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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{3}:
C07C 69/54; C08F 20/20; C08J 7/04; //C07C 35/37, 23/38, 61/135, 69/753, 31/27, 69/608, 39/17

A1

(11) International Publication Number: WO 81/03657

(43) International Publication Date: 24 December 1981 (24.12.81)

(21) International Application Number: PCT/EP81/00066

(22) International Filing Date: 9 June 1981 (09.06.81)

(31) Priority Application Number: 158,504

(32) Priority Date: 11 June 1980 (11.06.80)

(33) Priority Country: US

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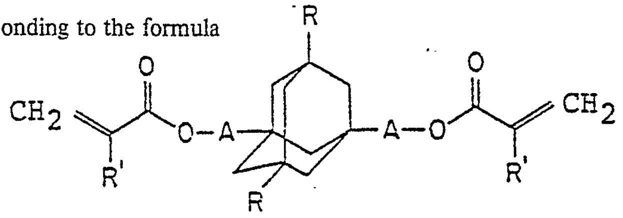
(81) Designated States: AT (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report

(54) Title: UNSATURATED ESTERS OF ADAMANTANE CONTAINING DIOLS AND THERMO-RESISTANT CROSS-LINKED POLYMERS THEREFROM

(57) Abstract

Diacrylate and dimethacrylate esters corresponding to the formula



wherein R and R' are hydrogen or methyl and A is either a sigma (σ) bond; a $(CH_2)n$ radical where n is an integer that may vary from one through four; or phenylene, or an alkyl derivative thereof. The new adamantane containing difunctional olefinic monomers can then be polymerized, or copolymerized with other acrylic type olefinic monomers to produce polymers with unusual physical properties, including unusual hardness, inertness to degradable agents, and resistance to heat.

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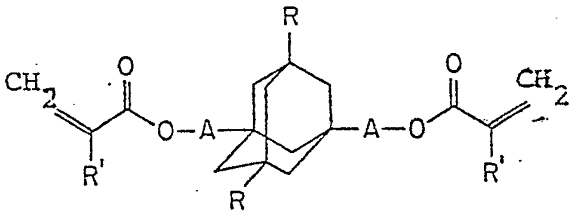
UNSATURATED ESTERS OF ADAMANTANE CONTAINING DIOLS AND THERMO-RESISTANT CROSS-LINKED POLYMERS THEREFROM

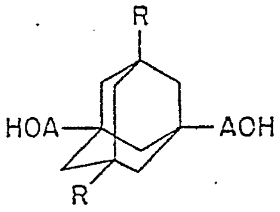
1. FIELD OF INVENTION

The present invention concerns new unsaturated esters (I) of adamantane diols and of adamantane containing dihydroxy-compounds (II), the polymerization thereof and the cross-linked polymers resulting from such polymerization.

The new ester monomers have the formula (I),



(I)



(II)

FORMULA (I)

FORMULA (II)

Wherein the R and R' are hydrogen or methyl group and A is either a sigma (σ) bond, a radical satisfying the formula $(CH_2)n$, a phenylene or an alkyl derivative thereof.

What follows is LIST I which lists some specific examples from FORMULA (I):

LIST I

1. Diacrylate and dimethacrylate esters of 1,3-adamantane diol
R = H; R' = H, CH_3; A = sigma (σ) bond

2. Diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-ada-

mantane diol

$R = CH_3$; $R' = H, CH_3$; A = sigma (σ) bond

3. Diacrylate and dimethacrylate esters of 1,3-bis-(hydroxymethyl) adamantane

$R = H$ $R' = H, CH_3$; $A = -CH_2-$

4. Diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-bis-(hydroxymethyl)-adamantane

$R = CH_3$; $R' = H, CH_3$; $A = -CH_2-$

5. Diacrylate and dimethacrylate esters of 1,3-bis-(2-hydroxyethyl)-adamantane

$R = H$; $R' = H, CH_3$; $A = -CH_2-CH_2-$

6. Diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-bis-(2-hydroxyethyl)-adamantane

$R = CH_3$; $R' = H, CH_3$; $A = -CH_2-CH_2-$

7. Diacrylate and dimethacrylate esters of 1,3-bis-(p-hydroxyphenyl)-adamantane

$R = H$; $R' = H, CH_3$; A = 

8. Diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-bis-(p-hydroxyphenyl)-adamantane

$R = CH_3$; $R' = H, CH_3$; A = 

Thus, the new monomers of the invention, i.e. the acrylic and methacrylic esters of the corresponding di-hydroxy containing adamantanes (II), are bifunctional, compounds, a condition for obtaining, by the polymerization thereof, cross-linked type resins having unusual hardness, inertness to degradation agents and resistance to heat.

2. <u>SUMMARY OF THE PRIOR ART</u>.

