

DESCRIPTION

TITLE OF THE INVENTION: PHOTOCURABLE COMPOSITION FOR
IMPRINTING

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TECHNICAL FIELD

[0001] The present invention relates to a photocurable composition for imprinting, the composition containing silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, a polyfunctional (meth)acrylate compound having an ethylenically unsaturated group, a polyrotaxane having an ethylenically unsaturated group, a photoradical initiator, and a polyfunctional thiol compound. More particularly, the present invention relates to a photocurable composition that can be formed into a cured product and molded product exhibiting the following characteristic features. Specifically, each of the cured product and the molded product highly adheres to and does not peel from a support even after undergoing a thermal shock test; i.e., continuous exposure to a low temperature of -20°C or lower and a high temperature of 80°C or higher. In addition, when an anti-reflective layer (AR layer) is formed on each of the cured product and the molded product and then subjected to thermal treatment, cracks do not occur in the anti-reflective layer.

BACKGROUND ART

[0002] A resin lens is used in electronic devices such as mobile phones, digital cameras, and in-vehicle cameras, and is required to have excellent optical characteristics in accordance with the intended use of the electronic devices. Moreover, in view of its applications, a resin lens is required to exhibit high durability (e.g., heat resistance and weatherability) and to have high productivity (i.e., capable of being molded at high yield). The material used for a resin lens satisfying such requirements is, for example, a thermoplastic transparent resin, such as a polycarbonate resin, a cycloolefin polymer, or a

methacrylic resin.

[0003] A plurality of lenses are used for a high-resolution camera module. In general, a lens having low wavelength dispersion (i.e., a lens having a high Abbe number) is used in a high-resolution camera module, and an optical material for forming such a lens is required. In the production of resin lenses, many attempts have been conducted to make a transition from injection molding of a thermoplastic resin to wafer level molding by extrusion molding using a curable resin that is in the form of liquid at room temperature, in order to improve yield and production efficiency, and to reduce optical axis shift during lamination of lenses. From the viewpoint of productivity, the wafer level molding generally involves a hybrid lens system wherein a lens is formed on a support such as a glass substrate.

[0004] The photocurable resin that has been conventionally used for the wafer level molding is a radical-curable resin composition, from the viewpoint of high transparency, heat yellowing resistance, and mold releasability (Patent Document 1).

[0005] There has been known a curable composition that can produce a cured product having a high Abbe number, the curable composition containing surface-modified oxide particles, such as silica particles having surfaces modified with a silane compound, or zirconium oxide particles having surfaces modified with a dispersant (e.g., Patent Documents 2 and 3).

[0006] Meanwhile, there has been known a polyrotaxane having a cyclic molecule with an opening, a linear molecule, and blocking groups (stoppers), wherein the blocking groups are disposed at both ends of a pseudo-polyrotaxane formed through skewered inclusion of the linear molecule in the opening of the cyclic molecule, and the cyclic molecule has a (meth)acrylic group (e.g., Patent Document 4). The linear molecule penetrates through the opening of the cyclic molecule, and the blocking groups are provided for preventing removal of the cyclic molecule from the linear molecule. As used herein, the term "inclusion" refers to incorporation of a molecule in the space of the opening of the cyclic molecule, and the term "pseudo-polyrotaxane" refers to a polyrotaxane that does not have the aforementioned blocking groups. A photocurable

composition containing the aforementioned polyrotaxane can produce a photocured product exhibiting high strength, high elastic modulus, and excellent toughness.

Prior Art Documents

5 Patent Documents

[0007] Patent Document 1: Japanese Patent No. 5281710 (International Publication WO 2011/105473)

Patent Document 2: Japanese Unexamined Patent Application Publication No. 2014-234458 (JP 2014-234458 A)

10 Patent Document 3: International Publication WO 2016/104039

Patent Document 4: International Publication WO 2016/072356

SUMMARY OF THE INVENTION

15 Problems to be Solved by the Invention

[0008] In the case where the molded product produced through wafer level molding is a lens, an anti-reflective layer composed of an inorganic material (e.g., silicon oxide or titanium oxide) is formed on the lens. Thus, thermal treatment of the lens coated with the anti-reflective layer causes a problem in that cracks occur in the anti-reflective layer. When a cured product produced from the aforementioned curable composition containing surface-modified oxide particles is subjected to a thermal shock test (i.e., continuous exposure to a low temperature of -20°C or lower and a high temperature of 80°C or higher), the cured product is problematically peeled from a support.

25 [0009] There has not yet been provided a curable resin material that can produce a molded product having a high Abbe number (e.g., 53 or more) and capable of being used as a lens for a high-resolution camera module, wherein no cracks occur in an anti-reflective layer formed on the molded product after thermal treatment of the molded product, and the molded product does not peel from a support even after undergoing a

thermal shock test. Therefore, a demand has arisen for development of such a curable resin material. The present invention has been conceived under such circumstances. Thus, an object of the present invention is to provide a photocurable composition that can form a molded product having a high Abbe number and exhibiting high thermal shock resistance, wherein no cracks occur in an anti-reflective layer formed on the molded product after thermal treatment of the molded product, and the molded product does not peel from a support even after undergoing a thermal shock test.

Means for Solving the Problems

[0010] A first aspect of the present invention is a photocurable composition for imprinting, the composition comprising the following components (a), (b), (c), (d), and (e):

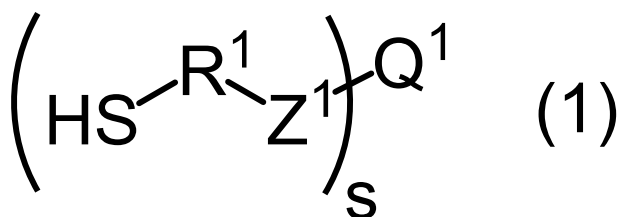
(a) silica particles having a primary particle diameter of 1 nm to 100 nm and having surfaces modified with a functional group having an ethylenically unsaturated group;

(b) a polyfunctional (meth)acrylate compound having an ethylenically unsaturated group;

(c) a polyrotaxane having an ethylenically unsaturated group;

(d) a photoradical initiator; and

(e) a polyfunctional thiol compound of the following Formula (1):



(wherein R^1 is a single bond or a linear or branched alkylene group having a carbon atom number of 1 to 6; Z^1 is a single bond, an ester bond, or an ether bond; Q^1 is a C_{2-12} organic group containing at least one heteroatom or containing no heteroatom, or a heteroatom; and s is an integer of 2 to 6).

[0011] The photocurable composition for imprinting of the present invention may further comprise the following component (f) and/or (g):

(f) a phenolic antioxidant; and

(g) a sulfide antioxidant.

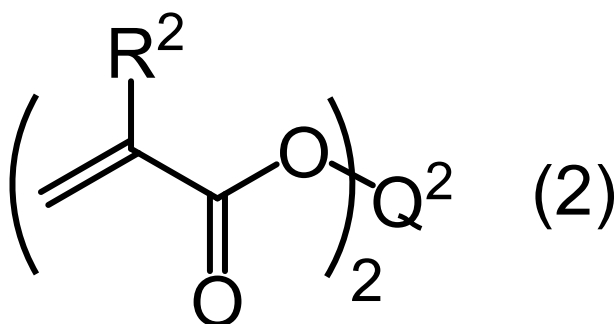
[0012] The photocurable composition for imprinting of the present invention may further comprise the following component (h):

5 (h) a monofunctional (meth)acrylate compound having an ethylenically unsaturated group.

[0013] The component (b) contains, for example, at least one of the following components (b1) and (b2):

(b1) a bifunctional (meth)acrylate compound of the following Formula (2); and

10 (b2) a urethane (meth)acrylate compound (except for the polyrotaxane having an ethylenically unsaturated group, which is the component (c)) or an epoxy (meth)acrylate compound:



(wherein R² is a hydrogen atom or a methyl group; and Q² is a linear or branched
15 hydrocarbon group having a carbon atom number of 2 to 16).

[0014] The component (b) contains, for example, the components (b1) and (b2).

[0015] The silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, which are the component (a), are, for example, silica particles having surfaces modified with a (meth)acryloyloxy group bonded to a
20 silicon atom via a divalent linking group. The divalent linking group is, for example, a C₁₋₅ alkylene group, and is preferably a C₂ or C₃ alkylene group.

