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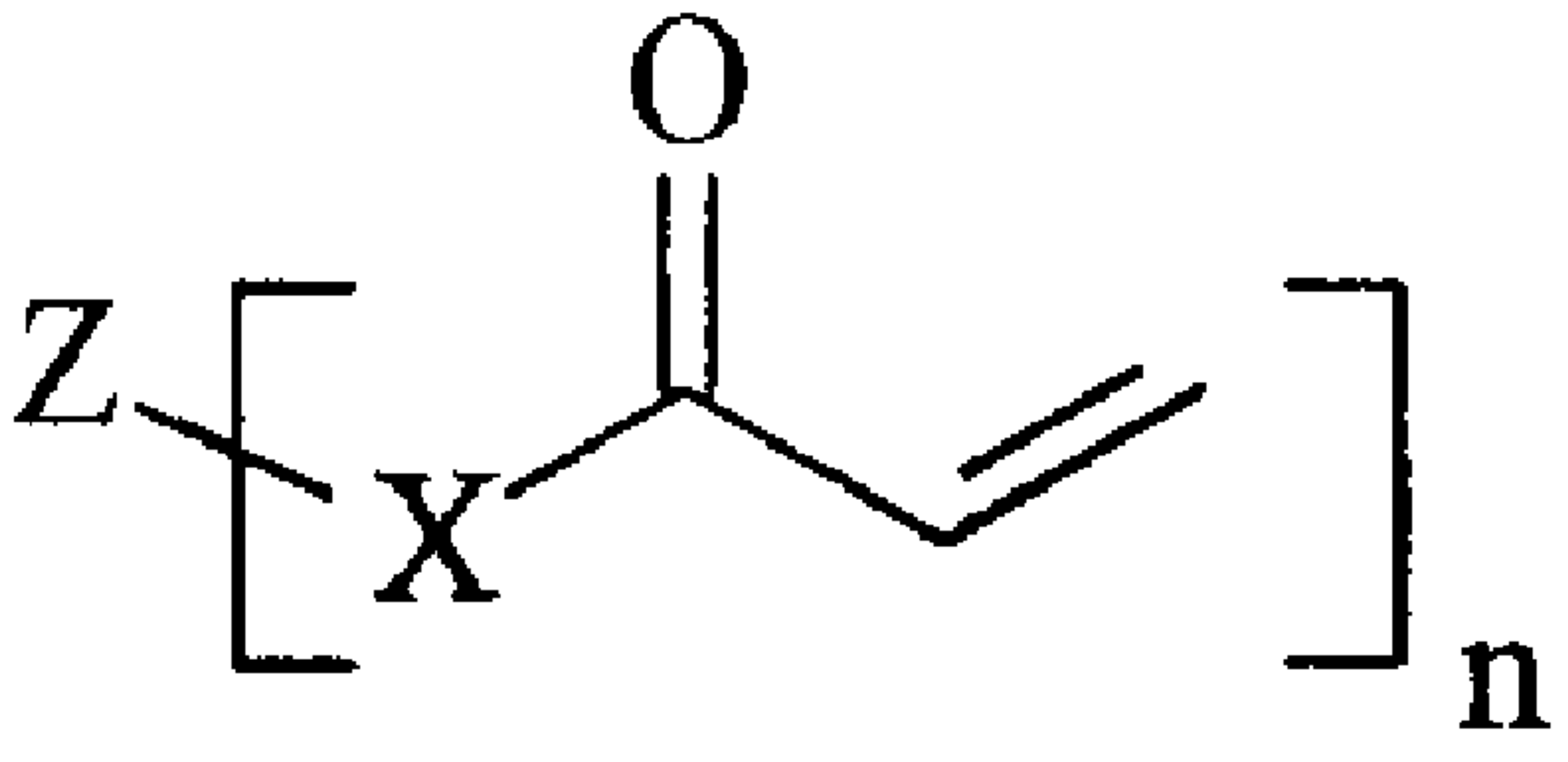
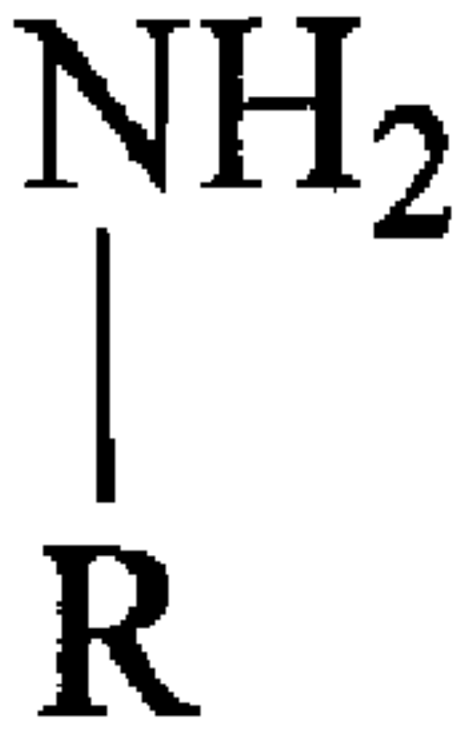
(54) Titre : COMPOSITION DE SCELLEMENT DU CANAL D'UNE RACINE DENTAIRE
(54) Title: DENTAL ROOT CANAL SEALING COMPOSITION



(I)



(II)

(57) **Abrégé/Abstract:**
The invention provides a dental root sealing composition curable in the absence of a polymerization initiator and having a viscosity at 23°C of less than 100 Pa*s, which comprises: (i) an amino terminated prepolymer having a viscosity at 23°C of less than 100

(57) **Abrégé(suite)/Abstract(continued):**

Pa*s obtained by reacting (a) one mole of a compound of formula (I) (see formula I) and (b) at least n moles of one or more compounds either of formula (II) (see formula II) or of formula (II) in combination with one or more di- or polyamine compounds; (ii) a di- or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound capable of undergoing polyaddition with the prepolymer (i); (iii) 40 to 85 wt% of a filler for providing a minimum radioopacity of at least 3 mm/mm Al; in the form of a two-component composition wherein a first component contains (i), a second component contains (ii) and (iii) is in one or both of the first and second components.

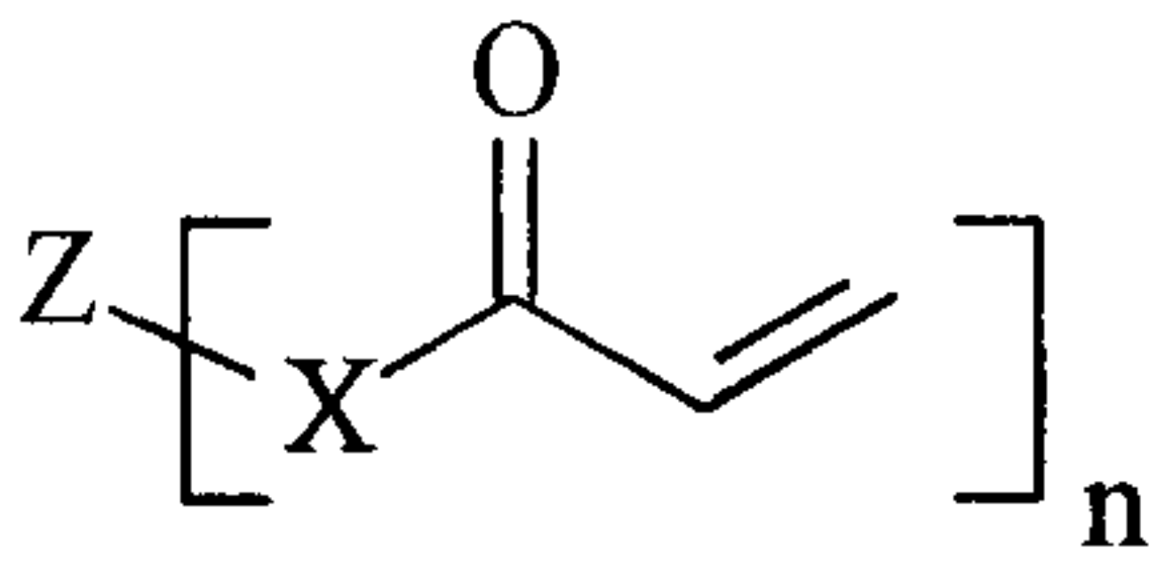
DENTAL ROOT CANAL SEALING COMPOSITION

Abstract

The invention provides a dental root sealing composition curable in the absence of a polymerization initiator and having a viscosity at 23°C of less than 100 Pa*s, which comprises:

(i) an amino terminated prepolymer having a viscosity at 23°C of less than 100 Pa*s obtained by reacting

(a) one mole of a compound of formula (I)



(I) and

(b) at least n moles of one or more compounds either of formula (II)

$R-NH_2$

(II)

or of formula (II) in combination with one or more di- or polyamine compounds;

(ii) a di- or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound capable of undergoing polyaddition with the prepolymer (i);

(iii) 40 to 85 wt% of a filler for providing a minimum radioopacity of at least 3 mm/mm Al;

in the form of a two-component composition wherein a first component contains (i), a second component contains (ii) and (iii) is in one or both of the first and second components.

Dental root canal sealing composition

Field of the invention

The present invention relates to a dental root canal sealing composition curable by addition polymerisation in the absence of a polymerisation catalyst.The dental root canal sealing composition of the invention is provided in the form of a two-component composition.

Background art

Dental root canal sealing compositions are frequently applied into the root canal through a canal of a needle. Due to the small dimensions of the needle canal, the compositions are required to have a low viscosity. Alternatively, dental root canal sealing compositions are applied by using lentulos or gutta percha tips. Accordingly, the viscosity must be low so that thin films may be formed. Independent from the application technique, the viscosity of the material must be low enough so that the composition may enter into dentine canals in the root canal.

The application of dental root canal sealing compositions is checked by using X-ray procedures. Due to the requirement for radioopacity, the compositions are required to contain a substantial amount of a radioopaque filler.

Dental root canal sealing compositions are known from WO 02/13767 disclosing in the application examples a two-component paste/paste system. The two-component paste/paste system is based on addition polymerisation of equimolar amounts of low-molecular diamines and low-molecular diacrylates optionally in the presence of a reactive diluent for ajusting the viscosity of the composition.

However, the presence of low molecular amines in the dental root canal sealing composition leads to severe drawbacks. Cytotoxic effects are frequently observed due to leaching of such amines from the root canal. Moreover, the cured compositions of WO 02/13767 show a considerable solubility whereby the cytotoxicity problem is aggravated and further application problems are created. Finally, the high vapor pressure of low molecular amines and the high penetration rate through plastic packaging render the compositions of WO 02/13767 problematic for industrial application.

Polyaminoesters specifically disclosed in WO 02/13767 are highly viscous and require the use of a substantial amount of reactive diluent in order to decrease the viscosity. However, reactive diluents cannot be polymerised by addition polymerisation, but require the presence of a polymerisation initiator.

