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WO 02/13767 A2

(54) Title: POLYAMINOESTER AND THEIR APPLICATION IN DENTAL COMPOSITIONS

(57) Abstract: Dental compositions comprising at least a polymerizable monomer and/or at least a polyaminoester that are prepared by reaction of bis- or polyacrylic esters and amines, pigments, organic and/or inorganic fillers, initiators and stabilizers.

Polyaminoester and their application in dental compositions

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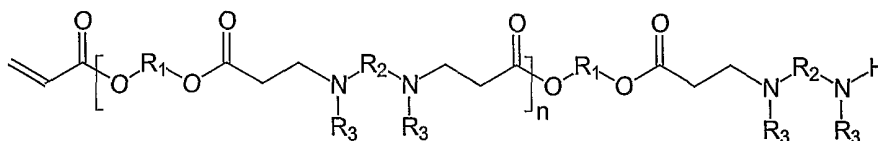
Technical background

Since some years, the addition polymerization of bisacrylamides and amines is well-known (P. Ferrutti et al., Polymer **26** (1985) 1336).
 10 Bisacrylamides are much more stable against hydrolysis compared to acrylic esters. The reaction of amines and esters lead to an transamidation reaction (H.-G. Elias, Makromoleküle, Hüttig&Wepf, Basel, 1990, p.555).
 Consequently, the assumption was that a reaction of acrylic esters and amines should lead to an cleavage of ester bonds. Therefore, the formation of
 15 addition polymers, prepolymers and macromonomers of amines and acrylic esters should be impossible.

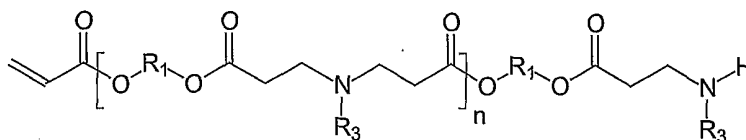
Recently, oligoamido amines and oligoester amines based on antibiotics containing .beta.-lactam rings were investigated (Panayotov, Eur. Polym. J. **32** (1996) 957-962). They were prepared by interaction between
 20 ampicillin and amoxicillin and methylenebisacrylamide, 1,4-diacryloylpiperazine and 1,3-propanediol diacrylate.

Description of the invention

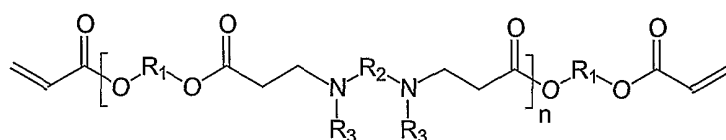
Dental compositions comprising at least a polymerizable monomer
 25 and/or at least a polyaminoester of formulas 1 to 6, pigments, organic and/or inorganic fillers, initiators and stabilizers.



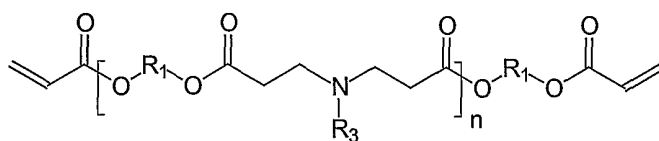
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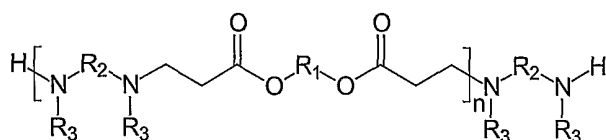
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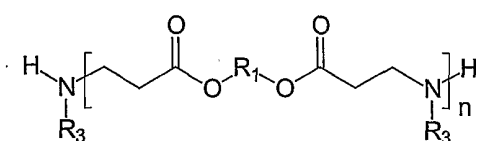
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5 wherein

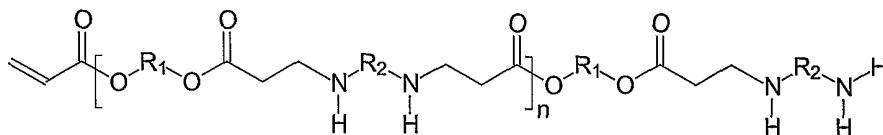
R₁ denotes is a difunctional substituted or unsubstituted C₁ to C₁₈ alkylene, difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C₅ to C₁₈ arylene or heteroarylene, difunctional substituted or unsubstituted C₅ to C₁₈ alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C₇ to C₃₀ alkylene arylene.