[0016] A second aspect of the present invention is a cured product produced from the photocurable composition for imprinting.

[0017] A third aspect of the present invention is a method for producing a resin

lens, the method comprising a step of imprint-molding the photocurable composition for imprinting.

[0018] A fourth aspect of the present invention is a method for producing a molded product from a photocurable composition for imprinting, the method comprising
5 a step of charging the photocurable composition for imprinting into a space between a support and a casting mold which are in contact with each other, or into a space in a separable casting mold; and a step of photocuring the photocurable composition for imprinting charged in the space through light exposure. The casting mold may also be referred to as "mold."

10 [0019] The method for producing a molded product of the present invention may further comprise, after the photocuring step, a step of releasing the resultant photocured product from the casting mold, and a step of heating the photocured product before, during, or after the releasing step.

[0020] The method may further comprise a developing step using an organic
15 solvent after the releasing step and before the heating step.

[0021] In the method for producing a molded product of the present invention, the molded product is, for example, a lens for a camera module.

Effects of the Invention

20 [0022] The photocurable composition for imprinting of the present invention contains the aforementioned components (a) to (e), and optionally contains the aforementioned component (f) and/or the aforementioned component (g) and the aforementioned component (h). Thus, a cured product and molded product produced from the photocurable composition exhibit optical characteristics desired for a lens for an
25 optical device (e.g., a high-resolution camera module); i.e., the products exhibit a high Abbe number. When an anti-reflective layer formed on each of the cured product and molded product produced from the photocurable composition of the present invention is subjected to thermal treatment at 175°C, no cracks occur in the anti-reflective layer. Even when each of the cured product and the molded product undergoes a thermal shock

test, the product does not peel from a support.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0023] [FIG. 1] FIG. 1 is a digital microscope photograph showing a corner of a cured film produced from a photocurable composition for imprinting 6 of Example 6.

[FIG. 2] FIG. 2 is a digital microscope photograph showing a corner of a cured film produced from a photocurable composition for imprinting 10 of Comparative Example 2.

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MODES FOR CARRYING OUT THE INVENTION

[0024] Components of the photocurable composition for imprinting of the present invention will be described in more detail. The term "ethylenically unsaturated
15 group" as used herein refers to a group having a double bond between two carbon atoms. Examples of such a group include a $(\text{CH}_2=\text{CH})$ - group and a $[\text{CH}_2=\text{C}(\text{CH}_3)]$ - group. The compound having an ethylenically unsaturated group contained in the photocurable composition for imprinting of the present invention is components (a) to (c) and (h).

[0025] [Component (a): Silica Particles Having Surfaces Modified with
20 Functional Group Having Ethylenically Unsaturated Group]

Silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, which can be used as a component (a) of the photocurable composition for imprinting of the present invention, have a primary particle diameter of 1 nm to 100 nm. The term "primary particle" as used herein refers to a
25 particle forming powder, and a particle composed of agglomerated primary particles is referred to as "secondary particle." The primary particle diameter can be calculated from the following relation: $D = 6/(\rho S)$ wherein S is the specific surface area (surface area per unit mass) of the aforementioned silica particles having surfaces modified with a functional group having an ethylenically unsaturated group as determined by the gas

adsorption method (BET method), ρ is the density of the surface-modified silica particles, and D is the primary particle diameter. The primary particle diameter calculated from this relation is an average particle diameter; i.e., the diameter of each primary particle.

The silica particles having surfaces modified with a functional group having an

5 ethylenically unsaturated group are, for example, silica particles having surfaces modified with a (meth)acryloyloxy group bonded to a silicon atom via a divalent linking group.

The aforementioned silica particles having surfaces modified with a functional group having an ethylenically unsaturated group may be used as is, or may be used in the form of a colloid prepared by previously dispersing the surface-modified silica particles in an

10 organic solvent serving as a dispersion medium (i.e., a sol prepared by dispersion of colloidal particles in a dispersion medium). When a sol containing the surface-modified silica particles is used, the solid content concentration of the sol may be 10% by mass to 60% by mass.

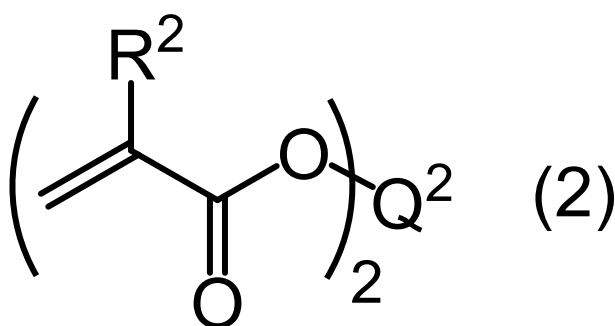
[0026] The sol containing the silica particles having surfaces modified with a
15 functional group having an ethylenically unsaturated group may be selected from, for example, MEK-AC-2140Z, MEK-AC-4130Y, MEK-AC-5140Z, PGM-AC-2140Y, PGM-AC-4130Y, MIBK-AC-2140Z, and MIBK-SD-L (available from Nissan Chemical Corporation) and ELCOM (registered trademark) V-8802 and V-8804 (available from JGC Catalysts and Chemicals Ltd.).

20 [0027] The amount of the component (a) contained in the photocurable composition for imprinting of the present invention is 10 parts by mass to 40 parts by mass, preferably 10 parts by mass to 30 parts by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition. When the amount of the component (a) is less than 10 parts by mass, occurrence of
25 cracks may fail to be prevented in an anti-reflective layer formed on each of a cured product and molded product produced from the photocurable composition for imprinting. When the amount of the component (a) is more than 40 parts by mass, a haze may be generated in each of the cured product and the molded product, resulting in a reduction in transmittance.

[0028] The silica particles having surfaces modified with a functional group having an ethylenically unsaturated group (i.e., component (a)) used in the present invention may be of a single type or a combination of two or more types.

[0029] [Component (b): Polyfunctional (Meth)acrylate Compound Having
5 Ethylenically Unsaturated Group]

The polyfunctional (meth)acrylate compound having an ethylenically unsaturated group, which can be used as the component (b) of the photocurable composition for imprinting of the present invention, is a (meth)acrylate compound having two or more ethylenically unsaturated groups in one molecule of the compound. Examples of the
10 polyfunctional (meth)acrylate compound include a urethane (meth)acrylate compound, an epoxy (meth)acrylate compound, and an additional bifunctional (meth)acrylate compound. In the present specification, a compound of the following Formula (2) (among additional bifunctional (meth)acrylate compounds) is referred to as "component (b1)," and the aforementioned urethane (meth)acrylate compound or epoxy
15 (meth)acrylate compound is referred to as "component (b2)." When the photocurable composition for imprinting of the present invention contains the component (b1), the composition exhibits excellent compatibility with the below-described polyrotaxane having an ethylenically unsaturated group (i.e., component (c)).



20 (In Formula (2), R² is a hydrogen atom or a methyl group, and Q² is a linear or branched hydrocarbon group having a carbon atom number of 2 to 16.)

[0030] Examples of the compound that is not represented by Formula (2) (among the aforementioned additional bifunctional (meth)acrylate compounds) include diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene

glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, and EO-modified hydrogenated bisphenol A di(meth)acrylate. The compound may be a commercially

5 available product. Examples of the commercially available product include 2G, 3G, 4G, 9G, 14G, 23G, A-200, A-400, A-600, A-1000, APG-100, APG-200, APG-400, APG-700, 3PG, 9PG, and A-PTMG-65 (available from SHIN-NAKAMURA CHEMICAL Co., Ltd.); LIGHT ACRYLATE 3EG-A, LIGHT ACRYLATE 4EG-A, LIGHT ACRYLATE 9EG-A, LIGHT ACRYLATE 14EG-A, and LIGHT ACRYLATE PTMGA-250 (available
10 from Kyoeisha Chemical Co., Ltd.); Viscoat #310HP and Viscoat #335HP (available from OSAKA ORGANIC CHEMICAL INDUSTRY LTD.); and HBPE-4 (available from DKS Co. Ltd.).

[0031] [Component (b1): Bifunctional (Meth)acrylate Compound of Formula (2)]

15 The bifunctional (meth)acrylate compound of Formula (2), which can be used as the component (b1) of the photocurable composition for imprinting of the present invention, is a compound having two (meth)acryloyloxy groups in one molecule of the compound.

