



(86) Date de dépôt PCT/PCT Filing Date: 2015/03/10
(87) Date publication PCT/PCT Publication Date: 2015/09/17
(45) Date de délivrance/Issue Date: 2022/05/17
(85) Entrée phase nationale/National Entry: 2016/08/10
(86) N° demande PCT/PCT Application No.: EP 2015/054993
(87) N° publication PCT/PCT Publication No.: 2015/135957
(30) Priorité/Priority: 2014/03/10 (EP14000839.2)

(51) Cl.Int./Int.Cl. *A61K 6/887* (2020.01),
A61K 6/20 (2020.01), *A61K 6/30* (2020.01),
A61K 6/54 (2020.01)

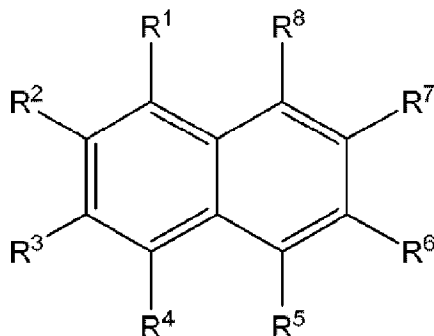
(72) Inventeurs/Inventors:
KLEE, JOACHIM E., DE;
WEBER, CHRISTOPH, DE;
MAIER, MAXIMILIAN, DE;
SZILLAT, FLORIAN, DE;
SCHEUFLER, CHRISTIAN, DE;
RITTER, HELMUT, DE

(73) Propriétaire/Owner:
DENTSPLY DETREY GMBH, DE

(74) Agent: SMART & BIGGAR LLP

(54) Titre : COMPOSITION DENTAIRE COMPRENANT UN COMPOSE POLYMERISABLE

(54) Title: DENTAL COMPOSITION COMPRISING A POLYMERIZABLE COMPOUND



(I)

(57) Abrégé/Abstract:

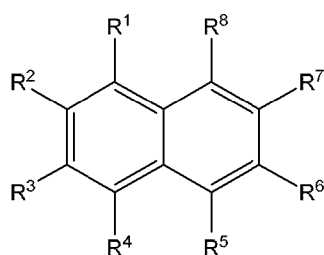
The present invention provides a dental composition comprising a polymerizable compound of the following formula (I):

(see formula I)

wherein R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are as defined herein. The dental composition of the present invention may be a dental adhesive composition, a dental pit and a fissure sealer, a dental composite, and a root canal filling composition.

ABSTRACT

The present invention provides a dental composition comprising a polymerizable compound of the following formula (I):



(I)

wherein R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are as defined herein. The dental composition of the present invention may be a dental adhesive composition, a dental pit and a fissure sealer, a dental composite, and a root canal filling composition.

DENTAL COMPOSITION COMPRISING A POLYMERIZABLE COMPOUND

Field of the Invention

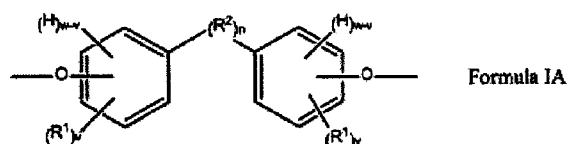
The present invention relates to a dental composition. The present invention also relates to processes for the preparation of a dental composition. Furthermore, the present invention relates to a dental composition obtainable by a process of the invention. Finally, the present invention relates to the use of the composition of the present invention in a dental composition.

A dental composition of the present invention may be a dental adhesive composition, a dental pit and fissure sealer, a dental composite, and a root canal filling composition. A dental composition according to the present invention does not require the use of 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (bis-GMA), bisphenol-A dimethacrylate, ethoxylated bis-GMA, or any other raw material based on bisphenol-A for providing superior properties including mechanical properties, refractive index, and viscosity even in the absence of solvents.

Background of the invention

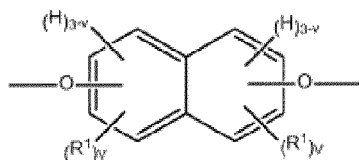
Conventional dental compositions often comprise polymerizable monomers. In view of reducing the polymerization shrinkage, conventional dental compositions frequently contain bis-GMA. However, bisphenol-A contained in bis-GMA and other polymerizable resins is problematic when leached from the polymerized dental composition. Bisphenol-A is an endocrine disruptor which may have adverse effects on the patient and the dentist alike. Therefore, the use of any bisphenol-A containing polymerizable resin such as bis-GMA in a dental composition is not preferred.

WO2014025406 discloses dental materials made from resin which include segments of the following Formula (IA) wherein w is 4.



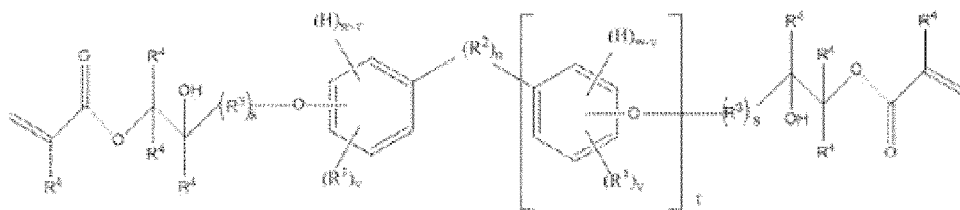
In formula (IA), R^2 may be present or absent. WO2014025406 observes that when R^2 is absent in the segment of Formula IA, either (i) a carbon atom of one phenylene ring is covalently attached to a carbon atom of the other phenylene ring (which occurs when w is 4) or (ii) the phenylene groups depicted in Formula IA join to form a fused ring system

(which occurs when w is 3 and the phenylene groups are so fused). WO2014025406 discloses an embodiment of the segment of Formula IA in which n is 0, and w is 3 such that two phenylene groups have joined to form a naphthalene group as follows:



Given that w in Formula IA can only be 4, the above embodiment wherein w is 3, is explicitly excluded from the disclosure of WO2014025406. Moreover, an embodiment wherein R^2 is absent and a carbon atom of one phenylene ring is covalently attached to a carbon atom of the other phenylene ring according to (i), is not preferred according to WO2014025406. Rather, according to WO2014025406 it is preferred that R^2 is present and is an organic groups containing less than 15 carbon atoms, which is reflected by the specific examples of WO2014025406.

Furthermore, WO2014025406 discloses that epichlorohydrin may be used to form a diepoxide and that the resulting diepoxide may be reacted with an ethylenically-unsaturated acid or acid anhydride to provide a resin with ethylenically unsaturated free- radically polymerizable groups. Formula IV below is disclosed as a resin formed by epichlorohydrin epoxidation to form a diepoxide followed by reaction with a (meth)acrylic acid:



The presence of hydroxyl groups close to the aromatic rings as a result of the synthetic route through diepoxides in compounds according to WO2014025406 results in an increased viscosity of the compounds whereby the presence of large amounts of solvents is required in order to provide a dental composition.

Summary of the Invention

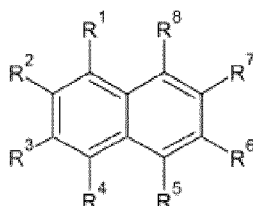
It is the problem of the present invention to provide a dental composition which does not require the use of 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (bis-

GMA), bisphenol-A dimethacrylate, ethoxylated bis-GMA, or any other raw material based on bisphenol-A for providing superior properties including mechanical properties, refractive index, and viscosity even in the absence of solvents.

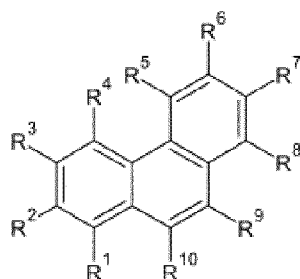
It is a further problem of the present invention to provide processes for the preparation of a dental composition whereby the composition provides superior properties including mechanical properties, refractive index, and viscosity even in the absence of solvents and which does not require the use of 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (bis-GMA), bisphenol-A dimethacrylate, ethoxylated bis-GMA, or any other raw material based on bisphenol-A.

Furthermore, it is the problem of the present invention to provide a use of the composition which does not require the use of 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (bis-GMA), bisphenol-A dimethacrylate, ethoxylated bis-GMA, or any other raw material based on bisphenol-A for providing superior properties including mechanical properties, refractive index, and viscosity even in the absence of solvents.

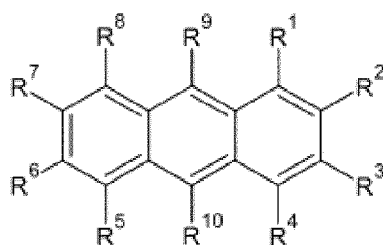
According to a first aspect, the present invention provides a dental composition comprising a polymerizable compound of the following formula (I), (II) and/or formula (III):



(I)



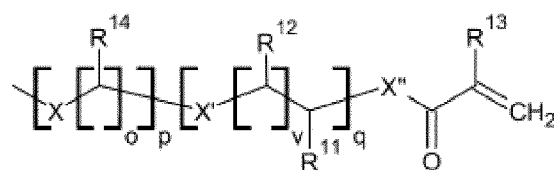
(II)



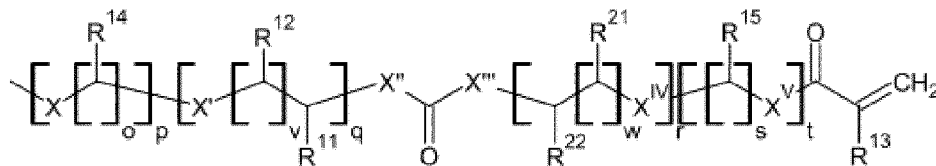
(III)

wherein

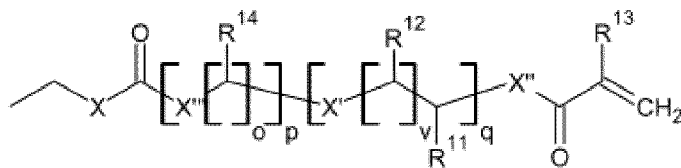
2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} , which are independent from each other, represent a group of the following formula (IV), (V), or (VI):



(IV)



(V)



(VI)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

X^{IV} is -NH-, an oxygen atom or a sulfur atom,

X^V is -NH-, an oxygen atom or a sulfur atom,

R^{11} , R^{12} , R^{21} and R^{22}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁴ and R¹⁵ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

o and s which may be the same or different, independently represent an integer of from 2 to 10,

p and t which may be the same or different, independently is an integer of from 0, 1 or 2;

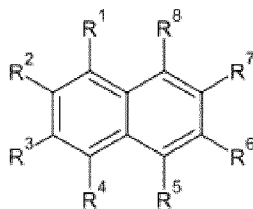
q and r which may be the same or different, independently represent an integer of from 0 to 10, preferably 1 to 10;

v and w which may be the same or different, independently represent an integer of from 1 to 10

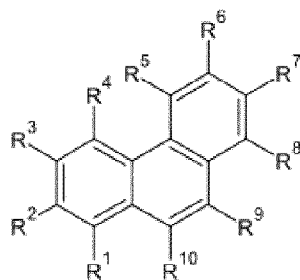
and the remaining groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, and, if present, R⁹, and R¹⁰ independently represent a hydrogen atom, a halogen atom, a straight chain or branched C₁₋₆ alkyl group, a C₃₋₆ cycloalkyl group, or a C₁₋₆ alkyl C₃₋₆ cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

Furthermore, according to a second aspect, the present invention provides a process for the preparation of a dental composition according to the first aspect, which process comprises the steps of

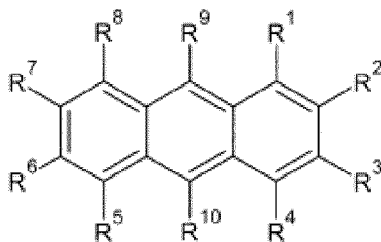
- (a) subjecting a reaction mixture comprising
 - (a1) one or more compounds of formula (VII), (VIII) and/or formula (IX):



(VII)



(VIII)



(IX)

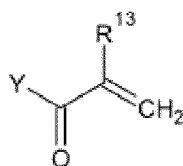
wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are -XH groups wherein X is -NH-, an oxygen atom or a sulfur atom, and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups, and

(a2) ethylene carbonate or a compound of the formula ZRZ' , wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group,

to an addition reaction for obtaining an addition product and

- (b1) reacting the addition product of ethylene carbonate with a compound of the following formula (XI):



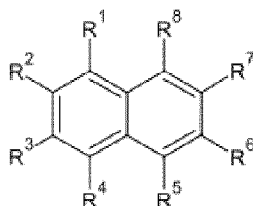
(XI)

wherein Y is a leaving group and R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group, or wherein Y and R^{13} form together with the carbon atoms to which they are bound a cyclic lactone ring or carboxylic acid anhydride ring having 4 to 8 carbon atoms;

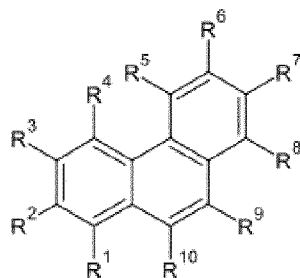
for obtaining a polymerizable compound of formula (I), (II) or (III) of the present invention; or

- (b2) reacting the addition product of the compound of the formula ZRZ' , wherein Z, Z' and R are as defined above, with a compound of formula (XI) wherein Y is OH, for obtaining a polymerizable compound of formula (I), (II) or (III) of the present invention.

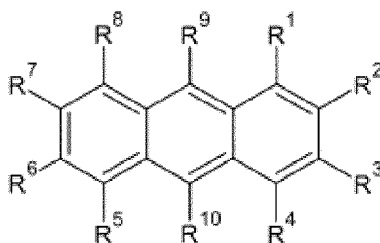
Furthermore, according to a third aspect, the present invention provides a process for the preparation of a dental composition according to the first aspect, comprising subjecting a reaction mixture comprising one or more compounds of formula (XII), (XIII) and/or formula (XIV):



(XII)



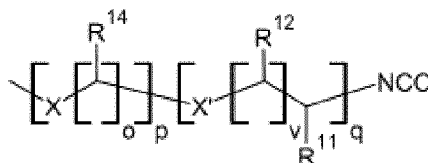
(XIII)



(XIV)

wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are independently a group of the following formula (XV):



(XV)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

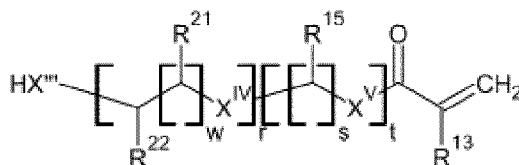
o independently represent an integer of from 2 to 10,

p independently is an integer of from 0, 1 or 2;

q independently represent an integer of from 0 to 10, preferably 1 to 10;

v independently represents an integer of from 1 to 10,

and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups, to an addition reaction with a compound of the following formula (XVI):



(XVI)

wherein

X''' is -NH-, an oxygen atom or a sulfur atom,

X^{IV} is -NH-, an oxygen atom or a sulfur atom,

X^V is -NH-, an oxygen atom or a sulfur atom,

R²¹ and R²²

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁵ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

s independently represent an integer of from 2 to 10,

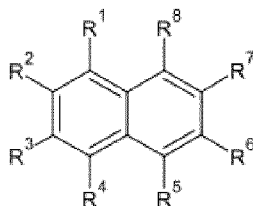
t independently is an integer of from 0, 1 or 2;

r which may be the same or different, independently represent an integer of from 0 to 10, preferably 1 to 10;

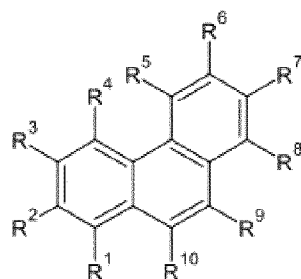
w independently represents an integer of from 1 to 10,

for obtaining a polymerizable compound of formula (I), (II) or (III) as defined in the present invention.

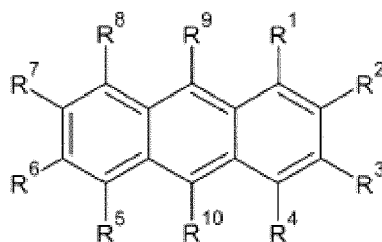
Furthermore, according to a fourth aspect, the present invention provides a process for the preparation of a dental composition according to the first aspect, comprising subjecting a reaction mixture comprising one or more compounds of formula (XVII), (XVIII) and/or formula (XIX):



(XVII)



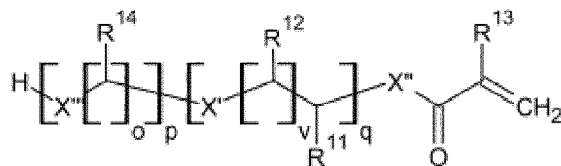
(XVIII)



(XIX)

wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are isocyanatomethyl groups, and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups, to an addition reaction with a compound of the following formula (XX):



(XX)

wherein

X' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

- which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,
- R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,
- R¹⁴ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,
- o which may be the same or different, independently represent an integer of from 2 to 10,
- p which may be the same or different, independently is an integer of from 0, 1 or 2;
- q which may be the same or different, independently represent an integer of from 0 to 10, preferably 1 to 10;
- v independently represents an integer of from 1 to 10,

for obtaining a polymerizable compound of formula (I), (II) or (III) as defined in the present invention.