R₂ denotes is a difunctional substituted or unsubstituted C₁ to C₁₈ alkylene, difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C₅ to C₁₈ arylene or heteroarylene, difunctional substituted or unsubstituted C₅ to C₁₈ alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C₇ to C₃₀ alkylene arylene,

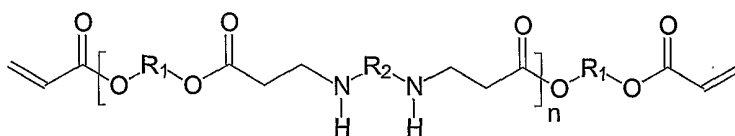
R₃ denotes H or a substituted or unsubstituted C₁ to C₁₈ alkylene, substituted or unsubstituted cycloalkylene, substituted or unsubstituted C₅ to C₁₈ arylene or heteroarylene, substituted or unsubstituted C₅ to C₁₈ alkylarylene or alkylheteroarylene, substituted or unsubstituted C₇ to C₃₀ alkylene arylene,

n is an integer.

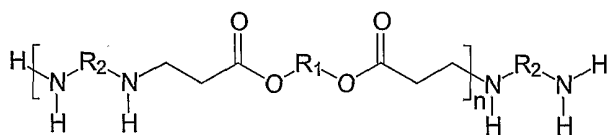
Preferably the invented dental composition contains a polyaminoester that are characterized by the following formulas



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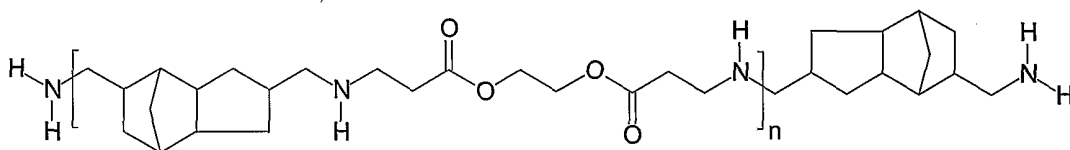


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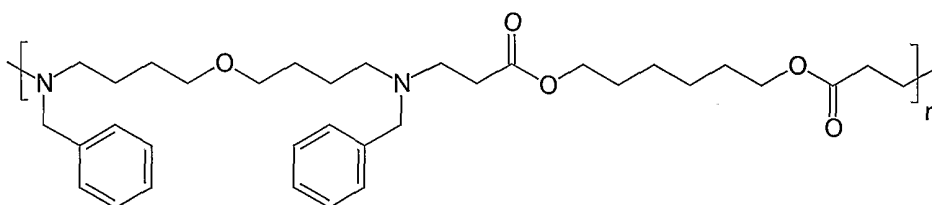
wherein

- 5 R_1 denotes is a difunctional substituted or unsubstituted C_1 to C_{18} alkylene, difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, difunctional substituted or unsubstituted C_5 to C_{18} alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C_7 to C_{30} alkylene arylene,
- 10 R_2 denotes is a difunctional substituted or unsubstituted C_1 to C_{18} alkylene, difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, difunctional substituted or unsubstituted C_5 to C_{18} alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C_7 to C_{30} alkylene arylene, and
- 15 n is an integer.

Most preferably polyaminoesters are applied characterized by the following formulas



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wherein n is an integer.

Said polymerizable monomer preferably are hydroxyethyl methacrylate, hydroxyethylacrylate, hydroxypropyl methacrylate, ethyleneglykol dimethacrylate, diethyleneglykol dimethacrylate, triethyleneglykol dimethacrylate, 3,(4),8,(9)-Dimethacryloyl-(oxymethyl)-tricyclo-5.2.1.0^{2,6} decane, trimethylolpropane triacrylate or trimethylolpropane trimethacrylate, N,N'-dimethylaminoethyl methacrylate.