Examples of the bifunctional (meth)acrylate compound include ethylene glycol di(meth)acrylate, 1,3-propanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate,
20 1,5-pentanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 3-methyl-1,5-pentanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,7-heptanediol di(meth)acrylate, 1,8-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,11-undecanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, 1,13-tridecanediol di(meth)acrylate,
25 1,14-tetradecanediol di(meth)acrylate, 1,15-pentadecanediol di(meth)acrylate, 1,16-hexadecanediol di(meth)acrylate, 1,3-octanediol di(meth)acrylate, 1,8-nonanediol di(meth)acrylate, 1,9-decanediol di(meth)acrylate, 1,10-undecanediol di(meth)acrylate, 1,3-dodecanediol di(meth)acrylate, 2,4,4-trimethyl-1,6-hexanediol di(meth)acrylate, 2,4-diethyl-1,5-pentanediol di(meth)acrylate, and 2,2,9,9-tetramethyl-1,10-decanediol

di(meth)acrylate.

[0032] The bifunctional (meth)acrylate compound may be a commercially available product. Examples of the commercially available product include Viscoat #195, Viscoat #230, and Viscoat #260 (available from OSAKA ORGANIC CHEMICAL INDUSTRY LTD.); BD, NPG, A-NPG, HD-N, A-HD-N, NOD-N, A-NOD-N, DOD-N, and A-DOD-N (available from SHIN-NAKAMURA CHEMICAL Co., Ltd.); and LIGHT ESTER EG and LIGHT ACRYLATE MPD-A (available from Kyoeisha Chemical Co., Ltd.).

[0033] [Component (b2): Urethane (Meth)acrylate Compound or Epoxy (Meth)acrylate Compound]

The urethane (meth)acrylate compound, which can be used as the component (b2) of the photocurable composition for imprinting of the present invention, is a compound having at least two (meth)acryloyloxy groups and at least two urethane structures represented by "-NH-C(=O)O-" in one molecule. The urethane (meth)acrylate compound does not include the below-described polyrotaxane having an ethylenically unsaturated group (i.e., component (c)). Examples of the urethane (meth)acrylate compound include EBECRYL (registered trademark) 230, 270, 280/15IB, 284, 4491, 4683, 4858, 8307, 8402, 8411, 8804, 8807, 9270, 8800, 294/25HD, 4100, 4220, 4513, 4738, 4740, 4820, 8311, 8465, 9260, and 8701, and KRM 7735, 8667, and 8296 (available from DAICEL-ALLNEX LTD.); UV-2000B, UV-2750B, UV-3000B, UV-3200B, UV-3210EA, UV-3300B, UV-3310B, UV-3500B, UV-3520EA, UV-3700B, UV-6640B, UV-6630B, UV-7000B, UV-7510B, and UV-7461TE (available from The Nippon Synthetic Chemical Industry Co., Ltd.); UA-306H, UA-306T, UA-306I, UA-510H, and UF-8001G (available from Kyoeisha Chemical Co., Ltd.); M-1100 and M-1200 (available from Toagosei Company, Limited); and NK Oligo U-2PPA, U-6LPA, U-200PA, U-200PA, U-160TM, U-290TM, UA-4200, UA-4400, UA-122P, UA-7100, and UA-W2A (available from SHIN-NAKAMURA CHEMICAL Co., Ltd.).

[0034] The epoxy (meth)acrylate compound, which can be used as the component (b2) of the photocurable composition for imprinting of the present invention,

is an ester prepared by reaction between a compound having at least two epoxy rings in one molecule and (meth)acrylic acid. Examples of the epoxy (meth)acrylate compound include EBECRYL (registered trademark) 645, 648, 860, 3500, 3608, 3702, and 3708 (available from DAICEL-ALLNEX LTD.); DA-911M, DA-920, DA-931, DA-314, DA-212 (available from Nagase ChemteX Corporation); HPEA-100 (available from KSM Co., Ltd.); and UNIDIC (registered trademark) V-5500, V-5502, and V-5508 (available from DIC Corporation).

[0035] The aforementioned urethane (meth)acrylate compound or epoxy (meth)acrylate compound (i.e., component (b2)) is preferably a compound having two or three (meth)acryloyloxy groups in one molecule of the compound. The aforementioned urethane (meth)acrylate compound or epoxy (meth)acrylate compound (i.e., component (b2)) may be used alone or in combination of two or more species.

[0036] When the photocurable composition for imprinting of the present invention contains at least one of the components (b1) and (b2) as the component (b), the amount of the component(s) satisfies all the relations of Formulae (3) to (5) described below, preferably satisfies all the relations of Formulae (3') to (5') described below, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition. In the following Formulae, X is the amount (parts by mass) of the component (b1), and Y is the amount (parts by mass) of the component (b2).

Formula (3): $30 \text{ parts by mass} \leq (X + Y) \leq 85 \text{ parts by mass}$

Formula (4): $0 \text{ part by mass} \leq X \leq 70 \text{ parts by mass}$

Formula (5): $0 \text{ part by mass} \leq Y \leq 80 \text{ parts by mass}$

Formula (3'): $30 \text{ parts by mass} \leq (X + Y) \leq 80 \text{ parts by mass}$

Formula (4'): $0 \text{ part by mass} \leq X \leq 60 \text{ parts by mass}$

Formula (5'): $0 \text{ part by mass} \leq Y \leq 70 \text{ parts by mass}$

When the amount of the component (b1) is more than 70 parts by mass, each of a cured product and molded product produced from the photocurable composition for imprinting may become brittle, leading to poor crack resistance of each of the cured product and the molded product. Meanwhile, when the amount of the component (b2) is

more than 80 parts by mass, each of a cured product and molded product produced from the photocurable composition for imprinting may exhibit lowered crosslink density, leading to an increase in change in the shape of each of the cured product and the molded product during heating.

5 [0037] [Component (c): Polyrotaxane Having Ethylenically Unsaturated Group]

The polyrotaxane having an ethylenically unsaturated group, which can be used as the component (c) of the photocurable composition for imprinting of the present invention, is a compound wherein blocking groups are disposed at both ends of a pseudo-polyrotaxane formed through skewered inclusion of a linear molecule in the
10 opening of a cyclic molecule such that the blocking groups prevent removal of the cyclic molecule, and the cyclic molecule has an ethylenically unsaturated group. The cyclic molecule, the linear molecule and the blocking groups, which are constituents of the polyrotaxane where the cyclic molecule has an ethylenically unsaturated group, will be described below.

15 [0038] <c-1. Cyclic Molecule>

No particular limitation is imposed on the cyclic molecule of the polyrotaxane having an ethylenically unsaturated group (i.e., component (c)), so long as the molecule has a cyclic structure and an opening, and the linear molecule is provided in the opening through skewered inclusion. Preferably, the cyclic molecule has the ethylenically
20 unsaturated group. The ethylenically unsaturated group may be directly bonded to the cyclic molecule, or may be bonded thereto via a spacer. Examples of the spacer include, but are not particularly limited to, an alkylene group, an alkylene oxide group, a hydroxyalkylene group, a carbamoyl group, an acrylate ester chain, a polyalkylene ether chain, and a polyalkylene carbonate chain. The cyclic molecule is preferably selected
25 from, for example, the group consisting of α -cyclodextrin, β -cyclodextrin, and γ -cyclodextrin.

[0039] <c-2. Linear Molecule>

No particular limitation is imposed on the linear molecule of the polyrotaxane having an ethylenically unsaturated group (i.e., component (c)), so long as the linear

molecule can be provided in the opening of the cyclic molecule through skewered inclusion. Examples of the linear molecule include compounds (polymers) exemplified in Patent Document 4. Of these compounds, preferred is a polymer selected from the group consisting of polyethylene glycol, polyisoprene, polyisobutylene, polybutadiene, polypropylene glycol, polytetrahydrofuran, polydimethylsiloxane, polyethylene, polypropylene, polyvinyl alcohol, and polyvinyl methyl ether. In particular, the linear molecule is preferably polyethylene glycol.

[0040] The linear molecule has a weight average molecular weight of 1,000 or more, preferably 3,000 to 100,000, more preferably 6,000 to 50,000. In the polyrotaxane having an ethylenically unsaturated group (i.e., component (c)), the combination of (cyclic molecule and linear molecule) is preferably (α -cyclodextrin-derived molecule and polyethylene glycol-derived molecule).

