Curable composition

Field of the invention

The present invention relates to a curable composition, preferably being a photo-curable composition, method for preparing a curable composition, method for preparing a cured layer, a cured layer and a stacked layer.

Background Art

Downscaling is an unbroken trend in the semiconductor industry to increase performance of microchips. However, achieving 7nm node technology and beyond significantly increases complexity and requires some new process and material solutions.

Inkjet Adaptive Planarization processes can be used to planarize surfaces of substrates. For this purpose, liquid drops of a photocurable composition are printed on the surface of substrates. The drop pattern can be tailored to existing topographies. A flat superstrate is brought into direct contact with the liquid to form a flat layer of liquid. The flat liquid layer is typically cured under the influence of UV-light, and after removal of the superstrate, a planar surface is obtained, which can be subjected to subsequent processing steps.

State-of-the-art photocurable compositions usually contain a high content of acrylate monomers.

US 2020/0339828 A1 describes the use of certain photocurable compositions comprising a polymerizable material and a photoinitiator, wherein at least 90 wt% of the polymerizable material comprise acrylate monomers including an aromatic group.

US 2021/0198400 A1 deals with a certain photocurable compositions including 1,3-benzoaxazine and acrylate monomers.

US 2020/201178 A1 describes certain photocurable compositions including a shrinkage compensating agent.

US 2021/0070906 A1 describes certain curable compositions that comprise a polymerizable material and an initiator, wherein the polymerizable material comprises a first monomer and a second monomer, the second monomer including a ring structure selected from a maleimide-ring, a pyrone ring, or a 2-furanone ring.

US 2022/0185914 A1 describes a photocurable composition including the polymerizable material, wherein the polymerizable material comprises at least one multifunctional vinylbenzene.

In another piece of prior art literature (US2023/0203210 A1), polymerizable compositions based on vinylbenzene or alkyne containing bis aromatic systems are reported. The compositions can contain acrylates, as allowed by the subclaim of the reference.

Patent Literature

1. US 2020/0339828 A1
2. US 2021/0198400 A1
3. US 2020/201178 A1
4. US 2021/0070906 A1
5. US 2022/0185914 A1
6. US 2023/0203210 A1

Non- Patent Literature

No literature

Summary of the invention

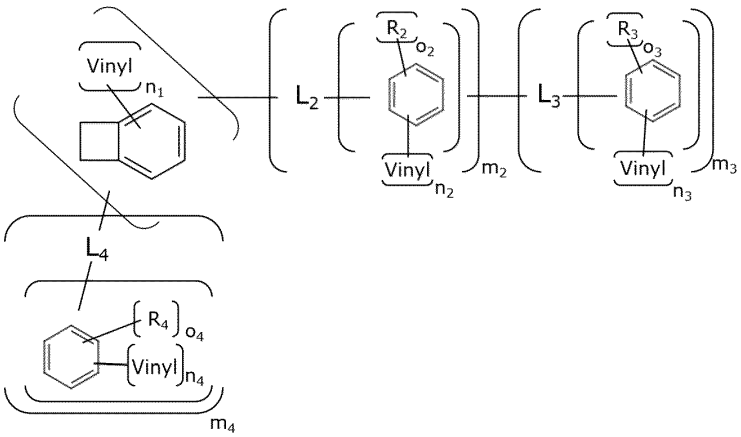
However, the inventors newly have found that there is still one or more of considerable problems for which improvement is desired, as listed below;

improved thermal stability after curing, preferably at about 350 C degree (°C) or more; lower shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer, namely over different pattern topographies of a substrate; low viscosity and/or low vapor pressure as a composition, preferably suitable for ink-jet printing; applicable for ink-jet printing to make a cured layer(s); and providing a cured layer with mechanical durability.

The inventors aimed to solve one or more of the above-mentioned problems.

Then, the present inventors have surprisingly found that one or more of the above-described technical problems can be solved by the features as defined in the claims.

Namely, it is found a novel curable composition, preferably being a photo-curable composition, comprising at least a 1st monomer compound and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I).



-(I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 1$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;

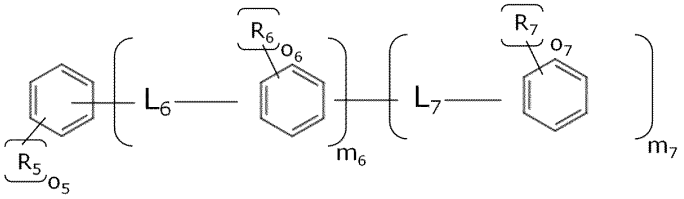
when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;

each of L_2 to L_4 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

The present invention also provides a composition further comprising a 2nd monomer compound represented by chemical formula (II).



-(II)

where

each of m_6 and m_7 is independently 0 or 1;

o_5 is 0, 1, 2, 3, 4, 5 or 6;

each of o_6 and o_7 is independently 0, 1 or 2;

each of R_5 to R_7 is independently C_{1-4} alkyl, vinyl or ethynyl;

the 2nd monomer has at least one of vinyl or ethynyl at present;

each of L_6 and L_7 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

As another aspect, the present invention also provides a method for preparing a composition, further comprising at least the following step (A);

(A) Mixing at least any embodiment of the 1st monomer compound and a polymerization initiator.

As the other embodiment, the present invention also provides a method for preparing a cured layer, comprising at least the following steps (i^a) and (i^b):

(i^a) providing any embodiment of the composition onto a substrate, preferably by printing, preferably by spin-coating, slit coating or ink-jetting;

(i^d) optionally bringing the composition into contact with a template;

(i^b) curing the composition by heat and/or by irradiating the composition with light to form a cured layer;

(i^e) optionally removing the template from the cured layer.

This invention also provides a cured layer which is obtained or obtainable by the method described above and below. As further another aspect, this invention provides a stacked layer comprising a substrate and any embodiment of the cured layer.

The present invention also provides a new compound represented by formula (I).

Formula (I) is same to described as above. $n_1+n_2+n_3+n_4 \geq 2$.

Unless otherwise specified, each of definition and detailed descriptions of each of parts in formula (I) referred in chemical compound is independently same to the ones of formula (I) referred in the curable composition.

Technical effects of the invention

The present invention provides one or more of the following technical effects:

improved thermal stability after curing, preferably at about 350 C degree or more; lower shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer, namely over

different pattern topographies of a substrate; low viscosity and/or low vapor pressure as a composition, preferably suitable for ink-jet printing; applicable for ink-jet printing to make a cured layer(s); and providing a cured layer with mechanical durability.

Brief description of the drawings

[Figure 1]

Grey (dashed): isothermal baking behavior of prior-art (100% compound B + 4 wt% OXE02).

Black (solid): isothermal baking behavior of W.E.1 (50 wt% compound A + 50 wt% compound + 4 wt% OXE02).

Definition of the terms

Unless otherwise specified in the present specification, the definitions and examples described in this paragraph are followed.

The singular form includes the plural form and “one” or “that” means “at least one”. An element of a concept can be expressed by a plurality of species, and when the amount (for example, mass % or mol %) is described, it means sum of the plurality of species.

“And/or” includes a combination of all elements and also includes single use of the element.

When a numerical range is indicated using “to” or “-“, it includes both endpoints and units thereof are common. For example, 5 to 25 mol % means 5 mol % or more and 25 mol % or less.

The descriptions such as “C_{x-y}”, “C_x-C_y” and “C_x” mean the number of carbons in a molecule or substituent. For example, C_{1-6} alkyl means an alkyl chain having 1 or more and 6 or less carbons (methyl, ethyl, propyl, butyl, pentyl, hexyl etc.).