As fillers are applied inorganic or organic, reactive or nonreactive, surface modified or nonmodified glasses such as polymer granulate or a combination of organic and/or inorganic fillers, strontium aluminosilicate glass, La₂O₃, BiPO₄, ZrO₂, BaWO₄, CaWO₄, SrF₂, Bi₂O₃.

Instead of primary monoamine and disecundary diamines the usage of polyamines is possible, too, leading to crosslinked polyaminoesters.

The invented dental composition preferably is applicable as root canal sealing material or as temporary crown & bridge material.

Example 1

5.000 g (22.097 mmol) Hexamethylendiacylate (Servo Delden) and 7.525 g (22.097 mmol) N,N'-Dibenzyl-5-nonandiamin-1,9 were mixed homogeneously and stirred at 60°C for 4 days. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm⁻¹.

Yield: 12.525 g (100 % of th.)

(C₃₄H₅₀N₂O₅)_n, (566.8)_n

[η] = 8.57 ml/g (Viscosity in THF solution)

IR: 2920 / 2865 (CH₂), 1735 (CO)

M_n (GPC) = 2225 (4661) g/mol

M_w (GPC) = 9398 (10200) g/mol

Example 2

20.000 g (88.39 mmol) Hexamethylendiacylate (Servo Delden) and 15.719 g (106.07 mmol) 3,6-Dioxaoctan-diamin-1,8 (Fluka) were mixed homogeneously and stirred at room temperature for 1.5 hours. After that time

a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm^{-1} .

Yield: 35.719 g (100 % of th.)

$(\text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_6)_n$, (347.5)_n

- 5 $\eta = 4.73 \pm 0.05 \text{ Pa}\cdot\text{s}$ (dynamic viscosity measured using Bohlin CS50 rheometer)

IR: 3325 (NH), 2920 / 2865 (CH_2), 1735 (CO)

^{13}C -NMR (CDCl_3): 172.6/172.4 (6), 73.4 (2); 70.5/70.2 (3); 64.2 (7), 49.8 (1), 45.0 (4), 41.7 (4), 34.8 (5), 28.4 (8), 25.5 (9)

- 10 IR: 3325 (NH), 2920 / 2865 (CH_2), 1735 (CO)

Example 3

10.000 g (58.77 mmol) Ethylene glycol diacrylate and 14.125 g (58.77 mmol) N,N'-Dibenzylethylenediamine were mixed homogeneously and stirred
15 at room temperature for 40 hours at 60°C. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm^{-1} .

Yield: 24.125 g (100 % of th.)

- 20 $\eta = 1557 \pm 17 \text{ Pa}\cdot\text{s}$ (dynamic viscosity measured using Bohlin CS50 rheometer)

$[\eta] = 9.176 \text{ ml/g}$ (viscosity in THF solution)

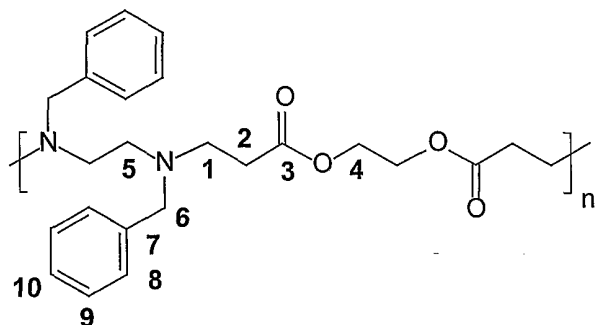
M_n (GPC) = 1575 g/mol

M_w (GPC) = 10060 g/mol

$(\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_4)_n$, (410.5)_n

- 25 IR: 3060 / 3028; 2953 / 2816 (CH_2), 1743 (CO)

^{13}C NMR (CDCl_3): 49.7 (1), 32.4 (2), 172.6 (3), 621.0 (4), 51.5 (5), 58.6 (6), 139.2 (7), 128.6 (8), 128.0 (9), 126.8 (10)



Example 4

10.000 g (58.77 mmol) Ethylene glykol diacrylate and 20.012 g (58.77 mmol) N,N'-Dibenzyl-5-oxanonane diamine-1.9 were mixed homogeneously and stirred at room temperature for 40 hours at 60°C. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm⁻¹.