Esters of unsaturated acids and hydroxy-containing adamantane compounds are already known. Thus, DULING et al (USP 3,533,947 and 3,639,362) disclose the mono-acrylates of 1-hydroxy-adamantane and of other hydroxy-adamantanes alkylated on the others bridge-head positions of the cage. Also S.S. NOVIKOV et al, Izvestiya Akademii Nauk SSSR, [12] 2765, (1977), report the preparation of acrylates and methacrylates of mono substituted adamantane compounds of formula HO-R-Ad in which Ad represents the adamantane cage and R represents the groups methylene, ethylene, $-CH_2-CH_2-O-CO-$, $-CH_2-CH_2-O-CO-CH_2-$. Also, REINHARDT (USP 3,342,880) discloses the preparation and the polymerization of adamantyl methacrylate and of 3,3'-dimethylacryl-1,1'-bis-adamantane, the latter giving a cross-linked resin.

Now, all the monofunctional monomers of the above prior-art provide straight chain polymer resins the properties of which do not come up to the level of cross-linked polymers and the difunctional monomer mentioned above, although it provides a cross-linked polymer, is rather expensive and not well suited for industrial developments.

OBJECTS OF THE INVENTION

Thus, one object of the present invention is to provide new adamantane monomers containing two olefinic groups suitable for making, by polymerization, or copolymerization with other monomers, cross-linked resins with unusual physical properties.

Another object of the invention is to provide adamantane polymerizable difunctional monomers, the adamantane cage of which is separated from the polymerizable function by means of a connecting chain the length of which can be varied in order that polymers and copolymers with a range of properties can be obtained by using appropriate mixtures of different monomers and copolymerizing such mixtures.

Still another object of the invention is to propose new difunctional adamantane monomers which can be prepared according to well defined and relatively inexpensive routes.

Still another object of the invention is to furnish difunctional adamantane polymerizable monomers which can easily and cheaply be polymerized by different methods, i.e. thermally, by means of free radicals or photochemically, thus ensuring a great versatility of end-uses.

Other objects of the invention will become apparent to those skilled in the art from the detailed discussion that follows:

DEFINITION OF THE INVENTION

The preferred compounds in the invention are the acrylates and methacrylates of 1,3-adamantane diol, of 1,3-bis(hydroxymethyl)-adamantane, of 1,3-bis(2-hydroxyethyl)-adamantane, of 1,3-bis-(p-hydroxyphenyl)-adamantane, and also the corresponding homologs with methyl groups in position 5 and 7 of the adamantane cage. All these monomers are liquids or solids which can be polymerized easily either thermally (around 150°C) or in the presence of radical initiators such as H_2O_2, organic peroxides such as benzoyl peroxide, dicumyl peroxide, lauroyl peroxide or azobis-isobutyronitrile and other common initiators. These monomers can also be polymerized by irradiation with actinic sources such as ultraviolet light (preferably below 320 nm), and electron beams.

The monomers can be polymerized either individually or copolymerized as mixtures of two or several other monomers. Said other monomers can be selected from difunctional monomers according to the invention or from monomers of the prior-art including monofunctional monomers or polyfunctional monomers. Among the monofunctional monomers, acrylic acid, acrylamide, and alkyl acrylates can be mentioned; among the polyfunctional monomers, ethylene glycol diacrylate, hexanediol diacrylate, and trimethylol propane triacrylate can be mentioned. The ratio of PTMM to the copolymers may range from 1:0 to 1:1.

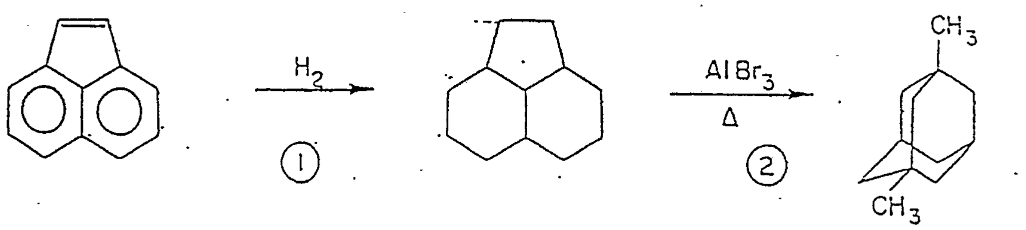
The polymers of the invention are hard, transparent resins which resist attack by heat and solvents and which have many end-uses. Depending on the method of polymerization, hardnesses in the range of 30(KNOOP) and more can be attained and the weight losses on being subjected to temperatures in the range of 400-450°C are only about one third of the losses for cross-linked resins from conventional monomers.

Therefore, the new resins can be used in many high temperature applications and, also, for improving the scratch and solvent resistance of organic glasses by means of coatings only a few microns thick.