According to a specific embodiment of the second to fourth aspect, the process further comprises a step of reacting a polymerizable compound of formula (I), (II) or (III) as defined in the first aspect, which contains hydroxyl groups in any of R¹³, with an isocyanate compound, a diisocyanate compound, isothiocyanate compound, a carboxylic acid halogenide compound, a cyclic carboxylic acid anhydride or a carboxylic acid compound for preparing a substituted hydroxyl group.

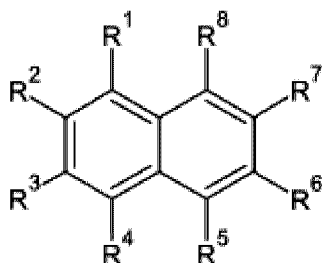
According to a fifth aspect, the present invention also provides a dental composition obtainable by any of the processes according to the present invention.

According to a sixth aspect, the present invention provides a use of a dental composition for the preparation of a dental composition as defined by the present invention.

11a

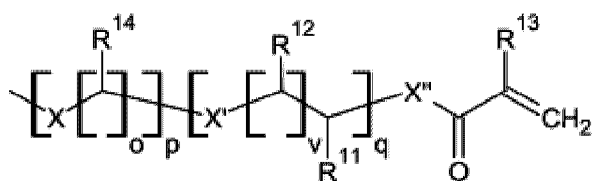
The present invention as claimed relates to:

- a dental composition comprising a polymerizable compound of the following formula (I):

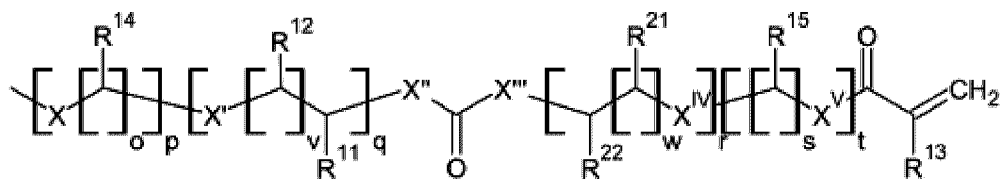


(I)

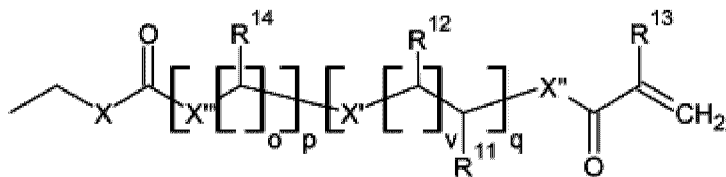
wherein 2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, which are independent from each other, represent a group of the following formula (IV), (V), or (VI):



(IV)



(V)



(VI)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

11b

X^{II} is -NH-, an oxygen atom or a sulfur atom,

X^{III} is -NH-, an oxygen atom or a sulfur atom,

X^{IV} is -NH-, an oxygen atom or a sulfur atom,

X^V is -NH-, an oxygen atom or a sulfur atom,

R¹¹, R¹², R²¹ and R²²

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁴ and R¹⁵

which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

o and s which may be the same or different, independently represent an integer of from 2 to 10,

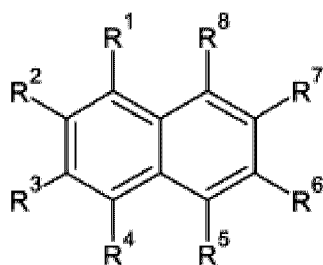
p and t which may be the same or different, independently is an integer of from 0, 1 or 2;

q and r which may be the same or different, independently represent an integer of from 0 to 10;

v and w which may be the same or different, independently represent an integer of from 1 to 10

and the remaining groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ independently represent a hydrogen atom, a halogen atom, a straight chain or branched C₁₋₆ alkyl group, a C₃₋₆ cycloalkyl group, or a C₁₋₆ alkyl C₃₋₆ cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups, and a filler and/or a solvent;
- a process for the preparation of a dental composition as described herein, wherein the dental composition comprises a polymerizable compound of the following formula (I):

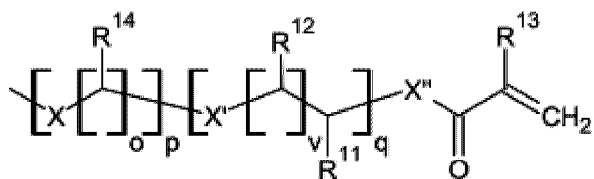
11c



(I)

wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , which are independent from each other, represent a group of the following formula (IV):

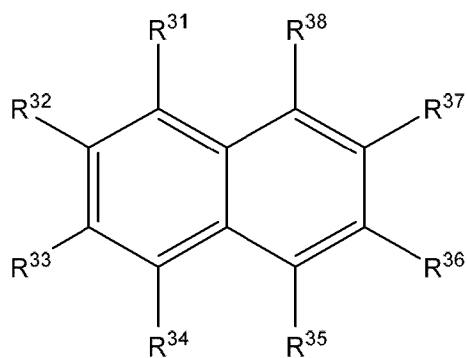


(IV)

the process comprising the steps of

(a) subjecting a reaction mixture comprising

(a1) one or more compounds of formula (VII):



(VII)

wherein

2 to 4 groups of R^{31} , R^{32} , R^{33} , R^{34} , R^{35} , R^{36} , R^{37} , and R^{38} are -XH groups wherein X is -NH-, an oxygen atom or a sulfur atom, and

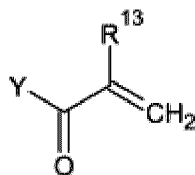
11d

the remaining groups of R^{31} , R^{32} , R^{33} , R^{34} , R^{35} , R^{36} , R^{37} , and R^{38} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups, and

- (a2) ethylene carbonate or a compound of the formula ZRZ' , wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group;

to an addition reaction to generate an addition product; and

- (b1) reacting the addition product of the one or more compounds of formula (VII) and ethylene carbonate with a compound of the following formula (XI)



(XI)

wherein Y is a leaving group and R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group, or wherein Y and R^{13} form together with the carbon atoms to which they are bound a cyclic lactone ring or carboxylic acid anhydride ring having 4 to 8 carbon atoms;

to generate the group of the formula (IV) and provide the polymerizable compound of formula (I); or

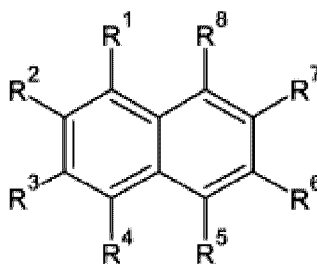
- (b2) reacting the addition product of the one or more compounds of formula (VII) and the compound of the formula ZRZ' , wherein Z and Z' independently are leaving groups and R is a straight chain

or branched alkylene group, with a compound of formula (XI)

wherein Y is OH;

to generate the group of the formula (IV) and provide the polymerizable compound of formula (I);

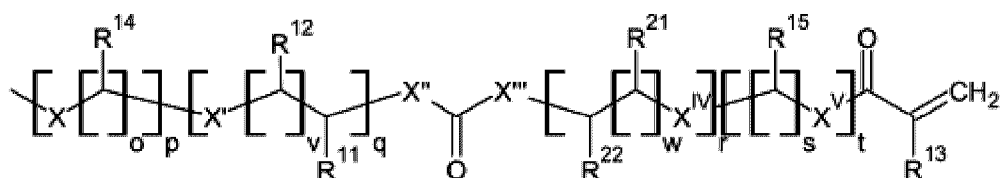
- a process for the preparation of a dental composition as described herein, wherein the dental composition comprises a polymerizable compound of the following formula (I):



(I)

wherein

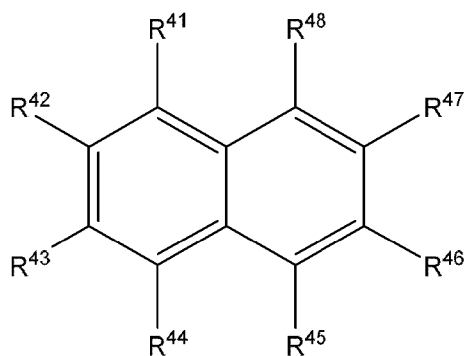
2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, which are independent from each other, represent a group of the following formula (V):



(V)

the process comprising subjecting a reaction mixture comprising one or more compounds of formula (XII):

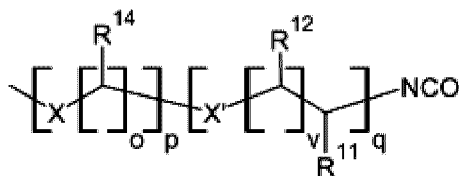
11f



(XII)

wherein

2 to 4 groups of R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , R^{46} , R^{47} , and R^{48} are independently a group of the following formula (XV):



(XV)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

o independently represent an integer of from 2 to 10,

p independently is an integer of from 0, 1 or 2;

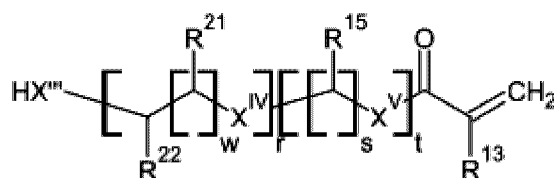
q independently represent an integer of from 0 to 10;

v independently represents an integer of from 1 to 10,

11g

and the remaining groups of R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , R^{46} , R^{47} , and R^{48} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups,

to an addition reaction with a compound of the following formula (XVI):



(XVI)

wherein

X''' is $NH-$, an oxygen atom or a sulfur atom,

X^{IV} is $NH-$, an oxygen atom or a sulfur atom,

X^V is $NH-$, an oxygen atom or a sulfur atom,

R^{21} and R^{22}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R^{15} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

s independently represent an integer of from 2 to 10,

t independently is an integer of from 0, 1 or 2;

r which may be the same or different, independently represent an integer of from 0 to 10;

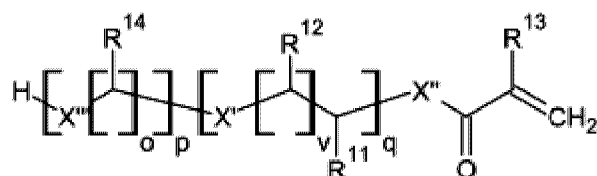
w independently represents an integer of from 1 to 10,

(XVII)

wherein

2 to 4 groups of R^{51} , R^{52} , R^{53} , R^{54} , R^{55} , R^{56} , R^{57} , and R^{58} are isocyanatomethyl groups, and the remaining groups of R^{51} , R^{52} , R^{53} , R^{54} , R^{55} , R^{56} , R^{57} , and R^{58} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups,

to an addition reaction with a compound of the following formula (XX):



(XX)

wherein

X' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

o which may be the same or different, independently represent an integer of from 2 to 10,

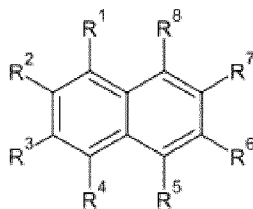
- p which may be the same or different, independently is an integer of from 0, 1 or 2;
- q which may be the same or different, independently represent an integer of from 0 to 10;
- v independently represents an integer of from 1 to 10,

wherein the addition reaction generates the group of the formula (VI) and provides the polymerizable compound of formula (I);

- a process for the preparation of a dental composition comprising a polymerizable compound comprising a substituted hydroxyl group, the process comprising a step of reacting the polymerizable compound of formula (I) as described herein, which comprises a hydroxyl group in any of R¹³, with an isocyanate compound, a diisocyanate compound, a isothiocyanate compound, a carboxylic acid halogenide compound, a cyclic carboxylic acid anhydride or a carboxylic acid compound;
- a dental composition obtained by the process as described herein; and
- use of the dental composition as described herein for the preparation of a dental composition.

Detailed Description of the Preferred Embodiments

The present invention provides a dental composition. The dental composition comprises a polymerizable compound. The polymerizable compound may be a compound of the following general formula (I) which is a naphthalene derivative:



(I)

In a naphthalene derivative according to formula (I), any of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ may be a hydrogen atom or the aromatic ring may be substituted at the respective position by a substituent group. The substituent groups may be groups having polymerizable substituent or saturated substituent groups which are not polymerizable. According to the present invention, 2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ represent a polymerizable group and the remaining groups are hydrogen atoms or saturated groups which are not polymerizable. Accordingly, the compounds of formula (I) act as crosslinking monomer in a radical polymerization.

According to a first preferred embodiment, a compound of formula (I) contains 2 polymerizable substituents. According to a second preferred embodiment, a compound of formula (I) contains 3 or 4 polymerizable substituents.

In case the compound of formula (I) contains 2 polymerizable substituents, it is preferable that the substituents do not share the same annelated benzene ring. Accordingly, a first polymerizable substituent is present at R¹, R², R³, or R⁴, and a second polymerizable substituent is present at R⁵, R⁶, R⁷, or R⁸.

Preferably, the first and second polymerizable substituent form a non-straight angle which is preferably obtuse. The angle being defined by the formal valence bonds in formula (I). Accordingly, the first and second polymerizable substituent are preferably not present at opposite positions across the aromatic ring system.

Specifically, when the first polymerizable substituent is present as R¹, then the second polymerizable substituent is preferably present as R⁶, R⁷, or R⁸. In this case it is less preferred that the second polymerizable substituent is present as R² or R³.

When the first polymerizable substituent is present as R² then the second polymerizable substituent preferably is present as R⁵, R⁷, or R⁸.

When the first polymerizable substituent is present as R^3 then the second polymerizable substituent is preferably present as R^5 , R^6 , or R^8 .

When the first polymerizable substituent is present as R^4 , then the second polymerizable substituent is preferably present as R^5 , R^6 , or R^7 . In this case it is less preferred that the second polymerizable substituent is present as R^2 or R^3 .

When the first polymerizable substituent is present as R^5 , then the second polymerizable substituent is preferably present as R^1 , R^2 , or R^3 . In this case it is less preferred that the second polymerizable substituent is present as R^6 or R^7 .

When the first polymerizable substituent is present as R^6 , then the second polymerizable substituent is preferably present as R^1 , R^3 , or R^4 .

When the first polymerizable substituent is present as R^7 then the second polymerizable substituent is preferably present as R^1 , R^2 , or R^4 .

When the first polymerizable substituent is present as R^8 , then the second polymerizable substituent is preferably present as R^1 , R^2 , or R^3 . In this case it is less preferred that the second polymerizable substituent is present as R^6 or R^7 .

The remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

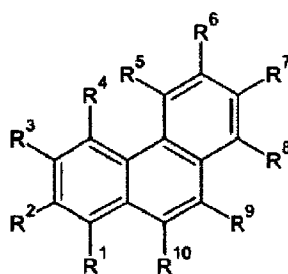
When the first polymerizable substituent is present as R^7 then the second polymerizable substituent preferably present as R^1 , R^2 , or R^4 .

When a compound of formula (I) contains 3 or 4 polymerizable substituents, then depending on the first polymerizable substituent, the second, third, and optionally fourth substituent are preferably present at the positions considered preferred for the second substituent in the

embodiment wherein a compound of formula (I) contains 2 polymerizable substituents above.

The remaining saturated substituent groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , are not polymerizable. Specifically, the remaining groups independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups. According to a preferred embodiment, the remaining groups are hydrogen atoms.

Alternatively, the polymerizable compound may be a compound of the following general formula (II) which is a phenanthrene derivative:



(II)

In a phenanthrene derivative according to formula (II), any of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} , may be a hydrogen atom or the aromatic ring may be substituted at the respective position by a substituent group. The substituent groups may be groups having polymerizable substituent or saturated substituent groups which are not polymerizable. According to the present invention, 2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} represent a polymerizable group and the remaining groups are hydrogen atoms or saturated groups which are not polymerizable. Accordingly, the compounds of formula (II) act as crosslinking monomer in a radical polymerization.

According to a first preferred embodiment, a compound of formula (II) contains 2 polymerizable substituents. According to a second preferred embodiment, a compound of formula (II) contains 3 or 4 polymerizable substituents.

In case the compound of formula (II) contains 2 polymerizable substituents, it is preferable that the substituents do not share the same annelated benzene ring. Accordingly, a first polymerizable substituent is present at R¹, R², R³, or R⁴, and a second polymerizable substituent is present at R⁵, R⁶, R⁷, or R⁸ or at R⁹ or R¹⁰.

Preferably, the first and second polymerizable substituent form a non-straight angle which is preferably obtuse. The angle being defined by the formal valence bonds in formula (II). Accordingly, the first and second polymerizable substituent are preferably not present at opposite positions across the aromatic ring system.