When a polymer has multiple types of repeating units, these repeating units undergo copolymerization. This copolymerization may be any of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization, or a mixture thereof. When a polymer or resin is

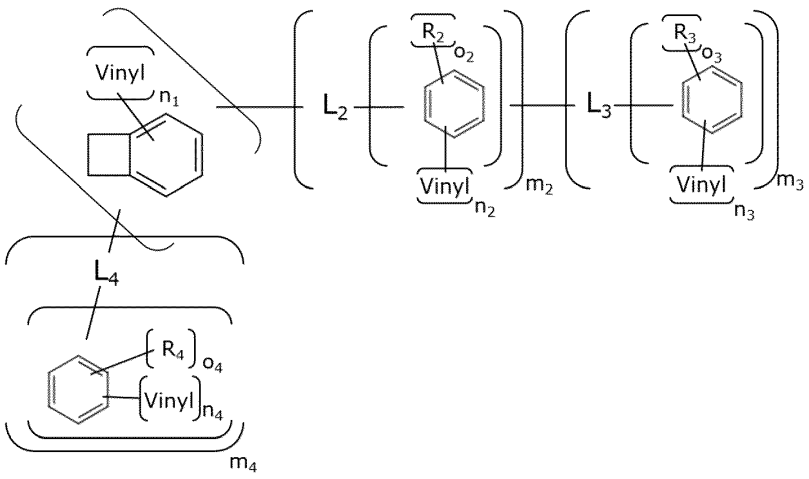
represented by a structural formula, n, m or the like that is attached next to parentheses indicate the number of repetitions.

Celsius is used as the temperature unit. For example, 20 degrees means 20 degrees Celsius.

The additive refers to a compound itself having a function thereof (for example, in the case of a base generator, a compound itself that generates a base). An embodiment in which the compound is dissolved or dispersed in a solvent and added to a composition is also possible. As one embodiment of the present invention, it is preferable that such a solvent is contained in the composition according to the present invention as the solvent (B) or another component.

Detailed description of the invention

According to the present invention, said curable composition, preferably being a photo-curable composition, comprises at least a 1st monomer compound, and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I):



- (I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 1$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;
when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;
each of L_2 to L_4 is independently selected from the group consisting of a direct bond, $C_{1\text{-}15}$ alkylene, and $C_{2\text{-}15}$ alkenylene,
where one or more non-adjacent methylene ($-CH_2-$) of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

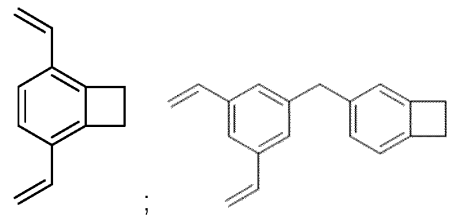
In a preferable embodiment of the present invention, said composition is a composition to be used for Inkjet Adaptive Planarization (IAP).

- **1st monomer compound**

According to the present invention, said 1st monomer compound represented by chemical formula (I).

Each of m_2 to m_4 is independently 0 or 1. M_2 is preferably 0 or 1; more preferably 0. M_3 is preferably 0 or 1; more preferably 1. It is also preferred embodiment of the invention that m_3 is 0. M_4 is preferably 0 or 1; more preferably 0.

As one embodiment of the invention, below left compound can be read as the 1st monomer in the present invention as “all of m_2 to m_4 are 0 and n_1=2”. As another embodiment, below right compound can be read as the 1st monomer in the present invention as “m_2 and m_4 are 0, m_3 is 1, n_3=2, o_3=0, and L_3 is methylene”.


;

Each of n_1 to n_4 is independently 0, 1 or 2.

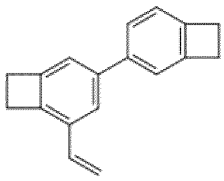
$n_1+n_2+n_3+n_4 \geq 1$. More preferably $n_1+n_2+n_3+n_4 \geq 2$. Further preferably $n_1+n_2+n_3+n_4=2$ or 3. Furthermore preferably $n_1+n_2+n_3+n_4=2$.

The 1st monomer has at least one vinyl group at present. Such embodiment is not included in the scope of the invention that $n_2=1$, $n_1=n_3=n_4=0$ and $m_2=0$, because vinyl bracketed with n_2 cannot be present in the 1st monomer. If any of the values n_1 to n_4 is 2, it is preferable to have two vinyl groups substituting the benzene ring at the meta- or para- position; with the meta- position being the more preferred option.

Each of o_2 to o_4 is independently 0 or 2.

When o_2 is 2, two R_2 are positioned as adjacent methyls, bonded to each other, forming a cyclobutene structure on the benzene ring. Same applies to each relation between o_3 and R_3, and o_4 and R_4.

As one embodiment of the invention, below compound can be read as the 1st monomer of the present invention as "m_2 and m_4 are 0, $m_3=1$, $n_1=1$, $n_3=0$, $o_3=2$, two R_3 are adjacent methyls to bond each other to make cyclobutene structure on the benzene bracketed with m_3, and L_3 is a direct bond".

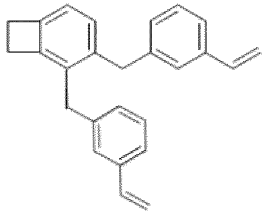


o_2 is preferably 0 or 2; more preferably 0. o_3 is preferably 0 or 2; more preferably 0. o_4 is preferably 0 or 2; more preferably 0.

The 1st monomer of the present invention comprises preferably one or two cyclobutene structure(s) at present; more preferably one cyclobutene structure at present.

Each of L_2 to L_4 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene. Such group is preferably a

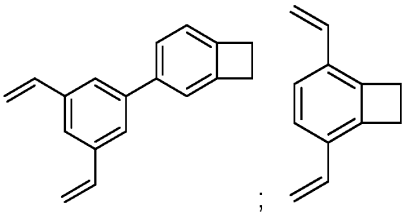
direct bond, C_{1-4} alkylene, and C_{2-4} alkenylene; more preferably a direct bond, methylene, and ethylene; further preferably a direct bond and methylene; furthermore preferably a direct bond. It is also one preferable embodiment of the present invention that each of L_2 to L_4 is methylene. As one embodiment of the invention, below compound can be read as the 1st monomer of the present invention as "m_2=0, m_3 and m_4 are 1, n_1=0, n_3=n_4=1, o_3=o_4=0, and L_3 and L_4 are methylene".



One or more non-adjacent methylene (-CH_2-) of said alkylene or alkenylene in any one or more of L_2 to L_4 can be optionally replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH. In a preferred embodiment of the invention, none of the methylene groups in L_2 to L_4 is replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH.

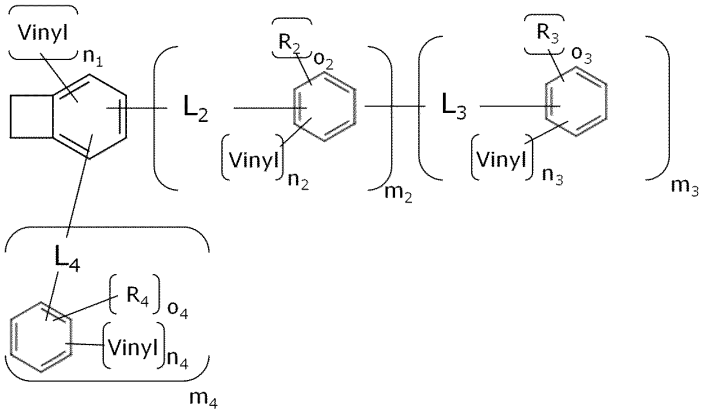
One or more H atoms in the 1st monomer can optionally be replaced by D (deuterium), F, Cl, Br, I, CN or NO_2. In a preferred embodiment of the invention, none of the H atoms in the 1st monomer are replaced by D, F, Cl, Br, I, CN or NO_2.