WO 02/13767 does not disclose a di-or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound which is capable of undergoing polyaddition.

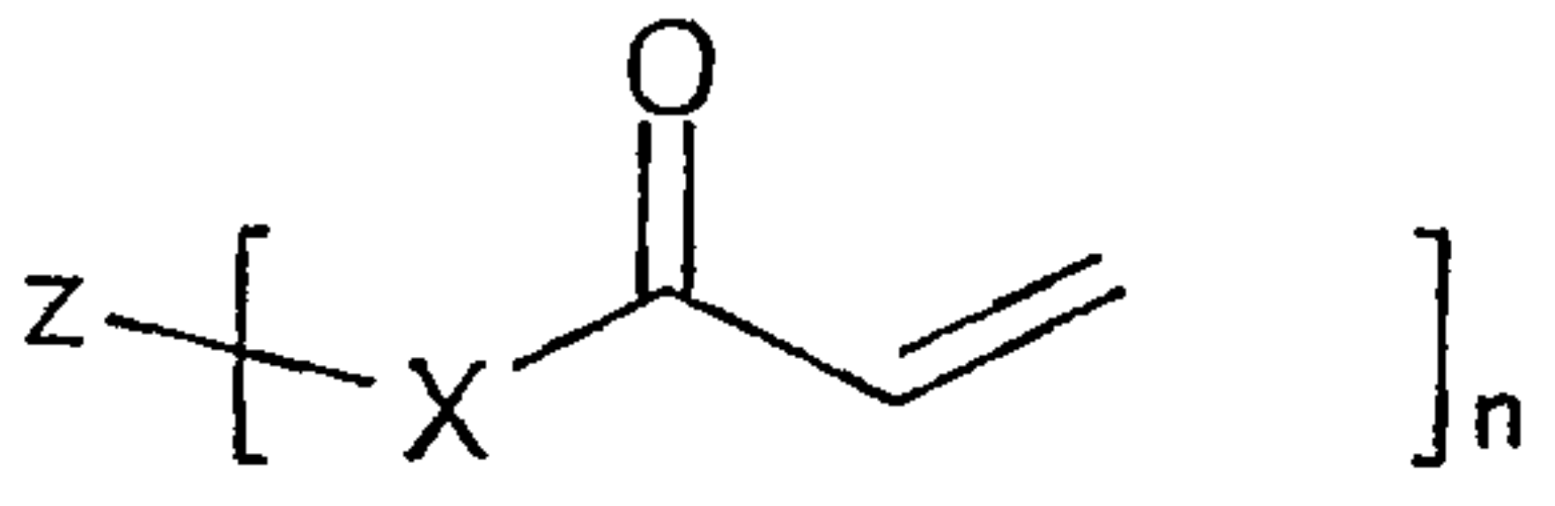
It is the problem of the present invention to provide a dental root canal sealing composition having a low viscosity, low cytotoxicity, and low solubility while having excellent mechanical properties such as low shrinkage and flexibility and which do not give rise to handling problems during manufacture and application.

Summary of the invention

The present invention provides a dental root canal sealing composition curable in the absence of a polymerisation initiator, which comprises

(i) an aminoterminated prepolymer having a viscosity at 23°C of less than 100 Pa*s, which is obtainable by reacting

  (a) one mole of a compound of the following formula (I)



(I)

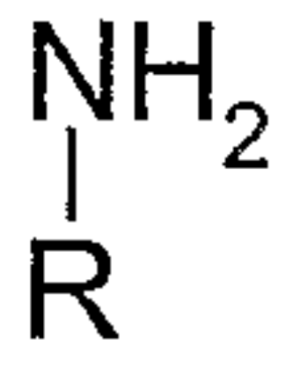
wherein

X represents a nitrogen or an oxygen atom;

Z represents an n-valent saturated aliphatic C_{2-16} hydrocarbon group or a divalent saturated cycloaliphatic C_{3-6} hydrocarbon group, which groups may contain 1 to 6 oxygen atoms, and which may be substituted by 1 to 6 C_{1-4} alkyl groups; and

n represents an integer of from 2 to 6; and

(b) at least n moles of one or more compounds either of the following formula (II)



$$\begin{array}{c} NH_2 \\ | \\ R \end{array}$$

(II)

wherein

R represents

a C_{1-6} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by one or more (up to six) members of the group selected from a C_{1-4} alkyl group, C_{1-4} alkoxy group, a phenyl group, and a hydroxy group,or

of formula (II) in combination with one or more di- or polyamine compounds.

(ii) a di-or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound which is capable of undergoing polyaddition with the aminoterminated prepolymer (i);

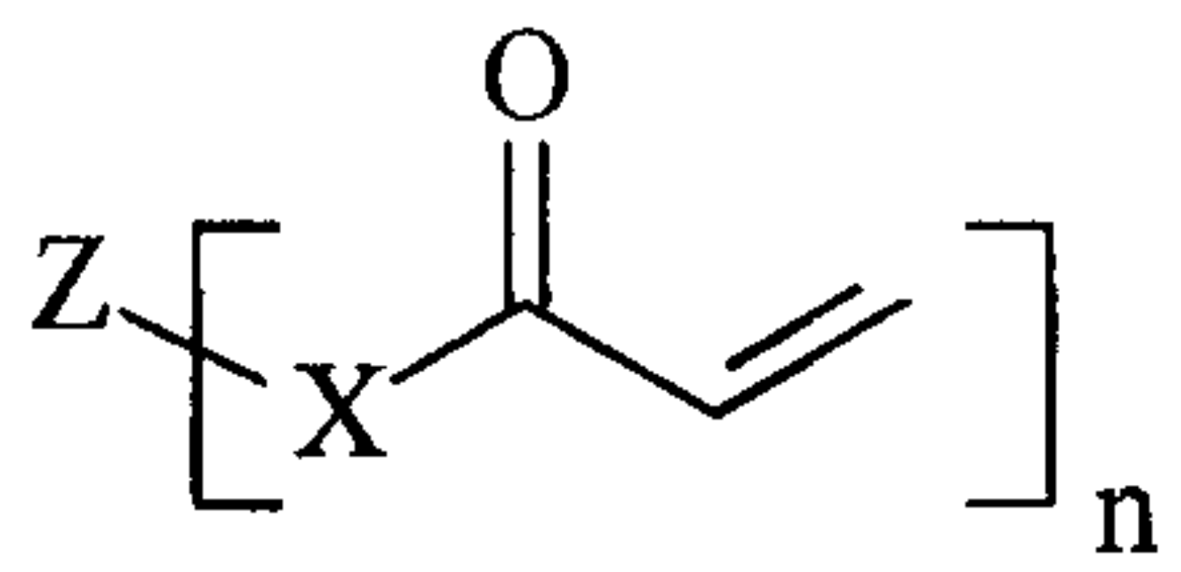
(iii) 40 to 85 wt.-% of a filler for providing a minimum radioopacity of at least 3mm/mm Al;

said compositon being in the form of a two-component composition wherein a first component contains the amino terminated prepolymer (i) and optionally filler (iii) and a second component contains the compound (ii) capable of undergoing polyaddition with the aminoterminated prepolymer (i) and optionally filler (iii).

According to one aspect of the present invention, there is provided a dental root canal sealing composition curable in the absence of a polymerisation initiator and having a viscosity at 23°C of less than 100 Pa*s, which comprises:

(i) an amino terminated prepolymer having a viscosity at 23°C of less than 100 Pa*s obtained by reacting

(a) one mole of a compound of formula (I)



(I)

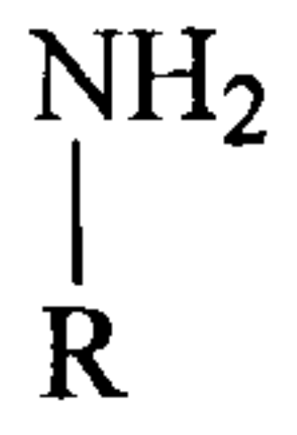
wherein

X represents NH or an oxygen atom;

Z represents an n-valent saturated aliphatic or cycloaliphatic C_{2-16} hydrocarbon group which may contain 1 to 6 oxygen atoms, and which may be substituted by one or more C_{1-4} alkyl groups; and

n represents an integer of from 2 to 6; and

(b) at least n moles of one or more compounds either of formula (II)



$$\begin{array}{c} NH_2 \\ | \\ R \end{array}$$

(II)

wherein

R represents

a C_{1-6} alkyl or a C3-14 cycloalkyl group, which may be substituted by 1 to 6 members of the group selected from a C_{1-4} alkyl group, C_{1-4} alkoxy group, a phenyl group and a hydroxy group, or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group or

of formula (II) in combination with one or more di- or polyamine compound;

(ii) a di- or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound which is capable of undergoing polyaddition with the aminoterminated prepolymer (i);

(iii) 40 to 85 wt.-% of a filler for providing a minimum radioopacity of at least 3 mm/mm Al;

said composition being in the form of a two-component composition wherein a first component contains the amino terminated prepolymer (i) and optionally filler (iii) and a second component contains the compound (ii) capable of undergoing polyaddition with the aminoterminated prepolymer (i) and optionally filler (iii).

In the formulae, X represents a nitrogen or an oxygen atom. In the formulae, Z is an n-valent saturated aliphatic C_{2-16} hydrocarbon group or a divalent saturated cycloaliphatic C_{3-6} hydrocarbon group, which groups may be based on linear or branched alkylene groups having 2 to 16 carbon atoms, preferably 4 to 10 carbon atoms, or cycloalkylene groups having 3 to 6 carbon atoms, preferably 4 to 6 carbon atoms. Z may be divalent (n=2), trivalent (n=3), tetravalent (n=4), pentavalent (n=5), or hexavalent (n=6). Preferable Z is divalent or trivalent. The hydrocarbon group may be substituted by one or more C_{1-4} alkyl groups. Specific examples of the alkyl groups are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl or tert.-butyl. The hydrocarbon group may contain 1 to 6 oxygen atoms in the carbon chain connecting the n acrylate substituents or in a side chain. Preferably the aliphatic or cycloaliphatic