Specifically, when the first polymerizable substituent is present as R¹, then the second polymerizable substituent is preferably present as R⁵, R⁷, R⁸, and R⁹. In this case it is less preferred that the second polymerizable substituent is present as R², R³, R⁴, R⁶ and R¹⁰.

When the first polymerizable substituent is present as R² then the second polymerizable substituent preferably is present as R⁵, R⁶, R⁸, R⁹ and R¹⁰. In this case it is less preferred that the second polymerizable substituent is present as R¹, R³, or R⁴.

When the first polymerizable substituent is present as R³ then the second polymerizable substituent is preferably present as R⁶, R⁷, and R¹⁰. In this case it is less preferred that the second polymerizable substituent is present as R¹, R², or R⁴.

When the first polymerizable substituent is present as R⁴, then the second polymerizable substituent is preferably present as R⁷, R⁸, and R⁹. In this case it is less preferred that the second polymerizable substituent is present as R¹, R² or R³.

When the first polymerizable substituent is present as R⁵, then the second polymerizable substituent is preferably present as R¹, R², or R³. In this case it is less preferred that the second polymerizable substituent is present as R⁶, R⁷ or R⁸.

When the first polymerizable substituent is present as R⁶, then the second polymerizable substituent is preferably present as R², R³, or R⁹. In this case it is less preferred that the second polymerizable substituent is present as R⁵, R⁷ or R⁸.

When the first polymerizable substituent is present as R^7 then the second polymerizable substituent is preferably present as R^1 , R^3 , or R^4 . In this case it is less preferred that the second polymerizable substituent is present as R^5 , R^6 or R^8 .

When the first polymerizable substituent is present as R^8 , then the second polymerizable substituent is preferably present as R^1 , R^2 , R^4 , or R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^6 or R^7 .

When the first polymerizable substituent is present as R^9 , then the second polymerizable substituent is preferably present as R^1 , R^2 , R^6 , R^7 , or R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^4 or R^5 .

When the first polymerizable substituent is present as R^{10} , then the second polymerizable substituent is preferably present as R^2 , R^3 , R^5 , R^7 , R^8 , or R^9 . In this case it is less preferred that the second polymerizable substituent is present as R^4 or R^5 .

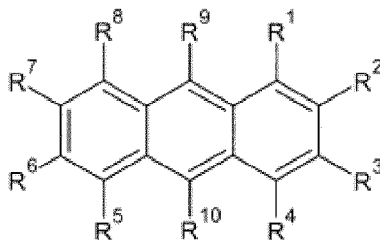
The remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

When a compound of formula (I) contains 3 or 4 polymerizable substituents, then depending on the first polymerizable substituent, the second, third, and optionally fourth substituent are preferably present at the positions considered preferred for the second substituent in the embodiment wherein a compound of formula (II) contains 2 polymerizable substituents above.

The remaining saturated substituent groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , are not polymerizable. Specifically, the remaining groups independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups. According to a first preferred embodiment, the remaining groups are hydrogen atoms. According to a second preferred embodiment, the

remaining groups comprise halogen atoms. Bromine and iodine atoms are preferable as halogen atoms in view of radioopacity and refractive index.

Alternatively, the polymerizable compound may be a compound of the following general formula (III) which is an anthracene derivative:



(III)

In an anthracene derivative according to formula (III), any of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} may be a hydrogen atom or the aromatic ring may be substituted at the respective position by a substituent group. The substituent groups may be groups having polymerizable substituent or saturated substituent groups which are not polymerizable. According to the present invention, 2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} represent a polymerizable group and the remaining groups are hydrogen atoms or saturated groups which are not polymerizable. Accordingly, the compounds of formula (III) act as crosslinking monomer in a radical polymerization.

According to a first preferred embodiment, a compound of formula (III) contains 2 polymerizable substituents. According to a second preferred embodiment, a compound of formula (III) contains 3 or 4 polymerizable substituents.

In case the compound of formula (III) contains 2 polymerizable substituents, it is preferable that the substituents do not share the same annelated benzene ring. Accordingly, a first polymerizable substituent is present at R^1 , R^2 , R^3 , or R^4 , and a second polymerizable substituent is present at R^5 , R^6 , R^7 , or R^8 or at R^9 or R^{10} .

Preferably, the first and second polymerizable substituent form a non-straight angle which is preferably obtuse. The angle being defined by the formal valence bonds in formula (III). Accordingly, the first and second polymerizable substituent are preferably not present at opposite positions across the aromatic ring system.

Specifically, when the first polymerizable substituent is present as R^1 , then the second polymerizable substituent is preferably present as R^6 and R^7 . In this case it is less preferred that the second polymerizable substituent is present as R^2 and R^3 .

When the first polymerizable substituent is present as R^2 then the second polymerizable substituent preferably is present as R^5 , R^7 , R^8 , R^9 and R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^1 , R^3 , or R^4 .

When the first polymerizable substituent is present as R^3 then the second polymerizable substituent is preferably present as R^5 , R^6 , R^8 , R^9 , and R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^1 , R^2 , or R^4 .

When the first polymerizable substituent is present as R^4 , then the second polymerizable substituent is preferably present as R^6 and R^7 . In this case it is less preferred that the second polymerizable substituent is present as R^2 and R^3 .

When the first polymerizable substituent is present as R^5 , then the second polymerizable substituent is preferably present as R^2 and R^3 . In this case it is less preferred that the second polymerizable substituent is present as R^2 and R^3 .

When the first polymerizable substituent is present as R^6 , then the second polymerizable substituent is preferably present as R^1 , R^3 , R^4 , R^9 , and R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^5 , R^7 , or R^8 .

When the first polymerizable substituent is present as R^7 then the second polymerizable substituent is preferably present as R^1 , R^2 , R^4 , R^9 , and R^{10} . In this case it is less preferred that the second polymerizable substituent is present as R^5 , R^6 , or R^8 .

When the first polymerizable substituent is present as R^8 , then the second polymerizable substituent is preferably present as R^2 and R^3 . In this case it is less preferred that the second polymerizable substituent is present as R^6 and R^7 .

When the first polymerizable substituent is present as R^9 , then the second polymerizable substituent is preferably present as R^2 , R^3 , R^6 , or R^7 . In this case it is less preferred that the second polymerizable substituent is present as R^{10} .

When the first polymerizable substituent is present as R^{10} , then the second polymerizable substituent is preferably present as R^2 , R^3 , R^6 , or R^7 . In this case it is less preferred that the second polymerizable substituent is present as R^{10} .

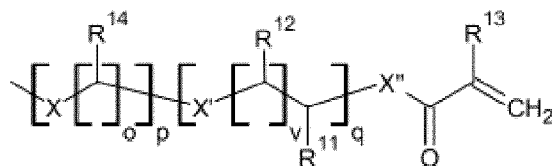
The remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

When a compound of formula (III) contains 3 or 4 polymerizable substituents, then depending on the first polymerizable substituent, the second, third, and optionally fourth substituent are preferably present at the positions considered preferred for the second substituent in the embodiment wherein a compound of formula (III) contains 2 polymerizable substituents above.

The remaining saturated substituent groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , are not polymerizable. Specifically, the remaining groups independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups. According to a first preferred embodiment, the remaining groups are hydrogen atoms.

The polymerizable substituents are independent from each other, and represent a group of the formula (IV), (V), or (VI).

Formula (IV) is as follows:



(IV)

In formula (IV), units p may be present or absent. Accordingly, p may be 0 or an integer of 1 or 2. In case unit p is absent, then X' is directly bonded to the group of Formula (I), (II), or (III). In case unit p is present, then X is directly bonded to the group of Formula (I), (II), or (III). In formula (IV), X may be -NH-, an oxygen atom or a sulfur atom. Preferably, X is an oxygen atom. In formula (IV), X' may be -NH-, an oxygen atom or a sulfur atom. Preferably, X' is an oxygen atom. Units p contains repeating units o, whereby o is an integer of from 2 to 10. Repeating units o contain groups R^{14} which may be the same or different, and independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group. According to a preferred embodiment, all R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group. According to a more preferred embodiment, all R^{14} are hydrogen atoms so that unit o is a straight chain C_{2-10} alkylene group, more preferably a C_{2-8} alkylene group, in particular ethylene, propylene, butylene, pentylene, hexylene, heptylene, or octylene.

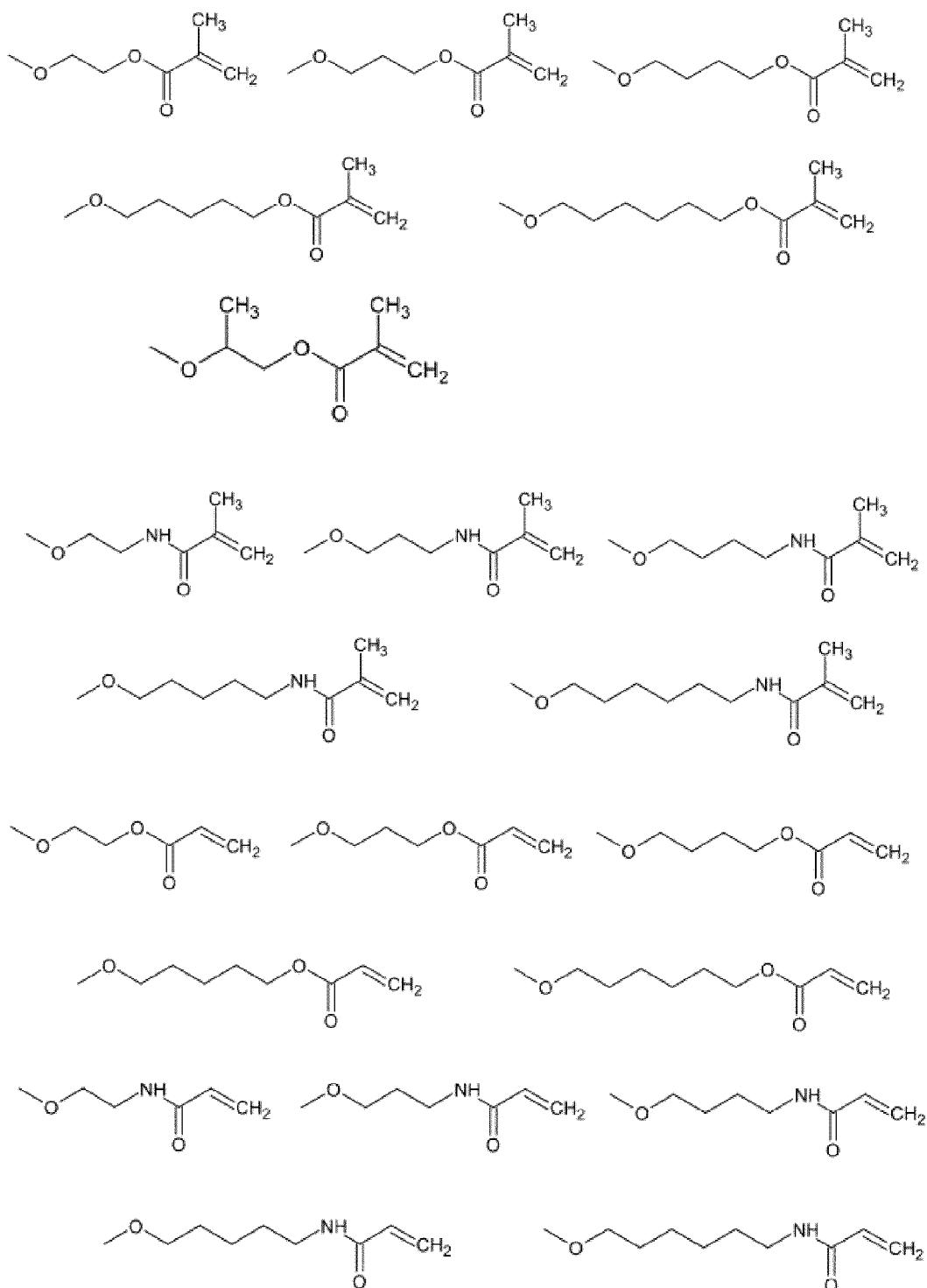
In formula (IV), q represents an integer of from 0 to 10, preferably 1 to 10. Units q contain group R^{11} and units v including groups R^{12} .

The R^{11} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{11} represent a hydrogen atom or a methyl group. The R^{11} may be the same or different when q is greater than 1.

v represents an integer of from 1 to 10. Units v may be the same or different when q is greater than 1. Moreover, groups R^{12} may be the same or different when v is greater than 1. Groups R^{12} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{12} represent a hydrogen atom or a methyl group.

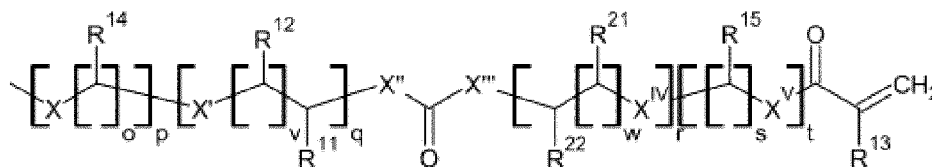
In formula (IV), a polymerizable group is attached to X''. X'' is -NH-, an oxygen atom or a sulfur atom. Preferably, X'' is -NH- or an oxygen atom. In the polymerizable group, R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group. Preferably, R^{13} represents a hydrogen atom or a methyl group.

Particularly preferred polymerizable substituents of the formula (IV) wherein p is 0 are as follows:



According to a preferred embodiment, a compound of formula (I), (II), or (III) contains the same 2 to 4 polymerizable substituents, which are groups of the formula (IV).

Formula (V) is as follows:



(V)

In formula (V), units p may be present or absent. Accordingly, p may be 0 or an integer of 1 or 2. In case unit p is absent, then X' is directly bonded to the group of Formula (I), (II), or (III). In case unit p is present, then X is directly bonded to the group of Formula (I), (II), or (III). In formula (V), X may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X is an oxygen atom. In formula (V), X' may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X'' is an oxygen atom. Units p contains repeating units o , whereby o is an integer of from 2 to 10. Repeating units o contain groups R^{14} which may be the same or different, and independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group. According to a preferred embodiment, all R^{14} are hydrogen atoms so that unit o is a straight chain C_{2-10} alkylene group, more preferably a C_{2-6} alkylene group, in particular ethylene, propylene, butylene, pentylene, hexylene, heptylene, or octylene.

In formula (V), q represents an integer of from 0 to 10, preferably 1 to 10. Units q contain group R^{11} and units v including groups R^{12} .

The R^{11} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{11} represent a hydrogen atom or a methyl group. The R^{11} may be the same or different when q is greater than 1.

v represents an integer of from 1 to 10. Units v may be the same or different when q is greater than 1. Moreover, groups R^{12} may be the same or different when v is greater than 1. Groups R^{12} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{12} represent a hydrogen atom or a methyl group.

In formula (V), r represents an integer of from 0 to 10, preferably 1 to 10. Units r contain group R^{22} and units w including groups R^{21} .

The R^{22} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, the R^{22} represent a hydrogen atom or a methyl group. The R^{22} may be the same or different when r is greater than 1.

w represents an integer of from 1 to 10. Units w may be the same or different when r is greater than 1. Moreover, groups R^{21} may be the same or different when w is greater than 1. Groups R^{21} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{21} represents a hydrogen atom or a methyl group.

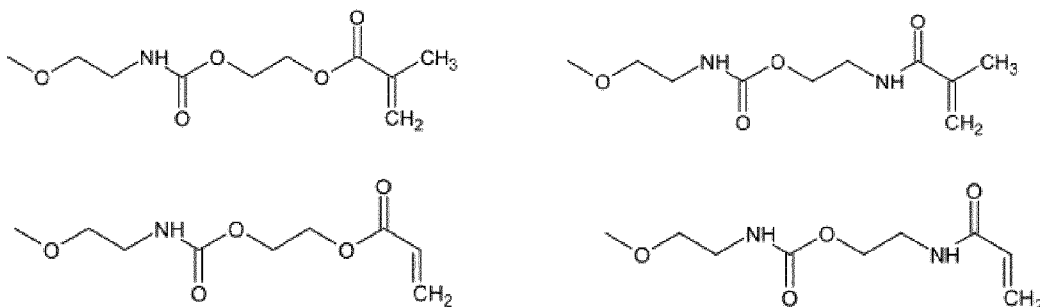
Units t contain repeating units s , whereby s is an integer of from 2 to 10. Repeating units s contain groups R^{15} which may be the same or different, and independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group. According to a preferred embodiment, all R^{15} are hydrogen atoms so that unit s is a straight chain C_{2-10} alkylene group, more preferably a C_{2-8} alkylene group, in particular ethylene, propylene, butylene, pentylene, hexylene, heptylene, or octylene.

In formula (V), units t may be present or absent. Accordingly, t may be 0 or an integer of 1 or 2. In case unit t is absent, then the polymerizable group is directly bonded to X^{IV} . In case unit p is present, then the polymerizable group is directly bonded to X^V . In the polymerizable group, R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group. Preferably, R^{13} represents a hydrogen atom or a methyl group.