[0041] <c-3. Blocking Group>

No particular limitation is imposed on the blocking group of the polyrotaxane having an ethylenically unsaturated group (i.e., component (c)), so long as blocking groups are disposed at both ends of a pseudo-polyrotaxane so as to prevent removal of the cyclic molecule used. Examples of the blocking group include blocking groups exemplified in Patent Document 4. Of these, preferred is a blocking group selected from the group consisting of a dinitrophenyl group, a cyclodextrin group, an adamantyl group, a trityl group, a fluorescein group, a silsesquioxane group, and a pyrene group. The blocking group is more preferably an adamantyl group or a cyclodextrin group. The blocking group is bonded to the linear molecule via, for example, a -NH-C(=O)-group.

[0042] The polyrotaxane having an ethylenically unsaturated group may be a commercially available product. Examples of the commercially available product include SeRM (registered trademark) Super Polymer SA1303P, SA1305P, SA1305P-10, SA2403P, SA2405P-10, SA3403P, SM1303P, SM2403P, and 3403P (available from Advanced Softmaterials Inc.).

[0043] The amount of the component (c) contained in the photocurable

composition for imprinting of the present invention is 1 part by mass to 15 parts by mass, preferably 3 parts by mass to 10 parts by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition. When the amount of the component (c) is less than 1 part by mass, each of a cured product and
5 molded product produced from the photocurable composition for imprinting may be insufficiently prevented from being peeled from a support in a thermal shock test. Meanwhile, when the amount of the component (c) is more than 15 parts by mass, a haze may be generated in each of the cured product and the molded product, resulting in a reduction in transmittance.

10 [0044] The polyrotaxane having an ethylenically unsaturated group (i.e., component (c)) may be used alone or in combination of two or more species.

[0045] [Component (d): Photoradical Initiator]

The photoradical initiator, which can be used as the component (d) of the photocurable composition for imprinting of the present invention, is selected from, for
15 example, an alkylphenone compound, a benzophenone compound, a Michler's ketone compound, an acylphosphine oxide compound, a benzoyl benzoate compound, an oxime ester compound, a tetramethylthiuram monosulfide compound, and a thioxanthone compound. In particular, a photofragmentation-type photoradical polymerization initiator is preferred. The photoradical initiator may be a commercially available
20 product. Examples of the usable commercially available product include OMNIRAD (registered trademark) 184, 369, 651, 500, 819, 907, 784, 2959, TPO, and 1173 (available from IGM Resins); [former IRGACURE (registered trademark) 184, 369, 651, 500, 819, 907, 784, 2959, TPO, and 1173 (available from BASF Japan Ltd.)]; IRGACURE (registered trademark) CGI1700, CGI1750, CGI1850, CG24-61, and 1116 (available
25 from BASF Japan Ltd.); and ESACURE KIP150, KIP65LT, KIP100F, KT37, KT55, KTO46, and KIP75 (available from Lamberti).

[0046] The amount of the component (d) contained in the photocurable composition for imprinting of the present invention is 0.1 parts by mass to 5 parts by mass, preferably 0.5 parts by mass to 3 parts by mass, relative to 100 parts by mass of the

total amount of the components (a), (b), (c), (e), and (h) contained in the composition.

When the amount of the component (d) is less than 0.1 parts by mass, each of a cured product and molded product produced from the photocurable composition for imprinting may exhibit lowered strength. Meanwhile, when the amount of the component (d) is

5 more than 5 parts by mass, each of the cured product and the molded product may exhibit impaired heat yellowing resistance.

[0047] The photoradical initiator (i.e., component (d)) may be used alone or in combination of two or more species.

[0048] [Component (e): Polyfunctional Thiol Compound of Formula (1)]

10 The polyfunctional thiol compound, which can be used as the component (e) of the photocurable composition for imprinting of the present invention, is a polyfunctional thiol compound of Formula (1). Examples of the polyfunctional thiol compound of Formula (1) include 1,2-ethanedithiol, 1,3-propanedithiol, bis(2-mercaptoethyl) ether, trimethylolpropane tris(3-mercaptopropionate),

15 tris-[(3-mercaptopropionyloxy)-ethyl]-isocyanurate, tetraethylene glycol bis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptobutyrate), 1,4-bis(3-mercaptobutyryloxy)butane, 1,3,5-tris(3-mercaptobutyryloxyethyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, trimethylolpropane tris(3-mercaptobutyrate), trimethylolethane tris(3-mercaptobutyrate),
20 and pentaerythritol tris(3-mercaptopropyl) ether. The polyfunctional thiol compound of Formula (1) may be a commercially available product. Examples of the commercially available product include Karenz MT (registered trademark) PE1, NR1, BD1, TPMB, and TEMB (available from Showa Denko K.K.); and TMMP, TEMPIC, PEMP, EGMP-4, DPMP, TMMP II-20P, PEMP II-20P, and PEPT (available from SC Organic Chemical
25 Co., Ltd.).

[0049] The amount of the component (e) contained in the photocurable composition for imprinting of the present invention is 1 part by mass to 15 parts by mass, preferably 3 parts by mass to 10 parts by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition. When

the amount of the component (e) is less than 1 part by mass, each of a cured product and molded product produced from the photocurable composition for imprinting may exhibit poor adhesion to a support. Meanwhile, when the amount of the component (e) is more than 15 parts by mass, each of the cured product and the molded product may exhibit lowered strength, leading to an increase in change in the shape of each of the cured product and the molded product during heating.

[0050] The polyfunctional thiol compound of Formula (1), which is the component (e), may be used alone or in combination of two or more species.

[0051] [Component (f): Phenolic Antioxidant]

Examples of the phenolic antioxidant that can be used as the component (f) of the photocurable composition for imprinting of the present invention include IRGANOX (registered trademark) 245, 1010, 1035, 1076, and 1135 (available from BASF Japan Ltd.); SUMILIZER (registered trademark) GA-80, GP, MDP-S, BBM-S, and WX-R (available from Sumitomo Chemical Company, Limited); and ADK STAB (registered trademark) AO-20, AO-30, AO-40, AO-50, AO-60, AO-80, and AO-330 (available from ADEKA CORPORATION).

[0052] When the photocurable composition for imprinting of the present invention contains the component (f), the amount of the component (f) is 0.05 parts by mass to 3 parts by mass, preferably 0.1 parts by mass to 1 part by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition.

[0053] The phenolic antioxidant, which is the component (f), may be used alone or in combination of two or more species.

[0054] [Component (g): Sulfide Antioxidant]

Examples of the sulfide antioxidant that can be used as the component (g) of the photocurable composition for imprinting of the present invention include ADK STAB (registered trademark) AO-412S and AO-503 (available from ADEKA CORPORATION); IRGANOX (registered trademark) PS802 and PS800 (available from BASF Japan Ltd); and SUMILIZER (registered trademark) TP-D (available from Sumitomo Chemical

Company, Limited).

[0055] When the photocurable composition for imprinting of the present invention contains the component (g), the amount of the component (g) is 0.05 parts by mass to 3 parts by mass, preferably 0.1 parts by mass to 1 part by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition.

[0056] The sulfide antioxidant, which is the component (g), may be used alone or in combination of two or more species.

[0057] [Component (h): Monofunctional (Meth)acrylate Compound Having Ethylenically Unsaturated Group]

The monofunctional (meth)acrylate compound having an ethylenically unsaturated group, which can be used as the component (h) of the photocurable composition for imprinting of the present invention, is a (meth)acrylate compound having one ethylenically unsaturated group in one molecule of the compound. Examples of the monofunctional (meth)acrylate compound include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, isooctyl (meth)acrylate, dodecyl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, 1-adamantyl (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, phenoxydiethylene glycol (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, methoxyethylene glycol (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxytetraethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate, methoxytripropylene glycol (meth)acrylate, ethylcarbitol (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, (meth)acryloyloxymethyltrimethoxysilane, (meth)acryloyloxymethyldimethoxysilane,

(meth)acryloyloxymethyltriethoxysilane, (meth)acryloyloxymethyldiethoxysilane, 2-(meth)acryloyloxyethyltrimethoxysilane, 2-(meth)acryloyloxyethyldimethoxysilane, 2-(meth)acryloyloxyethyltriethoxysilane, 2-(meth)acryloyloxyethyldiethoxysilane, 3-(meth)acryloyloxypropyltrimethoxysilane, 3-(meth)acryloyloxypropyldimethoxysilane, 3-(meth)acryloyloxypropyltriethoxysilane, 3-(meth)acryloyloxypropyldiethoxysilane, 8-(meth)acryloyloxyoctyltrimethoxysilane, 8-(meth)acryloyloxyoctyldimethoxysilane, 8-(meth)acryloyloxyoctyltriethoxysilane, and 8-(meth)acryloyloxyoctyldiethoxysilane.