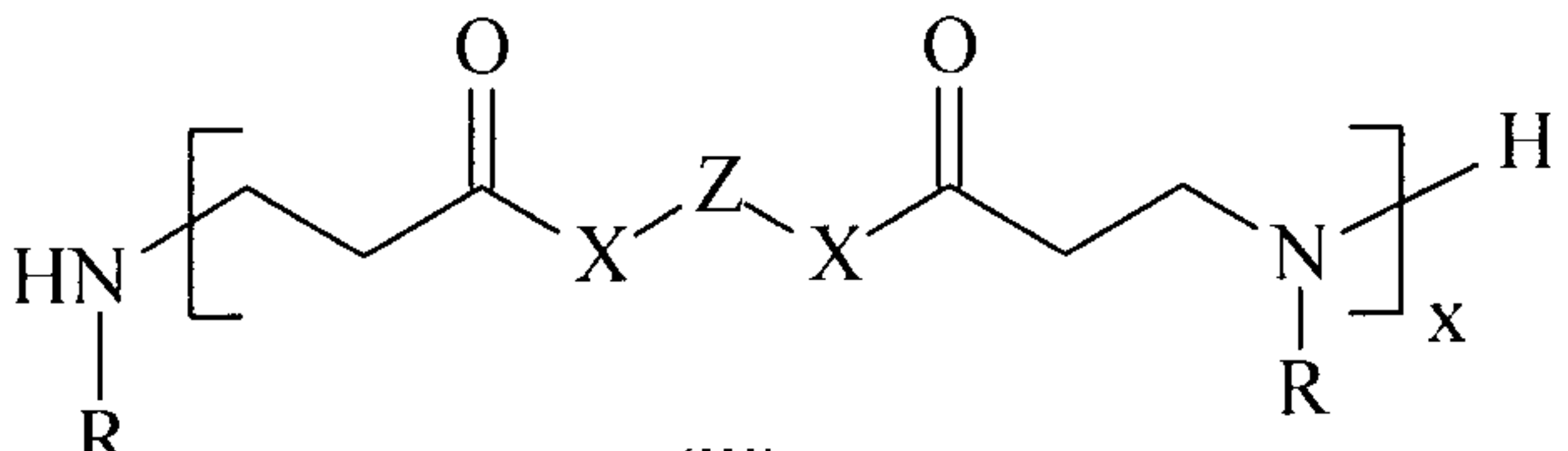
C_{2-16} hydrocarbon group is highly flexible due to the presence of ether bonds and the absence of bulky groups. In a preferred embodiment, Z is a divalent group based on a straight chain alkyl group which may contain ether bonds. Specifically, Z may be a C_{2-16} alkylene group.

In formula (II), R represents a C_{1-6} alkyl or a C_{3-14} cycloalkyl group. Examples for a C_{1-6} alkyl group can include linear or branched alkyl groups having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl and n-hexyl. Examples of the C_{3-14} cycloalkyl group can include those having 3 to 14 carbon atoms, for example, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The C_{1-6} alkyl group and the C_{3-14} cycloalkyl group may optionally be substituted by one or more members (up to six) of the group selected from a C_{1-4} alkyl group, C_{1-4} alkoxy group, a phenyl group, and a hydroxy group. Examples for C_{1-4} alkyl group can include linear or branched alkyl groups having 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl. Examples for an C_{1-4} alkoxy group can include linear or branched alkoxy groups having 1 to 4 carbon atoms, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, and tert-butoxy.

In the preparation of the prepolymer, the compound of formula (II) may be optionally used in combination with with one or more di- or polyamine compounds. The di- or polyamine compound may be used to replace up to n/1.5 moles, preferably n/20 to n/2 moles of the compound of formula (II) used in the reaction for preparing the prepolymer, wherein n is as defined above. The amount of the component used in combination with the amine of formula (II) must be chosen such that the viscosity of the prepolymer does not exceed 100 Pa*s, preferably 80 Pa*s, more preferably 20 Pa*s.

Description of the preferred embodiments

In a preferred embodiment the dental root canal sealing composition contains a prepolymer of the following formula (III)



(III)

wherein

X represents an oxygen or nitrogen atom;

Z represents an n-valent saturated aliphatic C_{2-16} hydrocarbon group or a divalent saturated cycloaliphatic C_{3-6} hydrocarbon group, which groups may contain 1 to 6 oxygen atoms, and which may be substituted by 1 to 6 C_{1-4} alkyl groups; and

R represent a C_{1-4} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by a C_{1-4} alkyl group, C_{1-4} alkoxy group, a phenyl group or a hydroxy group or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group; and

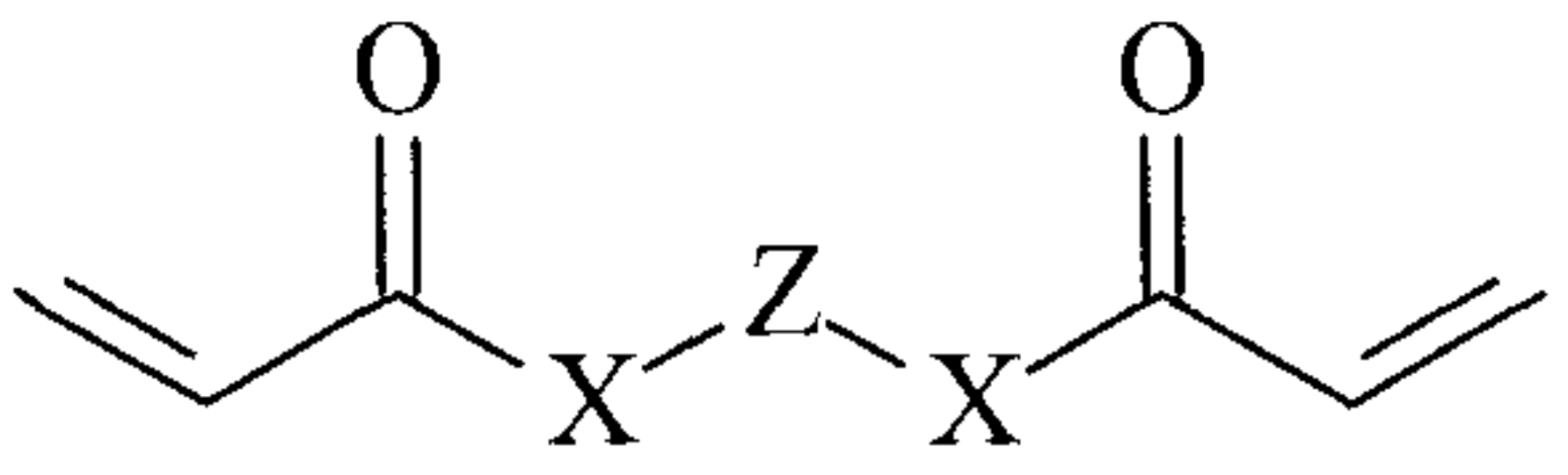
x is an integer of from 1 to 8;

(ii) a di- or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound which is capable of undergoing polyaddition with the aminoterminated prepolymer (i);

(iii) 40 to 85 wt.-% of a filler for providing a minimum radioopacity of at least 3 mm/mm Al.

In another preferred embodiment, there is provided the dental root canal sealing composition described herein, wherein the amino terminated prepolymer (i) is obtained by reacting

(a) one mole of a compound of formula (IV)



(IV)

wherein X and Z are as defined as in claim 2 for the compound of formula III; and

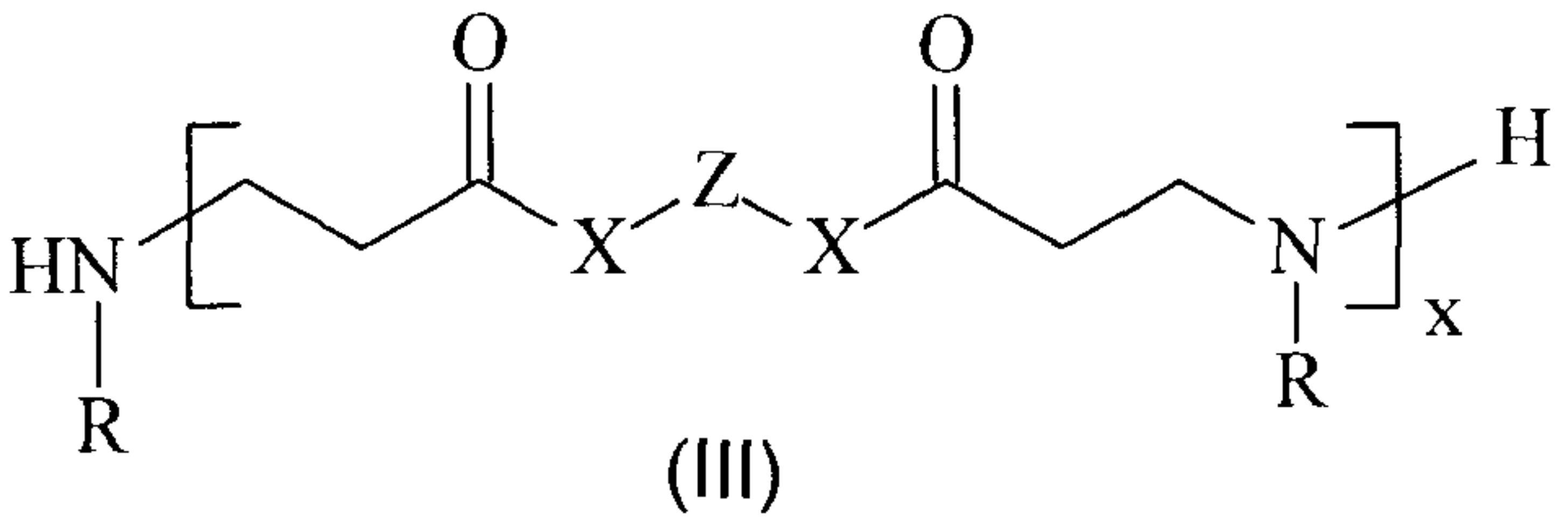
(b) at least two moles of one or more compounds of the following formula (II)


$$\mathrm{NH_2{-}R}$$

(II)

wherein R represents a C_{1-4} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by a C_{1-4} alkyl group, a phenyl group or a hydroxy group or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group.

