic characteristics	
Commercial name (manufacturer)	Amount (parts by weight)		Purified?	Name	Amount (ppm)	Haze	Yellow Index	Initial T% (@550 nm)	$\Delta T\%$ (@550 nm)
P85 (Aldrich)	2	Comp Ex 1	No	Reversacol Wembley grey Reversacol Heath green	513 282	0.27	2.71	83.7	69.8
	2	Ex 1	Yes	Reversacol Wembley grey Reversacol Heath green	513 282	0.24	2.60	85.6	71.4
PE10500 (BASF)	2	Comp Ex 2	No	Reversacol Wembley grey Reversacol Heath green	513 282	0.37	2.93	83.7	70.8
	2	Ex 2	Yes	Reversacol Wembley grey Reversacol Heath green	513 282	0.27	2.89	85.0	72.1
P123 (Aldrich)	2	Comp Ex 3	No	Reversacol Wembley grey Reversacol Heath green	513 282	0.61	3.48	86.3	73.8
	2	Ex 3	Yes	Reversacol Wembley grey Reversacol Heath green	513 282	0.51	3.16	86.5	73.8

[0118]

Table 3 shows the photochromic performance of the purified Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol),(Plurionics[®]) in the photochromic compound (b) and the polymerization reactive compound (c) of one embodiment of the present disclosure. As it is shown in Examples 1, 2, and 3, the purified Plurionics[®] P85, PE10500, and P123 exhibited improved Haze value, Yellow Index, Initial T% at 550 nm, and $\Delta T\%$ at 550 nm as compared to the non-purified Plurionics[®] P85, PE10500, and P123 used for the Comparative Examples 1, 2, and 3. From the results, the purification of Plurionics[®] dramatically improved the clarity and performance of the lenses, as it was exhibited in the examples. More specifically, it was found that the poly(thio)urethane resin molded body including the purified Plurionics[®] P85, PE10500, and P123 of the subject embodiment of the present disclosure effectively exhibited a sufficient clarity, and the poly(thio)urethane resin molded body including the purified Plurionics[®] P85, PE10500, and P123 of the subject embodiment of the present disclosure further effectively exhibited the fading speed faster than the fading speed of the poly(thio)urethane resin molded body including non-purified Plurionics[®] P85, PE10500, and P123.

[0119]

[Photochromic Characteristics Test 2]

(Comparative examples 4 and 5)

Preparation Method of Comparative Examples 4 and 5

[0120]

30.8 mg (684 ppm) of Reversacol Wembley Grey (manufactured by Vivimed) and 16.7 mg (376 ppm) of Reversacol Heath Green (manufactured by Vivimed) as photochromic compounds, 1.0 g (2 parts by weight) of the non-purified Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), and 150 mg (3000 ppm) of butoxyethyl acid phosphate were added to 25.35 g (50.7 parts by weight) of a 2,5-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane and 2,6-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, followed by stirring for dissolution using a stirring apparatus.

Subsequently, 11.95 g (23.9 parts by weight) of pentaerythritol tetrakis 3-mercaptopropionate was added to this solution, followed by stirring for 30 minutes. 12.75 g (25.4 parts by weight) of 4-mercaptomethyl-1,8-dimercapto-3,6-dithiaoctane in which 30 mg (600 ppm) of dibutyltin dichloride (manufactured by Sigma-Aldrich Co. LLC.) had been dissolved was added thereto, followed by stirring for 1 hour. After decompressing and degassing was performed in a degree of decompression of 133 to 400 Pa for 30 minutes using a vacuum pump, filtration through a 1 μ m membrane filter was performed, and while stirring, a decompressing and degassing operation was performed for 2 hours until foams disappeared using a vacuum pump. The prepared monomer was charged in a glass mold having a thickness of 2 mm, and resinification was performed by raising the temperature from room temperature to 120 °C in an oven to prepare a molded body.

[0121]

(Examples 4 and 5)

Preparation Method of Examples 4 and 5

(Purifying Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic[®]))

(1) A first mixture was prepared by dissolving 8.0 g of Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), in 30 ml of acetone (manufactured by Avantor Performance Materials, LLC). (2) A second mixture was prepared by adding 30 ml of hexane (manufactured by Avantor Performance Materials, LLC) to the first mixture and stirring the second mixture. (3) A third mixture was prepared by separating a hexane phase from the second mixture and removing the hexane phase from the second mixture. (4) Repeated the processes (2) with fresh hexane and the process (3) two more times. (5) A purified polymer composition (a) was prepared by removing volatiles using EYELA vacuum oven (manufactured by Tokyo Rikakikai Co., Ltd) from the third mixture.