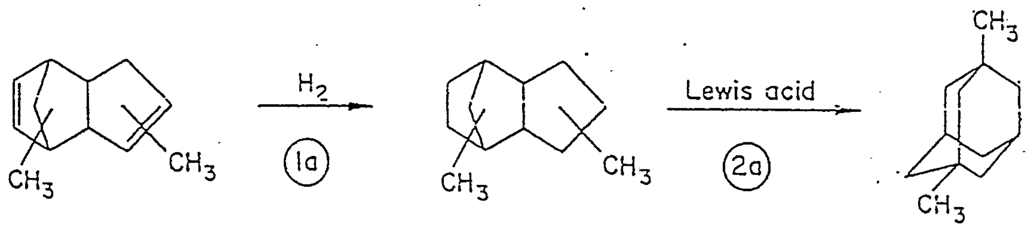
SOME ILLUSTRATIVE EMBODIMENTS OF THE INVENTION

The new monomers of the invention can be obtained according to several different routes some of which will be summarized in the following text below by way of illustration.

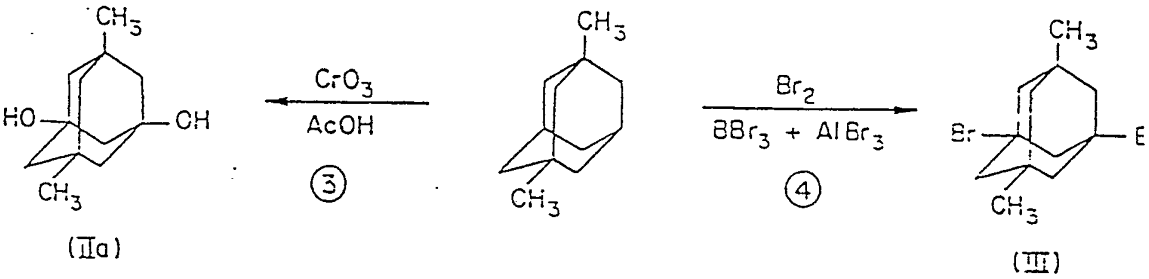
Adamantane itself is available commercially and is generally obtained from the catalyzed rearrangement of tricyclic compounds. Thus, for instance, the bridge-head dimethyl hydrocarbon can be obtained from acenaphtene by hydrogenation (reaction ①) and subsequent rearrangement in the presence of lewis acids (reaction ②).



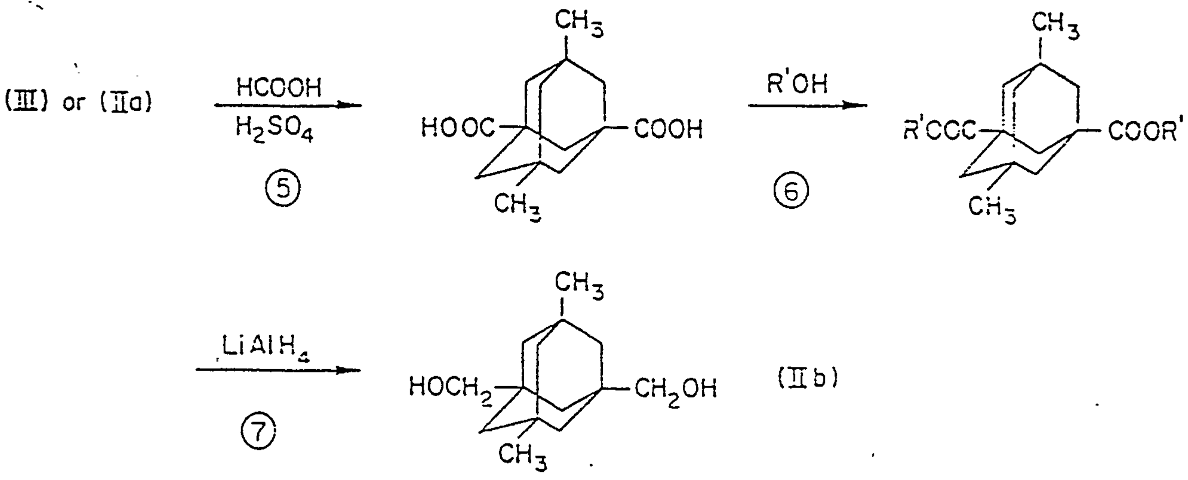
Another similar method consists in the hydrogenation of dimethyl dicyclopentadiene (reaction (1a)) and the subsequent rearrangement of the hydrogenated tricyclo compound into dimethyladamantane (reaction (2a)).



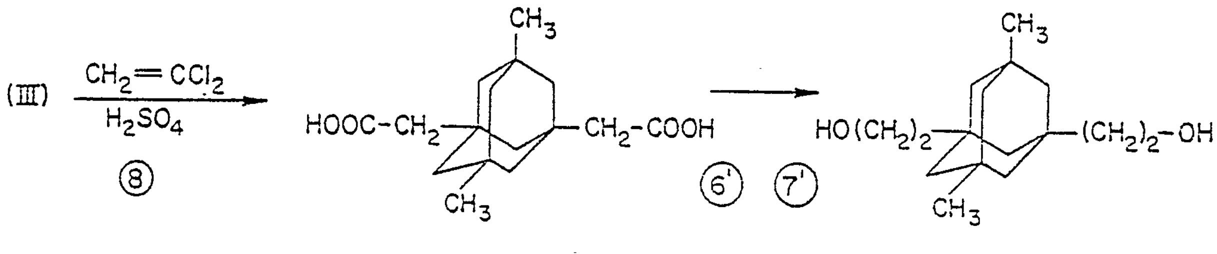
Then, dimethyl adamantane can be oxidized (reaction ③) with CrO_3 in acetic acid to the corresponding diol (IIa) such as described, for instance in French Patent No 1.461.287, or brominated to the corresponding dibromo-compound (III) with bromine in the presence of boron tribromide and $AlBr_3$ (reaction ④).