It goes without saying, for the sake of clarity, that the curable composition of the present invention can comprise multiple species of 1st monomer. As one embodiment, a curable composition of the present invention can comprise below two types of compounds as 1st monomers, both of which fall within chemical formula (I).



Although not to be bound by theory, it is believed that compounds containing high carbon content, preferably 80% or more in said compound, are useful for realizing carbon-rich flat underlayer, and low viscosity with relatively low vapor pressure can be ideally used in inkjet printing process, namely in the IAP process according to the present invention. It is further believed that the 1st monomer compound comprises benzocyclobutene which can form highly crosslinked thermosets after UV-induced radical polymerization. A high crosslinking density contributes to increasing chemical and thermal stability and is the key to its function as hard- mask.

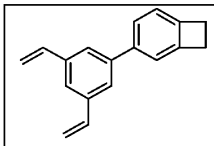
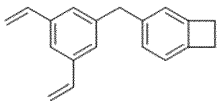
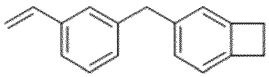
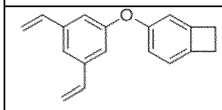
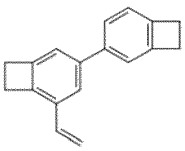
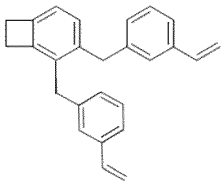
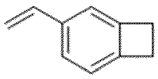
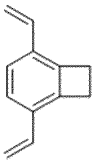
It is one of preferred embodiment of the invention that formula (I) is represented by below formula (I').



Each of definition, detailed description, explanation and embodiment of each part of the formula (I') is independently same to the formula (I) described above.

Below table A shows preferable examples of the 1st monomer compound.

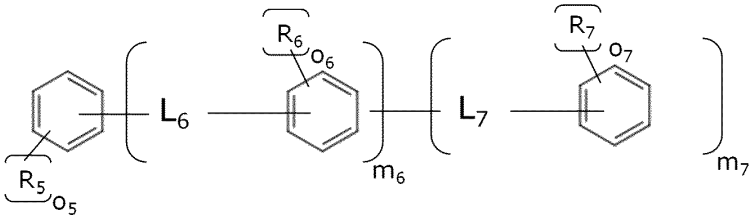
Table A:

In a preferred embodiment of the present invention, the total amount of the 1st monomer compound is in the range from 5 to 99.99 wt% based on the total amount of the composition; preferably it is from 20 to 99.99 wt%; more preferably from 40 to 99.9 wt%; further preferably 50 to 99.9 wt%; furthermore preferably 80 to 99 wt%.

- **2nd monomer compound**

According to the present invention, said composition can further comprises a 2nd monomer compound represented by chemical formula (II).



(II)

where

each of m_6 and m_7 is independently 0 or 1;

each of o_5 to o_7 is independently 0, 1 or 2;

the 2nd monomer has at least one of vinyl or ethynyl at present;

each of R_5 to R_7 is independently C_{1-4} alkyl, vinyl or ethynyl;

each of L_6 and L_7 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene,

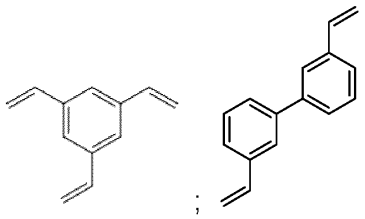
where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D (deuterium), F, Cl, Br, I, CN or NO_2.

The 1st monomer compound and the 2nd monomer compound are different of each other.

Each of m_6 and m_7 is independently 0 or 1. M_6 is preferably 0 or 1; more preferably 0. M_7 is preferably 0 or 1; more preferably 1. It is also another preferable embodiment of the present invention that m_7 is 0.

As one embodiment of the invention, below left compound can be read as the 2nd monomer in the present invention as "m_6 and m_7 are 0, o_5 is 3, and three R_5 are all vinyl". As another embodiment, below right compound can be read as the 2nd monomer in the present invention as "m_6 is 0, m_7 is 1, o_5 and o_7 are 1, and R_5 and R_7 are vinyl".



;

o_5 is 0, 1, 2, 3, 4, 5 or 6 (preferably 1, 2, 3 or 4; more preferably 1, 2 or 3; further preferably 1 or 2; furthermore preferably 2).

Each of o_6 and o_7 is independently 0, 1 or 2. o_6 is preferably 0, 1 or 2; more preferably 1 or 2; further preferably 1. o_7 is preferably 0, 1 or 2; more preferably 1 or 2; further preferably 1.

Each of R_5 to R_7 is independently C_{1-4} alkyl, vinyl or ethynyl; preferably methyl, vinyl or ethynyl; more preferably methyl or vinyl; further preferably vinyl.

The 2nd monomer has at least one of vinyl or ethynyl at present; preferably at least one of vinyl at present.

Such embodiment is not included in the scope of 2nd monomer of the present invention, that "o_6=1, o_5=o_7=0 and m_6=0", because R_6 (vinyl or ethynyl) bracketed with o_6 cannot be present in the 2nd monomer.
In the case any one of o_5 to o_7 is 2, any one or more of R_5 to R_7 substitute benzene at meta- or para- position is preferable; and at meta- position is more preferable.

Each of L_6 and L_7 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene (preferably selected from the group consisting of a direct bond, C_{1-6} alkylene, and C_{2-4} alkenylene; more preferably selected from the group consisting of a direct bond, methylene, ethylene (-CH_2-CH_2-), and propylene; further preferably selected from the group consisting of a direct bond, and ethylene: further more preferably ethylene.

One or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH. It is preferable embodiment of the invention that none methylene of L_6 and L_7 is replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH.

One or more H atoms in the 2nd monomer can optionally be replaced by D, F, Cl, Br, I, CN or NO_2. It is preferable embodiment of the invention that

none of H atom in the 2nd monomer is replaced by D, F, Cl, Br, I, CN or NO_2.

Although not to be bound by theory, it is believed that compounds containing high carbon content, preferably 80% or more in said compound, are useful for realizing carbon-rich flat underlayer, and low viscosity with relatively low vapor pressure can be ideally used in inkjet printing process, namely in the IAP process according to the present invention. Also, it is further believed that the 2nd monomer compound can form highly crosslinked thermosets after UV-induced radical polymerization. A high crosslinking density would contribute to increasing chemical and thermal stability and would be the key to its function as hardmask.