[0122]

30.8 mg (684 ppm) of Reversacol Wembley Grey (manufactured by Vivimed) and 16.7 mg (376 ppm) of Reversacol Heath Green (manufactured by Vivimed) as photochromic

compounds, 1.0 g (2 parts by weight) of Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), and 150 mg (3000 ppm) of butoxyethyl acid phosphate were added to 25.35 g (50.7 parts by weight) of a 2,5-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane and 2,6-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, followed by stirring for dissolution using a stirring apparatus. Subsequently, 11.95 g (23.9 parts by weight) of pentaerythritol tetrakis 3-mercaptopropionate was added to this solution, followed by stirring for 30 minutes. 12.75 g (25.4 parts by weight) of 4-mercaptomethyl-1,8-dimercapto-3,6-dithiaoctane in which 30 mg (600 ppm) of dibutyltin dichloride (manufactured by Sigma-Aldrich Co. LLC.) had been dissolved was added thereto, followed by stirring for 1 hour. After decompressing and degassing was performed in a degree of decompression of 133 to 400 Pa for 30 minutes using a vacuum pump, filtration through a 1 μ m membrane filter was performed, and while stirring, a decompressing and degassing operation was performed for 2 hours until foams disappeared using a vacuum pump. The prepared monomer was charged in a glass mold having a thickness of 2 mm, and resinification was performed by raising the temperature from room temperature to 120°C in an oven to prepare a molded body. The measurement results of the photochromic characteristics are shown in Table 4.

[0123]

As the Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), Example 4 includes 1.0 g (2 parts by weight) of Pluronic[®] P85 (manufactured by Sigma-Aldrich[®]) and Example 5 includes 1.0 g (2 parts by weight) of Pluronic[®] P123 (manufactured by Sigma-Aldrich[®]).

[0124]

[Table 4]

Name (manufacturer)	Polymer additive			Photochromic Dye		Haze	Yellow index	Photochromic characteristics	
	Amount (parts by weight)		Purified?	Name	Amount (ppm)			Initial T% (@550 nm)	Δ T% (@550 nm)
P85 (Aldrich)	2	Comp Ex 4	No	Reversacol Wembley grey Reversacol Heath green	684 376	0.38	2.87	85.5	70.5
	2	Ex 4	Yes	Reversacol Wembley grey Reversacol Heath green	684 376	0.38	2.81	87.6	72.3
P123 (Aldrich)	2	Comp Ex 5	No	Reversacol Wembley grey Reversacol Heath green	684 376	0.75	4.14	82.2	69
	2	Ex 5	Yes	Reversacol Wembley grey Reversacol Heath green	684 376	0.67	3.93	85.2	72

[0125]

Table 4 shows the photochromic performance of the purified Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol),(Plurionics®) in the photochromic compound (b) and the polymerization reactive compound (c) of one embodiment of the present disclosure. As it is shown in Example 1, the purified Plurionics® P85, PE10500, and P123 exhibited improved Haze value, Yellow Index, Initial T% at 550 nm, and Δ T% at 550 nm as compared to the

non-purified Pluronics[®] P85, PE10500, and P123. From the results, the purification of pluronic dramatically improved the clarity and performance of the lenses, as it was exhibited in the examples. More specifically, it was found that the poly(thio)urethane resin molded body including the purified Pluronics[®] P85, PE10500, and P123 of the subject embodiment of the present disclosure effectively exhibited a sufficient clarity, and the poly(thio)urethane resin molded body including the purified Pluronics[®] P85, PE10500, and P123 of the subject embodiment of the present disclosure further effectively exhibited the fading speed faster than the fading speed of the poly(thio)urethane resin molded body including non-purified Pluronics[®] P85, PE10500, and P123.

[0126]

These results indicate the benefit of the purified polyester polyol (a) of the present disclosure to achieve excellent optical properties while maintaining the excellent photochromic characteristics and handling properties.