[0058] The monofunctional (meth)acrylate compound may be a commercially available product. Examples of the commercially available product include AIB, TBA, NOAA, IOAA, LA, STA, ISTA, IBXA, 1-ADA, 1-ADMA, Viscoat #150, Viscoat #155, Viscoat #160, Viscoat #190, Viscoat #192, Viscoat #MTG, Vismer #MPE400A, Vismer #MPE500A, HEA, and 4-HBA (available from OSAKA ORGANIC CHEMICAL INDUSTRY LTD.); FA-BZM, FA-BZA, FA-511AS, FA-512M, FA-512MT, FA-512AS, FA-513M, and FA-513AS (available from Hitachi Chemical Co., Ltd.); LMA, LA, S, A-S, S-1800M, S-1800A, IB, A-IB, PHE-1G, AMP-10G, PHE-2G, AMP-20GY, M-20G, M-30G, AM-30G, M-40G, M-90G, AM-90G, M-130G, AM-130G, M-230G, AM-230G, M-30PG, AM-30PG, and 702A (available from SHIN-NAKAMURA CHEMICAL Co., Ltd.); LIGHT ESTER M, LIGHT ESTER E, LIGHT ESTER NB, LIGHT ESTER IB, LIGHT ESTER TB, LIGHT ESTER EH, LIGHT ESTER L, LIGHT ESTER S, LIGHT ESTER CH, LIGHT ESTER IB-X, LIGHT ESTER BZ, LIGHT ESTER PO, LIGHT ESTER THF (1000), LIGHT ESTER 130MA, LIGHT ESTER 041MA, LIGHT ESTER HO-250(N), LIGHT ESTER HOA(N), LIGHT ESTER DM, LIGHT ESTER DE, LIGHT ACRYLATE L-A, LIGHT ACRYLATE S-A, LIGHT ACRYLATE IB-XA, LIGHT ACRYLATE PO-A, LIGHT ACRYLATE THF-A, LIGHT ACRYLATE MTG-A, LIGHT ACRYLATE 130A, LIGHT ACRYLATE DPM-A, LIGHT ACRYLATE EC-A, and EPOXY ESTER M-600A (available from Kyoeisha Chemical Co., Ltd.); and KBM-5103, KBM-503, KBM-502, KBE-503, KBE-502, and KBM-5803 (available from Shin-Etsu Chemical Co., Ltd.).

[0059] When the photocurable composition for imprinting of the present

invention contains the component (h), the amount of the component (h) is 0.5 parts by mass to 20 parts by mass, preferably 1 part by mass to 10 parts by mass, relative to 100 parts by mass of the total amount of the components (a), (b), (c), (e), and (h) contained in the composition.

5 [0060] The monofunctional (meth)acrylate compound having an ethylenically unsaturated group, which is the component (h), may be used alone or in combination of two or more species.

 [0061] <Additional Additive>

 So long as the effects of the present invention are not impaired, the photocurable
10 composition for imprinting of the present invention may further contain an optional additive, such as a chain transfer agent, an antioxidant, an ultraviolet absorber, a photostabilizer, a leveling agent, a rheology adjusting agent, an adhesive adjuvant (e.g., a silane coupling agent), a pigment, a dye, or an antifoaming agent.

 [0062] <Preparation Method for Photocurable Composition for Imprinting>

15 No particular limitation is imposed on the preparation method for the photocurable composition for imprinting of the present invention. The preparation method involves, for example, mixing of the components (a), (b1), (b2), (c), (d), and (e) and optionally the components (f) and/or (g) and (h) in predetermined proportions, to thereby prepare a homogeneous solution.

20 [0063] The photocurable composition for imprinting of the present invention prepared in the form of solution is preferably used after filtration with, for example, a filter having a pore diameter of 0.1 μm to 10 μm .

 [0064] <Cured Product>

 The photocurable composition for imprinting of the present invention can be formed
25 into a cured product through light exposure (photocuring). The present invention encompasses the cured product. Examples of the rays used for light exposure include ultraviolet rays, electron beams, and X-rays. Examples of the light source used for ultraviolet irradiation include sunlight, a chemical lamp, a low-pressure mercury lamp, a high-pressure mercury lamp, a metal halide lamp, a xenon lamp, and UV-LED. After

the light exposure, the cured product may be subjected to post-baking for stabilizing the physical properties of the product. No particular limitation is imposed on the post-baking method, and the post-baking is generally performed with, for example, a hot plate or an oven at 50°C to 260°C for one minute to 24 hours.

5 [0065] The cured product produced through photocuring of the photocurable composition for imprinting of the present invention has a high Abbe number v_D of 53 or more. Thus, the photocurable composition for imprinting of the present invention can be suitably used for formation of a resin lens.

[0066] <Molded Product>

10 The photocurable composition for imprinting of the present invention can be readily produced into any molded product in parallel with formation of a cured product by, for example, an imprint-molding process. The production method for the molded product includes, for example, a step of charging the photocurable composition for imprinting of the present invention into a space between a support and a casting mold which are in
15 contact with each other, or into a space in a separable casting mold; a step of photocuring the photocurable composition for imprinting charged in the space through light exposure; a step of releasing a photocured product prepared through the photocuring step from the casting mold; and a step of heating the photocured product before, during, or after the releasing step. The method may further include a developing step of washing and
20 removing an uncured portion with an organic solvent after the step of releasing the photocured product prepared through the photocuring step from the casting mold and before the heating step. No particular limitation is imposed on the method for preparing the uncured portion. For example, the uncured portion (i.e., a portion that is not
25 exposed to light) can be prepared by exposing only a predetermined position to light using a mask or through projection exposure. After the developing step, the photocured product may optionally be subjected to light exposure again for photocuring.

[0067] The aforementioned photocuring step through light exposure can be performed under conditions for producing the aforementioned cured product. No particular limitation is imposed on the conditions for the step of heating the photocured

product, and the heating step is generally performed under appropriately determined conditions (i.e., 50°C to 260°C for one minute to 24 hours). Examples of the heating means include, but are not particularly limited to, a hot plate and an oven. The molded product produced by the aforementioned method can be suitably used as a lens for a camera module.

Examples

[0068] The present invention will next be described in more detail by way of examples. However, the present invention should not be construed as being limited to the following examples. In Examples and Comparative Examples described below, the following apparatuses and conditions were used for preparation of samples and analysis of the physical properties of the samples.

[0069] (1) Stirring-defoaming machine

Apparatus: planetary centrifugal mixer Awatori Rentaro (registered trademark)

ARE-310, available from THINKY CORPORATION

(2) UV light exposure

Apparatus: batch-type UV-LED irradiation apparatus (wavelength: 365 nm), available from CCS Inc.

(3) Abbe number v_D

Apparatus: multi-wavelength refractometer Abbemat MW, available from Anton Paar

Measurement temperature: 23°C

(4) Thermal shock tester

Apparatus: small thermal shock tester TSE-11-A, available from ESPEC CORP.

Conditions: -40°C/85°C, exposure time at -40°C and 85°C = 30 minutes, 50 cycles

(5) Digital microscope (observation of peeling in thermal shock test)

Apparatus: KH-7700, MXG-2500REZ, available from HIROX CO., LTD.

Conditions: reflection (dark field), Low-Range, $\times 100$

(6) Measurement of transmittance

Apparatus: ultraviolet-visible-near-infrared spectrophotometer V-670, available from JASCO Corporation

Reference: air

(7) Formation of anti-reflective layer

5 Apparatus: SRV4300 Series, available from SHINKO SEIKI CO., LTD.

System: RF sputtering magnetron type

Conditions: target material = SiO₂, vertical distance between target and substrate = 100 mm, temperature = room temperature, sputtering time = 29 minutes

(8) Optical microscope (observation of anti-reflective coating)

10 Apparatus: VHX-1000, VH-Z1000R, available from KEYENCE CORPORATION

Conditions: reflection (bright field), objective ×500

[0070] Suppliers of compounds used in Production Examples, Examples, and Comparative Examples are as follows.