According to another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein the amino terminated prepolymer (i) is of formula (III)



(III)

wherein

X represents an oxygen atom or NH;

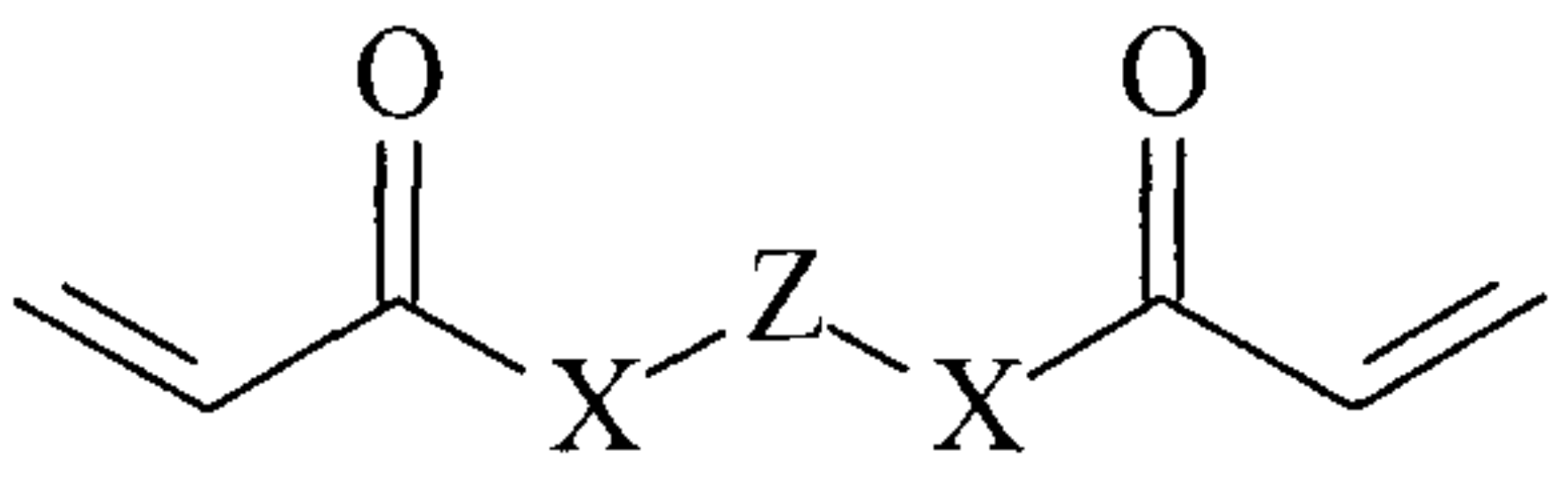
Z represents a divalent saturated aliphatic $C_{2\text{-}16}$ hydrocarbon group or a divalent saturated cycloaliphatic $C_{3\text{-}6}$ hydrocarbon group, which groups may contain 1 to 6 oxygen atoms, and which may be substituted by 1 to 6 $C_{1\text{-}4}$ alkyl groups; and

R represents a $C_{1\text{-}4}$ alkyl or a $C_{3\text{-}14}$ cycloalkyl group, which may be substituted by a $C_{1\text{-}4}$ alkyl group, a phenyl group or a hydroxy group or a $C_{1\text{-}4}$ alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group; and

x is an integer of from 1 to 8.

According to another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein the amino terminated prepolymer (i) is obtained by reacting

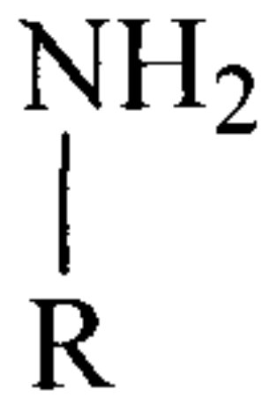
(a) one mole of a compound of formula (IV)



(IV)

wherein X and Z are as defined as in claim 2 for the compound of formula III; and

(b) at least two moles of one or more compounds of the following formula (II)



$$NH_2-R$$

(II)

wherein R represents a $C_{1\text{-}4}$ alkyl or a $C_{3\text{-}14}$ cycloalkyl group, which may be substituted by a $C_{1\text{-}4}$ alkyl group, a phenyl group or a hydroxy group or a

C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group.

According to still another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein Z represents a divalent saturated aliphatic C_{2-10} hydrocarbon chain, which may be substituted by 1 to 6 C_{1-4} alkyl groups.

According to yet another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein Z represents a C_{2-6} alkylene group.

According to a further aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein X represents an oxygen atom.

According to yet a further aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein X represents a nitrogen atom.

According to still a further aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein R is selected from a C_{1-4} alkyl group, which may be substituted by a phenyl group, a hydroxy group, or an amino group.

According to another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein the filler contains one or more of La_2O_3, ZrO_2, $BiPO_4$, $CaWO_4$, $BaWO_4$, SrF_2, and Bi_2O_3.

According to yet another aspect of the present invention, there is provided the dental root canal sealing composition described herein, wherein the two-component composition is a powder/liquid or a paste/paste system.

The dental root canal sealing composition is in the form of a two-component composition wherein a first component contains the amino terminated prepolymer (i) and optionally filler (iii) and a second component contains the compound (ii) capable of undergoing polyaddition with the aminoterminated prepolymer (i) and optionally filler (iii). At least one of the components contains filler.

The dental root canal sealing composition of the invention contains 40 to 85 wt.-% of a filler for providing a minimum radioopacity of the cured composition of at least 3mm/mm Al. The filler may contain one or more of La_2O_3, ZrO_2, $BiPO_4$, $CaWO_4$, $BaWO_4$, SrF_2, and Bi_2O_3. The radioopacity of the cured composition of the invention is at least 3 mm/mm Al, preferably at least 5 to 7 mm/mm Al, and most preferably at least 7 mm/mm Al.

Preferably, the dental root canal sealing composition of the invention does not contain a diluent, in particular a reactive diluent, having a viscosity which is lower than the viscosity of the prepolymer of the invention. Moreover, the dental root canal sealing composition does not need to contain a polymerisation initiator. In a preferred embodiment, the dental root canal sealing composition consists essentially of components (i) to (iii). A dental root canal sealing composition consisting essentially of components (i) to (iii) may contain common additives used in the dental field such as colorants, antibiotic agents and ion releasing agents, in a total amount of not more than 25 wt.-%, preferably not more than 10 wt.% of the composition.

A preferred embodiment of the dental root canal sealing composition of the invention contains 40 to 85 wt.-% of a filler and 15 to 60 wt.-% of the aminoterminated prepolymer and the compound capable of undergoing polyaddition with the aminoterminated prepolymer. The aminoterminated prepolymer used in the present invention is usually a mixture of oligomers. Accordingly, the amount of the aminoterminated prepolymer and the compound capable of undergoing polyaddition with the aminoterminated prepolymer is calculated based on the mixture of oligomers.

The dental root canal sealing composition of the present invention is a two component composition which is mixed prior to use.The two component composition is preferably a powder/liquid system, a powder/paste system, a paste/paste system or a liquid/paste system. The paste/paste system or a liquid/paste system may be applied by an applicator wherein both components are mixed by a static mixer.

The present invention is based on the recognition that the Michael addition of specific diamines to specific di- and oligoacrylate compounds provides prepolymers having low viscosity while at the same time eliminating the problems associated with the presence of low molecular amines. Surprisingly, the reaction kinetics of the Michael addition of diamines with acrylates differs from the reaction kinetics of other addition reactions of amines so that the reaction products are not crosslinked or high molecular highly viscous materials, but uncrosslinked prepolymers having low viscosity. It appears that the difference of the reaction rates between primary and secondary amines with acrylate compounds is the basis for the possibility of obtaining the compositions of the present invention. Based on the specific reaction kinetics of primary amines in the present invention, the content of residual primary amines in the prepolymer or in the dental root canal sealing composition of the present invention is substantially reduced as compared to systems using functional end groups showing the same reactivity towards primary and secondary amines, cf. J. Klee, H.-H. Hörhold, J. Raddatz; Acta Polymerica, 41 (1990) 557-560; "Telechele Prepolymere aus DGEBA und disekundären Diaminen. Unvernetzte Epoxid-Amin-

Additionspolymere, 29."; J.E. Klee; Acta Polym. 45 (1994) 73-82; "Telechelic prepolymers and macromonomers by step growth processes" (39); J. E. Klee, R.-E. Grützner, H.-H. Hörhold; Macromol. Chem. Phys. 197 (1996) 2305-2323; Linear arylamine/ Bis-2,2-[4-(2,3-epoxypropoxy)-phenyl]-propane addition polymers - synthesis and properteis, Uncrosslinked epoxide-amine addition polymers, 44." Primary amines react much faster as compared to secondary amines, in particular in the reaction with di- or polyfunctional acrylates or acrylamides, or bis- or polymaleimides.

The prepolymer contained in the dental root canal sealing composition of the present invention has a viscosity at 23°C of less than 100 Pa*s. Preferably, the viscosity of the prepolymer is in the range of from 1 to 80 Pa*s, more preferably from 1 to 20 Pa*s. If the viscosity is too high, then it will be difficult to apply the composition through the canal of a needle. If the viscosity is too low, then it will be difficult handle the composition.

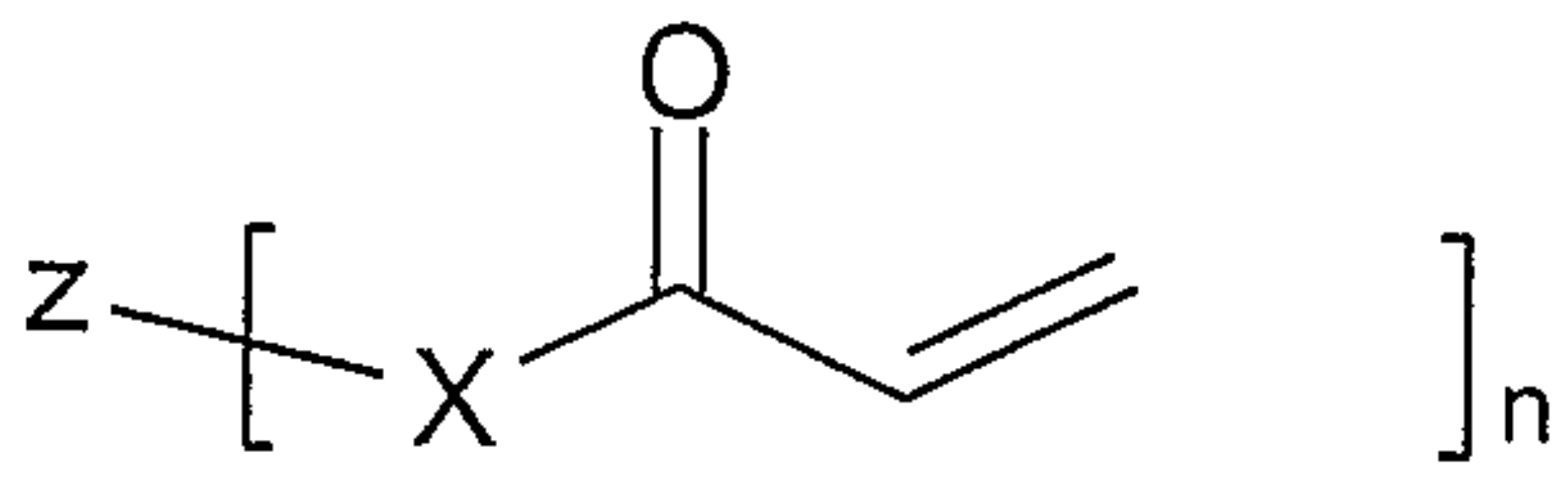
The dental root canal sealing composition of the present invention is curable in the absence of a polymerisation initiator. The curing mechanism is based on an addition reaction of an addition reaction between the aminoterminated prepolymer (i) and a compound capable of undergoing polyaddition with the aminoterminated prepolymer (i). The compound capable of undergoing polyaddition with the aminoterminated prepolymer (i) is a di- or polyfunctional acylate, or di- or polyfunctional maleimide. Di- or polyfunctional acrylates and di- or polyfunctional maleimides are preferred with regard to the selectivity in the reaction with primary and secondary amino groups. The compound capable of undergoing polyaddition with the aminoterminated prepolymer (i) may be the same or different as the compound as defined by formula (I) wherein X and Z are as defined above and n represents an integer of from 2 to 6.