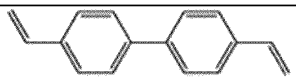
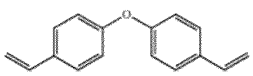
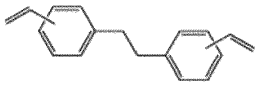
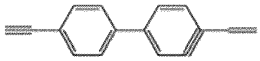
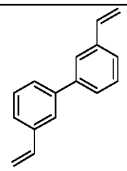
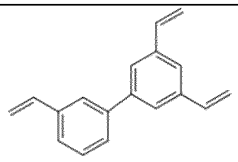
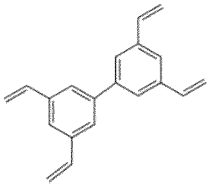
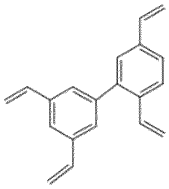
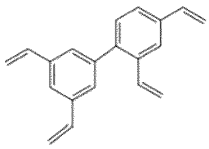
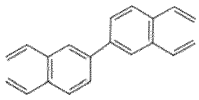
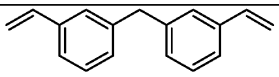
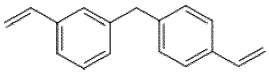
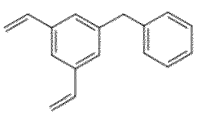
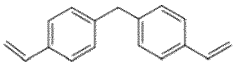
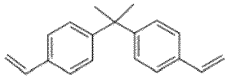
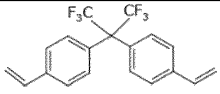
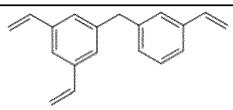
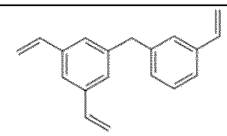
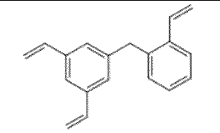
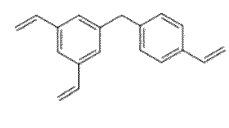
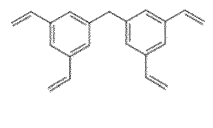
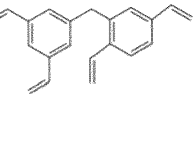
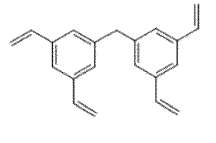
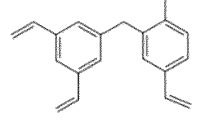
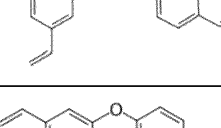
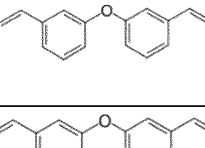
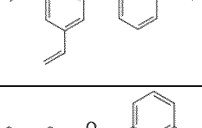
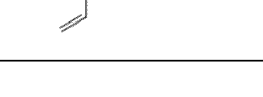
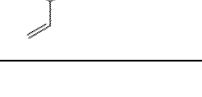
By adding the 2nd monomer compound in addition to the 1st monomer compound, and by controlling the mixing ratio, the viscosity, crosslinking property, vapor pressure of the composition and/or thermal stability, shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer; can be controlled.

As a preferred embodiment of the present invention, the sum amount of the 1st monomer compound and the 2nd monomer compound based on the total amount of the composition is in the range from 10 to 99.9wt% (preferably from 50 to 99.9 wt%; more preferably from 80 to 99 wt%).

As another embodiment of the present invention, the amount of the 2nd monomer compound based on the amount of the 1st monomer compound is in the range from 10 to 90 wt% (preferably 20 to 80 wt%; more preferably 30 to 70 wt%; further preferably 40 to 60 wt%).

Below Table B shows preferable examples of the 2nd monomer compound.

Table B:

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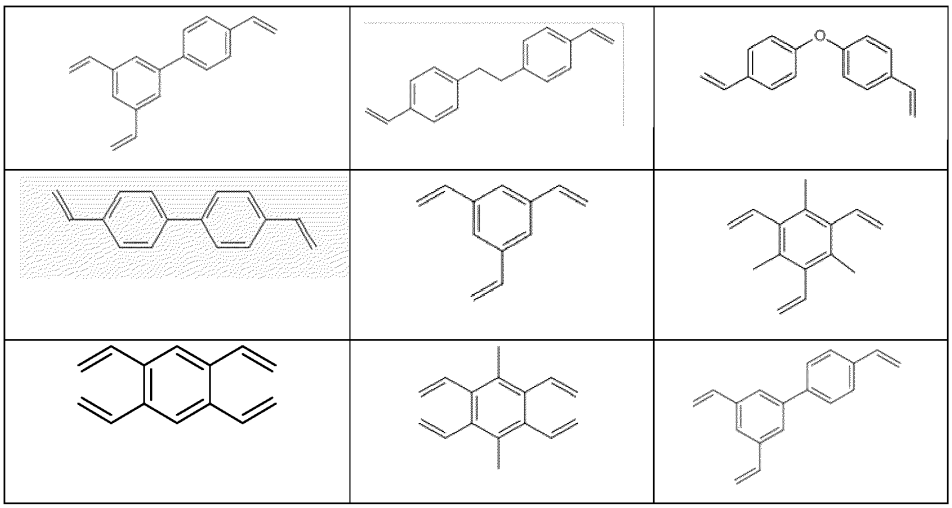


- 3rd/4th monomer compounds

In some embodiments of the present invention, the composition may optionally contain a 3rd and/or a 4th monomer compound. Said 3rd and/or 4th monomer compounds are different from each other, and it also differ from the 1st and the 2nd monomer compounds.

- Polymerization initiator

The polymerization initiator of the present invention includes a polymerization initiator that generates an acid, a base or a radical by radiation, and a polymerization initiator that generates an acid, a base or a radical by heat.

Preferably said polymerization initiator is selected from photo-radical initiators, photo-acid generators or a combination of photo-radical initiator and photo-acid generator. Examples are like Irgacure OXE02 (Boc Sciences, CAS: 478556-66-0), Omnirad 1316 (IGM Resins), Irgacure651 (Merck, CAS: 24650-42-8) and Irgacure819 (Merck, CAS: 162881-26-7).

According to the present invention, publicly available one like described in EP 3717966 A1 or WO 2021/099236 A1, can be used preferably.

- Composition

In a preferred embodiment of the present invention, the composition comprises an acrylate monomer 10 wt% or less based on the total amount of the composition, preferably it is in the rage from 0 to 10 wt%, more preferably it is in the range from 0 to 5 wt%, more preferably it is an acrylate free composition comprising 0 wt% of acrylate monomer.

Although not to be bound by theory, it is believed that containing an acrylate monomer 10 wt% or less leads significantly higher carbon content of a cured film obtained from the composition. Said higher carbon content leads improved etching resistance, which crucial for the function as carbon-rich hard mask and the pattern etch transfer. Furthermore, it is believed that acrylates reduce temperature stability of a cured film and leads higher degree of UV-induced shrinkage in photocurable systems. By reducing the total content of acrylate monomer in the composition 10 wt% or less based on the total amount of the composition, more preferably it is in the range from 0 to 5 wt%, such disadvantages of using acrylate can be reduced or resolved.

As another embodiment of the present invention, it is believed that adding small amount of acrylates may give flexibility on adjusting viscosity, inkjetability and/or vapor pressure of the composition. It can also increase photo curing speed of the composition.

Preferably, the composition of the present invention comprises a solvent 10 wt% or less based on the total amount of the composition, preferably it is in the rage from 0 to 10 wt%, more preferably it is in the range from 0 to 5 wt%, more preferably it is a solvent free composition comprises 0 wt% of solvent.

Although not to be bound by theory, it is believed that setting the total content of solvent(s) in the composition 10 wt% or less based on the total amount of the composition is beneficial for reducing process steps, minimizing processing time, easy handling, namely for inkjetting, and/or minimizing/avoiding impurity contamination.