Yield: 30.012 g (100 % of th.)

η = 188.8 ± 1.3 Pa*s (dynamic viscosity measured using Bohlin CS50 rheometer)

10 [η] = 10.051 ml/g (viscosity in THF solution)

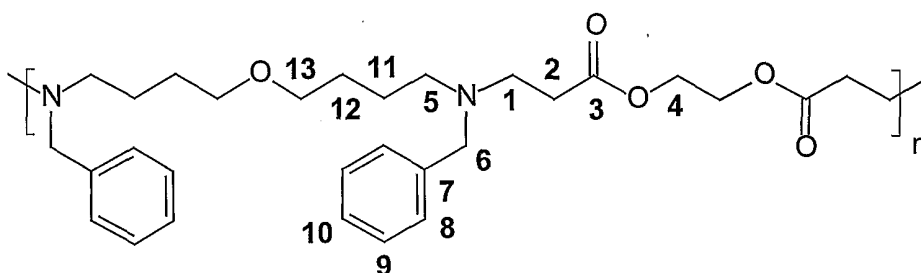
M_n (GPC) = 4281 g/mol

M_w (GPC) = 12110 g/mol

(C₃₀H₄₂N₂O₅)_n, (510.7)_n

IR: 3060 / 3026 / 2943 / 2860 / 2802 (CH₂), 1740 / 1731 (CO)

15 ¹³C NMR (CDCl₃): 49.1 (1), 32.4 (2), 172.3 (3), 62.1 (4), 53.2 (5), 58.2 (6), 139.5 (7), 128.0 (8), 127.9 (9), 126.7 (10), 27.5 (11), 23.5 (12)

**Example 5**

20 10.000 g (58.77 mmol) Ethylene glykol diacrylate and 11.420 g (58.77 mmol) N,N'-Dibenzyl-4,4'-dicyclohexylmethane were mixed homogeneously and stirred at room temperature for 40 hours at 60°C. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm⁻¹.

25 Yield: 21.420 g (100 % of th.)

IR: 3060 / 3026 / 2943 / 2860 / 2802 (CH₂), 1740 / 1731 (CO)

Example 6

30 10.000 g (58.77 mmol) Ethylene glykol diacrylate and 5.710 g (29.384 mmol) 3,(4),8,(9)-Bis(aminomethyl)-tricyclo-5.2.1.0^{2,6} decane were mixed homogeneously and stirred at room temperature for 2 hours at room

temperature. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm^{-1} .

Yield: 15.710 g (100 % of th.)

η = Pa*s (dynamic viscosity measured using Bohlin CS50 rheometer)

5 $(\text{C}_{28}\text{H}_{42}\text{N}_2\text{O}_8)_n$, (534.7)_n

IR: 3445 / 3332 (NH), 2947 / 2875 / 2821(CH_2), 1729 (CO); 1637 / 1619 ($\text{C}=\text{C}$)

Example 7

10 10.000 g (58.77 mmol) Ethylene glykol diacrylate and 22.840 5.710 g (117.54 mmol) 3,(4),8,(9)-Bis(aminomethyl)-tricyclo-5.2.1.0^{2,6} decane were mixed homogeneously and stirred at room temperature for 2 hours at room temperature. After that time a complete conversion was found indicated by disappearance of the double bonds at 1635 / 1619 cm^{-1} .