The use of the specific amino terminated prepolymers eliminates or at least strongly reduces the problems associated with low molecular amines. Moreover, it is surprising that the use of the specific prepolymers provides a dental root canal sealing composition which has a low viscosity. For this purpose, it is essential that rigid moieties in the prepolymers are avoided.

The compositions of the pesent invention may be applied to a root canal by using conventional techniques. Specifically, the compositions of the present invention may be applied via the canal of a syringe into the root canal. Moreover, the compositions of the present invention may also be used for the manufacture of prefabricated root canal cones. If cones made of the compositions of the invention are used in combination with the respective dental root canal sealing composition of the invention, compatibility of the cones with the sealing composition can be guaranteed whereby a tight seal may be obtained. The cured product obtained with the composition according to the invention has superior mechanical properties, in particular with regard to flexibility, which is essential for the application as a root canal sealing composition.

Now, the general process for the preparation of the an amino terminated prepolymer is described. The amino terminated prepolymer may be obtained by reacting

(a) one mole of a compound of the following formula (I)



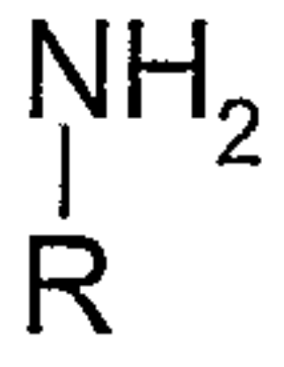
(I)

wherein

X and Z are as defined above and

n represents an integer of from 2 to 4;

(b) at least n moles of one or more compounds either of the following formula (II)



$$NH_2-R$$

(II)

wherein

R is as defined above, or of formula (II) in combination with one or more di- or polyamine compound.

The reaction may be carried out in the absence of a solvent or in the presence of a suitable solvent. The temperature of the reaction is preferably in the range of from 10 °C to 150 °C, more preferably in the range of 20 °C to 80 °C. The reaction time depends on the temperature and the reactivity of the reaction system and is usually in the range of from hours to several days. The termination of the reaction may be checked by conventional methods sucha s an IR spectrum whereby the end of the reaction is reached when all acrylic carbon-carbon double bonds have disappeared. In case the reaction is carried out in the absence of a solvent, the prepolymers obtained by the reaction of compounds (I) and (II) may be used as such without further work-up of the reaction mixture. In the preparation of the prepolymer, the compound of formula (II) may be used in combination with one or more di- or polyamine compounds. The di- or polyamine compound may be used to replace of from n/10 to n/2 moles of the compound of formula (II) used in the reaction for preparing the prepolymer.

The present invention will now be further explained with reference to specific examples. Dynamic viscosities were measured by using a Bohlin CS50 rheometer at 23°C.

EXAMPLES

Example 1

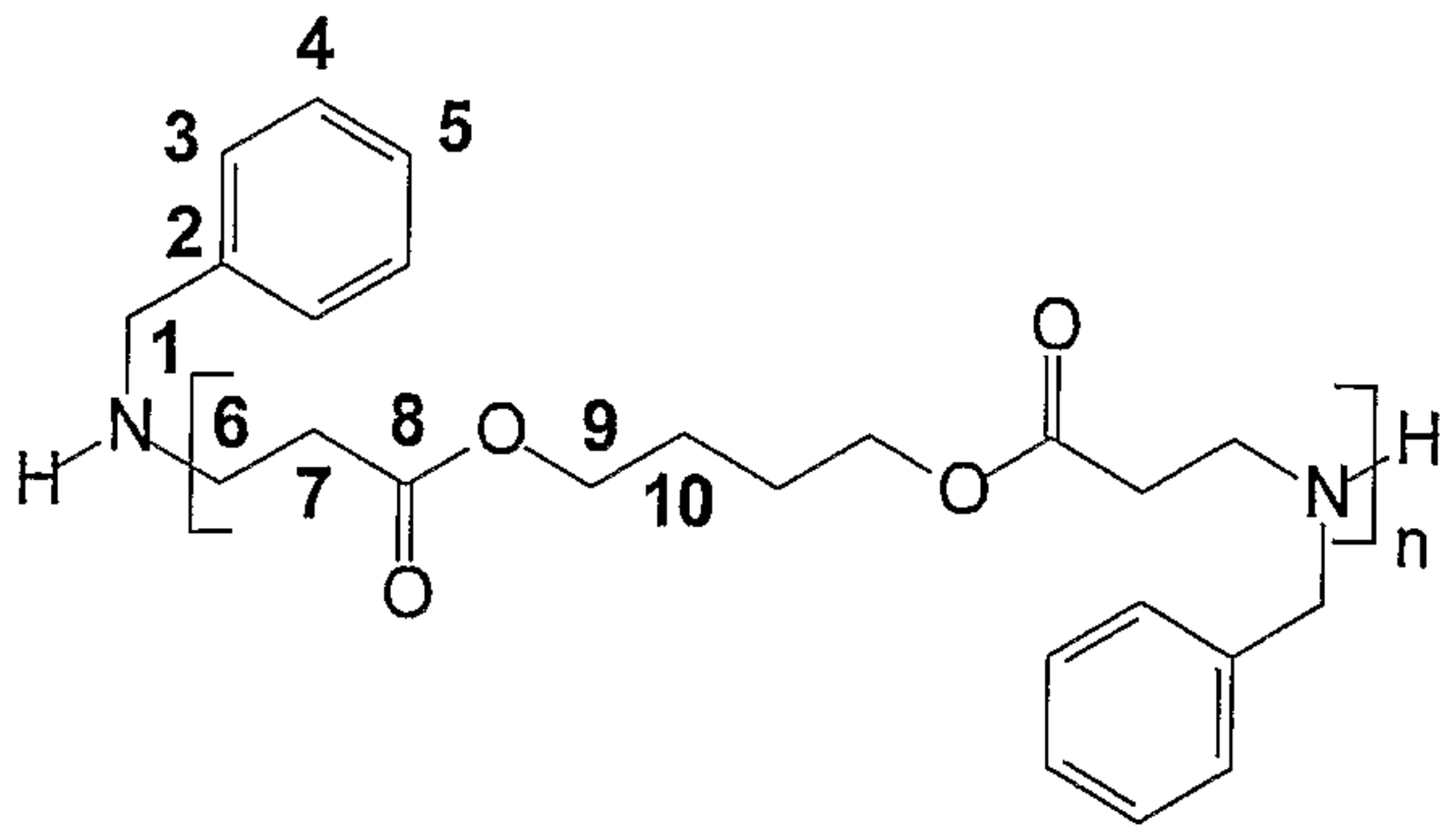
In a 250 ml flask equipped with stirrer, and condenser 29.982 g (279.79 mmol) benzyl amine and 27.730 g (139.89 mmol) butanediol diacrylate were homogeneously mixed and stirred for 3 days at room temperature. Thereafter no double bonds were found in the IR-spectrum at 1609 and 809 cm^{-1}

Yield: 57.71 g (100 % d. Th), $h_{23\,°C} = 0.627 \pm 0.011$ Pa*s

$C_{24}H_{32}N_2O_4$; 412.53

IR: 3027, 2954, 2837 (CH_2/CH_3), 1726 (CO), 1453, 1403, 1353, 1170 (CH_2/CH_3) cm^{-1}

^{13}C-NMR ($CDCl_3$): 171.9 (8), 139.6 (2), 128.2-126.5 (3-5), 63.4 (9), 53.2 (1), 44.0 (6), 42.7 (7), 24.8 (10), ppm



FAB-MS m/z= 413, 718, 1022, 1327, 1633

HPLC analysis, content benzyl amine: 7.17 % (theor. 19.68 %)

GC analysis, content benzyl amine: 6.36 % (theor. 19.68 %).

Examples 2-4

Analogous to example 1 benzyl amine BA and butanediol diacrylate BDODA were reacted. The used quantities of monomers, their mol ratio, calculated molecular mass and remaining benzyl amine, calculated and measured by using of GC as well as their viscosities are summarised in Table 1.

Table 1 Amino terminated prepolymers

BA		BDODA		mol ratio	Mn (calc)	benzyl amine residue		Viscosity
G	mmol	g	mmol		g/mol	Calc. %	GC %	Pa*s
19.694	183.78	24.286	122.52	3 / 2	717.92	8.17	0.20	0.507 ± 0.004
21.241	198.22	29.468	148.66	4 / 3	1023.30	4.45	0.03	0.474 ± 0.007
20.110	187.66	29.759	150.13	5 / 4	1328.68	2.79	0.02	0.438 ± 0.005

Example 5

In a 250 ml flask equipped with stirrer, and condenser 29.849 g (197.35 mmol) 1-aminoadamantan and 19.559 g (98.67 mmol) butanediol diacrylate were homogeneously mixed and stirred for 5 days at room temperature. Thereafter no double bonds were found in the IR-spectrum at 1609 and 809 cm^1.