- Additives

According to the present invention, in some embodiments, the composition may optionally comprise an additive selected from one or more members of the group consisting of surfactants, wetting agents, release agents, oxygen quenchers and stabilizers.

It is another embodiment of the present invention, that the composition comprises one or more of additive(s) and the sum of these additives are 0 to 10 wt% (preferably 0 to 5 wt%; more preferably 0 to 2 wt%; further preferably 0 wt%) based on the total amount of the composition.
The composition doesn't comprise additive(s) (0 wt%) is also other preferable embodiment of the present invention.

As said additive(s), publicly known materials preferably used in semiconducting industry can be used in the present invention.

It is believed that surfactants, release agents can be used to reduce adhesion force of the composition, preferably to the superstrate material for improved processibility.

- Viscosity

In a preferred embodiment of the present invention, the viscosity of the composition at 23 C degree is in the range from 2 to 100 cP, preferably it is 5 to 50 cP, more preferably it is 5 to 20 cP, further preferably 7 to 20 cP from the viewpoint of realizing smooth inkjetting.

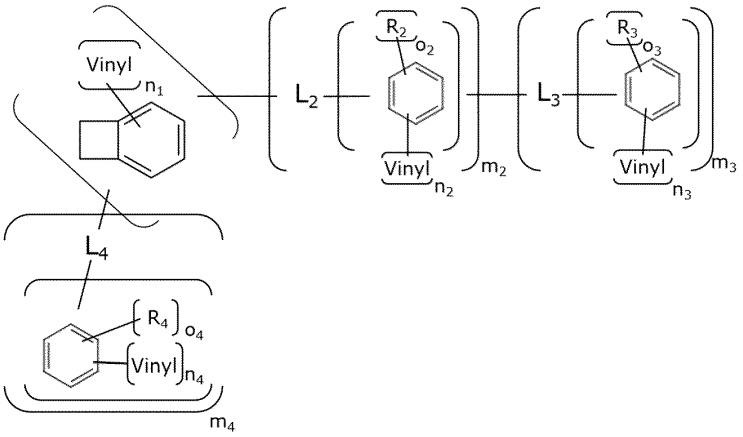
The viscosity of the composition can be controlled, for examples, by changing the type of the 1st monomer and/or the 2nd monomer, the amount of the 1st monomer and/or the 2nd monomer.

The viscosity of the composition of the present invention can be measured using an Anton Paar MCR 92 rheometer (Anton Paar, Graz, Austria) using a cone-plate geometry. Viscosity value is determined at a shear rate of 500s-1 using a rotational cone-plate geometry (d=25mm) at 23 C degree.

-Method for preparing the composition

In another aspect, the present invention relates to method for preparing the composition of the present invention, comprises at least the following step (A);

(A) Mixing at least a 1st monomer compound of formula (I) and a polymerization initiator.



- (I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 1$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;

when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;

each of L_2 to L_4 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

In another aspect, the present invention further relates to method for preparing the cured layer, comprising at least the following steps (i^a) and (i^b):

(i^a) providing the composition of the present invention onto a substrate, preferably by printing, more preferably by spin-coating, slit coating or ink-jetting, further preferably ink-jetting;

(i^d) optionally bringing the composition into contact with a template;

(i^b) curing the composition by heat and/or by irradiating the composition with light to form a cured layer;

(i^e) optionally removing the template from the cured layer.

As one embodiment the template used in step (i^d) and (i^e) is preferably patterned or not patterned; more preferably not patterned. One embodiment of such not patterned template is superstrate.

As for superstrate, publicly known one can be used. For example, the superstrate and it is method like described in Niyaz Khusnatdinov et. al., “Development of an inkjet-enabled Adaptive Planarization Process“, Proceedings Volume 10451, Photomask Technology 2017; 104511A (2017), can be used preferably.

In some embodiments, said curing can be a photo combination of photo curing, heat curing or a combination of photo curing and heat curing.

In a preferred embodiment, said photo curing is performed by irradiating the composition with UV light with curing energies in the range from 0.1 to 30 J/cm^2, more preferred is from 0.3 to 25 J/cm^2.Further preferred one is from 0.5 to 2 J/cm^2. Preferred UV light wavelength is 250 nm to 400 nm, more preferably around 350 nm.

In a preferred embodiment, said method further contains following step (i^c) after step (i^b);
(i^c) baking the cured layer at the temperature in the range from 180 to 450 C degree, for the time in the range from 0.5 min to 10 min.

Although not to be bound by theory, it is believed that thermal treatment, either through a suitable post-exposure bake or the heat from subsequent thermal processes, triggers the ring opening of the cyclobutene ring in the chemical compound represented by formula (I) or formula (I'). This process generates a reactive o-quinodimethane intermediate, which undergoes cycloaddition reactions. These reactions contribute to the increased mechanical strength and enhanced thermal stability of the cured material.

In a preferred embodiment, said method for preparing the cured layer is Inkjet Adaptive Planarization (IAP).

In another aspect, the present invention further relates to a cured layer, preferably a photo-cured layer. More preferably, this cured layer is obtained or can be obtained through a combination of photo-curing and thermal curing (dual-cured) using the method of the present invention. Another aspect of the present invention involves providing a method for manufacturing the aforementioned cured layer.

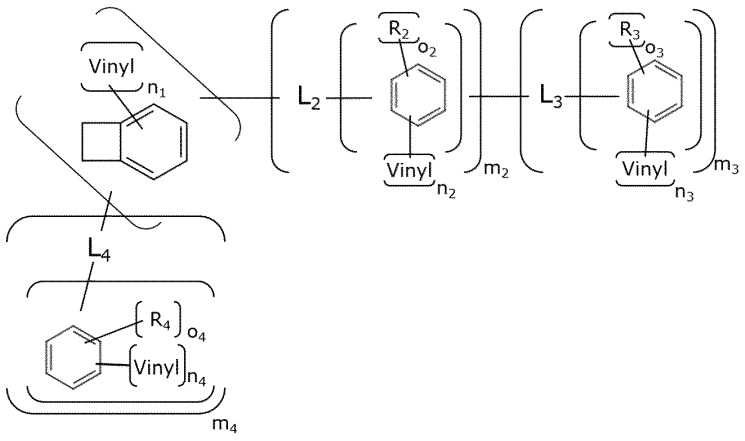
In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer, and more preferably a dual-cured layer,

formed from the composition of the present invention. In a preferred embodiment, said cured layer can be used as an interlayer insulating film in a semiconductor device or as an underlayer Spin-on carbon (SOC) for fabricating semiconductors. Such as LSI, system LSI, DRAM, SDRAM, RDRAM or D-RDRAM.

In another aspect, the present invention further relates to a stacked layer comprising a substrate and the cured layer of the present invention at least partly overlying the substrate. As the other aspect, the present invention provides a method of manufacturing of the stacked layer as described above.

-A new compound

The present invention also provides a new compound represented by chemical formula (I).