The dibromo-compound (III), as well as the diol (IIa), can be converted to the corresponding dicarboxylic acid by reaction with formic acid in concentrated H_2SO_4, (reaction ⑤) then the diacid is esterified with a lower alcohol (reaction ⑥) and the obtained ester is reduced to the corresponding diol (IIb) with lithium aluminium hydride (reaction ⑦):

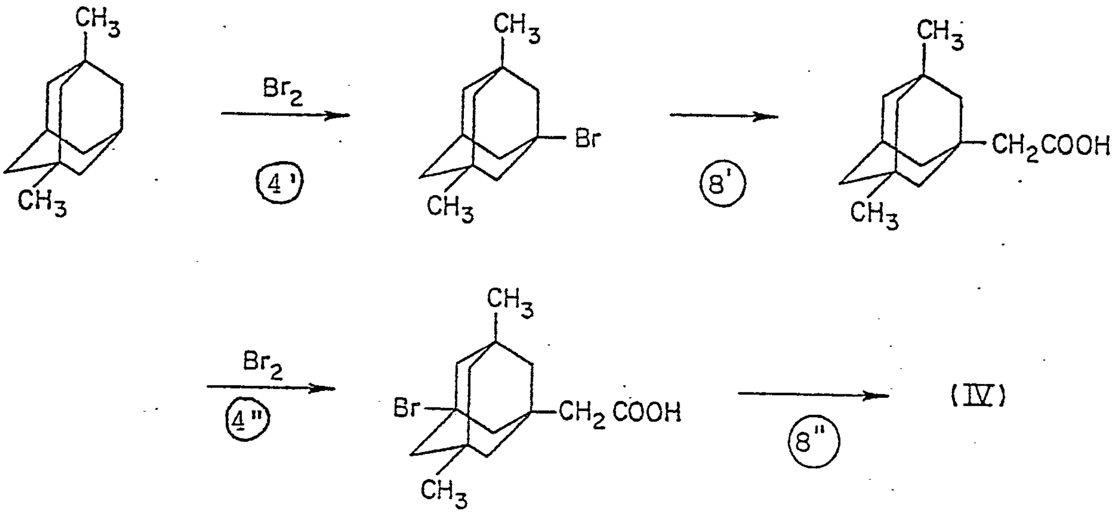


Alternatively, the dibromo-compound (III) can be converted to the corresponding diacetic acid derivative (IV), for instance by heating with vinylidene chloride in sulfuric acid (reaction ⑧), according to K. BOTT, Chem.Ber. 101, 564-573 (1968). The diacid being thereafter esterified and the ester reduced with $LiAlH_4$ in a manner analogous to reactions ⑥ and ⑦ above (reactions (6') and (7')) to give the dimethylol compound (IIc).

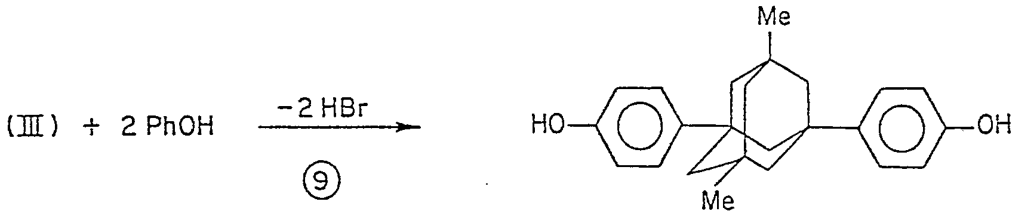


(IV) (IIc)

However, since the sequence of reactions ⑧, (6') and (7') does not provide very good yields, a two stage analogous sequence of reactions involving the corresponding monobromo-adamantane derivative is preferably used. In this sequence, dimethyl adamantane is first monobrominated using refluxing bromine (reaction (4')) and the dimethyl-bromo-adamantane is converted to the mono-methyl-carboxylic acid by the same type of reaction as reaction ⑧ above, after which the mono-carboxylic compound is brominated yielding 1-bromo-3-carboxymethyl-5,7-dimethyl adamantane which then is once more reacted with vinylidene chloride in H_2SO_4 according to ⑧ to give, finally, the diacetic acid (IV):



The dibromo-dimethyl-adamantane (III) can also be reacted with phenols according to the conditions disclosed in USP 3,594,427 (reaction ⑨) to give the desired bishydroxyphenyl compounds (IId). This is illustrated by the following scheme involving ordinary unsubstituted phenol:



(IId)

It should be pointed out that the same reactions can be used for obtaining the corresponding non-methylated adamantane bishydroxy-compounds.