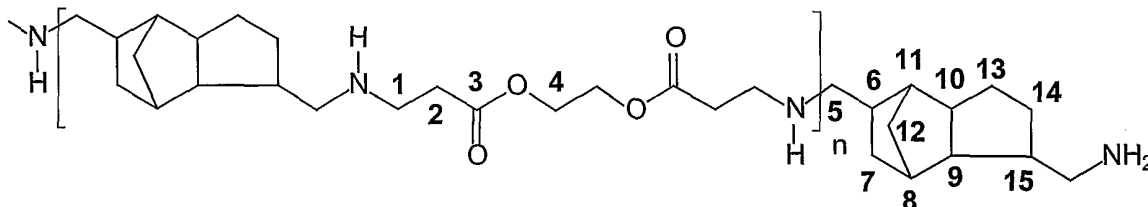
15 Yield: 32.840 g (100 % of th.)

η = 218800 $\pm$ 1990 Pa*s (dynamic viscosity measured using Bohlin CS50 rheometer)

$(\text{C}_{32}\text{H}_{54}\text{N}_4\text{O}_4)_n$, (558.8)_n

IR: 3373 / 3286 (NH), 2960 / 2888 (CH_2), 1743 / 1731 (CO)

20 ^{13}C NMR (CDCl_3): 47.5 (1), 34.3/34.7 (2), 172.9 (3), 66.0 (4), 55.3 (5), signals of (6) to (15) between 24.5 and 63.5 ppm



25 Example 8

To 10.000 g (58.77 mmol) Ethylene glykol diacrylate dissolved in 50 ml THF were slowly added at 0 to 5°C under stirring a solution of 8.709 g (58.77 mmol) 3,6-Dioxaoctane diamine-1,8 in 50 ml THF. After adding the amine the solution was stirred at room temperature for 1.5 hours. After that time a complete conversion was found due to the disappearance of the double bonds at 1635 / 1619 cm^{-1} . Then the solvent was removed and the addition polymer was dried in vacuum.

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Yield: 18.709 g (100 % of th.)

η = Pa*s (dynamic viscosity measured using Bohlin CS50 rheometer)

$(C_{14}H_{26}N_2O_6)_n$, (318.4)_n

IR: 3373 / 3286 (NH), 2960 / 2888 (CH₂), 1743 / 1731 (CO)

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Application Example 1 (Dental root canal sealer)

Paste A

8.404 g (37.14 mmol) Hexamethylendiacrylate (Servo Delden), 25.968
10 g CaWO₄, 6.492 g ZrO₂ and 0.325 g aerosil were mixed homogeneously.

Paste B

7.217 g (37.14 mmol) 3,(4),8,(9)-Bis(aminomethyl)-tricyclo-5.2.1.0^{2,6}
decane, 28.867 g CaWO₄, 7.217 g ZrO₂ and 0.722 g aerosil were mixed
15 homogeneously.

Dental root canal sealer

Immediately before use 0.214 g of Paste A and 0.200 g of Paste B
were mixed homogeneously. The setting time of the root canal sealing
20 material is 30 minutes. The radiopacity of 12.8 mm/ mm Al.

Application Example 2 (Dental root canal sealer)

Paste A

25 2.5213 g (11.14 mmol) Hexamethylendiacrylate (Servo Delden),
12.9298 g CaWO₄, 3.2325 g ZrO₂ and 0.0385 g aerosil were mixed
homogeneously.

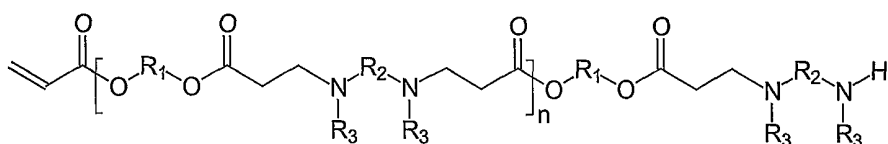
Paste B

30 0.801 g (5.29 mmol) 1-Aminoadamantane, 1.802 g (5.29 mmol) N,N'-
Dibenzyl-5-oxanonandiamin-1,9, 0.103 g (0.53 mmol) 3,(4),8,(9)-
Bis(aminomethyl)-tricyclo-5.2.1.0^{2,6} decane, 10.411 g CaWO₄, 2.603 g ZrO₂
and 0.315 g aerosil were mixed homogeneously.