- (I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 2$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;

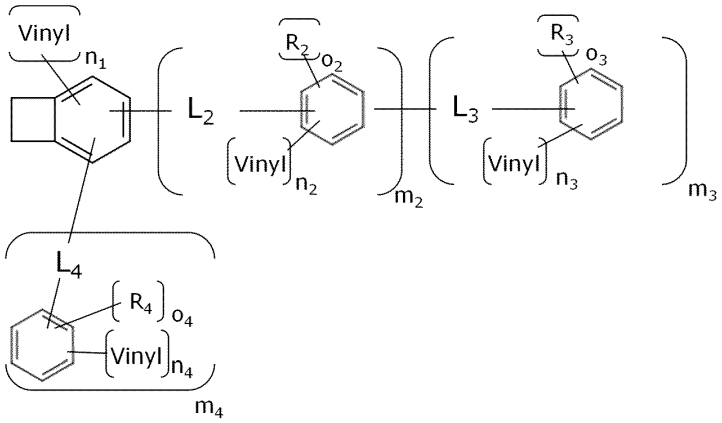
when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;

each of L_2 to L_4 is independently selected from the group consisting of a direct bond, $C_{1\text{-}15}$ alkylene, and $C_{2\text{-}15}$ alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

It is one of preferred embodiment of the invention that the new compound is represented by below formula (I').



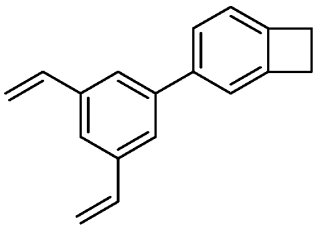
Each of definition, detailed description, explanation and embodiment of each part of the new compound represented by formula (I) and formula (I') is independently same to the formula (I) and formula (I') described above in 1st monomer section.

The present invention is further illustrated by the examples following hereinafter which shall in no way be construed as limiting. The skilled person will acknowledge that various modifications, additions and alternations may be made to the invention without departing from the spirit and scope of the invention as defined in the appended claims.

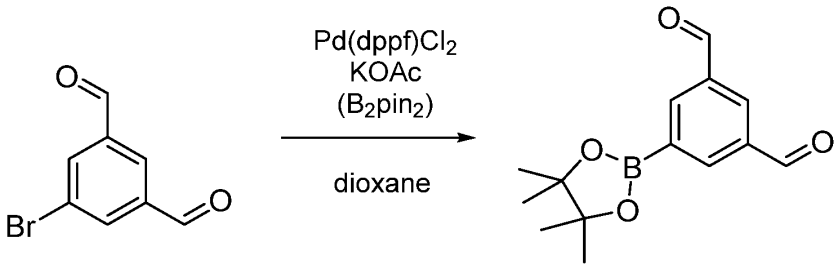
Examples

Part A: Synthesis examples

Example 1: 3-(3,5-divinylphenyl)bicyclo[4.2.0]octa-1,3,5-triene



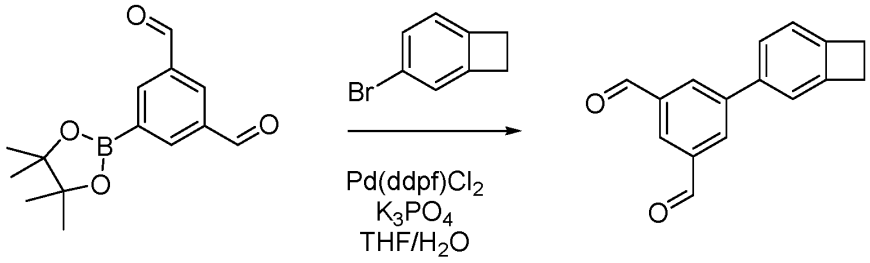
Step 1: Synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalaldehyde



To a flask, 5-bromoisophthalaldehyde (Amadis chemical, CAS: 120173-41-3, 28.2 mmol, 6 g), KOAc (Merck, CAS: 127-08-2, 84.5 mmol, 8.3 g) and bis(pinacolato)diboron (Merck, CAS: 73183-34-3, 31 mmol, 7.9 g) are dissolved in 1,4-dioxane (100 mL) and purged with nitrogen. Palladium catalyst (Merck, CAS: 72287-26-4, 0.85 mmol, 618 mg) is then introduced and the reaction mixture is heated to 80 C degree overnight. Afterward, the reaction mixture is diluted with water and extracted with ethyl acetate. The organic phase is subsequently washed with water (2 times by volume) and brine, dried using Na_2SO_4, filtered and evaporated. To purify the crude mixture, it is dissolved in ethyl acetate and passed through silica using a mixture of heptane/ethyl acetate (1:1 by volume). The appropriate fractions are combined and evaporated, resulting in the formation of a yellow-colored solid (6.2 g, 84.6%).

^{1}H NMR (500 MHz, Chloroform-*d*): δ = 10.14 (s, 2H), 8.56 (d, *J* = 1.6 Hz, 2H), 8.46 (t, *J* = 1.7 Hz, 1H), 1.39 (s, 12H) ppm.

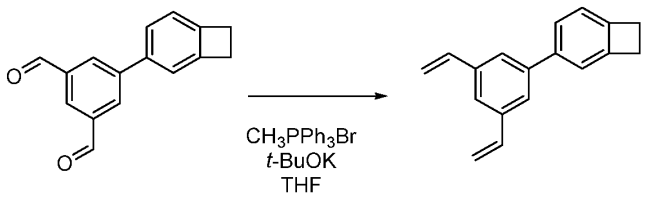
Step 2: Synthesis of 5-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-isophthalaldehyde



A suspension of boronic ester (step 1, 19 mmol, 5 g), along with Pd catalyst (Merck, CAS: 72287-26-4, 0.78 mmol, 574 mg) and potassium phosphate (57 mmol, 12.2 g) in THF/water (75 mL/1.8 mL), is prepared. Under a nitrogen atmosphere, 4-bromobenzoxyclobutene (Merck, CAS: 1073-39-8, 19 mmol, 3.5 g) is added to the solution, and the resulting mixture is stirred at 70 C degree overnight. The reaction mixture is subsequently extracted with water and ethyl acetate, dried using Na_2SO_4, filtered, and concentrated. To purify the crude mixture, column chromatography on silica gel is performed using a mixture of heptane/ethyl acetate (15:1) as the eluent. This process yields a colorless solid (3.7 g, 82%).

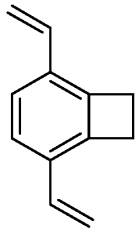
1H NMR (500 MHz, Chloroform-*d*): δ = 10.16 (s, 2H), 8.31 (s, 3H), 7.48 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35 (d, *J* = 1.6, 1H), 7.19 (d, *J* = 7.6, 1H) 3.26 (s, 4H) ppm.

Step 3: Synthesis of 3-(3,5-divinylphenyl)bicyclo[4.2.0]octa-1,3,5-triene



Methyltriphenylphosphonium bromide (Merck, CAS: 1779-49-3, 14 mmol, 5 g) is dissolved in THF (35 mL) and cooled to -18 C degree. t-BuOK (Merck, CAS: 865-47-4, 14 mmol, 1.6 g) is added to the solution. Dialdehyde (step2, 6.3 mmol, 1.5 g) is dissolved in 15 mL of THF and slowly added dropwise at 0 C degree under temperature control. The mixture is stirred overnight, then diluted with water and extracted with DCM (dichloromethane). The organic phase is washed twice with water and once with a NaCl solution. It is then dried over Na_2SO_4, filtered, and concentrated. The crude product is purified using a silica gel column with heptane as the eluent, resulting in the isolation of 1.1 g of a colorless oil (75%).