In formula (V), X may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X is an oxygen atom. In formula (V), X' may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X' is an oxygen atom. In formula (V), X'' may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X'' is an oxygen atom. In formula (V), X''' may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X''' is an oxygen atom. In formula (V), X^{IV} may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X^{IV} is an oxygen atom. In formula (V), X^V may be $-NH-$, an oxygen atom or a sulfur atom. Preferably, X^V is an oxygen atom.

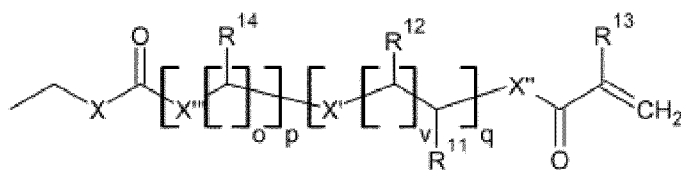
In formula (V), the moiety $-X''COX'''$ is preferably selected from a urethane group and a urea group. In case of a urethane group, X'' may be an oxygen atom and X''' may be an $-NH-$, or X'' may be an $-NH-$ and X''' may be an oxygen atom.

Particularly preferred polymerizable substituents of the formula (V) wherein p is 0 are as follows:



According to a preferred embodiment, a compound of formula (I), (II), or (III) contains the same 2 to 4 polymerizable substituents, which are groups of the formula (V).

Formula (VI) is as follows:



(VI)

In formula (VI), units p may be present or absent. Accordingly, p may be 0 or an integer of 1 or 2. In case unit p is absent, then X' is directly bonded to the -X''CO group of formula (VI). In case unit p is present, then X''' is directly bonded to the -X''CO group of formula (VI).

In formula (VI), X may be -NH-, an oxygen atom or a sulfur atom. Preferably, X is -NH- or an oxygen atom. In formula (VI), X' may be -NH-, an oxygen atom or a sulfur atom. Preferably, X' is -NH- or an oxygen atom. In formula (VI), X''' may be -NH-, an oxygen atom or a sulfur atom. Preferably, X'' is -NH- or an oxygen atom.

Units p contains repeating units o, whereby o is an integer of from 2 to 10. Repeating units o contain groups R¹⁴ which may be the same or different, and independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group. According to a preferred embodiment, all R¹⁴ are hydrogen atoms so that unit o is a straight chain C₂₋₁₀ alkylene group, more preferably a C₂₋₈ alkylene group, in particular ethylene, propylene, butylene, pentylene, hexylene, heptylene, or octylene.

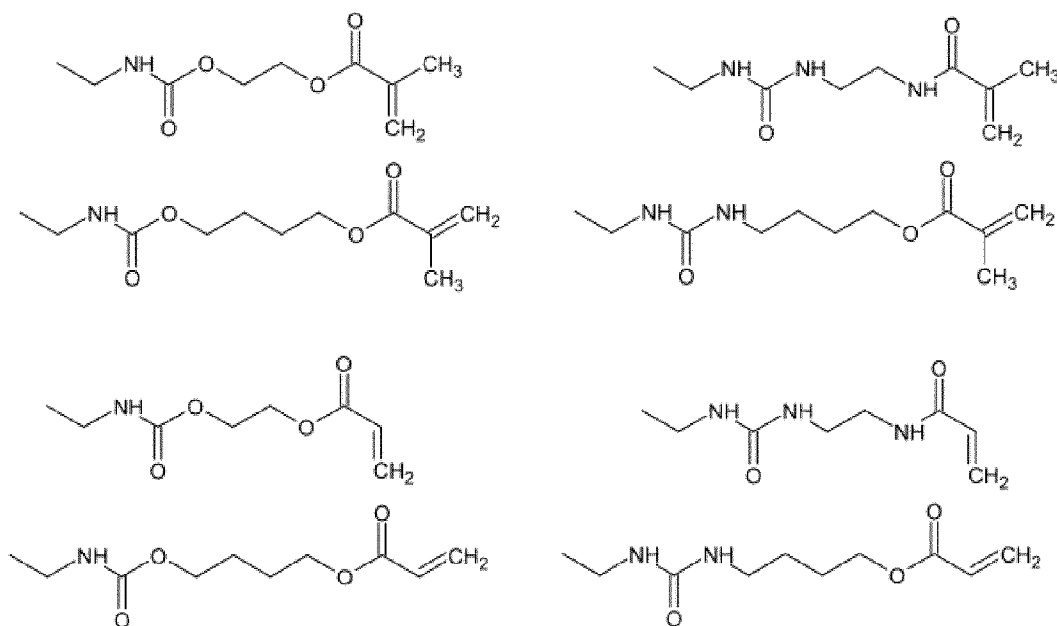
In formula (VI), q represents an integer of from 0 to 10, preferably 1 to 10. Units q contain group R^{11} and units v including groups R^{12} .

The R^{11} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{11} represent a hydrogen atom or a methyl group. The R^{11} may be the same or different when q is greater than 1.

v represents an integer of from 1 to 10. Units v may be the same or different when q is greater than 1. Moreover, groups R^{12} may be the same or different when v is greater than 1. Groups R^{12} independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group. Preferably, R^{12} represent a hydrogen atom or a methyl group.

In formula (VI), a polymerizable group is attached to X'' . X'' is -NH-, an oxygen atom or a sulfur atom. Preferably, X'' is -NH- or an oxygen atom. In the polymerizable group, R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group. Preferably, R^{13} represents a hydrogen atom or a methyl group.

Particularly preferred polymerizable substituents of the formula (VI) wherein p is 0 are as follows:



According to a preferred embodiment, a compound of formula (I), (II), or (III) contains the same 2 to 4 polymerizable substituents, which are groups of the formula (VI).

According to a preferred embodiment, the dental composition comprises a compound of formula (I).

Moreover, according to a further preferred embodiment, the dental composition comprises a compound, wherein 2 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} , represent a group of the formula (IV). Preferably, the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} represent a hydrogen atom.

According to a further preferred embodiment, the dental composition according to the present invention comprises a compound, wherein R^2 and R^7 , which may be the same or different, represent a group of formula (IV). Preferably, R^1 , R^3 , R^4 , R^5 , R^6 and R^8 represent a hydrogen atom in this embodiment.

According to an alternative preferred embodiment, the dental composition comprises a compound of formula (II).

A preferred specific compound for use in the present invention is selected from (naphthalene-2,7-diylbis(oxy))bis(hexane-6,1-diyl)bis(2-methacrylate), naphthalene-2,7-diylbis(oxy))bis(propane-3,1-diyl)bis(2-methacrylate), and (naphthalene-2,7-diylbis(oxy))bis(hydroxypropane-3,1-diyl)bis(2-methacrylate).

Preferably, the dental composition further comprises a filler and/or a solvent. Preferably, the dental composition further comprises a polymerization initiator system. The dental composition of the present invention may be a dental adhesive composition, a dental pit and fissure sealer, a dental composite, and a root canal filling composition. A dental composite may be a flowable dental composite, a universal dental composite, or packable dental composite. The dental composition is preferably selected from a dental adhesive composition, a dental pit and fissure sealer, a dental composite, and a root canal filling composition.

The dental composite of the present invention may comprise a particulate filler. A particulate filler is a powdered metal oxide or hydroxide, mineral silicate, or ion leachable glass or

ceramic, or mixtures thereof. Examples of particulate fillers may be selected from fillers currently used in dental restorative compositions.

The particulate filler may have a unimodal or polymodal (e.g., bimodal) particle size distribution. The particulate filler can be an inorganic material. It can also be a crosslinked organic material that is insoluble in the polymerizable resin, and is optionally filled with inorganic filler. The particulate filler can be radiopaque, radiolucent or non-radiopaque.

Examples of suitable particulate inorganic fillers are naturally-occurring or synthetic materials such as quartz, nitrides such as silicon nitride, glasses derived from, for example Ce, Sb, Sn, Zr, Sr, Ba and Al, colloidal silica, feldspar, borosilicate glass, kaolin, talc, titania, and zinc glass, and submicron silica particles such as pyrogenic silicas. Examples of suitable particulate organic filler particles include filled or unfilled pulverized polycarbonates or polyepoxides.

Preferably the surface of the filler particles is treated with a coupling agent in order to enhance the bond between the particulate filler and the matrix. The use of suitable coupling agents include gamma-methacryloxypropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane and gamma-aminopropyltrimethoxysilane.

The particulate filler usually has an average particle size of from 0.005 to 100 μm , preferably of from 0.01 to 40 μm as measured using, for example, by electron microscopy or by using a conventional laser diffraction particle sizing method as embodied by a MALVERN MastersizerTM S or MALVERN MastersizerTM 2000 apparatus.

A dental composition of the present invention may contain nano-scale particles. As the nano-scale particles in the present invention, any known nano-scale particles used in dental compositions may be used without any limitation. Preferable examples of the nano-scale particles include particles of inorganic oxides such as silica, alumina, titania, zirconia, particles of composite oxides of any of these oxides, and particles of calcium phosphate, hydroxyapatite, yttrium fluoride and ytterbium fluoride. Preferably, the nano-scale particles are particles of silica, alumina, titania, prepared by flame pyrolysis.

The average particle size of the nano-scale particles is preferable 1 to 50 nm, and more preferably 3 to 40 nm. The average particle size of the nano-scale particles can be measured by taking electron micrographs of these nano-scale particles and calculating the

average value of the diameters of the 100 randomly-selected nano-scale particles. It is desirable that the inorganic nano-scale particles be subjected previously to surface treatment with a surface treating agent to improve the affinity between the inorganic filler and the polymerizable composition of the present invention, and to increase the chemical bonding between the inorganic filler and the polymerizable composition so as to enhance the mechanical strength of the cured product.

The total amount of the particulate filler is preferably 0.1 to 500 parts by weight per 100 parts by weight of the polymerizable composition, more preferably 75 to 350 parts by weight, and particularly preferably 100 to 300 parts by weight. The amount of the nano-scale particles is preferably 0.1 to 50 parts by weight per 100 parts by weight of the polymerizable composition, more preferably 1 to 40 parts by weight, and particularly preferably 3 to 30 parts by weight.

Moreover, the polymerizable compound contained in the dental composition according to the present invention has a refractive index of from 1.500 to 1.540.

The dental composition of the present invention may comprise a solvent. A suitable solvent may be selected from water, alcohols, ketones, and ethers. Suitable alcohols may be selected from ethanol, iso-propanol, tert.-butanol and n-butanol. Suitable ketones may be selected from acetone and methyl ethyl ketone. Suitable ethers may be selected from diethyl ether and tetrahydrofuran. The solvent may be a mixture of two or more solvents.

The dental composite of the present invention may contain further polymerizable monomers other than the polymerizable compound of formula (I), (II), and (III). The polymerizable monomers may be mono-, bi-, tri- or polyfunctional monomers. The polymerizable monomers may be selected from methyl (meth)acrylate, isobutyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, 2-(N,N-dimethylamino)ethyl (meth)acrylate, 2,3-dibromopropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 10-hydroxydecyl (meth)acrylate, propylene glycol mono(meth)acrylate, glycerol mono(meth)acrylate, erythritol mono(meth)acrylate, N-methylol (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N-(dihydroxyethyl)(meth)acrylamide, (meth)acryloyloxydodecylpyridinium bromide, (meth)acryloyloxydodecylpyridinium chloride, (meth)acryloyloxyhexadecylpyridinium chloride, (meth)acryloyloxydecylammonium chloride, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,10-

decanediol di(meth)acrylate, bisphenol A diglycidyl (meth)acrylate (2,2-bis[4-[3-(meth)acryloyloxy-2-hydroxypropoxy]phenyl]propane, commonly known as "BisGMA"), 2,2-bis[4-(meth)acryloyloxyethoxyphenyl]propane, 2,2-bis[4-(meth)acryloyloxyethoxyphenyl]propane, 2,2-bis[4-[3-((meth)acryloyloxy-2-hydroxypropoxy]phenyl]propane, 1,2-bis[3-(meth)acryloyloxy-2-hydroxypropoxylethane, pentaerythritol di(meth)acrylate, [2,2,4-trimethylhexamethylenebis(2-carbamoyloxyethyl)] dimethacrylate (commonly known as "UDMA trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, N,N'-(2,2,4-trimethylhexamethylene)bis[2-(aminocarbonyloxy)propane-1,3-diol] tetramethacrylate, and 1,7-diacryloyloxy-2,2,6,6-tetraacryloyloxymethyl-4-oxyheptane.

The total amount of the polymerizable monomers contained in the dental composition besides the polymerizable compound of formula (I), (II), and (III) is preferably in the range of from 1 part to 100 part by weight per 100 part by weight of the polymerizable compound of formula (I), (II), and (III).

The dental composition of the present invention preferably contains a polymerization initiator. The type of the polymerization initiator is not particularly limited and can be selected from polymerization initiators commonly used in the dental field. Particularly, photopolymerization initiators and chemical polymerization initiators may be used alone, or two or more of them may be used in combination.

Examples of suitable photopolymerization initiators include alpha-diketones or (bis)acylphosphine oxides.

Examples of the alpha-diketones used as the photopolymerization initiator include camphorquinone, 9,10-phenanthrenequinone, 2,3-pentadione, 2,3-octadione, 4,4'-oxybenzyl, and acenaphthenequinone. Camphorquinone having the maximum absorption wavelength in the visible light range is preferred.

Examples of the acylphosphine oxides include 2,4,6-trimethylbenzoylmethoxyphenylphosphine oxide, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2,6-dimethoxybenzoyldiphenylphosphine oxide, 2,6-dichlorobenzoyldiphenylphosphine oxide, 2,4,6-trimethylbenzoylethoxyphenylphosphine

oxide, 2,3,5,6-tetramethylbenzoyldiphenylphosphine oxide, and benzoyl di-(2,6-dimethylphenyl)phosphonate.

Examples of the bisacylphosphine oxides include bis-(2,6-dichlorobenzoyl)phenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-4-propylphenylphosphine oxide, bis-(2,6-dichlorobenzoyl)-1-naphthylphosphine oxide, bis-(2,6-dimethoxybenzoyl)phenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,5-dimethylphenylphosphine oxide, bis-(2,4,6-trimethylbenzoyl)phenylphosphine oxide, and (2,5,6-trimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide.

A chemical polymerization initiator may be an organic peroxide selected from ketone peroxide, hydroperoxide, diacyl peroxide, dialkyl peroxide, peroxyketal, peroxyester, and peroxydicarbonate.

A ketone peroxide may be selected from methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, methylcyclohexanone peroxide, and cyclohexanone peroxide.

A hydroperoxide may be selected from 2,5-dimethylhexane-2,5-dihydroperoxide, diisopropylbenzene hydroperoxide, cumene hydroperoxide, and t-butyl hydroperoxide.

A diacyl peroxide may be selected from acetyl peroxide, isobutyryl peroxide, benzoyl peroxide, decanoyl peroxide, 3,5,5-trimethylhexanoyl peroxide, 2,4-dichlorobenzoyl peroxide, and lauroyl peroxide.

A dialkyl peroxide may be selected from di-t-butyl peroxide, dicumyl peroxide, t-butyleumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 1,3-bis(t-butylperoxyisopropyl)benzene, and 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne.

A peroxyketal may be selected from 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane, and 4,4-bis(t-butylperoxy)valeric acid-n-butyl ester.

A peroxyester may be selected from t-butylperoxy acetate, t-butylperoxy-2-ethyl hexanoate, alpha-cumyl peroxyneodecanoate, t-butyl peroxyneodecanoate, t-butyl peroxyipivate, 2,2,4-trimethylpentylperoxy-2-ethyl hexanoate, t-amylperoxy-2-ethyl hexanoate, di-t-

butylperoxy isophthalate, di-t-butylperoxy hexahydroterephthalate, t-butylperoxy-3,3,5-trimethyl hexanoate, t-butylperoxy benzoate, and t-butylperoxymaleic acid.

A peroxydicarbonate maybe selected from di-3-methoxy peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, bis(4-t-butylelohexyl)peroxydicarbonate, diisopropyl peroxydicarbonate, di-n-propyl peroxydicarbonate, di-2-ethoxyethyl peroxydicarbonate, and diallyl peroxydicarbonate.

Benzoyl peroxide is preferred.

The amount of the polymerization initiator to be added in the present invention is not particularly limited. Preferably, 0.01 to 10 parts by weight of the polymerization initiator per 100 parts by weight of the polymerizable composition may be used. When the amount of the polymerization initiator is less than 0.01 part by weight, polymerization may not proceed sufficiently and thereby mechanical strength may be reduced. Therefore, the amount is more preferably at least 0.1 part by weight. On the other hand, when the amount of the polymerization initiator exceeds 10 parts by weight, in the case where the polymerization initiator itself has low polymerization performance, sufficient mechanical strength may not be obtained and furthermore precipitation from the composition may occur.

The dental composition of the present invention may further contain a polymerization accelerator. Examples of the polymerization accelerator are amines and sulfinic acids and salts thereof.