[0127]

Fig. 4 shows a lens manufactured using non-purified Pluronic[®] P105 (manufactured by Sigma-Aldrich[®]) on the left and a lens manufactured using Pluronic[®] P105 (manufactured by Sigma-Aldrich[®]) purified by the purification method of the present disclosure on the right. The lens on the left has an apparent whitishness due to the light scattering caused by the impurities from the non-purified Pluronic[®] P105. The lens using the Pluronic[®] P105 after purification of the present disclosure on the right does not have this apparent whitishness. This indicates that the purifying process of the present disclosure improves the clarity of the lens.

[0128]

What has been described above includes examples of the subject invention. It is, of course, not possible to describe every conceivable combination of components or methodologies for purposes of describing the subject invention, but one of ordinary skill in the art may recognize that many further combinations and permutations of the subject invention are possible. Accordingly, the subject invention is intended to embrace all such alterations, modifications and variations that fall within the spirit and scope of the

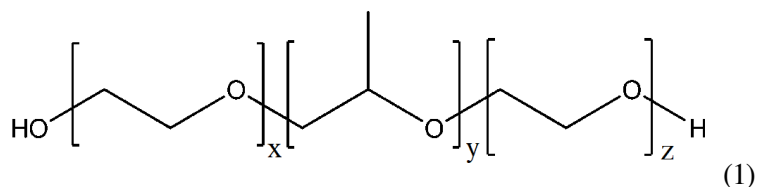
appended claims. Furthermore, to the extent that the terms “contain,” “have,” “include,” and “involve” are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term “comprising” as “comprising” is interpreted when employed as a transitional word in a claim. In some instances, however, to the extent that the terms “contain,” “have,” “include,” and “involve” are used in either the detailed description or the claims, such terms are intended to be partially or entirely exclusive in a manner similar to the terms “consisting of” or “consisting essentially of” as “consisting of” or “consisting essentially of” are interpreted when employed as a transitional word in a claim.

CLAIMS

What is claimed is:

1. A polymerizable composition for optical materials comprising:

a polymer composition (a) comprising a tri-block copolymer of formula (1):



wherein x represents an integer of 3 or more and 300 or less,

y represents an integer of 3 or more and 300 or less, and

z represents an integer of 3 or more and 300 or less;

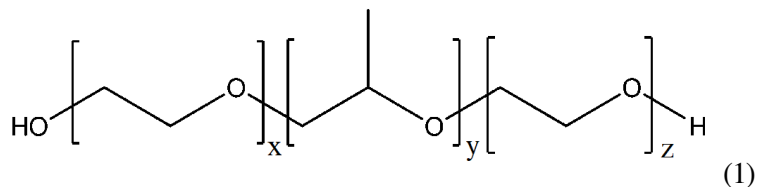
a photochromic compound (b); and

a polymerization reactive compound (c) other than the polymer composition (a),

wherein the polymer composition (a) comprises an impurity comprising di-block copolymer and mono polymer; and a weight percent of the impurity in the polymer composition (a) is less than 25 %.

2. A polymerizable composition for optical materials comprising:

a polymer composition (a) comprising a tri-block copolymer of formula (1):



wherein x represents an integer of 3 or more and 300 or less,

y represents an integer of 3 or more and 300 or less, and

z represents an integer of 3 or more and 300 or less;

a photochromic compound (b); and

a polymerization reactive compound (c) comprising at least one selected from the group consisting of metaxylylene diisocyanate, 5,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, 4,7-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane, and 4,8-dimercaptomethyl-1,11-dimercapto-3,6,9-trithiaundecane,

wherein the polymer composition (a) has a weight average molecular weight of 4,000 g/mol to 7,000 g/mol.

3. A cured body obtained by curing the polymerizable composition of claim 2.

4. The polymerizable composition of claim 2, wherein the polymer composition (a) has a weight average molecular weight of about 4,600 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.852.

5. A cured body obtained by curing the polymerizable composition of claim 4.

6. The cured body of claim 5, wherein a haze value of the cured body is less than 0.27, an yellow index of the cured body is less than 2.71, Initial T% at 550 nm is more than 83.7, and $\Delta T\%$ at 550 nm is more than 69.8.

7. The polymerizable composition of claim 2, wherein the polymer composition (a) has a weight average molecular weight of about 5,800 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.473.

8. A cured body obtained by curing the polymerizable composition of claim 7.

9. The cured body of claim 8, wherein a haze value of the cured body is less than 0.61, an yellow index of the cured body is less than 3.48, Initial T% at 550 nm is more than 86.3, and $\Delta T\%$ at 550

nm is more than 73.8.