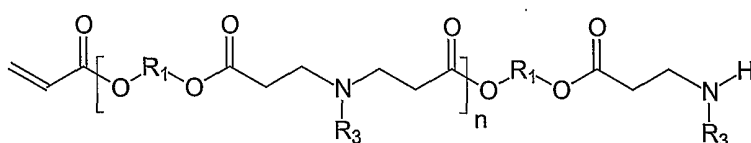
Dental root canal sealer

Immediately before use 0.173 g of Paste A and 0.200 g of Paste B were mixed homogeneously. The setting time of the root canal sealing material is 30 minutes. The radiopacity of 13.8 mm/ mm Al.

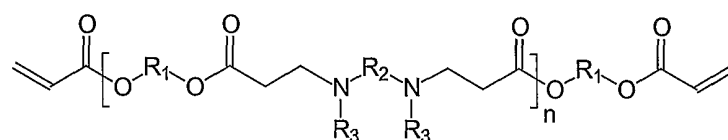
1. Dental compositions comprising at least a polymerizable monomer and/or
at least a polyaminoester of formulas 1 to 6, pigments, organic and/or
5 inorganic fillers, initiators and stabilizers.



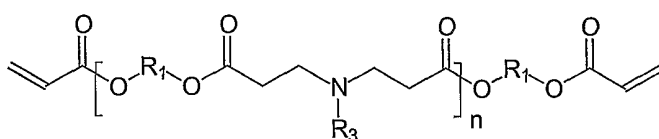
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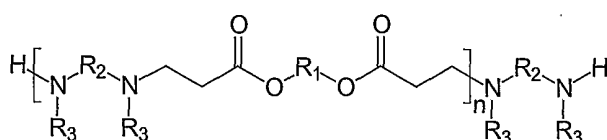
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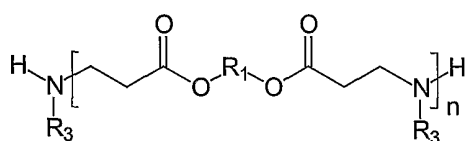


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wherein

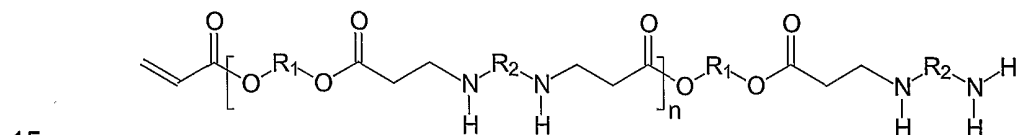
- R₁ denotes is a difunctional substituted or unsubstituted C₁ to C₁₈ alkylene,
difunctional substituted or unsubstituted cycloalkylene, difunctional
substituted or unsubstituted C₅ to C₁₈ arylene or heteroarylene, difunctional
15 substituted or unsubstituted C₅ to C₁₈ alkylarylene or alkylheteroarylene,
difunctional substituted or unsubstituted C₇ to C₃₀ alkylene arylene,

R_2 denotes is a difunctional substituted or unsubstituted C_1 to C_{18} alkylene, difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, difunctional substituted or unsubstituted C_5 to C_{18} alkylarylene or alkylheteroarylene, 5 difunctional substituted or unsubstituted C_7 to C_{30} alkylene arylene,

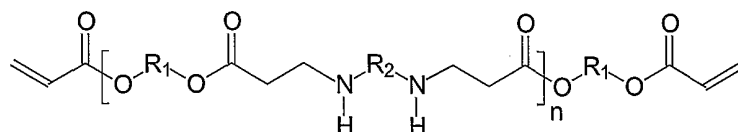
R_3 denotes H or a substituted or unsubstituted C_1 to C_{18} alkylene, substituted or unsubstituted cycloalkylene, substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, substituted or unsubstituted C_5 to C_{18} alkylarylene or alkylheteroarylene, substituted or unsubstituted C_7 to C_{30} 10 alkylene arylene,

n is an integer.