Amines may be aliphatic amines or aromatic amines. Examples of aliphatic amines include primary aliphatic amines such as n-butylamine, secondary aliphatic amines such as diisopropylamine, and tertiary aliphatic amines such as N-methyldiethanolamine, N-ethyl-diethanolamine, N-n-butyl-diethanolamine, N-lauryldiethanolamine, 2-(dimethylamino)ethyl methacrylate, N-methyldiethanolamine dimethacrylate, N-ethyl-diethanolamine dimethacrylate, triethanolamine monomethacrylate, triethanolamine dimethacrylate, triethanolamine trimethacrylate, triethanolamine, trimethylamine, triethylamine, and tributylamine, tertiary aliphatic amines are preferred. Aromatic amines may be selected from N,N-di(2-hydroxyethyl)-p-toluidine, 4-N,N-dimethylaminobenzoic acid ethyl ester, N,N-dimethylaminobenzoic acid n-butoxyethyl ester, and 4-N,N-dimethylaminobenzophenone.

A sulfinic acid or salt thereof may be selected from sodium benzenesulfinate, sodium p-toluenesulfinate, and sodium 2,4,6-triisopropylbenzenesulfinate.

The amount of polymerization accelerator is not particularly limited. The amount may be selected from the range of from 0.001 to 5 parts by weight of polymerization accelerator per 100 parts by weight of the polymerizable composition.

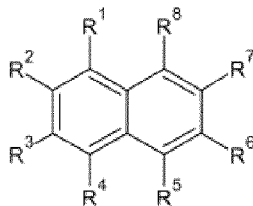
The dental composition of the present invention may further contain a pH adjuster, an ultraviolet absorber, an antioxidant, a polymerization inhibitor, a colorant, an antibacterial agent, an X-ray contrast agent, a thickening agent, a fluorescent agent.

The dental composition of the present invention may further contain a fluorine ion sustained-releasable filler, such as sodium fluoride, calcium fluoride, fluoroaluminosilicate glass, or sodium monofluorophosphate.

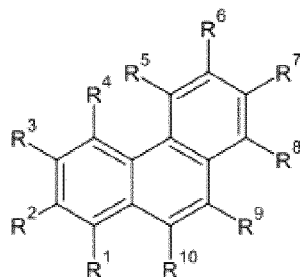
The dental composition may contain an antimicrobial agent. The antimicrobial agent may be a surfactant having an antibacterial activity, such as 12-(meth)acryloyloxydodecylpyridinium bromide or cetylpyridinium chloride.

The present invention also provides processes for the preparation of a dental composition according to the invention.

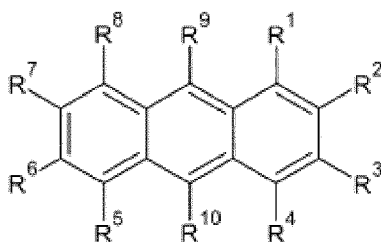
According to a first process, a reaction mixture is subjected to an addition reaction for obtaining an addition product. The reaction mixture comprises one or more compounds of formula (VII), (VIII) and/or formula (IX):



(VII)



(VIII)



(IX)

formula (VII), (VIII) and/or formula (IX), 2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are -XH groups wherein X is -NH-, an oxygen atom or a sulfur atom, and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups, and The reaction mixture further comprises ethylene carbonate or a compound of the formula ZRZ', wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group.

The reaction using ethylene carbonate may be carried out by mixing, preferably during heating, of components (VII), (VIII) and/or (IX) and ethylene carbonate in a reaction vessel and reacting the mixture in a single step in the presence of an addition catalyst for providing an addition product.

The reaction time is not particularly limited and may be selected in the range from 5 minutes to 8 hours. Preferably, the reaction time is selected in the range of from 20 minutes to 5 hours, more preferably, from 30 minutes to 4 hours.

The reaction temperature is not particularly limited and may be selected in the range from ambient temperature to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from 50 °C to the 250 °C, more preferably from 70 °C to 200 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

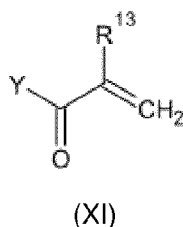
The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether.

The reaction may be carried out in the presence of a catalyst. The catalyst may be a base. A suitable base may be selected from alkali metal hydroxides such as sodium hydroxide or potassium hydroxide or alkali metal carbonates such as sodium carbonate and potassium carbonate.

The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 15 percent by weight, more preferably 0.1 to 10 percent by weight, based on the total weight of components (VII), (VIII), and (IX) present in the reaction mixture.

The obtained addition product may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

Subsequently, the process further comprises reacting the ethylene carbonate addition product with a compound of the following formula (XI):



wherein Y is a leaving group and R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group, or wherein Y and R¹³ form together with the carbon atoms to which they are bound a cyclic lactone or carboxylic acid anhydride ring having 4 to 8 carbon

atoms, for obtaining a polymerizable compound of formula (I), (II) or (III) of the present invention.

The reaction may be carried out by mixing, preferably during heating, of the addition product with ethylene carbonate and one or more compounds of the formula (XI) in a reaction vessel and reacting the mixture in a single step for providing a polymerizable compound of formula (I), (II) or (III) of the present invention.

The reaction time is not particularly limited and may be selected in the range from 30 minutes to 48 hours. Preferably, the reaction time is selected in the range of from 1 hours to 30 hours, more preferably, from 2 hours to 24 hours.

The reaction temperature is not particularly limited and may be selected in the range from -50 °C to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from -30 °C to the 60 °C, more preferably from -10 °C to 40 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as dichloromethane, chloroform, dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether.

The reaction may be carried out in the presence of a catalyst. The catalyst may be a base. A suitable base may be selected from amines such as triethyl amine.

The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 5 percent by weight, more preferably 0.1 to 3 percent by weight, based on the total weight of the addition product present in the reaction mixture.

When component (XI) is present in the reaction mixture, the reaction may be carried out in the presence of an inhibitor. The inhibitor may be any conventionally known inhibitor which does not interfere with the desired reaction. The inhibitor may be selected from 2,6-di-tert-butyl-p-cresol (BHT), hydroquinone, hydroquinone monomethyl ether, tert.-butyl

hydroquinone (TBHQ), TEMPO, and phenothiazin. Preferably, 2,6-di-tert-butyl-p-cresol may be used.

The amount of the inhibitor is not particularly limited and may be selected in a range of from 0.001 to 0.5 percent by weight, more preferably 0.01 to 0.3 percent by weight, based on the total weight of the addition product present in the reaction mixture.

The obtained methacrylate terminated macromer is may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

The reaction using a compound of the formula ZRZ' , wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group, may be carried out by mixing, preferably during heating, of components (VII), (VIII) and/or (IX) and a compound of the formula ZRZ' , in a reaction vessel and reacting the mixture in a single step in the presence of an addition catalyst for providing an addition product.

In the formula ZRZ' , Z and Z' independently are leaving groups. The leaving groups may be selected from halogen atoms, a hydroxyl group and a tosyl group. A halogen atom may be a chlorine atom, a bromine atom and an iodine atom. A bromine atom is preferred. In the formula ZRZ' , R is a straight chain or branched alkylene group. The alkylene group is preferably, a C_{2-10} alkylene group, more preferably, a straight chain C_{2-8} alkylene group. Examples of the alkylene group is ethylene, propylene, butylene, pentylene, hexylene, heptylene, and octylene. Preferably, a compound of the formula ZRZ' is a compound of the following formula $Br(CH_2)_nBr$, wherein n is an integer of from 2 to 10, more preferably, from 2 to 8, still more preferably, 6.

The reaction time is not particularly limited and may be selected in the range from 1 hour to 36 hours. Preferably, the reaction time is selected in the range of from 2 hours to 30 hours, more preferably, from 5 hours to 24 hours.

The reaction temperature is not particularly limited and may be selected in the range from -30 °C to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from -10°C to the 100 °C, more preferably from 0 °C to 80 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

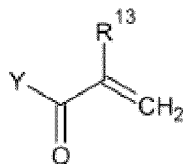
The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as acetone, dichloromethane, dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether.

The reaction may be carried out in the presence of a catalyst. The catalyst may be a base. A suitable base may be selected from alkali metal hydroxides such as sodium hydroxide or potassium hydroxide or alkali metal carbonates such as sodium carbonate and potassium carbonate.

The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 15 percent by weight, more preferably 0.1 to 10 percent by weight, based on the total weight of components (VII), (VIII), and (IX) present in the reaction mixture.

The obtained addition product may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

Subsequently, the process further comprises reacting the ethylene carbonate addition product with a compound of the following formula (XI):



(XI)

wherein Y is a leaving group and R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group, or wherein Y and R^{13} form together with the carbon atoms to which they are bound a cyclic lactone or carboxylic acid anhydride ring having 4 to 8 carbon atoms, for obtaining a polymerizable compound of formula (I), (II) or (III) of the present invention.

The reaction may be carried out by mixing, preferably during heating, of the addition product with a compound of the formula ZRZ' , wherein Z and Z' independently are leaving groups

and R is a straight chain or branched alkylene group, and one or more a compounds of the formula (XI) in a reaction vessel and reacting the mixture in a single step for providing a polymerizable compound of formula (I), (II) or (III) of the present invention.

The reaction time is not particularly limited and may be selected in the range from 30 minutes to 48 hours. Preferably, the reaction time is selected in the range of from 1 hours to 36 hours, more preferably, from 2 hours to 24 hours.

The reaction temperature is not particularly limited and may be selected in the range from - 50 °C to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from 0°C to the 100 °C, more preferably from 10 °C to 90 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as ethyl acetate, acetone, dichloromethane, chloroform, dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether.

The reaction may be carried out in the presence of a catalyst. The catalyst may be quaternary amine such as tetrabutylammonium iodide.

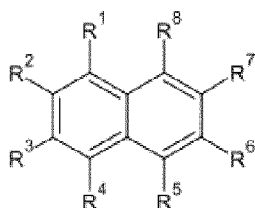
The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 5 percent by weight, more preferably 0.1 to 3 percent by weight, based on the total weight of the addition product present in the reaction mixture.

When component (XI) is present in the reaction mixture, the reaction may be carried out in the presence of an inhibitor. The inhibitor may be any conventionally known inhibitor which does not interfere with the desired reaction. The inhibitor may be selected from 2,6-di-tert-butyl-p-cresol (BHT), hydroquinone, hydroquinone monomethyl ether, tert.-butyl hydroquinone (TBHQ), TEMPO, and phenothiazin. Preferably, 2,6-di-tert-butyl-p-cresol may be used.

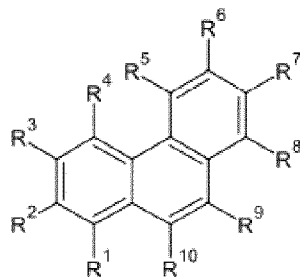
The amount of the inhibitor is not particularly limited and may be selected in a range of from 0.001 to 0.5 percent by weight, more preferably 0.01 to 0.3 percent by weight, based on the total weight of the addition product present in the reaction mixture.

The obtained methacrylate terminated macromer is may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

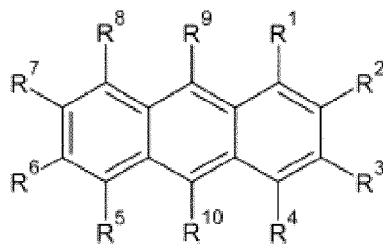
According to a second process of the present invention a reaction mixture is subjected to an addition reaction. The reaction mixture comprises one or more compounds of formula (XII), (XIII) and/or formula (XIV):



(XII)



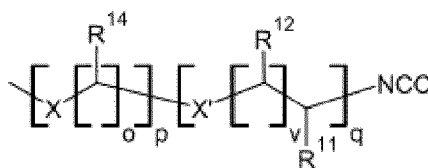
(XIII)



(XIV)

wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are independently a group of the following formula (XV):



(XV)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

o independently represent an integer of from 2 to 10,

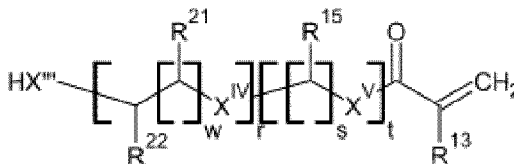
p independently is an integer of from 0, 1 or 2;

q independently represent an integer of from 0 to 10, preferably 1 to 10;

v independently represents an integer of from 1 to 10,

and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

The addition reaction is carried out with a compound of the following formula (XVI):



(XVI)

wherein

X''' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X^V is -NH-, an oxygen atom or a sulfur atom,

R^{21} and R^{22}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{13} represents a hydrogen atom or a straight chain or branched C_{1-6} alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R^{15} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

s independently represent an integer of from 2 to 10,

t independently is an integer of from 0, 1 or 2;

r which may be the same or different, independently represent an integer of from 0 to 10, preferably 1 to 10;

w independently represents an integer of from 1 to 10,

for obtaining a polymerizable compound of formula (I), (II) or (III) as defined above.

The reaction may be carried out by mixing, preferably during heating, of components (XII), (XIII) and/or (XIV), and (XVI) in a reaction vessel and reacting the mixture in a single step for providing a compound of the present invention. Preferably, r and t are not 0 at the same time.

The reaction time is not particularly limited and may be selected in the range from 30 minutes to 48 hours. Preferably, the reaction time is selected in the range of from 1 hours to 12 hours, more preferably, from 2 hours to 10 hours.

The reaction temperature is not particularly limited and may be selected in the range from ambient temperature to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from 50 °C to the 150 °C, more preferably from 70 °C to 130 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether.

The reaction may be carried out in the presence of a catalyst. The catalyst may be a phase transfer catalyst. A suitable phase transfer catalyst may be selected from quaternary ammonium and phosphonium salts. Specifically, the phase transfer catalyst may be triethylbenzyl ammonium chloride, benzyltrimethyl ammonium chloride and hexadecyltributylphosphonium bromide. Preferably, triethylbenzyl ammonium chloride may be used.

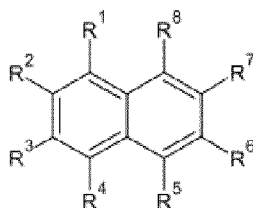
The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 5 percent by weight, more preferably 0.1 to 3 percent by weight, based on the total weight of components (XI), (XII), and (XIII) present in the reaction mixture.

When component (XVI) is present in the reaction mixture, the reaction may be carried out in the presence of an inhibitor. The inhibitor may be any conventionally known inhibitor which does not interfere with the desired reaction. The inhibitor may be selected from 2,6-di-tert-butyl-p-cresol (BHT), hydroquinone, hydroquinone monomethyl ether, tert.-butyl hydroquinone (TBHQ), TEMPO, and phenothiazin. Preferably, 2,6-di-tert-butyl-p-cresol may be used.

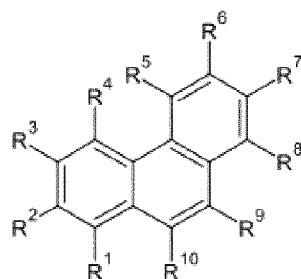
The amount of the inhibitor is not particularly limited and may be selected in a range of from 0.001 to 0.5 percent by weight, more preferably 0.01 to 0.3 percent by weight, based on the total weight of components (XI), (XII), and (XIII) present in the reaction mixture.

The obtained polymerizable compound is may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

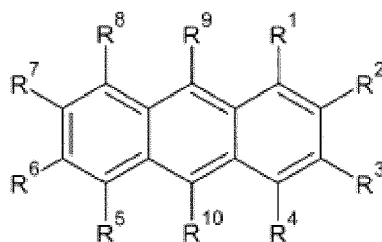
According to a third process, a reaction mixture is subjected to an addition reaction for obtaining an addition product. The reaction mixture comprises one or more compounds of formula (XVII), (XVIII) and/or formula (XIX):



(XVII)



(XVIII)

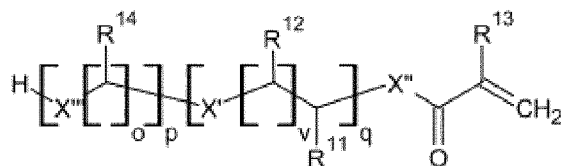


(XIX)

wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} are isocyanatomethyl groups, and the remaining groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , and, if present, R^9 , and R^{10} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from halogen atoms or hydroxy groups.

The addition reaction is carried out with a compound of the following formula (XX):



(XX)

wherein

X' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

- which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,
- R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,
- R¹⁴ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,
- o which may be the same or different, independently represent an integer of from 2 to 10,
- p which may be the same or different, independently is an integer of from 0, 1 or 2;
- q which may be the same or different, independently represent an integer of from 0 to 10, preferably 1 to 10;
- v independently represents an integer of from 1 to 10,
- for obtaining a polymerizable compound of formula (I), (II) or (III) as defined above.

The reaction may be carried out by mixing, preferably during heating, of components (XVII), (XVIII) and/or (XIX), and (XX) in a reaction vessel and reacting the mixture in a single step for providing a polymerizable composition of the present invention. Preferably, p and q are not 0 at the same time.