MEK-AC-2140Z: available from Nissan Chemical Corporation, trade name:

15 ORGANO SILICA SOL MEK-AC-2140Z

APG-200: available from SHIN-NAKAMURA CHEMICAL Co., Ltd., trade name: NK Ester APG-200

V#260: available from OSAKA ORGANIC CHEMICAL INDUSTRY LTD., trade name: Viscoat #260

20 V#230: available from OSAKA ORGANIC CHEMICAL INDUSTRY LTD., trade name: Viscoat #230

SA1303P: available from Advanced Softmaterials Inc., trade name: SeRM (registered trademark) Super Polymer SA1303P

25 UA-4200: available from SHIN-NAKAMURA CHEMICAL Co., Ltd., trade name: NK Oligo UA-4200

EBECRYL 4513: available from DAICEL-ALLNEX LTD., trade name: EBECRYL4513

I184: available from IGM Resins, trade name: OMNIRAD (registered trademark) 184 (former IRGACURE (registered trademark) 184)

I245: available from BASF Japan Ltd., trade name: IRGANOX (registered trademark) 245

AO-503: available from ADEKA CORPORATION, trade name: ADK STAB (registered trademark) AO-503

5 BA: available from Tokyo Chemical Industry Co., Ltd., compound name: butyl acrylate

HEMA: available from Tokyo Chemical Industry Co., Ltd., compound name: 2-hydroxyethyl methacrylate

KBM-503: available from Shin-Etsu Chemical Co., Ltd., trade name: KBM-503

10 PEPT: available from SC Organic Chemical Co., Ltd., trade name: PEPT [0071] [Production Example 1]

A 500 mL eggplant-shaped flask was charged with 200 g of V#260 (i.e., a bifunctional (meth)acrylate compound of Formula (2), component (b1)), and V#260 was dissolved in 200 g of methyl ethyl ketone (hereinafter abbreviated as "MEK"). To the resultant solution was added 441 g of MEK-AC-2140Z (MEK dispersion (solid content concentration: 45% by mass) of silica particles having surfaces modified with a (meth)acryloyloxy group and having a primary particle diameter of 10 nm to 15 nm) (i.e., silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, component (a)), and the resultant mixture was stirred for 15 homogenization. Thereafter, MEK was distilled off with an evaporator at 50°C and a reduced pressure of 133.3 Pa or less, to thereby produce a V#260 dispersion of the silica particles having surfaces modified with a functional group having an ethylenically unsaturated group (amount of the surface-modified silica particles: 50% by mass).

[0072] [Production Example 2]

25 A 500 mL eggplant-shaped flask was charged with 50 g of V#230 (i.e., a bifunctional (meth)acrylate compound of Formula (2), component (b1)), and V#230 was dissolved in 50 g of MEK. To the resultant solution was added 111 g of MEK-AC-2140Z (MEK dispersion (solid content concentration: 45% by mass) of silica particles having surfaces modified with a (meth)acryloyloxy group and having a primary

particle diameter of 10 nm to 15 nm) (i.e., silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, component (a)), and the resultant mixture was stirred for homogenization. Thereafter, MEK was distilled off with an evaporator at 50°C and a reduced pressure of 133.3 Pa or less, to thereby produce a V#230 dispersion of the silica particles having surfaces modified with a functional group having an ethylenically unsaturated group (amount of the surface-modified silica particles: 50% by mass).

[0073] [Production Example 3]

A 500 mL eggplant-shaped flask was charged with 50.0 g of UA-4200 (i.e., a urethane (meth)acrylate compound, component (b2)), and UA-4200 was dissolved in 50.0 g of MEK. To the resultant solution was added 111 g of MEK-AC-2140Z (MEK dispersion (solid content concentration: 45% by mass) of silica particles having surfaces modified with a (meth)acryloyloxy group and having a primary particle diameter of 10 nm to 15 nm) (i.e., silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, component (a)), and the resultant mixture was stirred for homogenization. Thereafter, MEK was distilled off with an evaporator at 60°C and a reduced pressure of 133.3 Pa or less, to thereby produce a UA-4200 dispersion of the silica particles having surfaces modified with a functional group having an ethylenically unsaturated group (amount of the surface-modified silica particles: 50% by mass).

[0074] [Production Example 4]

A 500 mL eggplant-shaped flask was charged with 20.0 g of V#260 (i.e., a bifunctional (meth)acrylate compound of Formula (2), component (b1)). Subsequently, 40.0 g of SA1303P (MEK dispersion (solid content concentration: 50% by mass) of a polyrotaxane containing a cyclic molecule of cyclodextrin having an acrylic group on its side chain) (i.e., a polyrotaxane having an ethylenically unsaturated group, component (c)) was added to V#260, and the resultant mixture was stirred for homogenization. Thereafter, MEK was distilled off with an evaporator at 50°C and a reduced pressure of 133.3 Pa or less, to thereby produce a V#260 solution of the polyrotaxane having an

ethylenically unsaturated group (amount of the polyrotaxane having an ethylenically unsaturated group: 50% by mass).

[0075] [Production Example 5]

A 500 mL eggplant-shaped flask was charged with 20.0 g of V#230 (i.e., a bifunctional (meth)acrylate compound of Formula (2), component (b1)). Subsequently, 40.0 g of SA1303P (MEK dispersion (solid content concentration: 50% by mass) of a polyrotaxane containing a cyclic molecule of cyclodextrin having an acrylic group on its side chain) (i.e., a polyrotaxane having an ethylenically unsaturated group, component (c)) was added to V#230, and the resultant mixture was stirred for homogenization.

Thereafter, MEK was distilled off with an evaporator at 50°C and a reduced pressure of 133.3 Pa or less, to thereby produce a V#230 solution of the polyrotaxane having an ethylenically unsaturated group (amount of the polyrotaxane having an ethylenically unsaturated group: 50% by mass).

[0076] [Production Example 6]

A 500 mL eggplant-shaped flask was charged with 11.0 g of UA-4200 (i.e., a urethane (meth)acrylate compound, component (b2)). Subsequently, 18.0 g of SA1303P (MEK dispersion (solid content concentration: 50% by mass) of a polyrotaxane containing a cyclic molecule of cyclodextrin having an acrylic group on its side chain) (i.e., a polyrotaxane having an ethylenically unsaturated group, component (c)) was added to UA-4200, and the resultant mixture was stirred for homogenization. Thereafter, MEK was distilled off with an evaporator at 50°C and a reduced pressure of 133.3 Pa or less, to thereby produce a UA-4200 solution of the polyrotaxane having an ethylenically unsaturated group (amount of the polyrotaxane having an ethylenically unsaturated group: 45% by mass).

[0077] [Example 1]

The solid content of the V#260 dispersion produced in Production Example 1 (i.e., the silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, component (a)), V#260 (i.e., a bifunctional (meth)acrylate compound of Formula (2), component (b1)), UA-4200 (i.e., a urethane

(meth)acrylate compound having an ethylenically unsaturated group, component (b2)), the solid content of the V#260 solution produced in Production Example 4 (i.e., a polyrotaxane having an ethylenically unsaturated group, component (c)), I184 as a photoradical initiator (component (d)), I245 as a phenolic antioxidant (component (f)), and AO-503 as a sulfide antioxidant (component (g)) were mixed in proportions shown in Table 1 below. The proportion of V#260 shown in Table 1 below includes the V#260 component contained in the V#260 dispersion and the V#260 solution. Thereafter, the resultant mixture was shaken at 50°C for 16 hours, and then PEPT as a polyfunctional thiol compound of Formula (1) (component (e)) was added to the mixture, followed by stirring and defoaming with the aforementioned stirring-defoaming machine for 10 minutes, to thereby prepare a photocurable composition for imprinting 1. In Table 1 below, the term "parts" refers to "parts by mass."