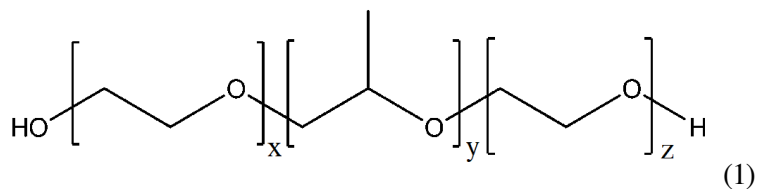
10. The polymerizable composition of claim 2, wherein the polymer composition (a) has a weight average molecular weight of about 6,500 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.953.

11. A cured body obtained by curing the polymerizable composition of claim 10.

12. The cured body of claim 11, wherein a haze value of the cured body is less than 0.37, an yellow index of the cured body is less than 2.93, Initial T% at 550 nm is more than 83.7, and $\Delta T\%$ at 550 nm is more than 70.8.

13. A polymerizable composition for optical materials comprising:

a polymer composition (a) comprising a tri-block copolymer of formula (1):



wherein x represents an integer of 3 or more and 300 or less,

y represents an integer of 3 or more and 300 or less, and

z represents an integer of 3 or more and 300 or less;

a photochromic compound (b); and

a polymerization reactive compound (c) comprising at least one selected from the group consisting of 2,5-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane and 2,6-bis(isocyanatomethyl) bicyclo-[2.2.1]-heptane, pentaerythritol tetrakis 3-mercaptopropionate, and 4-mercaptopomethyl-1,8-dimercapto-3,6-dithiaoctane,

wherein the polymer composition (a) has a weight average molecular weight of 4,000

g/mol to 7,000 g/mol.

14. A cured body obtained by curing the polymerizable composition of claim 13.

15. The polymerizable composition of claim 13, wherein the polymer composition (a) has a weight average molecular weight of about 4,600 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.852.

16. A cured body obtained by curing the polymerizable composition of claim 15.

17. The cured body of claim 16, wherein a yellow index of the cured body is less than 2.87, Initial T% at 550 nm is more than 85.5, and $\Delta T\%$ at 550 nm is more than 70.5.

18. The polymerizable composition of claim 13, wherein the polymer composition (a) has a weight average molecular weight of about 5,800 g/mol and a ratio of a weight of ethylene glycol units to a weight of propylene glycol units in the polymer composition (a) is higher than 0.473.

19. A cured body obtained by curing the polymerizable composition of claim 18.

20. The cured body of claim 19, wherein a haze value of the cured body is less than 0.75, a yellow index of the cured body is less than 4.14, Initial T% at 550 nm is more than 82.2, and $\Delta T\%$ at 550 nm is more than 69.

21. The polymerizable composition for optical materials according to any one of claims 1 to 20, wherein the photochromic compound (b) is a naphthopyran derivative.

22. A molded body obtained by curing the polymerizable composition in a mold for optical

materials according to any one of claims 1 to 21.

23. An optical material formed of the molded body according to claim 22.

24. A plastic lens formed of the molded body according to claim 23.

25. A method of removing an impurity from a polymer composition (a) comprising a tri-block copolymer, the method comprising:

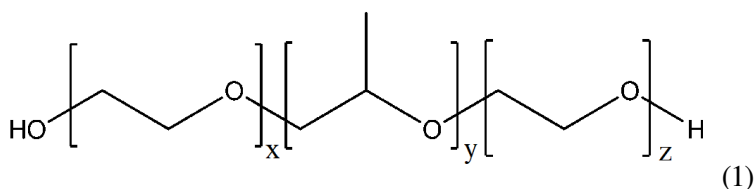
dissolving the polymer composition (a) in acetone to prepare a first mixture;

adding hexane to the first mixture to prepare a second mixture and stirring the second mixture;

separating a hexane phase from the second mixture and removing the hexane phase from the second mixture to prepare a third mixture; and

removing volatiles from the third mixture to prepare a purified polymer composition (a),

wherein the polymer composition (a) comprises a tri-block copolymer of formula (1):



wherein x represents an integer of 3 or more and 300 or less,

y represents an integer of 3 or more and 300 or less, and

z represents an integer of 3 or more and 300 or less;

the impurity comprises di-block copolymer and mono polymer;

the purified polymer composition (a) comprises the impurity less than 25 weight percent in the purified polymer composition (a).