Now, the compounds of formula (II) can be converted to the monomers (I) by esterification, preferably with acrylyl chloride or methacrylyl chloride in the presence of a tertiary amine, according to well known techniques (see for example USP 3,533,947). The reaction is carried out by dissolving the alcohol in a solvent such as benzene, toluene tetrahydrofurane or the like, adding a tertiary amine to the mixture in molar excess relative to the alcohol, and than slowly adding the acid chloride thereto. The amine used preferably is triethylamine, although other tertiary amines such as pyridine, tributylamine, N,N,N',N'-tetramethyl-ethylenediamine, triethylenediamine, picolines, quinoline and the like can be employed. Upon addition of the acid chloride, the initial reaction that takes place involves the formation of a complex between it and the amine. Slow addition of the acid chloride is continued preferably until the amount added is in molar excess of the alcohol. The resulting slurry is then stirred at a temperature in the range of 10-80°C, preferably 20-60°C, to effect the esterification reaction. A temperature above 80°C should be avoided in most instances as this tends to cause a messy reaction, and it is most preferable to maintain the temperature in the range of 25-60°C. Time required for completion of the reaction will depend upon the reaction temperature used, but generally is in the range of 1-20 hours.

As the reaction occurs the amine-acid chloride complex is replaced by an amine HCl complex which is insoluble in the solvent. The alkyladamantyl-acrylate product on the other hand remains in solution. After completion of the reaction, the mixture is filtered to remove the amine-HCl complex and the solvent is removed by evaporation. The crude product ester obtained is a nearly colorless liquid or solid which can be purified by liquid partition chromatography, by column chromatography (on Al_2O_3) or, when crystallization occurs, by recrystallization in a suitable solvent. The purified products are colorless liquids or solids. In the absence of suitable stabilizing additives, the liquids may, in some cases, polymerize spontaneously on storage but this generally occurs slowly enough to allow end use application beforehand.

For polymerizing the monomers of the invention, conventional techniques can be used. For instance, the monomers can be heated, either pure or in admixture with other monomers, at temperatures where polymerization will occur thermally. Temperatures in the range of 150°C and over are ordinarily suitable.

Otherwise, free radical promoters or irradiation in the presence of photoinitiators can be used when polymerization is to be carried out at lower temperature, e.g. room temperature. Conditions for photopolymerization are also conventional and can be found in the following references: U.V. Curing Science K Technology, Editor: Technology Marketing Corp. (1978) Stamford, Conn.06902, USA.

For instance, a coating of protective polymer according to the invention can be applied on organic glasses made, for example, of transparent resins such as polycarbonate or polymethacrylate. For this, the monomers of the invention (either pure or in admixture with other monomers) and a photoinitiator are applied as a thin layer over the surface of said organic glass and the whole is subjected to irradiation for periods ranging from a few seconds to several minutes by means of ultraviolet radiation, e.g. a high pressure mercury lamp, the emission of which is mainly in the ultraviolet wavelengths (300-330 nm) or the short visible wavelengths. The pieces of organic glasses thus acquire a very hard, solvent-resistant and transparent protective film enabling them to be used in applications where resistance to solvents, especially chlorinated solvents, and mechanical abuse is a problem, e.g. transparent construction plates, optical material, etc...

The examples below further illustrate the invention in more detail.

EXPERIMENTAL

Example 1

Preparation of the diacrylate ester of 1,3-dimethyl-5,7-adamantane-diol

(Compound (I), R = CH_3; R' = H)

a) Oxidation of 1,3-dimethyladamantane with chromic anhydride: This reaction was carried out as described in French Patent No. 1.461.287 and gave the corresponding diol in yields of about 85%.

b) Esterification of diol (IIa) with acrylyl chloride

9.55 g (48.6 mmole) of 1,3-dimethyl-5,7-adamantane-diol were dissolved in a solution of 14 ml (100 mmole) of triethylamine in 400 ml of anhydrous tetrahydrofurane (THF) at 40°C. The solution was kept between 40 and 50°C while adding, dropwise with stirring, 8.1 ml (100 mmole) of acrylyl chloride. The addition lasted 45 min. Stirring was continued for 1 hr afterwards and the insoluble triethylamine hydrochloride was removed by filtration. The solid was dried and weighted, the result corresponding practically to the expected theoretical weight and showing that the reaction is about quantitative. The filtrate was concentrated under reduced pressure (12 Torr; below 50°C) until 14,8 g of the crude diacrylate was obtained. The crude product was easily purified by column chromatography on Al_2O_3 using hexane or chloroform as eluent. MP of the pure diacrylate was 45,5- 46°C. The NMR spectrum was taken in $CDCl_3$, using TMS as the internal standard. The chemical shifts are given in ppm (δ).