The reaction time is not particularly limited and may be selected in the range from 30 minutes to 48 hours. Preferably, the reaction time is selected in the range of from 1 hours to 12 hours, more preferably, from 2 hours to 10 hours.

The reaction temperature is not particularly limited and may be selected in the range from ambient temperature to the boiling temperature of the mixture. Preferably, the reaction temperature is selected in the range of from 50 °C to the 150 °C, more preferably from 70 °C to 130 °C.

The reaction pressure is not particularly limited and may be selected in the range from ambient pressure to an elevated pressure. Preferably, the reaction pressure is ambient pressure.

The reaction may be carried out in the presence or absence of a solvent. Suitable solvent may be selected from aprotic solvents such as dimethyl sulfoxide, toluene, DMF, and ethyleneglycol monomethyl ether. Preferably, the reaction is carried out in the absence of a solvent.

The reaction may be carried out in the presence of a catalyst. The catalyst may be a phase transfer catalyst. A suitable phase transfer catalyst may be selected from quaternary ammonium and phosphonium salts. Specifically, the phase transfer catalyst may be triethylbenzyl ammonium chloride, benzyltrimethyl ammonium chloride and hexadecyltributylphosphonium bromide. Preferably, triethylbenzyl ammonium chloride may be used.

The amount of the catalyst is not particularly limited and may be selected in a range of from 0.01 to 5 percent by weight, more preferably 0.1 to 3 percent by weight, based on the total weight of components (XVII), (XVIII), and (XIX) present in the reaction mixture.

When component (XX) is present in the reaction mixture, the reaction may be carried out in the presence of an inhibitor. The inhibitor may be any conventionally known inhibitor which does not interfere with the desired reaction. The inhibitor may be selected from 2,6-di-tert-butyl-p-cresol (BHT), hydroquinone, hydroquinone monomethyl ether, tert.-butyl hydroquinone (TBHQ), TEMPO, and phenothiazin. Preferably, 2,6-di-tert-butyl-p-cresol may be used.

The amount of the inhibitor is not particularly limited and may be selected in a range of from 0.001 to 0.5 percent by weight, more preferably 0.01 to 0.3 percent by weight, based on the total weight of components (XVII), (XVIII), and (XIX) present in the reaction mixture.

The obtained methacrylate terminated macromer is may be soluble in organic solvents such as chloroform, DMF and THF and in reactive diluents such as triethyleneglycol dimethacrylate.

According to a specific embodiment, a polymerizable compound of formula (I), (II) or (III), which contains hydroxyl groups in any of R^{13} may be further reacted with an isocyanate compound, a diisocyanate compound, isothiocyanate compound, a carboxylic acid halogenide compound, a cyclic carboxylic acid anhydride or a carboxylic acid compound for preparing a substituted hydroxyl group. Preferably, a polymerizable compound of formula (I), (II) or (III), which contains hydroxyl groups in any of R^{14} , and/or R^{15} is substituted.

An isocyanate compound may be aliphatic and/or aromatic. As examples of an isocyanate, methylisocyanate (MIC), allyl isocyanate, 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl

acrylate, 3-isocyanatopropyl methacrylate, 4-isocyanatobutyl methacrylate, and 6-isocyanatohexyl methacrylate may be mentioned.

A diisocyanate compound may be aliphatic and/or aromatic. As examples of a diisocyanate compound, methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) may be mentioned.

An isothiocyanate compound may be aliphatic and/or aromatic. As examples of an isothiocyanate, methylisothiocyanate, allyl isothiocyanate, 2-isothiocyanatoethyl methacrylate, 2-isothiocyanatoethyl acrylate, 3-isothiocyanatopropyl methacrylate, 4-isothiocyanatobutyl methacrylate, and 6-isothiocyanatohexyl methacrylate may be mentioned.

A carboxylic acid halogenide compound may preferably be a carboxylic acid chloride or a carboxylic acid bromide. As examples of a carboxylic acid halogenide compound, acryloyl chloride, methacryloyl chloride, acryloyl bromide, methacryloyl bromide may be mentioned.

A cyclic carboxylic acid anhydride may be selected from pentandioic anhydride, phthalic anhydride, itaconic anhydride or maleic anhydride.

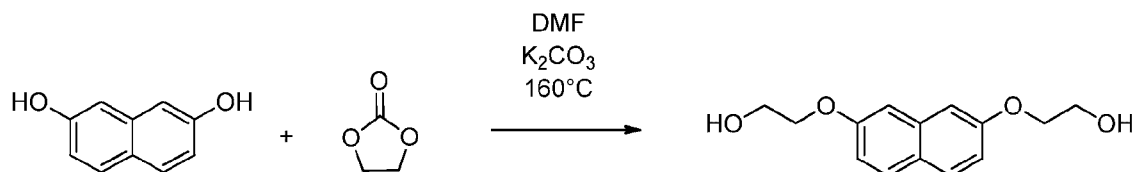
A carboxylic acid compound may be aliphatic and/or aromatic and may be selected from acrylic acid and methacrylic acid.

The present invention will now be further illustrated based on the following examples.

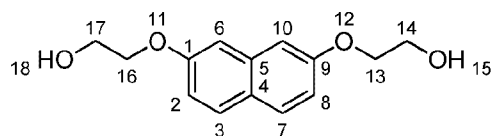
Examples

Example 1 - Naphthalene-2,7-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate)

2,2'-(naphthalene-2,7-diylbis(oxy))diethanol



5.00 g 2,7-dihydroxynaphthalene (31.21 mmol), 6.05 g ethylene carbonate (68.66 mmol; 2.2 eq.), and 8.62 g potassium carbonate (68.43 mmol) were solved in 100 ml DMF. The mixture was heated to 160°C for 2 h. After that, the mixture was concentrated via rotary evaporator before the product was precipitated in 1000 mL NaOH (1M). The slightly brown solid was filtrated and washed several times with 500 mL water. The obtained dark brown solid was dried under high vacuum.



Yield: 5.02g (64%)

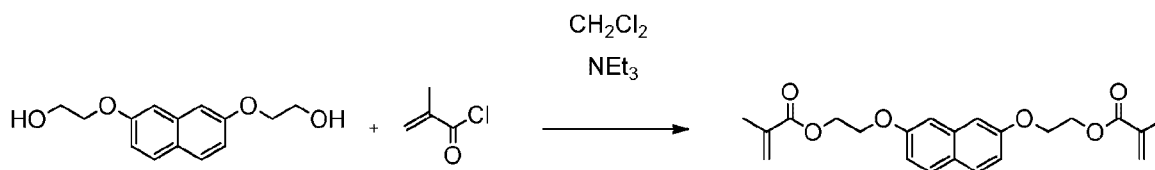
Elementary analysis: theor. [%] C: 68.74; H: 6.29

pract. [%] C: 67.29; H: 6.28

¹H-NMR [ppm]: [300MHz; DMSO-d₆]: δ 7.70 (d, 2H, Pos. 3, 7); δ 7.20 (d, 2H, Pos. 6, 10); δ 7.00 (dd, 2H, Pos. 2, 8); δ 4.91 (s, 2H, Pos. 15, 18); δ 4.08 (t, 4H, Pos. 13, 16); δ 3.78 (m broad, 4H, Pos. 14, 17)

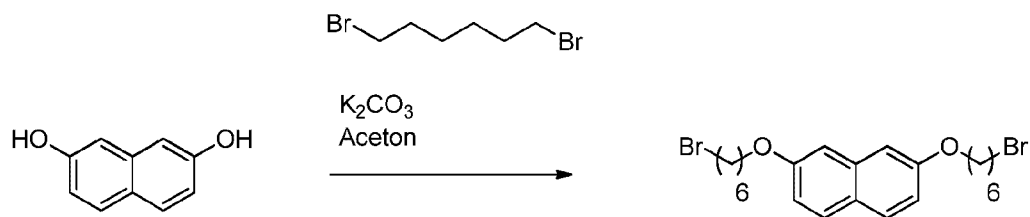
¹³C-NMR [ppm]: [150MHz; DMSO-d₆]: δ 157.11 (C1, 9); δ 135.77 (C5); δ 128.97 (C3, 7); δ 123.68 (C4); δ 115.98 (C2, 8); δ 106.10 (C6, 10); δ 64.47 (C13, 16); δ 59.57 (C14, 17)

(Naphthalene-2,7-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate)

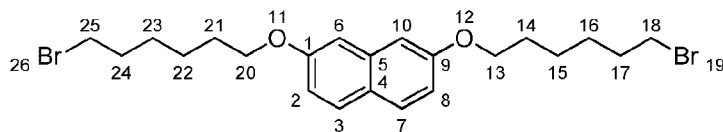


5.00 g 2,2'-(naphthalene-2,7-diylbis(oxy))diethanol (20.14 mmol) and 4.89 g triethylamine (19.33 mmol; 2.4 eq.) were added to 80 mL CH₂Cl₂ and cooled down to 0°C. Under high stirring, 5.05 g methacryloyl chloride (48.33 mmol; 2.4 eq.) solved in 20 mL CH₂Cl₂, was added slowly to the reaction mixture. The mixture was allowed to stay at 0°C for 60 min. before the mixture was stirred for 24 h at room temperature. After that, the mixture was concentrated via rotary evaporator. The mixture was washed two times with 100 mL Na₂CO₃ (1M) and one time with 100 mL water. The organic layer was dried with MgSO₄.

Example 2 - (Naphthalene-2,7-diylbis(oxy))bis(hexane-6,1-diyl)bis(2-methacrylate)

2,7-bis((6-bromohexyl)oxy)naphthalene

5 g 2,7-dihydroxynaphthalene (31.21 mmol) and 9.49 g potassium carbonate (68.60 mmol) were added in a 500 ml one neck flask and solved with 250 ml Acetone. The reaction mixture was refluxed for 2 h and cooled down to room temperature, before 60.92 g 1,6-dibromohexane (249.70 mmol) was added. After that, the reaction mixture was refluxed for 48h. Next, the solvent was removed via rotary evaporator and the residual was solved in 80ml CHCl₃, before the solution was washed with 2M HCl (2x80 ml) and H₂O (2x80 ml). The collected organic layers were dried over MgSO₄. After removal of the solvent via rotary evaporator a brown/green mixture was obtained. To this, 300 mL Ethanol was added whereat a yellow/green solid precipitated. The product was obtained as a colorless powder via column chromatography (CHCl₃:n-hexane= 9:1).



Yield: 4.55g (29%)

Elementary analysis: theor. [%] C: 54.34; H: 6.22

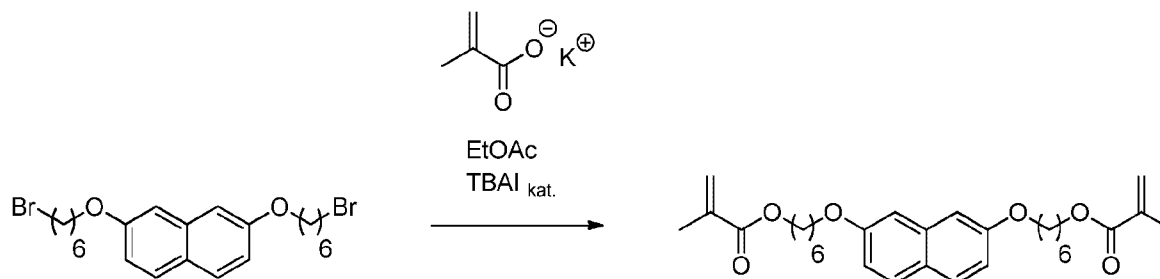
pract. [%] C: 54.20; H: 6.21

¹H-NMR [ppm]: [300MHz; CDCl₃]: δ 7.64 (d, 2H, Pos. 3, 7); δ 7.01 (d, 2H, Pos. 6, 10); δ 6.95 (d, 2H, Pos. 2, 8); δ 4.05 (t, 4H, Pos. 13; 20); δ 3.42 (t, 4H, Pos. 18, 25); δ 1.92 – 1.82(m, 8H, Pos. 14, 17, 21, 24); δ 1.52 (m, 4H, Pos. 15, 16, 22, 23)

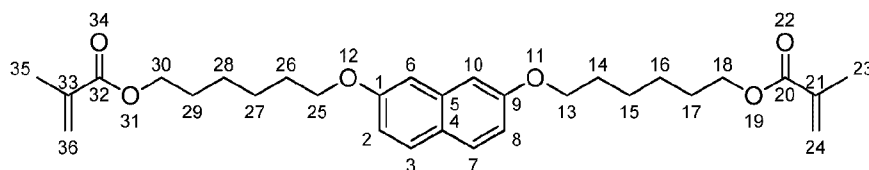
¹³C-NMR [ppm]: [150MHz; [CDCl₃]: δ 157.78 (C1, 9); δ 136.13 (C5); δ 129.28 (C4); δ 116.43 (C2, 8); δ 106.21 (C6, 10); δ 67.88 (C13, 20); δ 34.04 (C18, 25); δ 32.91 (C17, 24); δ 29.30 (C14, 21); δ 28.16 (C16, 23); δ 25.58 (C15, 22)

ESI (MS): 487:1 M+H⁺ [m/z]

(Naphthalene-2,7-diylbis(oxy))bis(hexane-6,1-diyl)bis(2-methacrylate)



3.6 g 2,7-bis((6-bromohexyl)oxynaphthalene) (7.40 mmol), 3.67 g potassium methacrylate (29.61 mmol; 4 eq.) and 0.054 g tetrabutylammonium iodide (0.1 mmol) were solved in 60 mL ethylacetate. The suspension was heated to 75°C for 24 h. After that, the suspension was filtered and the solvent was removed via rotary evaporator. The residual was solved in 50 mL diethylether and some crystals BHT were added. The solution was washed with 50 mL 1M HCl, 50 mL 1M NaOH and 50 mL water. The organic layer was dried over MgSO_4 . The product was obtained as slightly yellow viscous oil.



Yield: 2.5g (68%)

Elementary analysis: theor. [%] C: 72.55; H: 8.12

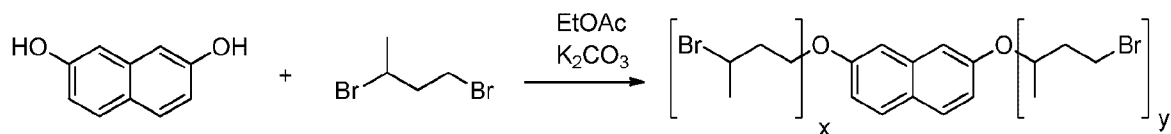
pract. [%] C: 72.55; H: 8.01

$^1\text{H-NMR}$ [ppm]: [300MHz; CDCl_3]: δ 7.63 (d, 2H, Pos. 3, 7); δ 7.00 (d, 2H, Pos. 6, 10); δ 6.95 (dd, 2H, Pos. 2, 8); δ 6.08 (m, 2H, Pos. 24a; 36a); δ 5.52 (m, 2H, Pos. 24b, 36b); δ 4.15 (t, 4H, Pos. 13, 25); δ 4.04 (t, 4H, Pos. 18, 30); δ 1.93 (m, 6H, Pos. 23, 35); δ 1.84 (m, 4H, Pos. 14, 26); δ 1.71 (m, 4H, Pos. 17, 29); δ 1.50 (m, 8H, Pos. 15, 16, 27, 28)

$^{13}\text{C-NMR}$ [ppm]: [150MHz; CDCl_3]: δ 167.72 (C20, 32); δ 157.78 (C1, 9); δ 136.99 (C21, 33); δ 136.13 (C5); δ 129.25 (C3, 7); δ 125.41 (C24, 36); δ 124.37 (C4); δ 116.41 (C2, 8); δ 106.19 (C6, 10); δ 67.92 (C13, 25); δ 64.86 (C18, 30); δ 29.36 (C14, 26); δ 28.78 (C15, 16, 27, 28); δ 18.53 (C23, 35)

ESI (MS): 497.5 $\text{M}+\text{H}^+$ [m/z]

Example 3 – 4-((7-((4-((methacryloyloxy)butane-2-yl)oxy)naphthalen-2-yl)oxy)butane-2-yl)methacrylate

2-((4-bromobutane-2-yl)oxy)7-(3-bromobutoxy)naphthalene

5 g 2,7-dihydroxynaphthalene (31.21 mmol) and 9.49 g potassium carbonate (68.60 mmol) were added in a 500 ml one neck flask and solved with 250 ml Acetone. The reaction mixture was refluxed for 2 h and cooled down to room temperature, before 40.43 g 1,3-dibromobutane (187.26 mmol) was added. After that, the reaction mixture was refluxed for 24 h. Next, the solvent was removed via rotary evaporator. The product was obtained as slightly yellow solid via column chromatography (CHCl_3 :n-hexane= 10:1; R_f = 0.8).