Yield: 49.408 g (100 % d. Th), $\eta_{23 ^\circ C}$ = 0.835 ± 0.020 Pa*s

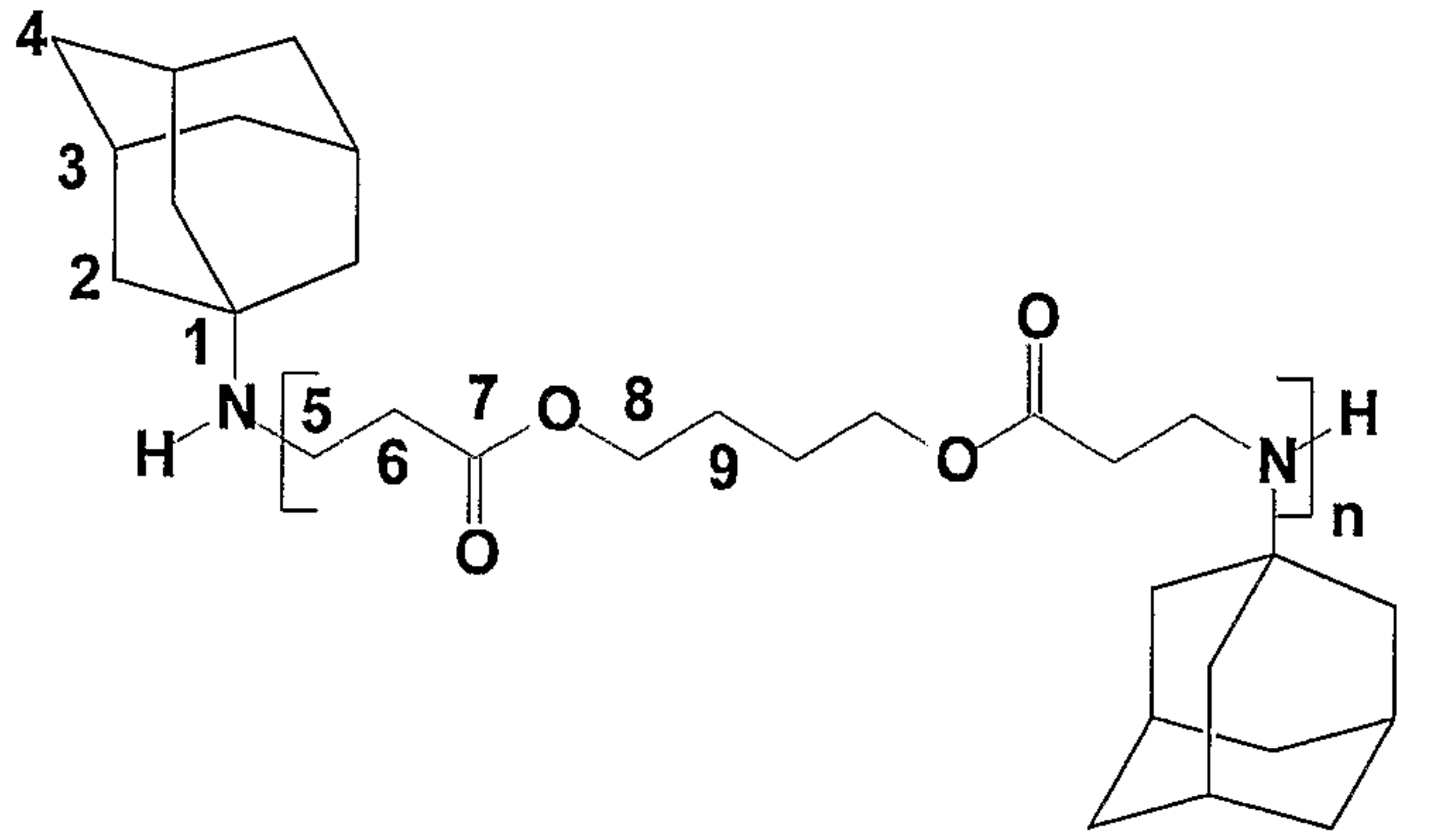
$C_{30}H_{48}N_2O_4$; 500.72

IR: 3303 (OH), 2958, 2924 (CH_2/CH_3), 1725, 1720 (CO), 1458, 1408, 1355, 1170 (CH_2/CH_3) cm^{-1}

^{13}C-NMR: 173.1 (7), 64.5/62.0/61.3 (8), 51.7/50.8 (5), 46.2 (1), 42.7 (2), 36.8/36.4/36.1 (4), 35.6/35.5 (6), 29.7/29.3 (9), 25.4 (3) ppm

FAB-MS m/z= 500

GC analysis, content 1-aminoadamantan: 3,23 % (theor. 18.10 %).



Example 6

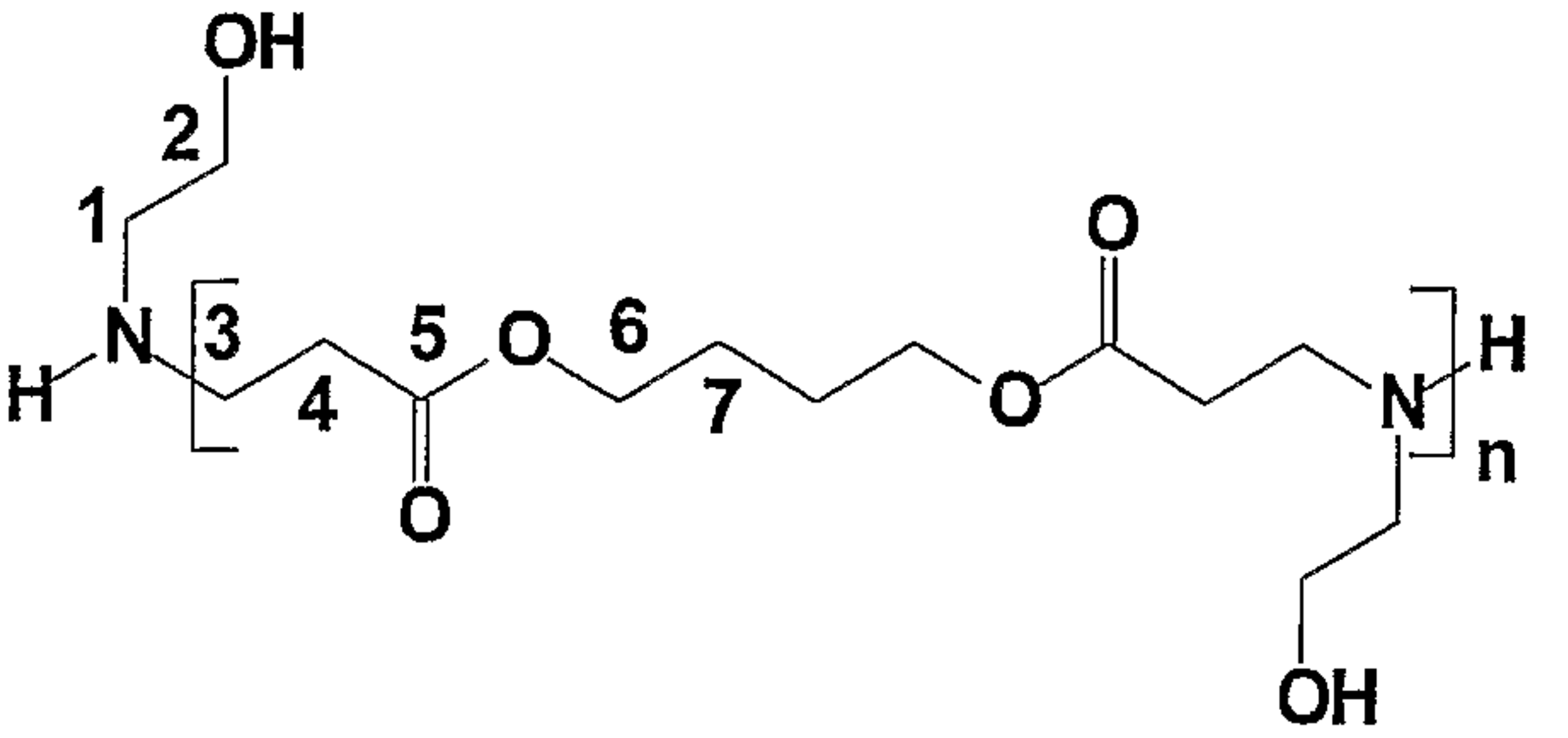
In a 250 ml flask equipped with stirrer, and condenser 17.079 g (279.62 mmol) ethanol amine and 27.713 g (139.81 mmol) butanediol diacrylate were homogeneously mixed and stirred for 5 days at room temperature. Thereafter no double bonds were found in the IR-spectrum at 1609 and 809 cm^{-1}.

Yield: 44.79 g (100 % d. Th), h $_{23\,°C}$ = 6.257 ± 0.180 Pa*s

$C_{14}H_{28}N_2O_6$; 320.39

IR: 3303 (OH), 2958, 2924 (CH_2/CH_3), 1725, 1720 (CO), 1458, 1408, 1355, 1170 (CH_2/CH_3) cm^{-1}

^{13}C-NMR: 173.4/172:9 (5), 64.7/64.2 (6), 62.3/61.7/60.8 (2), 51.3 (1), 44.9 (3), 34.6 (4), 29.9 29.3/25.1/25.3 (7) ppm



FAB-MS m/z= 321, 579, 839, 1097

GC analysis, content ethanol amine: 0.05 % (theor. 21.66 %).

Example 7

In a 250 ml flask equipped with stirrer, and condenser 22.857 g (213.30 mmol) benzyl amine and 21.067 g (71.10 mmol) trimethylol propane triacrylate were homogeneously mixed and stirred for 3 days at room temperature. Thereafter no double bonds were found in the IR-spectrum at 1609 and 809 cm^{-1}.

Yield: 43.924 g (100 % d. Th), $\eta_{23\,°C} = 1.142 \pm 0.018$ Pa*s

$C_{36}H_{47}N_3O_6$; 617.79

GC analysis, content benzyl amine: 7.19 %.

Example 8

25.000 g (233.30 mmol) benzyl amine and 23.592 g (116.65 mmol) 1,4-butandiol diglycidyl ether were homogeneously mixed under heating and polymerised for 24 hours at 50°C.

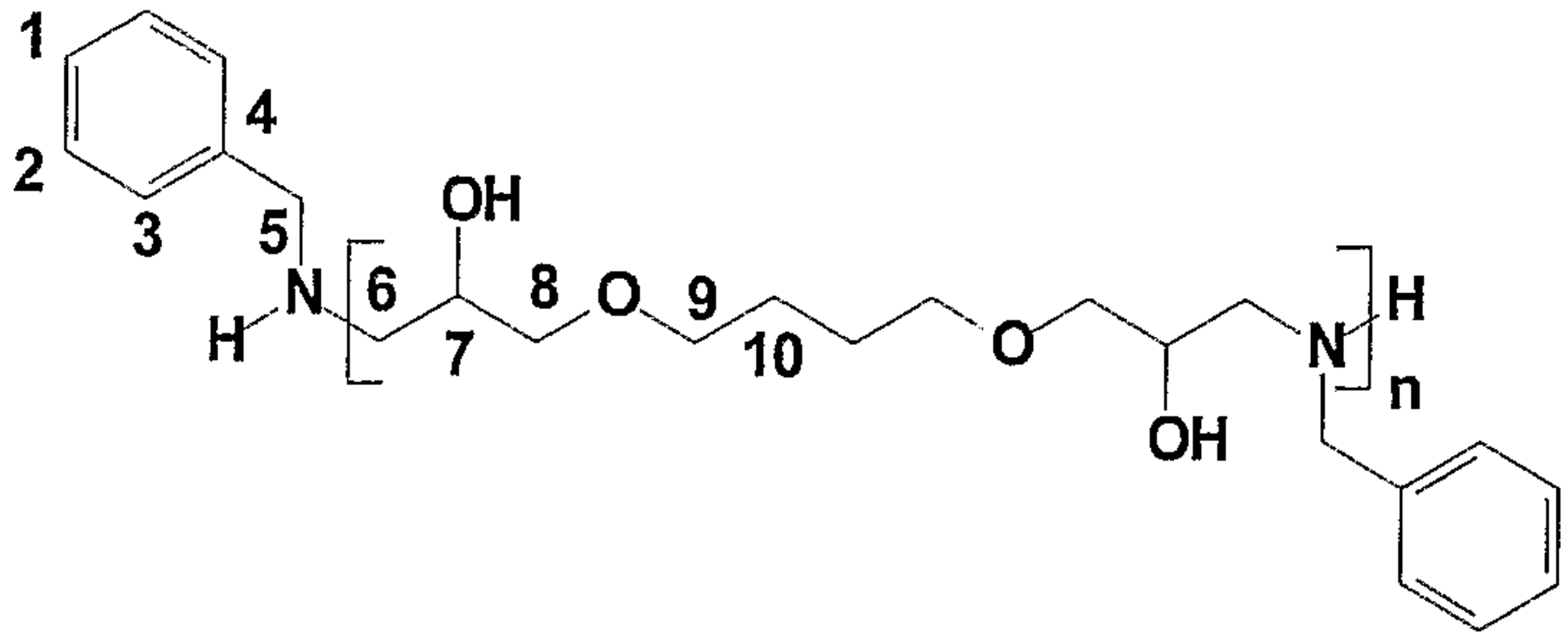
Yield: 48.592 (100 % of th.)