1.00 (s,6H) : $-\overset{|}{\underset{|}{C}}-CH_3$; 1.20 (s,2H) : adamantane-CH_2- ; 1.86 (s,8H) : adamantane-CH_2- ; 2.48 (s,2H) : adamantane-CH_2- ; 5.65 (m (complex), 6H) : $-CO-CH=CH_2$.

Example 2

Preparation of diacrylate and dimethacrylate ester of 1,3-dimethyl-5,7-bis-(2-hydroxymethyl) adamantane

a) Dibromination of dimethyladamantane (reaction ④).

This dibromination to 1,3-dimethyl-5,7-dibromoadamantane can be carried out according to known techniques using bromine in the presence of Lewis acids such as $AlBr_3$ and BBr_3. The present preparation was performed according to E.R. TALATY et al, J. Chem, Soc. (C) 1968, 1902. Thus, 328 g of dimethyladamantane (2 mole) were treated with 1.04 l of anhydrous bromine in the presence of 50 ml BBr_3 and 2.2 g of $AlBr_3$ to give 510 g of the desired product (80% yield).

b) Conversion of the dibromo-dimethyl-adamantane (III) or the corresponding dihydroxy-compound (IIa) to the corresponding dicarboxylic acid (IIIa).

This reaction was carried out according to the directions given in French Patent No 1.476.992. Thus, treating 165 g (0.51 mole) of 1,3-dimethyl-5,7-dibromoadamantane in 1.8 l of sulfuric acid (103%

H_2SO_4 equiv.) with 190 ml of HCOOH at 10°C gave, after hydrolysis, 121.3 g of the desired dicarboxylic acid (yield 94%).

Similar results were obtained when using, as the starting material, the corresponding 1,3-dimethyl-5,7-adamantane-diol.

c) Esterification of the dimethyl-adamantane-dicarboxylic acid (IIIa)

Esterification of the above compound can be performed according to conventional techniques, e.g. by the direct interaction with a lower alcohol such as MeOH, EtOH in the presence of catalysts such as H_2SO_4, BF_3, tosylic acid and the like. Another route is the conversion of the diacid into its dichloride followed by reaction of the latter with the lower alcohols. Thus, 31 g (0.12 mole) of 1,3-dimethyladamantane-5,7-dicarboxylic acid was boiled for 4 hours under reflux with 160 ml $SOCl_2$. The excess of thionyl chloride was removed under reduced pressure and the residue was dissolved into 100 ml CCl_4 to which was added an excess of absolute ethanol. The solvent and excess alcohol were stripped off and the crude diester was distilled under reduced pressure (B.P./0.8 Torr: 135 - 139°C); yield 34,9 g (92%) NMR spectrum (CCl_4; TMS; ppm δ).

0.92 (s,6H): $-C-CH_3$; 1.17 (s,2H): adamantane-CH_2-;
1.23 (t,6H, J = 7.2 cps): $-CH_3$ (of ethoxy);
1.48 (s,8H) adamantane-CH_2;
1.82 (s,2H): adamantane-CH_2;
4.10 (g,4H, J = 7.2 cps): $-CH_2-$ (of ethoxy).

d) Reduction of the dimethyl-adamantane dicarboxylate with $LiAlH_4$ (reaction ⑦).

Six g of lithium-aluminum hydride (0.158 mole) was stirred with 200 ml of absolute ether and to this was added dropwise 24.15 g (0.078 mole) of diethyl 1,3-dimethyladamantane-5,7-dicarboxylate in 50 ml of absolute ether at a rate such as to maintain gentle refluxing of the solvent. Refluxing was continued for 2 hrs and the excess $LiAlH_4$ was decomposed with moist AcOEt. The reaction mixture was acidified with 20% H_2SO_4 which gave, by crystallization, 15.3 g of 1,3-dimethyl-5,7-bis(hydroxymethyl)-adamantane(IIb) which was collected by filtration. Another 1.8 g crop was obtained from the filtrate after separating the water phase and evaporating the organic layer.

Yield was 17.1 g (97%). MP was 158-161°C. Recrystallization from ethyl acetate afforded a product MP 160-162°C.

NMR spectrum ($DMSO-d_6 + CDCl_3$, TMS, ppm δ).
0.87 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$;
1.10 (s,12H): adamantane-CH_2-;
3.16 (d,4H, J = 6 cps): $-CH_2-OH$;
3,93 (t,2H, J = 6 cps): $-CH_2-OH$.

e) Esterification of the 1,3-dimethyl-5,7-bis(hydroxymethyl)-adamantane (IIb) into the corresponding diacrylic and dimethacrylic esters (I), R = CH_3; R' = H, CH_3; A = $-CH_2-$.