[0078] [Examples 2 to 12 and Comparative Examples 1 and 2]

In Examples 2, 3, 5, 6, and 9, photocurable compositions for imprinting 2, 3, 5, 6, and 9 were prepared by mixing components (a) to (g) in proportions shown in Table 1 below in the same manner as in Example 1. In Example 4, a photocurable composition for imprinting 4 was prepared by mixing components (a) to (g) in proportions shown in Table 1 below in the same manner as in Example 1, except that the solid content of the V#230 dispersion produced in Production Example 2 was used as component (a), and the solid content of the V#230 solution produced in Production Example 5 was used as component (c). In Examples 7 and 8, photocurable compositions for imprinting 7 and 8 were prepared by mixing components (a) to (g) in proportions shown in Table 1 below in the same manner as in Example 1, except that the solid content of the UA-4200 dispersion produced in Production Example 3 was used as component (a), and the solid content of the UA-4200 solution produced in Production Example 6 was used as component (c). In Examples 10, 11, and 12, photocurable compositions for imprinting 10, 11, and 12 were prepared through the following procedure: the solid content of the V#230 dispersion produced in Production Example 2 was used as component (a); the solid content of the V#230 solution produced in Production Example 5 was used as

component (c); components (a) to (d) and (f) to (h) were mixed in proportions shown in Table 1 below; the resultant mixture was shaken at 50°C for 16 hours; component (e) was added to the mixture; and the mixture was subjected to stirring and defoaming with the aforementioned stirring-defoaming machine for 10 minutes. In Comparative Example 1, a photocurable composition for imprinting 13 was prepared by mixing components in proportions shown in Table 1 below in the same manner as in Example 1, except that the solid content of the V#230 dispersion produced in Production Example 2 was used as component (a), and component (c) was not used. In Comparative Example 2, a photocurable composition for imprinting 14 was prepared by mixing components (a) to (g) in proportions shown in Table 1 below in the same manner as in Example 1, except that component (e) was not used.

[0079]

Table 1

		(a)		(b)		(c)		(d)		(e)		(f)		(g)		(h)	
		Parts		Parts		Parts		Parts		Parts		Parts		Parts		Parts	
Example 1	Photocurable composition 1	16	MEK-AC-2140Z	V#260 UA-4200	47 25	SA1303P	7	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 2	Photocurable composition 2	23	MEK-AC-2140Z	V#260 UA-4200	43.5 21.5	SA1303P	7	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 3	Photocurable composition 3	24	MEK-AC-2140Z	V#260 UA-4200	44 22	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 4	Photocurable composition 4	24	MEK-AC-2140Z	V#230 UA-4200	35 31	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 5	Photocurable composition 5	16	MEK-AC-2140Z	V#260 EBECRYL 4513	37 35	SA1303P	7	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 6	Photocurable composition 6	16	MEK-AC-2140Z	V#260 UA-4200	47 25	SA1303P	7	I184	1	NR1	5	I245	0.7	AO-503	0.5	-	-
Example 7	Photocurable composition 7	24	MEK-AC-2140Z	UA-4200	66	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 8	Photocurable composition 8	24	MEK-AC-2140Z	APG-200 UA-4200	35 31	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 9	Photocurable composition 9	23	MEK-AC-2140Z	V#260 APG-200 UA-4200	34.5 5 27.5	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Example 10	Photocurable composition 10	23	MEK-AC-2140Z	V#230 UA-4200	34.5 27.5	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	BA	5
Example 11	Photocurable composition 11	23	MEK-AC-2140Z	V#230 UA-4200	37.5 27.5	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	HEMA	2
Example 12	Photocurable composition 12	23	MEK-AC-2140Z	V#230 UA-4200	37.5 27.5	SA1303P	5	I184	1	PEPT	5	I245	0.7	AO-503	0.5	KBM-503	2
Comparative Example 1	Photocurable composition 13	24	MEK-AC-2140Z	V#230 UA-4200	38 33	-	-	I184	1	PEPT	5	I245	0.7	AO-503	0.5	-	-
Comparative Example 2	Photocurable composition 14	24	MEK-AC-2140Z	V#260 UA-4200	44 27	SA1303P	5	I184	1	-	-	I245	0.7	AO-503	0.5	-	-

[0080] [Formation of Cured Film]

Each of the photocurable compositions for imprinting prepared in Examples 1 to 12 and Comparative Examples 1 and 2 and a silicone rubber-made spacer (thickness: 500 μm) were sandwiched between two glass substrates subjected to release treatment by application of NOVEC (registered trademark) 1720 (available from 3M Japan Limited) and subsequent drying. The thus-sandwiched photocurable composition for imprinting was subjected to UV light exposure with the aforementioned UV-LED irradiation apparatus at 30 mW/cm^2 for 200 seconds. After the light exposure, the resultant cured product was removed from the release-treated glass substrates, and then heated on a hot plate at 100°C for 10 minutes, to thereby form a cured film having a diameter of 1 cm and a thickness of 0.5 mm.

[0081] [Evaluation of Transmittance]

The transmittance of the cured film formed as described above was measured at a wavelength of 410 nm with the aforementioned spectrophotometer. Subsequently, the cured film was subjected to a heat resistance test (i.e., heating in an oven at 125°C for 94 hours) and then cooled to room temperature. The transmittance of the thus-cooled cured film was measured in the same manner as described above. The results are shown in Table 2 below.

[0082] [Evaluation of Abbe Number ν_D]

The cured film formed as described above was cut out with a cutter into a size of about 6 mm $\times$ about 6 mm, and the Abbe number ν_D of the cured film was measured with the aforementioned multi-wavelength refractometer. The results are shown in Table 2 below.

[0083] [Evaluation of Peeling Resistance of Cured film in Thermal Shock Test]

An appropriate amount of each of the photocurable compositions for imprinting prepared in Examples 1 to 12 and Comparative Examples 1 and 2 was applied onto a photomask substrate (having an opening of 1 cm $\times$ 1 cm) subjected to release treatment by application of NOVEC (registered trademark) 1720 (available from 3M Japan Limited) and subsequent drying. Thereafter, the photocurable composition for

imprinting was sandwiched, via a silicone rubber-made spacer (thickness: 500 μm), between the release-treated photomask substrate and a non-alkaline glass substrate (10 cm $\times$ 10 cm, thickness: 0.7 mm). The non-alkaline glass substrate was subjected to adhesion treatment by application of a solution prepared by dilution of an adhesive
5 adjuvant (product name: KBM-5803, available from Shin-Etsu Chemical Co., Ltd.) with propylene glycol monomethyl ether acetate (hereinafter abbreviated as "PGMEA") to 10% by mass and subsequent drying of the applied solution. The thus-sandwiched photocurable composition for imprinting was subjected to UV light exposure with the aforementioned UV-LED irradiation apparatus at 115 mW/cm² for 2.2 seconds. After
10 the light exposure, the resultant cured product was removed from the release-treated photomask substrate, and then immersed (developed) in stirred PGMEA, followed by rinsing with PGMEA, to thereby remove an unexposed portion. Consequently, a cured film having a size of 1 cm $\times$ 1 cm and a thickness of 0.5 mm was formed on the adhesion-treated non-alkaline glass substrate. The cured film was again subjected to
15 UV light exposure with the aforementioned UV-LED irradiation apparatus at 30 mW/cm² for 191.7 seconds, and then heated on a hot plate at 100°C for 10 minutes. Thereafter, the cured film was placed in the aforementioned thermal shock tester (available from ESPEC CORP.). After the thermal shock test was performed for 50 cycles, the cured film was removed from the tester, and a corner of the cured film was observed with the
20 aforementioned digital microscope (available from HIROX CO., LTD.). Evaluation "×" was given when the peeling of the cured film from the adhesion-treated non-alkaline glass substrate was determined, whereas evaluation "○" was given when the peeling of the cured film was not determined. The results are shown in Table 2 below. For example, FIG. 1 is a photograph showing a corner of a cured film produced from the
25 photocurable composition for imprinting 6 of Example 6 (evaluation "○"), and FIG. 2 is a photograph showing a corner of a cured film produced from the photocurable composition for imprinting 14 of Comparative Example 2 (evaluation "×").