$h_{23\,°C} = 2.377 \pm 0.041$ Pa*s

$C_{24}H_{36}N_2O_4$; 416.56

IR: 3028, 2863, 2860 (CH_2/CH_3), 1451, 1105, 738 (CH_2/CH_3) cm^{-1}

^{13}C-NMR: 137.2 (4), 128.3 (2), 128.1 (3), 126.8 (1), 75.2 (8), 71.5 (7), 70.5 (9), 57.8 (5), 55.5 (6), 27.3 (10) ppm (calc.)



2.784 g (6.683 mmol) of the prepared prepolymer were homogeneously mixed with 3.422 g (6.683 mmol) ethoxylated bisphenol A diacrylate (SR-601, Sartomer™) and reacted at 37 °C.

Example 9

10.000 g (29.375 mmol) bis-2,2-[4-(2,3-epoxypropoxy)-phenyl]-propane and 6.296 g (58.751 mmol) benzyl amine were homogeneously mixed under heating and polymerised for 20 hours at 100°C.

Yield: 16.296 (100 % of th.)

$C_{35}H_{42}N_2O_4$; 554.73M_n(vpo) 620 g/mol, T_g 11°C

Example 10

10.000 g (29.375 mmol) bis-2,2-[4-(2,3-epoxypropoxy)-phenyl]-propane and 4.722 g (44.063 mmol) benzyl amine were homogeneously mixed under heating and polymerised for 20 hours at 100°C.

Yield: 14.722 (100 % of th.)

$C_{63}H_{75}N_3O_8$; 1002.30 g/molM_n(vpo) 1100 g/mol, T_g 30°C

Application Example 1

1.198 g of amino terminated prepolymer prepared by addition reaction of benzylamine and trimethylol propane triacrylate according of example 7 and 3.133 g of a powder composed of cyclohexane dimethanol diacrylate 16.439 %, calcium tungstate 66.849 % and zirconium oxide 16.712 % were homogeneously mixed and polymerised at 37 °C for 17 hours. The radio-opacity according ISO 6876 is 10.6 mm/mm Al.

Application Example 2

1.267 g (2.16 mmol) of amino terminated prepolymer prepared by addition reaction of benzylamine and trimethylol propane triacrylate according of example 7 and 3.313 g (2.16 mmol) of a powder composed of cyclohexane dimethanol diacrylate 20.00 % and bismuth oxide 80.00 % were homogeneously mixed and polymerised at 37 ° for 10 hours.

The radio-opacity according ISO 6876 is 8.1 mm/mm Al.

Application Example 3

Acrylate Paste: 5.000 g (9.77 mmol) ethoxylated bisphenol A diacrylate (SR-601, Sartomer). 9.917 g calcium tungstate, 2.479 g zirconium oxide, 0.050 g Aerosil™ A 200 and 0.025 g iron (III) oxide were homogeneously mixed.

Prepolymer Paste: 4.830 g (9.77 mmol) aminoterminated prepolymer according example 6, 9.500 g calcium tungstate, 2.375 g zirconium oxide and 0.536 g Aerosil™ A 200 were homogeneously mixed.

Immediately before application 1.00 g of the acrylate paste and 0.987 g of the Amino-Prepolymer Paste were mixed homogeneously and polymerised at 37 °C for 3 hours.

Reference Example

In a 250 ml flask equipped with stirrer and condenser 25.000 g (128.70 mmol) 3,(4),8,(9)-bis(aminomethyl) tricyclo-5.2.1.0 ^{2,6} decane, 12.755 g (64.35 mmol) butanediol diacrylate were homogeneously mixed and stirred at 20 to 25 °C for 3 days. Thereafter no double bonds were found in the IR-spectrum at 1609 and 809 cm^{-1}. Yield: 37.764 g (100 % d. Th), η 23 °C = 7157 ± 100 Pa*s (after storage for 1 month at room temperature)

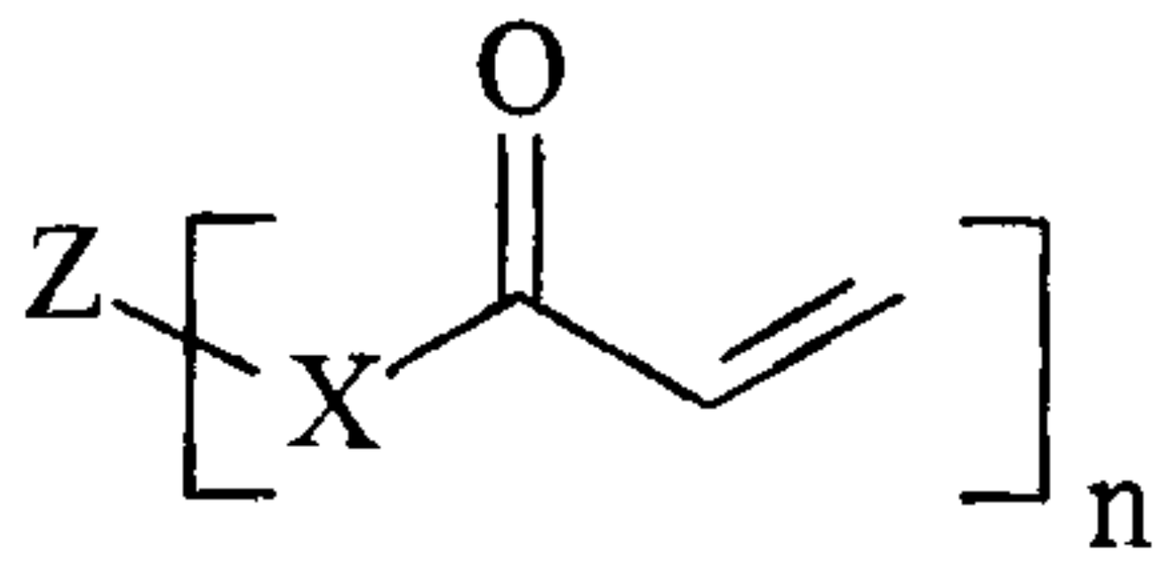
2.127 g (3.624 mmol) of the prepared prepolymer were homogeneously mixed with 0.716 g (2.416 mmol) trimethylol propane triacrylate and reacted at 37 °C. The mixture has a gel time of 30 minutes at 37 °C. The prepolymer has a viscosity which is not suitable for the application as a root canal sealing composition.

CLAIMS:

1. A dental root canal sealing composition curable in the absence of a polymerisation initiator and having a viscosity at 23°C of less than 100 Pa*s, which comprises:

(i) an amino terminated prepolymer having a viscosity at 23°C of less than 100 Pa*s obtained by reacting

(a) one mole of a compound of formula (I)



(I)

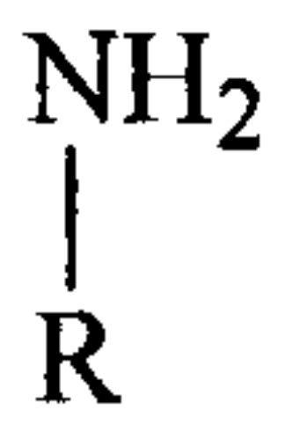
wherein

X represents NH or an oxygen atom;

Z represents an n-valent saturated aliphatic or cycloaliphatic C_{2-16} hydrocarbon group which may contain 1 to 6 oxygen atoms, and which may be substituted by one or more C_{1-4} alkyl groups; and

n represents an integer of from 2 to 6; and

(b) at least n moles of one or more compounds either of formula (II)



$$R-NH_2$$

(II)

wherein

R represents

a C_{1-6} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by 1 to 6 members of the group selected from a C_{1-4} alkyl group, C_{1-4} alkoxy group, a phenyl group and a hydroxy group or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group, or

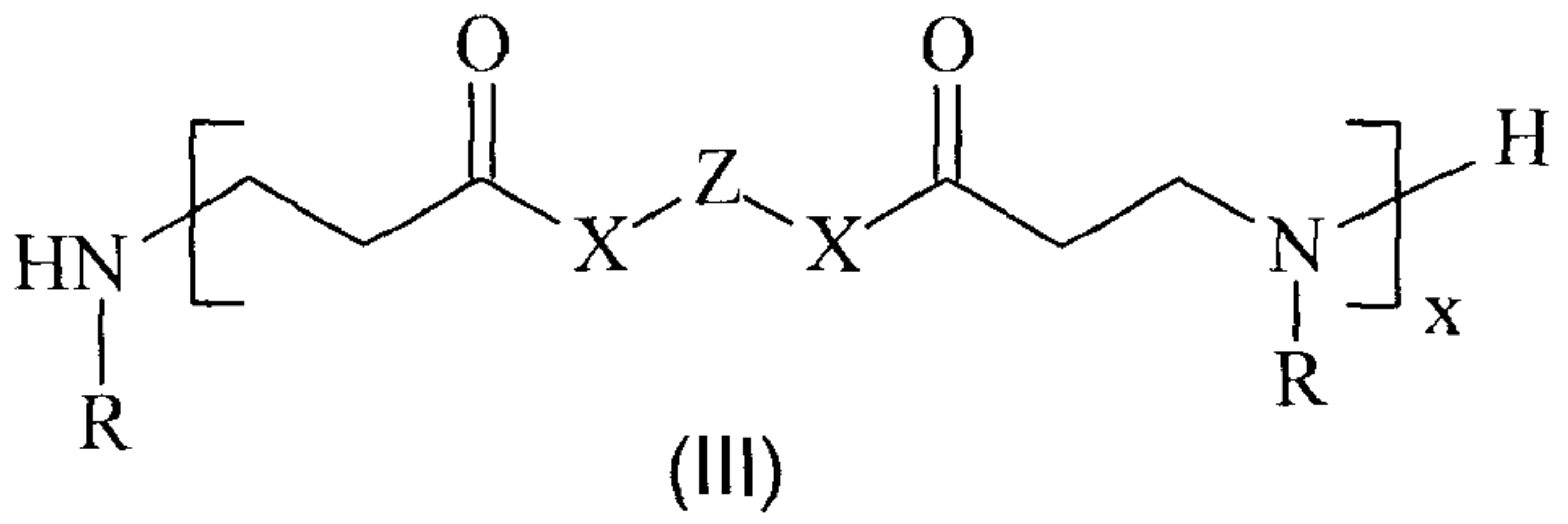
of formula (II) in combination with one or more di- or polyamine compound;

(ii) a di- or polyfunctional acrylate compound or a di- or polyfunctional maleimide compound which is capable of undergoing polyaddition with the aminoterminated prepolymer (i);

(iii) 40 to 85 wt.-% of a filler for providing a minimum radioopacity of at least 3 mm/mm Al;

said composition being in the form of a two-component composition wherein a first component contains the amino terminated prepolymer (i) and optionally filler (iii) and a second component contains the compound (ii) capable of undergoing polyaddition with the aminoterminated prepolymer (i) and optionally filler (iii).