1. Reaction with acrylyl chloride.

To a solution of 11.15 g of 1,3-dimethyl-5,7-bis(hydroxymethyl)-adamantane (49.7 mmole) in 280 ml of benzene and 16.7 ml (120 mmole) of triethylamine was added, dropwise at room temperature, 8.84 ml (109 mmole) of acrylyl chloride over a 45 min period. The temperature rose to about 40°C and triethylamine hydrochloride separated. The suspension was further stirred for 1 hr at 40°C after which it was filtered and the solid was washed with benzene. The combined washings and filtrate were extracted with, successively, water, saturated aqueous $NaHCO_3$, 5% HCl and finally water. The benzene solution was dried on anhydrous Na_2SO_4 and concentrated below 40°C, leaving a viscous colorless residue that crystallized on standing in the cold. Yield 13.2 g (80%) of diacrylate (I), R = CH_3; R' = H; A = $-CH_2-$. The product was crystallized from $EtOH-H_2O$ giving colorless crystals having a MP 49-50.5°C.

NMR spectrum (CCl_4, TMS, ppm δ)
0.87 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$;
1.16 (s,12H): adamantane-CH_2-;
3.80 (s,4H): $-CH_2O-$;
5.6-6.7 (complex m,6H): $-CO-CH=CH_2$

2. Reaction with methacrylyl-chloride

Methacryl chloride (12.3 ml, 127.3 mmole) was added dropwise at 40°C to a solution of 12.97 g (57.8 mmole) of 1,3-dimethyl-5,7-bis(hydroxymethyl)adamantane in 315 ml of dry benzene containing 17.7 ml (127.3 mmole) of Et_3N. After the addition was complete, stirring was continued for 5 hrs at 60°C and, thereafter, the precipitated hydrochloride was filtered off and washed with benzene. The combined filtrate and washings were scrubbed as described abvove in the case of the diacrylate and, after drying the organic phase and evaporating the solvent, 18.7 g (90%) of the dimethycrylate (I), R = R' = CH_3; A = $-CH_2-$, was recovered as a viscous residue. This was further purified by column chromatography on Al_2O_3 using $CHCl_3$ as eluent. Analysis showed that it was reasonably pure but it dit not crystallize.

NMR spectrum ($CDCl_3$, TMS, ppm δ)

0.87 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$;

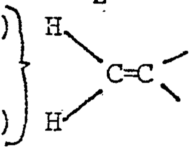
1.18 (s,12H): adamantane$-CH_2-$;

1.97 (d,6H, J = ~1 cps): $-CH_3$ (of the methacryl group)

3.85 (s,4H): $-CH_2-O-$;

5.61 (m,2H)

6.16 (m,2H)



Example 3

Preparation of diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-bis(2-hydroxyethyl)adamantane

(I), R = CH_3; R' = H, CH_3; A = $-CH_2-CH_2-$

a) 1,3-dimethyl-5,7-adamantanediacetic-acid diethylester

1,3-dimethyl-5,7-adamantanediacetic acid (IV) was prepared by known techniques (K. BOTT, Chem.Ber.,101, 564(1968). Esterification can be achieved by the same conventional techniques mentioned under Example 2C. Thus, 28.7 g of 1,3-dimethyl-5,7-adamantane diacetic acid (0.10 mole) was boiled with an excess of absolute ethanol and 1.2 ml concentrated sulfuric acid for 12 hrs under reflux to yield 31.7 g of diethyl ester (91%) BP 0.45 Torr 140 - 145°C.

NMR Spectrum (CCl_4 solution, TMS as internal standard, ppm (δ)

0.85 (s,6H): $-C-CH_3$

1.20 (s,12H): adamantane$-CH_2-$

1.20 (t,6H, J = 7 cps): $-O-CH_2-CH_3$

2.05 (s,4H): $-\overset{|}{\underset{|}{C}}-CH_2-\underset{\underset{O}{\|}}{C}-$

4.05 (q,4H, J = 7 cps): $-O-CH_2-CH_3$

b) 1,3-dimethyl-5,7-bis(2-hydroxyethyl)adamantane (IIc)

The diol (IIc) was obtained by reducing the 1,3-dimethyl-5,7-adamantanediacetic acid diethylester with Lithium aluminum hydride: To 7.5 g $LiAlH_4$ (197.6 mmole) in 250 ml dry ether was added 30.2 g of diester (89.8 mmole) dissolved in 50 ml ether at such a rate that a gentle refluxing of the solvent is maintained. Refluxing was continued for an additional 2 hrs after which time the excess $LiAlH_4$ was decomposed with ethyl acetate and water. The reaction mixture was acidified with H_2SO_4 20% and filtered, leaving 6.15 g of diol IIc. A further 13.3 g of diol was obtained from the filtrate after separating and evaporating the organic layer. Yield 19.45 g (86%) of diol (IIc) MP: 133 - 135°C (from ether).