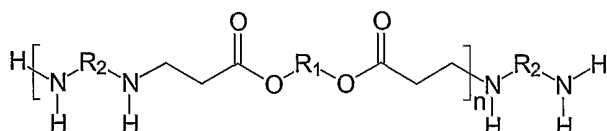
2. Dental composition of claim 1, wherein said polyaminoester is characterized by the following formulas



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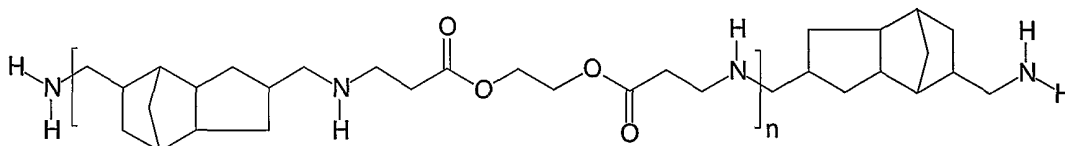
wherein

R_1 denotes is a difunctional substituted or unsubstituted C_1 to C_{18} alkylene, 20 difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, difunctional substituted or unsubstituted C_5 to C_{18} alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C_7 to C_{30} alkylene arylene,

R_2 denotes is a difunctional substituted or unsubstituted C_1 to C_{18} alkylene, 25 difunctional substituted or unsubstituted cycloalkylene, difunctional substituted or unsubstituted C_5 to C_{18} arylene or heteroarylene, difunctional

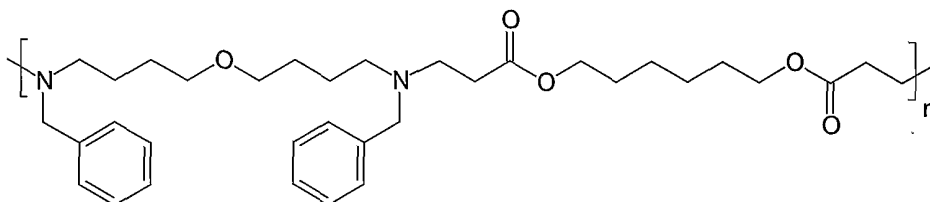
substituted or unsubstituted C₅ to C₁₈ alkylarylene or alkylheteroarylene, difunctional substituted or unsubstituted C₇ to C₃₀ alkylene arylene, and n is an integer.

- 5 3. Dental composition of claim 1, wherein said polyaminoesters preferably is characterized by the following formula



wherein n is an integer.

- 10 4. Dental composition of claim 1, wherein said polyaminoesters preferably is characterized by the following formula



wherein n is an integer.

- 15 5. Dental composition of claim 1, wherein said polyaminoesters are composed of polyamines and bis- or polyacrylates.
6. Dental composition of claim 1, wherein said polyaminoesters are copolymerized with monomers that are usable for step-growth polymerization, preferably with di- or polyepoxides or di- or polyisocyanates.
- 20 7. Dental composition of claim 1, wherein said polymerizable monomer preferably is hydroxyethyl methacrylate, hydroxyethylacrylate, hydroxypropyl methacrylate, ethyleneglykol dimethacrylate, diethyleneglykol dimethacrylate, triethyleneglykol dimethacrylate, 3,(4),8,(9)-Dimethacryloyl-(oxymethyl)-tricyclo-5.2.1.0^{2,6} decane, trimethylolpropane triacrylate or trimethylolpropane trimethacrylate, N,N'-dimethylaminoethyl methacrylate.
- 25

8. Dental composition of claim 1, wherein said fillers are functionalized or non-functionalized organic polymers or wherein said fillers are inorganic or organic, reactive or non-reactive, surface modified or non-modified glasses such as polymer granulate or a combination of organic and/or inorganic fillers, strontium aluminosilicate glass, La_2O_3 , BiPO_4 , ZrO_2 , BaWO_4 , CaWO_4 , SrF_2 , Bi_2O_3 .
9. Dental composition of claim 1, applicable as root canal sealing material.
10. Dental composition of claim 1, applicable as temporary crown & bridge material.