Yield: 7.50g (55%)

Elementary analysis: theor. [%] C: 50.26; H: 5.15

pract. [%] C: 56.69; H: 5.58

El (MS): 430 [M]⁺ [m/z]

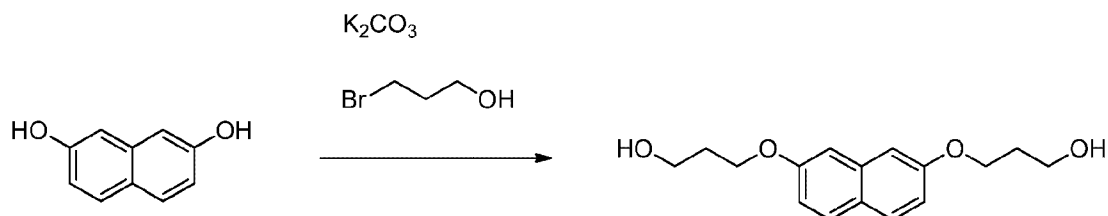
4-((7-((4-(methacryloyloxy)butane-2-yl)oxy)naphthalen-2-yl)oxy)butane-2-yl-methacrylate

7.5 g 2-((4-bromobutane-2-yl)oxy)7-(3-bromobutoxy)naphthalene (17.43 mmol), 8.66 g potassium methacrylate (69.73 mmol; 4eq.) and 0.110 g tetrabutylammonium iodide (0.35 mmol) were solved in 200 mL ethylacetate. The suspension was heated to 75°C for 24 h. After that, the suspension was filtered and the solvent was removed via rotary evaporator. The residual was solved in 100 mL diethylether and some crystals BHT were added. The solution was washed with 100 mL 1M HCl, 100mL 1M NaOH and 100 mL water. The organic layer was dried over MgSO_4 . The product was obtained as slightly yellow viscous oil.

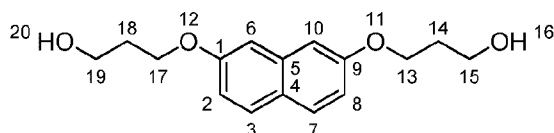
Yield: 4.60g (59%)

ESI (MS): 441 [M+H]⁺; 458.3 [M+NH₄]⁺ [m/z]

Example 4 - (Naphthalene-2,7-diylbis(oxy))bis(propane-3,1-diyl)bis(2-methacrylate)3,3'-(naphthalene-2,7-diylbis(oxy))bis(propane-1-ol)



2.5 g 2,7-dihydroxynaphthalene (15.60 mmol) and 4.89 g potassium carbonate (35.43 mmol) were solved in 125 ml acetone. The reaction mixture was refluxed for 2 h and cooled down to room temperature, before 4.77 g 1,3-dibromopropane (34.44 mmol) was added. After that, the reaction mixture was refluxed for 24 h. Next, the solvent was removed via rotary evaporator. The product was obtained as colorless solid via column chromatography (ethyl acetate:n-hexane = 10:1).



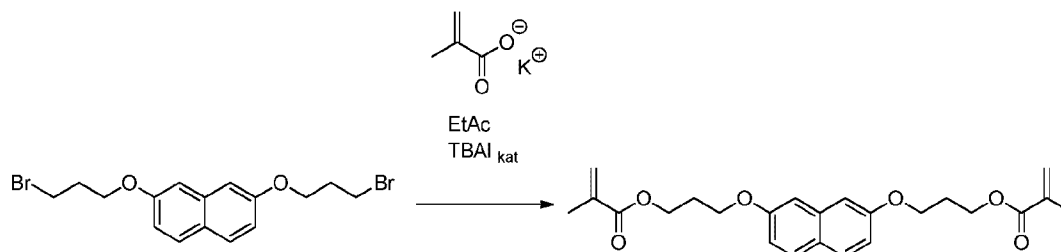
Yield: 0.9g (21%)

^1H -NMR [ppm]: [300MHz; Methanol- d_4]: δ 7.63 (d, 2H, Pos. 3, 7); δ 7.13(d, 2H, Pos. 6, 10); δ 6.96 (dd, 2H, Pos. 2, 8); δ 4.16(t, 4H, Pos. 13, 17); δ 3.78 (t, 4H, Pos. 15, 19); δ 2.03 (quint., 4H, Pos. 14, 18)

^{13}C -NMR [ppm]: [75MHz; Methanol- d_4]: δ 159.07 (C1,9); δ 137.72 (C23,27); δ 130.10 (C3,7); δ 125.89 (C4); δ 117.30 (C2,8); δ 107.31 (C6,10); δ 65.81 (C13,17) δ 59.81 (C15,19); δ 33.53 (C14, 18)

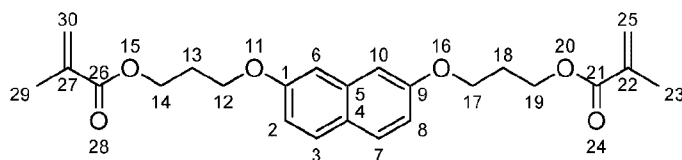
EI (MS): 276 M; 277 M+ H^+

(Naphthalene-2,7-diylbis(oxy))bis(propane-3,1-diyl)bis(2-methacrylate)



4.00 g 2,7-bis(3-bromopropoxy)naphthalene (9.94 mmol), 4.93 g potassium methacrylate (39.76 mmol; 4 eq.) and 0.073 g tetrabutylammonium iodide (0.2 mmol) were solved in 60 mL ethyl acetate. The suspension was heated to 75°C for 24 h. After that, the suspension

was filtered and the solvent was removed via rotary evaporator. The residual was solved in 50 mL diethyl ether and some crystals BHT were added. The solution was washed with 50 mL 1M HCl, 50 mL 1M NaOH and 50 mL water. The organic layer was dried over MgSO_4 . The product was obtained as colorless solid.



Yield: 2.73g (66%)

Mp: ~ 60°C (opt.)

Elementary analysis: theor. [%] C: 69.88; H: 6.84

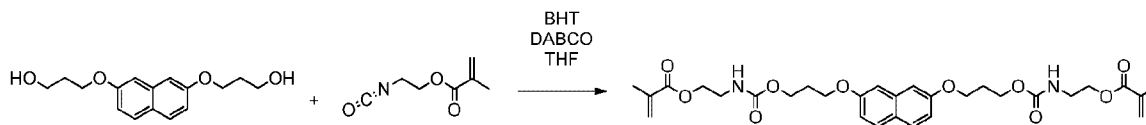
pract. [%] C: 69.88; H: 6.68

$^1\text{H-NMR}$ [ppm]: [300MHz; CDCl_3]: δ 7.58 (d, 2H, Pos. 3, 7); δ 6.96 (d, 2H, Pos. 6, 10); δ 6.93 (dd, 2H, Pos. 2, 8); δ 6.05 (m, 2H, Pos. 25a; 30a); δ 5.49 (m, 2H, Pos. 25b, 30b); δ 4.31 (t, 4H, Pos. 12, 17); δ 4.09 (t, 4H, Pos. 14, 19); δ 2.15 (qui., 4H, Pos. 13, 18); δ 1.88 (m, 6H, Pos. 23, 29)

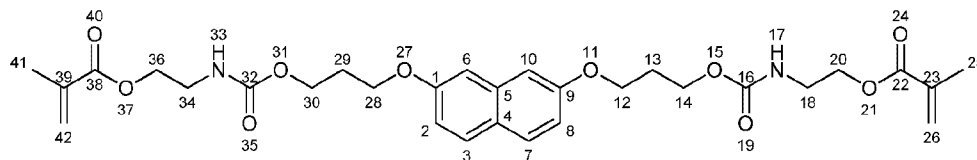
$^{13}\text{C-NMR}$ [ppm]: [150MHz; CDCl_3]: δ 167.57 (C21, 26); δ 157.53 (C1, 9); δ 136.50 (C22, 27); δ 136.00 (C5); δ 129.37 (C3, 7); δ 125.73 (C25, 30); δ 124.81 (C4); δ 116.47 (C2, 8); δ 106.23 (C6, 10); δ 64.58 (C12, 17); δ 61.78 (C14, 19); δ 28.88 (C13, 18); δ 18.53 (C23, 29)

ESI (MS): 413.2 $\text{M}+\text{H}^+$; 435.2 $\text{M}+\text{Na}^+$ [m/z]

Example 5 – {[(naphthalene-2,7-diylbis(oxy))bis(propylene glycol))bis(oxy))bis(carbonyl)] bis(azanediy)]bis(ethane-2,1-diyl)bis(2-methacrylate)



2 g 3,3'-(naphthalene-2,7-diylbis(oxy))bis(propylene glycol) (7.23 mmol), 2.69 g isocyanatoethyl methacrylate (17.37 mmol; 2.4 eq.), 0.081 g 1,4-diazabicyclo[2.2.2]octane (0.723 mmol) and 0.0031 g 2,6-di-tert-butyl-p-cresol (0.014 mmol) were solved in 50 mL THF. The solution was heated to 75°C for 24 h. After that, the solvent was removed via rotary evaporator. The product was obtained as colorless solid via column chromatography (ethyl acetate:n-hexane = 2:1).



Yield: 2.12g (52%)

Elementary analysis: theor. [%] C: 61.42; H: 6.53; N: 4.78

pract. [%] C: 61.46; H: 6.44; N: 4.77

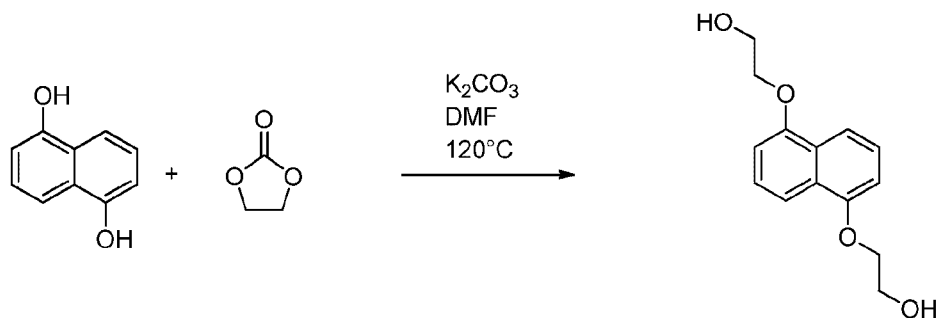
$^1\text{H-NMR}$ [ppm]: [300MHz; CDCl_3]: δ 7.64 (d, 2H, Pos. 3, 7); δ 7.00 (d, 2H, Pos. 6, 10); δ 6.95 (dd, 2H, Pos. 2, 8); δ 6.09 (m, 2H, Pos. 26a; 42a); δ 5.56 (m, 2H, Pos. 26b, 42b); δ 4.93 (s, 2H, Pos. 17, 33); δ 4.29 (t, 4H, Pos. 20, 36); δ 4.21 (t, 4H, Pos. 12, 28); δ 4.12 (t, 4H, Pos. 14, 30); δ 3.49 (q, 4H, Pos. 18, 34); δ 2.15 (quin., 4H, Pos. 13, 29); δ 1.91 (m, 6H, Pos. 25, 41)

$^{13}\text{C-NMR}$ [ppm]: [150MHz; CDCl_3]: δ 167.50 (C22, 38); δ 157.57 (C16, 32); δ 156.63 (C1, 9); δ 136.15 (C5); δ 136.03 (C23, 39); δ 129.37 (C3, 7); δ 126.28 (C26, 42); δ 124.58 (C4); δ 116.47 (C2, 8); δ 106.29 (C6, 10); δ 64.55 (C20, 36); δ 63.93 (C12, 28); δ 62.17 (C14, 30); δ 40.43 (C18, 34); δ 29.23 (C13, 29); δ 18.52 (C25, 41)

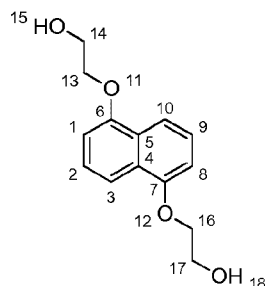
ESI (MS): 587.5 $\text{M}+\text{H}^+$ [m/z]

Example 6 – (Naphthalene-1,5-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate)

2,2'-(naphthalene-1,5-diylbis(oxy))diethanol



5.00 g 1,5-dihydroxynaphthalene (31.21 mmol), 6.05 g ethylene carbonate (68.66 mmol; 2.2 eq.), and 8.62 g potassium carbonate (68.43 mmol) were solved in 100 ml DMF. The mixture was heated to 160°C for 2 h. After that, the mixture was concentrated via rotary evaporator before the product was precipitated in 1000 mL NaOH (1M). The slightly brown solid was filtrated and washed several times with 500 mL water. The obtained slightly brown solid was dried under high vacuum.



Yield: 4.65g (60%)

Elementary analysis: theor. [%] C: 67.73; H: 6.50

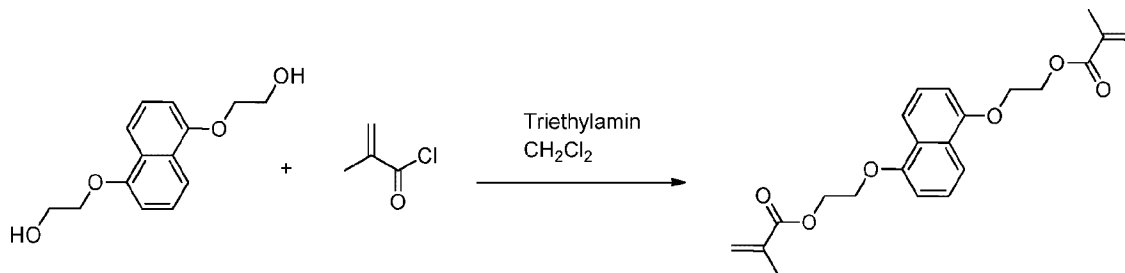
pract. [%] C: 66.85; H: 6.24

$^1\text{H-NMR}$ [ppm]: [300MHz; DMSO- d_6]: δ 7.80 (d, 2H, Pos. 3, 10); δ 7.37 (t, 2H, Pos. 2, 9); δ 6.98 (d, 2H, Pos. 1, 8); δ 4.98 (s, 2H, Pos. 15, 18); δ 4.14 (t, 4H, Pos. 13, 16); δ 3.86 (t, 4H, Pos. 14, 17)

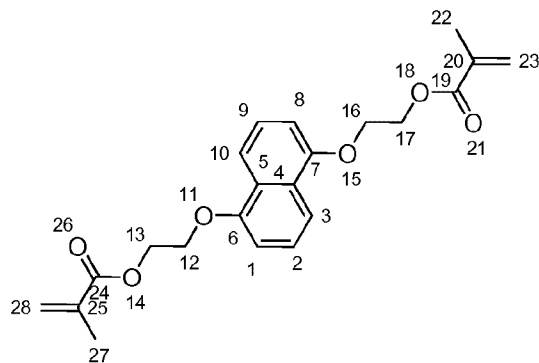
$^{13}\text{C-NMR}$ [ppm]: [75MHz; DMSO- d_6]: δ 154.07 (C7,6); δ 126.07 (C4,5); δ 125.29 (C2,9); δ 113.96 (C3,10); δ 105.78 (C1,8); δ 69.92 (C13, 16); δ 59.74 (C14,17)

EI (MS): 248 M; 249 M+ H^+

(Naphthalene-1,5-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-methacrylate)



2.00 g 2,2'-(naphthalene-1,5-diylbis(oxy))diethanol (8.05mmol) and 1.95g triethylamine (19.33 mmol; 2.4 eq.) were added to 50 mL CH_2Cl_2 and cooled down to 0°C. Under high stirring, 2.02 g methacryloyl chloride (19.33 mmol; 2.4 eq.) solved in 10 mL CH_2Cl_2 , were added slowly to the reaction mixture. The mixture was allowed to stay at 0°C for 60 min. before the mixture was stirred for 24 h at room temperature. After that, the mixture was concentrated via rotary evaporator. The mixture was washed two times with 100 mL Na_2CO_3 (1M) and one time with 100 mL water. The organic layer was dried with MgSO_4 . The product was obtained as colorless solid via column chromatography (CH_2Cl_2 :n-hexane = 4:1).