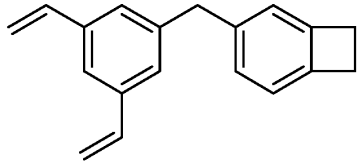
Example 2: 2,5-divinylbicyclo[4.2.0]octa-1,3,5-triene



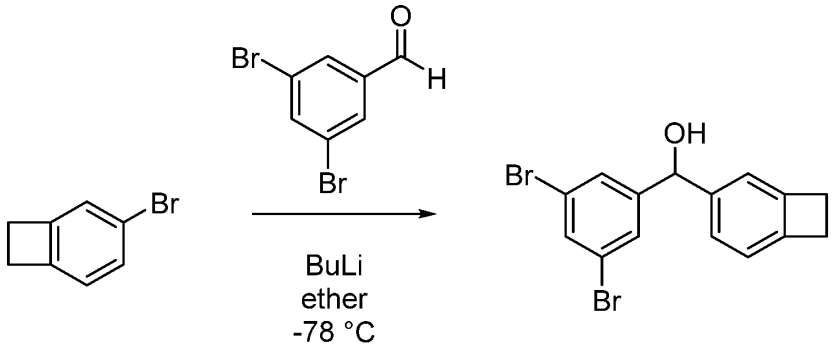
2,5-dibromobicyclo[4.2.0]octa-1,3,5-triene (Merck, CAS: 145708-71-0, 9.5 mmol, 2.5 g) is dissolved in dried THF (130 mL). NaOH is dissolved in water (40 mL) and cooled while treated with potassium vinyltrifluoroborate (Merck, CAS: 13682-77-4, 2.8 g, 21 mmol). Then Pd(amphos)Cl_2 (Merck, CAS: 887919-35-9, 0.27 g, 0.38 mmol) is added, and the reaction mixture is stirred for 15 minutes under argon. Subsequently, the prepared reactant solution in THF is added dropwise, and the mixture is stirred overnight at 50 C degree. Afterward, the mixture is cooled to room temperature, and the aqueous phase is separated. The organic phase is washed once with saturated sodium chloride and twice with water, dried over Na_2SO_4, and concentrated to dryness. The crude product is dissolved in heptane and subjected to purification using a silica plug, resulting in the isolation of 1.3 g (87%) of the desired product as a colorless liquid.

1H NMR (500 MHz, Chloroform-*d*): δ = 7.11 (s, 2H), 6.64 (dd, *J* = 17.7, 10.9 Hz, 2H), 5.67 (dd, *J* = 17.6, 1.3, 2H), 5.31 (dd, *J* = 10.8, 1.3, 2H) 3.34 (s, 4H) ppm.

Example 3 (prophetic): 3(3,5-divinylbenzyl)bicyclo[4.2.0]octa-1,3,5-triene

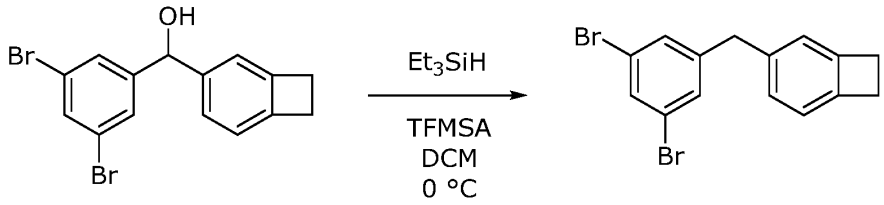


Step 1: Synthesis of bicyclo[4.2.0]octa-1,3,5-trien-3-yl(3,5-dibromophenyl)methanol



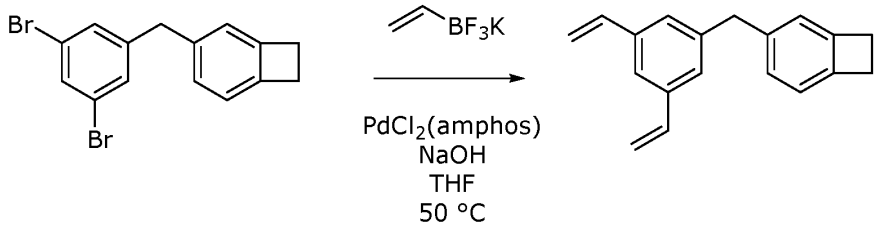
4-Bromobenzocyclobutene (Merck, CAS: 173-39-8, 2.6 g, 14.3 mmol) is dissolved in anhydrous diethyl ether (Merck, 60 mL). The solution is cooled to -78 C degree and n-butyllithium solution (1.6 M in hexane, 10 mL, 1.6 mmol) is added dropwise. Then, 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4, 3.4 g, 13 mmol) is added and the reaction mixture stirred while it is brought to room temperature. The mixture is carefully quenched with 50 mL brine, separated and the aqueous phase extracted 3 times with DCM. The combined organic phases are dried over Na_2SO_4, filtered and the solvent removed under vacuum, resulting 4.7 g (99 %) of a brown oil that is used without further purification.

Step 2: Synthesis of 3-(3,5-dibromobenzyl)bicyclo[4.2.0]octa-1,3,5-triene



Bicyclo[4.2.0]octa-1,3,5-trien-3-yl(3,5-dibromophenyl)methanol (4.7 g, 12.8 mmol) is dissolved in 40 mL DCM, treated with triethylsilane (Merck, CAS: 617-86-7, 4.1 mL, 25.6 mmol) and cooled to 0 C degree. Trifluoromethanesulfonic acid (Merck, CAS: 1493-13-6, 2.2 mL, 25.6 mmol) is added dropwise and the mixtures stirred at room temperature for 3 h. Ice is carefully added and the aqueous phase is separated 3 times with DCM. The combined organic phases are dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product is subject of purification by crystallization in ethanol resulting 3.6 g (80 %) of the desired product.

Step 3: Synthesis of 3-(3,5-divinylbenzyl)bicyclo[4.2.0]octa-1,3,5-triene



3-(3,5-dibromobenzyl)bicyclo[4.2.0]octa-1,3,5-triene (3.6 g, 10 mmol) is dissolved in anhydrous THF (0.2 L), treated with potassium vinyltrifluoroborate (Merck, CAS:13682-77-4, 21.8 mmol, 2.9 g) and stirred under nitrogen at room temperature for 1 h. A NaOH solution (30 mL, 10 wt%) and $Pd(amphos)Cl_2$ (Merck, CAS: 887919-35-9, 0.28 g, 0.4 mmol) are added and the reaction mixture stirred at 50 C degree for 12 h. The mixture is cooled to room temperature, treated with water and extracted 3 times with ethyl acetate. The combined organic phases are dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude product is purified with silica column chromatography using heptane as solvent, which eventually yields 1.85 g (75 %) of a colorless liquid.

Part B: Thermal Stability of Photo-Cured Layers

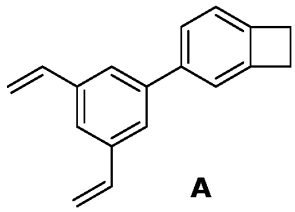
Cured films are prepared by applying a 60 μm thick layer (each of which is made from the working composition and the comparative composition described below) in a sandwich set-up consisting of two glass slides and curing the film at room temperature with UV light with a wavelength of 365 nm using 5 J/cm^2 dose. Subsequently, the films are baked after UV-curing at 300 C degree for 2 min on a hotplate and then measured via TGA (TA Discovery or TA TGA Q50). The thermal stability of a composition can be assessed using the weight loss percentage per minute at different temperatures, which is measured with an isothermal baking test by heating the sample to a pre-determined temperature (for example 400 C degree) in 20 min and holding the temperature constant for 60 min.

The formulation comprising the 1st monomer of the present invention exhibits better thermal stability than the comparative example formulation (refer to Table 1 and Figure 1).