[0084] [Formation of Anti-Reflective Layer (AR Layer) and Evaluation of Crack Resistance Thereof]

Firstly, 0.03 g of each of the photocurable compositions for imprinting prepared in Examples 3 and 4 and Comparative Example 1 was applied onto a glass substrate subjected to release treatment by application of NOVEC (registered trademark) 1720 (available from 3M Japan Limited) and subsequent drying. Thereafter, the photocurable composition for imprinting was sandwiched, via a silicone rubber-made spacer (thickness: 500 μm), between the release-treated glass substrate and a non-alkaline glass substrate (6 cm $\times$ 6 cm, thickness: 0.7 mm). The non-alkaline glass substrate was subjected to adhesion treatment by application of a solution prepared by dilution of an adhesive adjuvant (product name: KBM-5103, available from Shin-Etsu Chemical Co., Ltd.) with PGMEA to 30% by mass and subsequent drying of the applied solution. The thus-sandwiched photocurable composition for imprinting was subjected to UV light exposure with the aforementioned UV-LED irradiation apparatus at 30 mW/cm² for 200 seconds. After the light exposure, the resultant cured product was removed from the release-treated glass substrate, and then heated on a hot plate at 100°C for 10 minutes, to thereby form a cured film having a diameter of 1 cm, a thickness of 0.5 mm, and a mass of 0.03 g on the non-alkaline glass substrate.

[0085] On the cured film formed on the non-alkaline glass substrate, a silicon oxide layer (thickness: 200 nm) serving as an anti-reflective layer was formed with the aforementioned RF sputtering apparatus under the aforementioned conditions. The anti-reflective layer on the cured film was observed with the aforementioned optical microscope (available from KEYENCE CORPORATION), to thereby determine the presence or absence of cracks. Thereafter, the non-alkaline glass substrate was heated on a hot plate at 175°C for 2 minutes and 30 seconds, to thereby perform a heat resistance test. Regarding the non-alkaline glass substrate after the heat resistance test, the presence or absence of cracks was determined in the anti-reflective layer on the cured film through observation with the optical microscope (available from KEYENCE CORPORATION), to thereby evaluate the crack resistance of the anti-reflective layer. Evaluation "×" was given when cracks were visually observed in the anti-reflective layer on the cured film, whereas evaluation "○" was given when neither cracks nor wrinkles

were visually observed in the anti-reflective layer on the cured film. The results are shown in Table 2 below.

[0086]

Table 2

	Peeling resistance of cured film	Transmittance (410 nm)		Abbe number	Resistance to formation of AR
		Before heat resistance test	After heat resistance test		
Example 1	○	91%	88%	56	-
Example 2	○	91%	88%	57	-
Example 3	○	91%	89%	57	○
Example 4	○	91%	89%	57	○
Example 5	○	89%	87%	56	-
Example 6	○	90%	90%	57	-
Example 7	○	90%	85%	57	-
Example 8	○	92%	84%	57	-
Example 9	○	91%	89%	55	-
Example 10	○	91%	89%	55	-
Example 11	○	91%	89%	56	-
Example 12	○	91%	90%	56	-
Comparative Example 1	×	91%	88%	57	○
Comparative Example 2	×	90%	90%	57	-

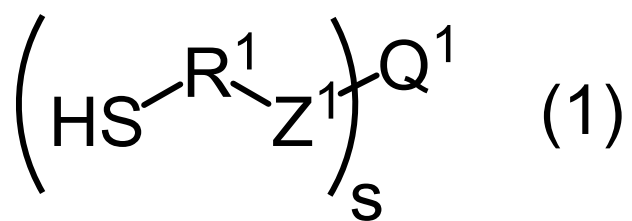
5 [0087] The cured film formed from the photocurable composition for imprinting 13 of Comparative Example 1 (not containing component (c)) and the cured film formed from the photocurable composition for imprinting 14 of Comparative Example 2 (not containing component (e)) were peeled from the non-alkaline glass substrate after the thermal shock test. In contrast, the cured film formed from each of the photocurable compositions for imprinting of Examples 1 to 12 (containing components (a) to (e)) was not peeled from the non-alkaline glass substrate after the thermal shock test. The cured film formed from the photocurable composition for imprinting of the present invention exhibited an Abbe number v_D of 53 or more. Thus, these results indicated that a cured film (molded product) produced from the photocurable composition for imprinting of the present invention exhibits a high Abbe number, exhibits excellent adhesion to a support (i.e., does not peel from the support even after undergoing a thermal shock test), and cracks do not occur in an anti-reflective layer formed on the cured film (molded product) after thermal treatment at 175°C; i.e., the cured film has properties desired for a lens for a

high-resolution camera module.

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CLAIMS

1. A photocurable composition for imprinting, the composition comprising the following components (a), (b), (c), (d), and (e):

- 5 (a) silica particles having a primary particle diameter of 1 nm to 100 nm and having surfaces modified with a functional group having an ethylenically unsaturated group;
- (b) a polyfunctional (meth)acrylate compound having an ethylenically unsaturated group;
- (c) a polyrotaxane having an ethylenically unsaturated group;
- 10 (d) a photoradical initiator; and
- (e) a polyfunctional thiol compound of the following Formula (1):



- (wherein R^1 is a single bond or a linear or branched alkylene group having a carbon atom number of 1 to 6; Z^1 is a single bond, an ester bond, or an ether bond; Q^1 is a C_{2-12}
- 15 organic group containing at least one heteroatom or containing no heteroatom, or a heteroatom; and s is an integer of 2 to 6).

2. The photocurable composition for imprinting according to claim 1, wherein the composition further comprises the following component (f) and/or (g):

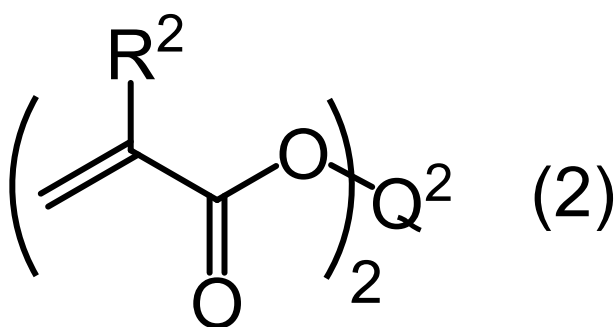
- 20 (f) a phenolic antioxidant; and
- (g) a sulfide antioxidant.

3. The photocurable composition for imprinting according to claim 1 or 2, wherein the composition further comprises the following component (h):

- 25 (h) a monofunctional (meth)acrylate compound having an ethylenically unsaturated group.

4. The photocurable composition for imprinting according to any one of claims 1 to 3, wherein the component (b) contains at least one of the following components (b1) and (b2):

- 5 (b1) a bifunctional (meth)acrylate compound of the following Formula (2); and
 (b2) a urethane (meth)acrylate compound (except for the polyrotaxane having an ethylenically unsaturated group, which is the component (c)) or an epoxy (meth)acrylate compound:



- 10 (wherein R² is a hydrogen atom or a methyl group; and Q² is a linear or branched alkylene group having a carbon atom number of 2 to 16).

5. The photocurable composition for imprinting according to claim 4, wherein the component (b) contains the components (b1) and (b2).

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6. The photocurable composition for imprinting according to any one of claims 1 to 5, wherein the silica particles having surfaces modified with a functional group having an ethylenically unsaturated group, which are the component (a), are silica particles having surfaces modified with a (meth)acryloyloxy group bonded to a silicon atom via a divalent

20 linking group.

7. A cured product produced from the photocurable composition for imprinting according to any one of claims 1 to 6.

8. A method for producing a resin lens, the method comprising a step of imprint-molding the photocurable composition for imprinting according to any one of claims 1 to 6.

5 9. A method for producing a molded product from a photocurable composition for imprinting, the method comprising a step of charging the photocurable composition for imprinting according to any one of claims 1 to 6 into a space between a support and a casting mold which are in contact with each other, or into a space in a separable casting mold; and a step of photocuring the photocurable composition for imprinting charged in
10 the space through light exposure.

 10. The method for producing a molded product according to claim 9, wherein the method further comprises, after the photocuring step, a step of releasing the resultant photocured product from the casting mold, and a step of heating the photocured product
15 before, during, or after the releasing step.

 11. The method for producing a molded product according to claim 10, wherein the method further comprises a developing step using an organic solvent after the releasing step and before the heating step.

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 12. The method for producing a molded product according to any one of claims 9 to 11, wherein the molded product is a lens for a camera module.