Yield: 0.87g (28%)

$^1\text{H-NMR}$ [ppm]: [300MHz; CDCl_3]: δ 7.84 (d, 2H, Pos. 3, 10); δ 7.35(t, 2H, Pos. 2, 9); δ 6.85 (d, 2H, Pos. 1, 8); δ 6.14(m, 2H, Pos. 23a/28a); δ 5.56 (m, 2H, Pos. 23b, 23b); δ 4.62 (m, 4H, Pos. 13, 17); δ 4.36 (m, 4H, Pos. 12,16); δ 1.94 (dd, 6H, Pos. 22, 27)

$^{13}\text{C-NMR}$ [ppm]: [75MHz; CDCl_3]: δ 167.59 (C19,24); δ 154.33 (C6,7); δ 136.24 (C20,25); δ 127.01 (C4,5); δ 126.26 (C2,9); δ 125.38 (C23,28); δ 115.06 (C3,10); δ 106.11 (C1,8); δ 66.61 (C12,16); δ 63.22 (C13,17); δ 18.53 (C22,27)

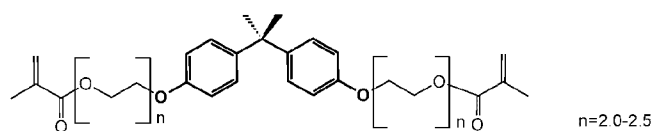
Application Example 1

(Naphthalene-2,7-diylbis(oxy))bis(hexane-6,1-diyl)bis(2-methacrylate) (FSE4C6KM) according to example 2 was mixed with 1.0 mol-% camphorquinone (CQ) and 1.3 mol-% ethyl 4-dimethylaminobenzoate (DMABE) until a homogenous mixture was obtained. 6 samples were taken and prepared to cured specimen according to ISO 4049. Subsequently, flexural strengths and E-modulus of the samples, measuring (25 ± 2) mm x (2 ± 0.2) mm x (2 ± 0.2) mm were tested according to ISO 4049.

The procedure was repeated with a mixture of FSE4C6KM and 30 wt.-% triethylene glycol dimethacrylate (FSE4C6KM-T30).

Batch		FSE4C6KM	FSE4C6KM-T30
Concentration TEGDMA	wt.-%	0	30
Viscosity	Pa·s	0.51	-
Refractive Index	-	1.539	-
Flexural Strength	MPa	77.5 ± 5.3	83.4 ± 8.6
E-modulus	MPa	1369 ± 53	1636 ± 68

Comparative Example 1

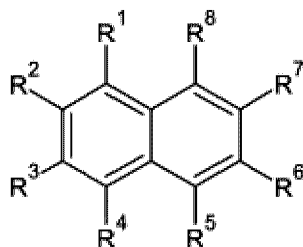


2,2-Bis-[4-(methacryloyloxydiethoxy)phenyl]-propane (EBA) was mixed with 1.3 mol-% campherquinone (CQ) and 1.3 mol-% ethyl 4-dimethylaminobenzoate (DMABE) until a homogenous mixture was obtained. 6 samples were taken and prepared to cured specimen according to ISO 4049. Subsequently, flexural strengths and E-modulus of the samples, measuring (25 ± 2) mm x (2 ± 0.2) mm x (2 ± 0.2) mm were tested according to ISO 4049. The procedure was repeated with a mixture of EBA and 30 wt.-% triethylene glycol dimethacrylate (AG 18-92-1).

Batch		EBA	AG 18-92-1
Concentration TEGDMA	wt.-%	0	30
Viscosity	Pa·s	0.65	0.158
Refractive Index	-	1.535	1.513
Flexural Strength	MPa	76.6 ± 4.6	95.3 ± 0.7
E-modulus	MPa	1223 ± 116	1923 ± 48

CLAIMS:

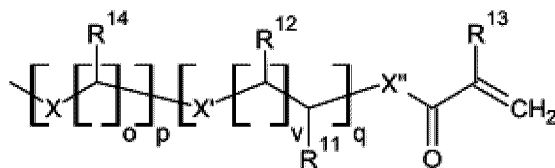
1. A dental composition comprising a polymerizable compound of the following formula (I):



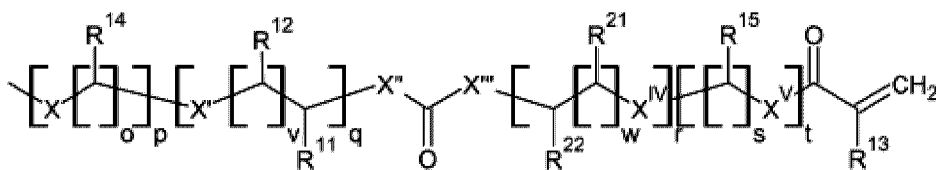
(I)

wherein

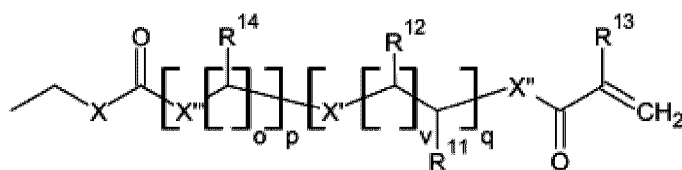
2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, which are independent from each other, represent a group of the following formula (IV), (V), or (VI):



(IV)



(V)



(VI)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

X'' is -NH-, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

X^{IV} is -NH-, an oxygen atom or a sulfur atom,

X^V is -NH-, an oxygen atom or a sulfur atom,

R¹¹, R¹², R²¹ and R²²

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁴ and R¹⁵

which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

o and s which may be the same or different, independently represent an integer of from 2 to 10,

p and t which may be the same or different, independently is an integer of from 0, 1 or 2,

q and r which may be the same or different, independently represent an integer of from 0 to 10,

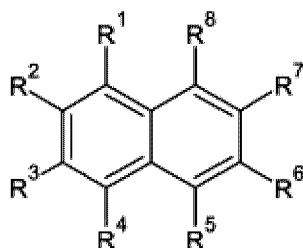
v and w which may be the same or different, independently represent an integer of from 1 to 10,

and the remaining groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ independently represent a hydrogen atom, a halogen atom, a straight chain or branched C₁₋₆ alkyl group, a C₃₋₆ cycloalkyl group, or a C₁₋₆ alkyl C₃₋₆ cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups,

and a filler and/or a solvent.

2. The dental composition according to claim 1, wherein 2 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ represent a group of the formula (IV).
3. The dental composition according to claim 2, wherein the remaining groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ represent a hydrogen atom.
4. The dental composition according to any one of claims 1-3, wherein R² and R⁷, which may be the same or different, represent a group of formula (IV).
5. The dental composition according to any one of claims 1-4, wherein the R¹⁴ in formula (IV) are all hydrogen atoms.
6. The dental composition according to any one of claims 1-5, which further comprises a polymerization initiator system.
7. The dental composition according to any one of claims 1-6, which is selected from the group consisting of a dental adhesive composition, a dental pit and fissure sealer, a dental composite, and a root canal filling composition.

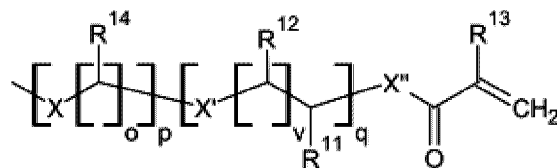
8. A process for the preparation of a dental composition according to claim 1, wherein the dental composition comprises a polymerizable compound of the following formula (I) as defined in claim 1:



(I)

wherein

2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, which are independent from each other, represent a group of the following formula (IV) as defined in claim 1:



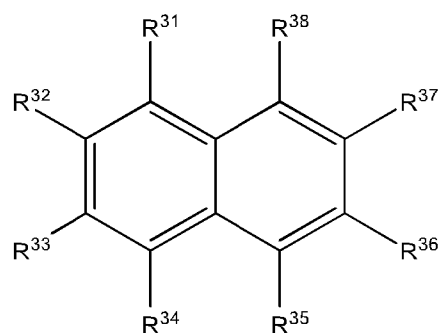
(IV)

the process comprising the steps of

(a) subjecting a reaction mixture comprising

(a1) one or more compounds of formula (VII):

61



(VII)

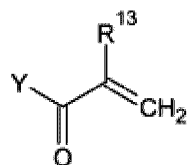
wherein

2 to 4 groups of R³¹, R³², R³³, R³⁴, R³⁵, R³⁶, R³⁷, and R³⁸ are -XH groups wherein X is -NH-, an oxygen atom or a sulfur atom, and the remaining groups of R³¹, R³², R³³, R³⁴, R³⁵, R³⁶, R³⁷, and R³⁸ independently represent a hydrogen atom, a halogen atom, a straight chain or branched C₁₋₆ alkyl group, a C₃₋₆ cycloalkyl group, or a C₁₋₆ alkyl C₃₋₆ cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups, and

- (a2) ethylene carbonate or a compound of the formula ZRZ', wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group;

to an addition reaction to generate an addition product;

- (b1) reacting the addition product of the one or more compounds of formula (VII) and ethylene carbonate with a compound of the following formula (XI)



(XI)

wherein Y is a leaving group and R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group, or wherein Y and R¹³ form together with the carbon atoms to which they are bound a cyclic lactone ring or carboxylic acid anhydride ring having 4 to 8 carbon atoms;

to generate the group of the formula (IV) and provide the polymerizable compound of formula (I); or

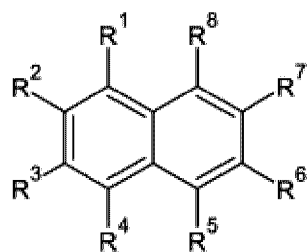
- (b2) reacting the addition product of the one or more compounds of formula (VII) and the compound of the formula ZRZ', wherein Z and Z' independently are leaving groups and R is a straight chain or branched alkylene group, with a compound of formula (XI) wherein Y is OH;

to generate the group of the formula (IV) and provide the polymerizable compound of formula (I); and

- (c) adding a filler and/or a solvent.

9. A process for the preparation of a dental composition according to claim 1, wherein the dental composition comprises a polymerizable compound of the following formula (I) as defined in claim 1:

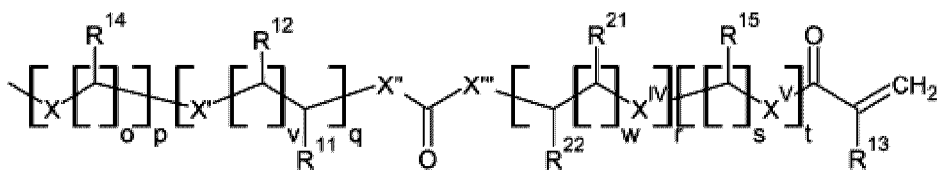
63



(I)

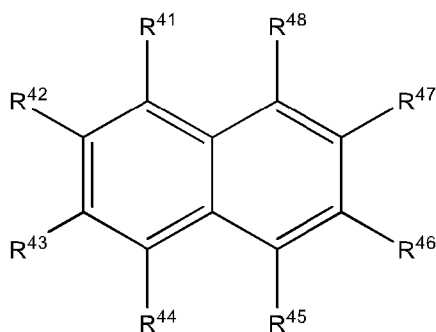
wherein

2 to 4 groups of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 , which are independent from each other, represent a group of the following formula (V) as defined in claim 1:



(V)

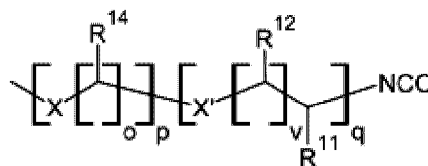
the process comprising subjecting a reaction mixture comprising one or more compounds of formula (XII):



(XII)

wherein

2 to 4 groups of R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , R^{46} , R^{47} , and R^{48} are independently a group of the following formula (XV):



(XV)

wherein

X is -NH-, an oxygen atom or a sulfur atom,

X' is -NH-, an oxygen atom or a sulfur atom,

R^{11} and R^{12}

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C_{1-6} alkyl group,

R^{14} which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C_{1-6} alkyl group,

o independently represent an integer of from 2 to 10,

p independently is an integer of from 0, 1 or 2;

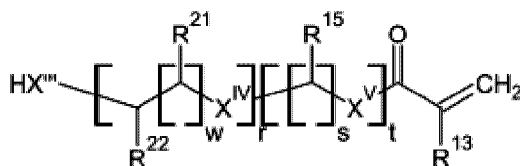
q independently represent an integer of from 0 to 10;

v independently represents an integer of from 1 to 10,

and the remaining groups of R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , R^{46} , R^{47} , and R^{48} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3

substituents selected from the group consisting of halogen atoms and hydroxy groups,

to an addition reaction with a compound of the following formula (XVI):



(XVI)

wherein

X^{III} is NH-, an oxygen atom or a sulfur atom,

X^{IV} is NH-, an oxygen atom or a sulfur atom,

X^V is NH-, an oxygen atom or a sulfur atom,

R²¹ and R²²

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁵ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

s independently represent an integer of from 2 to 10,

t independently is an integer of from 0, 1 or 2;

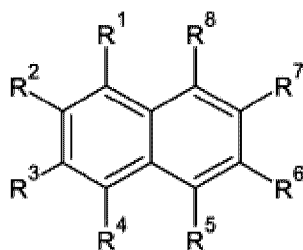
r which may be the same or different, independently represent an integer of from 0 to 10;

w independently represents an integer of from 1 to 10,

wherein the addition reaction generates the group of the formula (V) and provides the polymerizable compound of formula (I),

and adding a filler and/or a solvent.

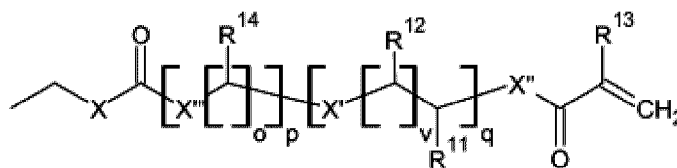
10. A process for the preparation of a dental composition according to claim 1, wherein the dental composition comprises a polymerizable compound of the following formula (I) as defined in claim 1:



(I)

wherein

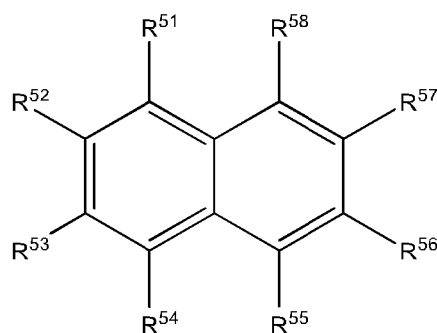
2 to 4 groups of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸, which are independent from each other, represent a group of the following formula (VI) as defined in claim 1:



(VI)

the process comprising subjecting a reaction mixture comprising one or more compounds of formula (XVII):

67

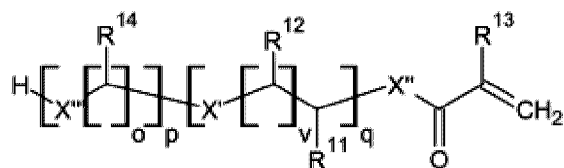


(XVII)

wherein

2 to 4 groups of R^{51} , R^{52} , R^{53} , R^{54} , R^{55} , R^{56} , R^{57} , and R^{58} are isocyanatomethyl groups, and the remaining groups of R^{51} , R^{52} , R^{53} , R^{54} , R^{55} , R^{56} , R^{57} , and R^{58} independently represent a hydrogen atom, a halogen atom, a straight chain or branched C_{1-6} alkyl group, a C_{3-6} cycloalkyl group, or a C_{1-6} alkyl C_{3-6} cycloalkyl group, which groups may contain 1 to 3 heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur atoms or be substituted by 1 to 3 substituents selected from the group consisting of halogen atoms and hydroxy groups,

to an addition reaction with a compound of the following formula (XX):



(XX)

wherein

X' is $-NH-$, an oxygen atom or a sulfur atom,

X'' is $-NH-$, an oxygen atom or a sulfur atom,

X''' is -NH-, an oxygen atom or a sulfur atom,

R¹¹ and R¹²

which may be the same or different, independently represent a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group,

R¹³ represents a hydrogen atom or a straight chain or branched C₁₋₆ alkyl group which may be substituted by a hydroxyl group or carboxyl group,

R¹⁴ which may be the same or different, independently represent a hydrogen atom, or a straight chain or branched C₁₋₆ alkyl group,

o which may be the same or different, independently represent an integer of from 2 to 10,

p which may be the same or different, independently is an integer of from 0, 1 or 2;

q which may be the same or different, independently represent an integer of from 0 to 10;

v independently represents an integer of from 1 to 10,

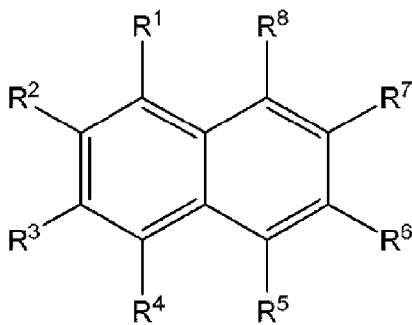
wherein the addition reaction generates the group of the formula (VI) and provides the polymerizable compound of formula (I),

and adding a filler and/or a solvent.

11. A process for the preparation of a dental composition comprising (i) a polymerizable compound comprising a substituted hydroxyl group and (ii) a filler and/or a solvent, the process comprising a step of reacting the polymerizable compound of formula (I) as defined in claim 1, which comprises a hydroxyl group in any one or more of R¹³, with an isocyanate compound, a diisocyanate compound, a isothiocyanate compound, a

carboxylic acid halogenide compound, a cyclic carboxylic acid anhydride or a carboxylic acid compound.

12. A dental composition obtained by the process according to any one of claims 8 to 10.
13. Use of the dental composition according to claim 12 for the preparation of a dental composition of claim 6 or 7.
14. A dental composition obtained by the process according to claim 11.



(I)