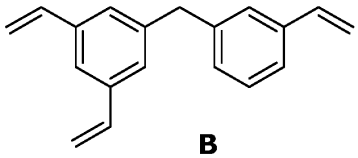
Composition	Weight loss/min at 400 C degree
Working example 1	0.11%/min
Comparative example 1	0.43%/min

The Working example 1 composition is prepared by mixing below compound A (1st monomer, 50 wt%) and compound B (2nd monomer, 50 wt%). Then, Irgacure OXE02 is added to 4 wt% comparing to the resultant formulation.

The Comparative example 1 composition is prepared by Irgacure OXE02 is added to compound B until 4 wt% comparing to the resultant formulation.



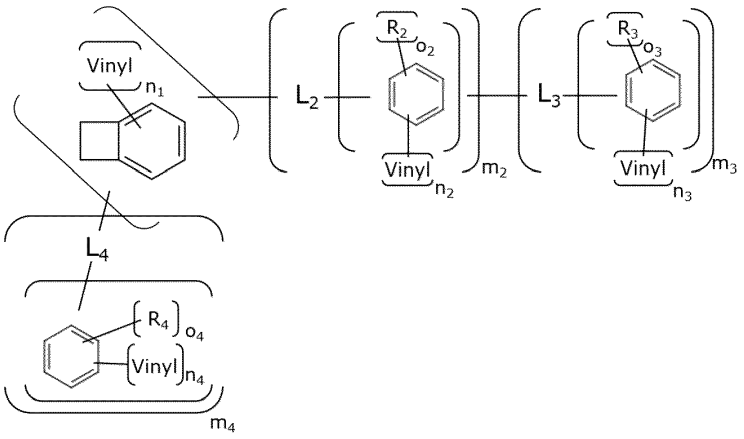
A



B

Patent Claims

1. A curable composition, preferably being a photo-curable composition, comprising a 1st monomer compound and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I);



- (I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 1$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;

when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;

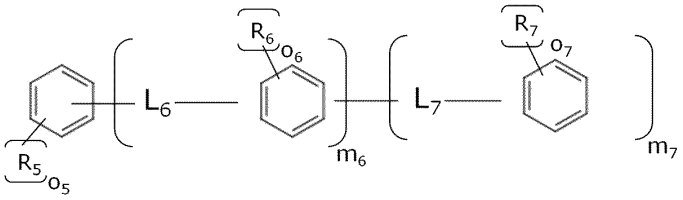
each of L_2 to L_4 is independently selected from the group consisting of a direct bond, $C_{1\text{-}15}$ alkylene, and $C_{2\text{-}15}$ alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

2. The composition according to claim 1, wherein the total amount of the 1st monomer compound is in the range from 5 to 99.99 wt% based on the total amount of the composition; preferably it is from 20 to 99.99 wt%; more preferably from 40 to 99.9 wt%.

3. The composition according to claim 1 or 2, further comprises a 2nd monomer compound represented by chemical formula (II);



(II)

where

each of m_6 and m_7 is independently 0 or 1;

o_5 is 0, 1, 2, 3, 4, 5 or 6;

each of o_6 and o_7 is independently 0, 1 or 2;

each of R_5 to R_7 is independently C_{1-4} alkyl, vinyl or ethynyl;

the 2nd monomer has at least one of vinyl or ethynyl at present;

each of L_6 and L_7 is independently selected from the group consisting of a direct bond, C_{1-15} alkylene, and C_{2-15} alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.

4. The composition according to any one or more of claim 1 to 3, wherein the sum amount of the 1st monomer compound and the 2nd monomer compound is in the range from 10 to 99.99 wt% based on the total amount of the composition.

5. The composition according to any one or more of claim 1 to 4, comprises an acrylate monomer 10 wt% or less based on the total amount of the

composition; preferably 0 to 10 wt%; more preferably 0 to 5 wt%, further preferably 0 wt%.

6. The composition according to any one or more of claims 1 to 5, comprises a solvent 10 wt% or less based on the total amount of the composition; preferably 0 to 10 wt%; more preferably 0 to 5 wt%, further preferably 0 wt%.

7. The composition according to any one or more of claims 1 to 6, comprises an additive selected from one or more members of the group consisting of surfactants, wetting agents, release agents, oxygen quenchers and stabilizers.

8. The composition of according to any one or more of claims 1 to 7, wherein the viscosity at 23 C degree is in the range from 2 to 100cP.

9. Method for preparing a composition of any one or more of claims 1 to 8, comprises at least the following step (A);
(B) Mixing at least a 1st monomer compound and a polymerization initiator.

10. Method for preparing a cured layer, comprising at least the following steps (i^a) and (i^b):
(i^a) providing the composition of any one of claims 1 to 10 onto a substrate, preferably by printing, more preferably by spin-coating, slit coating or ink-jetting;
(i^d) optionally bringing the composition into contact with a template;
(i^b) curing the composition by heat and/or by irradiating the composition with light to form a cured layer;
(i^e) optionally removing the template from the cured layer.

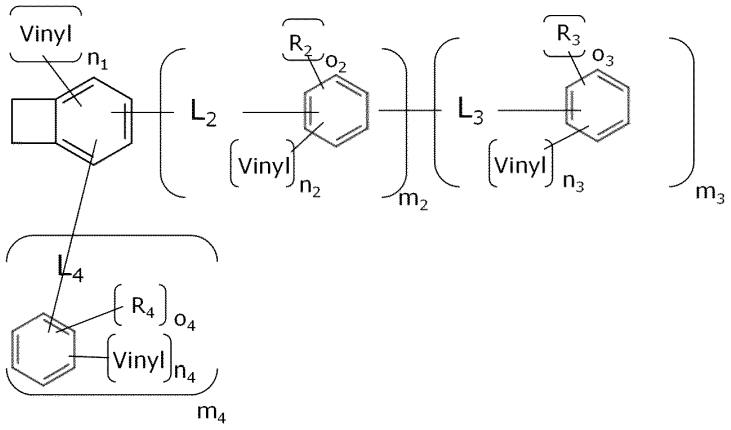
11. Method of claim 10, further contains following step (i^c) after step (i^b);
(i^c) baking the cured layer at the temperature in the range from 180 to 450°C, for the time in the range from 0.5 to 10min.

12. A cured layer, preferably it is a photo-cured layer obtained or obtainable by the method of any one or more of claims 9 to 11.

13. A cured layer, preferably it is a photo-cured layer formed from the composition of any one of claims 1 to 8.

14. A stacked layer comprising a substrate and the cured layer of claim 12 or 13 at least partly overlying the substrate.

15. A compound represented by chemical formula (I);



- (I)

where

each of m_2 to m_4 is independently 0 or 1;

each of n_1 to n_4 is independently 0, 1 or 2; $n_1+n_2+n_3+n_4 \geq 2$

the 1st monomer has at least one vinyl group at present;

each of o_2 to o_4 is independently 0 or 2;

when o_2 is 2, two R_2 are adjacent methyls to bond each other to make cyclobutene structure on the benzene; and same applies to each relation between o_3 and R_3, and o_4 and R_4;

each of L_2 to L_4 is independently selected from the group consisting of a direct bond, $C_{1\text{-}15}$ alkylene, and $C_{2\text{-}15}$ alkenylene,

where one or more non-adjacent methylene of said alkylene or alkenylene can be replaced by O, C=S, C=Se, C=NH, SiH_2, SO, SO_2, OS, or CONH; and

where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2.