2. The dental root canal sealing composition according to claim 1, wherein the amino terminated prepolymer (i) is of formula (III)



(III)

wherein

X represents an oxygen atom or NH;

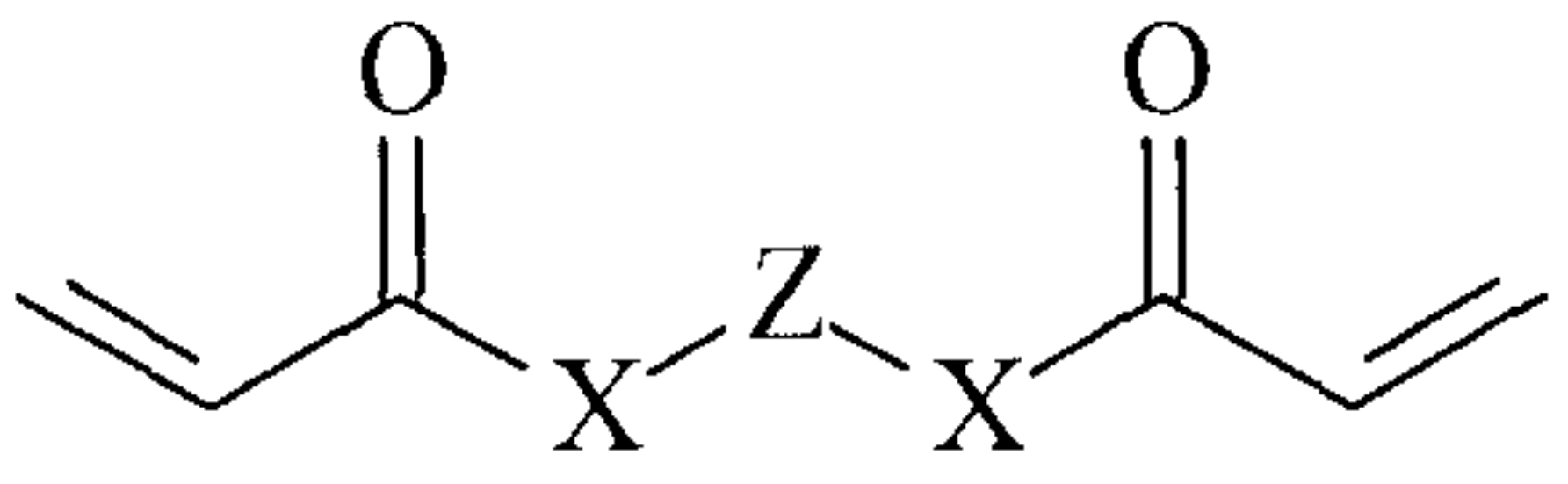
Z represents a divalent saturated aliphatic C_{2-16} hydrocarbon group or a divalent saturated cycloaliphatic C_{3-6} hydrocarbon group, which groups may contain 1 to 6 oxygen atoms, and which may be substituted by 1 to 6 C_{1-4} alkyl groups; and

R represents a C_{1-4} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by a C_{1-4} alkyl group, a phenyl group or a hydroxy group or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group; and

x is an integer of from 1 to 8.

3. The dental root canal sealing composition according to claim 2, wherein the amino terminated prepolymer (i) is obtained by reacting

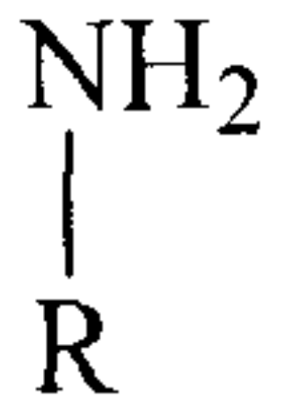
(a) one mole of a compound of formula (IV)



(IV)

wherein X and Z are as defined as in claim 2 for the compound of formula III; and

(b) at least two moles of one or more compounds of the following formula (II)



$$\overset{NH_2}{\underset{R}{|}}$$

(II)

wherein R represents a C_{1-4} alkyl or a C_{3-14} cycloalkyl group, which may be substituted by a C_{1-4} alkyl group, a phenyl group or a hydroxy group or a C_{1-4} alkyl group which may be substituted by a phenyl group, a hydroxy group or an amino group.

4. The dental root canal sealing composition according to any one of claims 1 to 3, wherein

Z represents a divalent saturated aliphatic C_{2-10} hydrocarbon chain, which may be substituted by 1 to 6 C_{1-4} alkyl groups.

5. The dental root canal sealing composition according to any one of claims 1 to 3, wherein Z represents a C_{2-6} alkylene group.

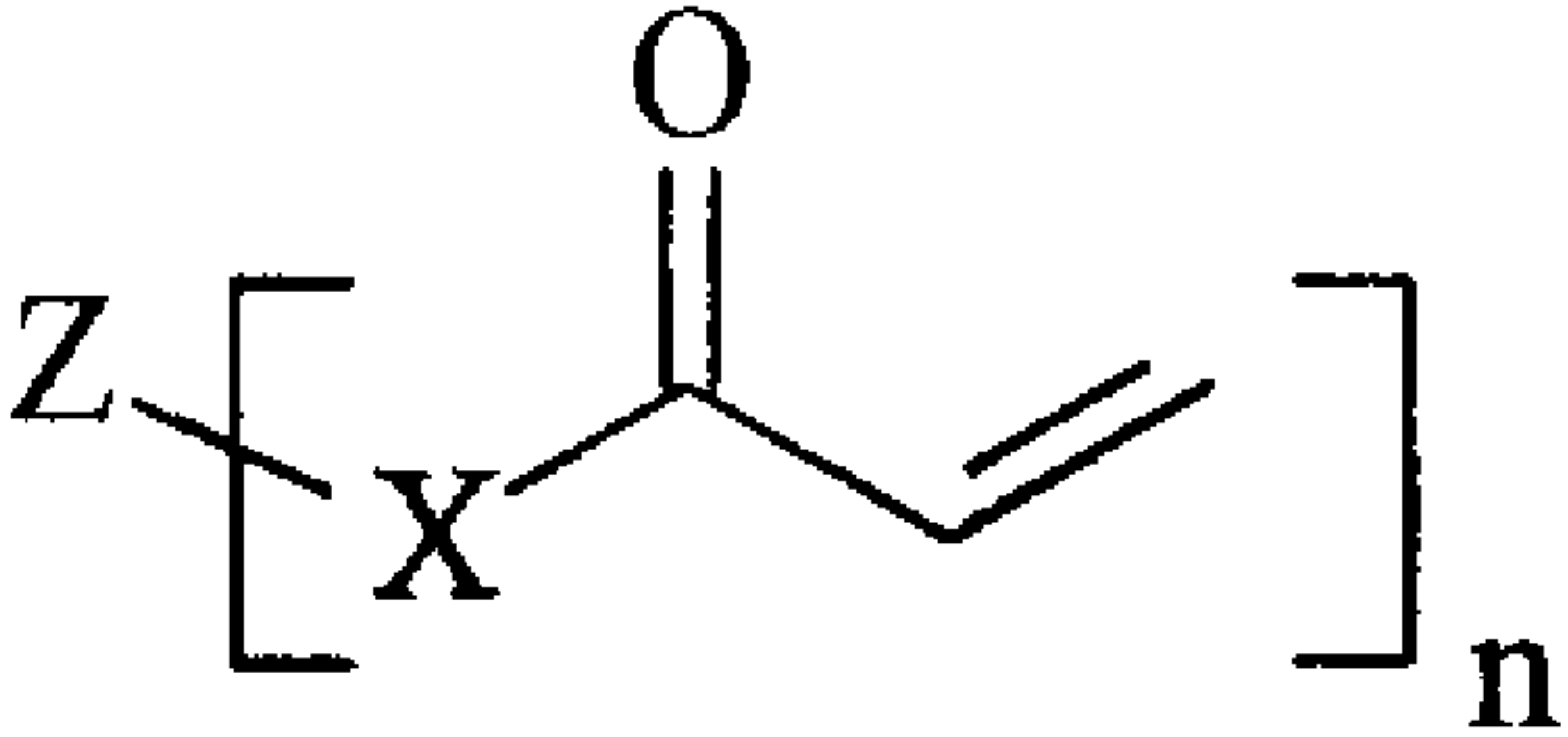
6. The dental root canal sealing composition according to any one of claims 1 to 5, wherein X represents an oxygen atom.

7. The dental root canal sealing composition according to any one of claims 1 to 5, wherein X represents NH.

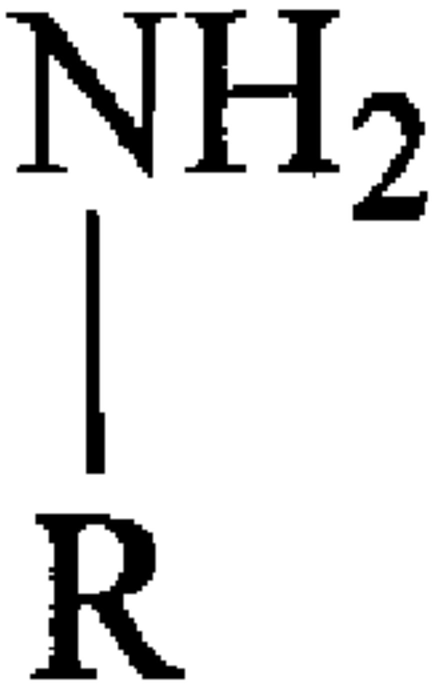
8. The dental root canal sealing composition according to any one of claims 1 to 7, wherein R is selected from a C_{1-4} alkyl group, which may be substituted by a phenyl group, a hydroxy group, or an amino group.

9. The dental root canal sealing composition according to any one of claims 1 to 8, wherein the filler contains one or more of La_2O_3, ZrO_2, $BiPO_4$, $CaWO_4$, $BaWO_4$, SrF_2, and Bi_2O_3.

10. The dental root canal sealing composition according to any one of claims 1 to 9, wherein the two-component composition is a powder/liquid or a paste/paste system.



(I)



$$\mathrm{R{-}NH_2}$$

(II)