NMR Spectrum (DMSO-d_6 solution, TMS as internal standard, ppm (δ)

0.77 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$

1.04 (s,12H): adamantane-CH_2-

1.27 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

3.43 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

c) Esterification of 1,3-dimethyl-5,7-bis(2-hydroxyethyl)adamantane into the corresponding diacrylic and dimethacrylic esters, (I), R = CH_3, R' = H, CH_3; A = $-CH_2-CH_2-$

1. Reaction with acrylyl chloride

To 5 g of 1,3-dimethyl-5,7-bis-(2-hydroxyethyl)adamantane (19.8 mmole) in 120 ml dry tetrahydrofurane (THF) containing 6.08 ml triethylamine (43.6 mmole) was added 3.52 ml acrylyl chloride (43.6 mmole) during a 25 min period, while maintaining the temperature at 45 - 50°C. Stirring was continued for 5 hrs at 60°C. The precipitated triethylamine hydrochloride was filtered off and washed with THF. The filtrate and washings were evaporated to dryness and the residue redissolved in benzene. The benzene was successively extracted with water, saturated bicarbonate solution and water and finally dried. Evaporation of the solvent provided 6.7 g (94%) of diacrylate (I), R = CH_3; R' = H A = $-CH_2-CH_2-$. Further purification was achieved by column chromatography on Al_2O_3 using chloroform as the eluent.

NMR Spectrum (CCl_4, TMS as internal standard, ppm (δ)

0.82 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$

1.11 (s,12H): adamantane-CH_2-

1.45 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

4.15 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

5.6 - 6.6 (complex m,6H): $-\underset{\underset{O}{\|}}{C}-CH=CH_2$

2.Reaction with methacrylyl chloride

The same condition as for the reaction with acrylyl chloride were found suitable, except for using instead 4.2 ml methacrylyl chloride (43.6 mmole). The yield was 7.3 g (95%) of dimethacrylate (I), R = R' = CH_3, A = $-CH_2-CH_2-$. Further purification was achieved by column chromatography on Al_2O_3 using chloroform as the eluent.

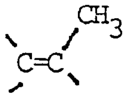
NMR Spectrum (CCl_4 solution, TMS as internal standard, ppm (δ)

0.83 (s,6H): $-C-CH_3$

1.13 (s,12H): adamantane-CH_2-

1.48 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

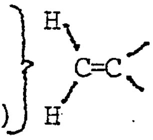
1.92 (d,6H, J = 1 cps):



4.12 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$

5.5 (m,2H)

6.03 (m,2H)



Example 4

Preparation of diacrylate and dimethacrylate esters of 1,3-bis-(2-hydroxyethyl)adamantane

(I), R = H; R' = H, CH_3; A = $-CH_2-CH_2-$

a) 1,3-adamantane-diacetic acid diethylester

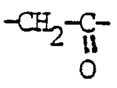
Esterification of commercially available 1,3-adamantane diacetic acid (Aldrich Chemical Co,Inc.) can be achieved by conventional techniques as mentioned heretofore. In this case, the acid chloride method was used. Thus, 20.8 g of 1,3-adamantane-diacetic acid (82.4 mmole) was boiled with 100 ml thionylchloride under reflux for 4 hrs. The excess thionylchloride was then evaporated off and the resulting crude acid chloride was dissolved in 65 ml carbon tetrachloride and subsequently treated with an excess absolute ethanol. The solvent and excess alcohol were stripped off and the crude diester was distilled under vacum.

BP 0.1 Torr = 149°-150°C. Yield 22.6 g (89%).

NMR spectrum (CCl_4 solution, TMS as internal standard, ppm(δ)

1.17 (t,6H, J = 7cps): $-O-CH_2-CH_3$

1.33 - 1,63: (complex m,12H) adamantane-CH_2-

1.97 (s,4H): 

$-CH_2-\underset{\underset{O}{\|}}{C}-$

2 (m,2H): 

adamantane-$\overset{|}{\underset{|}{C}}$-H

4.05 (q,4H, J = 7cps): $-O-CH_2-CH_3$

b) 1,3-bis-(2-hydroxyethyl)adamantane

This diol can be obtained by reducing the 1,3-adamantane-diacetic acid diethylester with lithium aluminium hydride:

To 5.65 g $LiAlH_4$ (148.9 mmole) in 185 ml dry ether was added 22.5 g of the diester (73 mmole) in 40 ml ether at such a rate as to maintain the solvent under gentle reflux. Refluxing was continued for a further 2.5 hrs and, thereafter, the excess $LiAlH_4$ was decomposed with ethylacetate and water. The reaction mixture was acidified with 20% H_2SO_4 and the organic layer was separated and washed to neutrality with water. Crystals of the pure diol then separated. Yield 12.6 g (77%)

NMR Spectrum (DMSO-d_6 solution, TMS as internal standard, ppm (δ)

$$1.03 - 1.7 \begin{cases} \text{(complex m, 12H): adamantane-CH}_2\text{-} \\ \text{(t,4H, J = 7.5 cps): -CH}_2\text{-CH}_2\text{-OH} \end{cases}$$

1.95 (m,2H): adamantane -C-H

3.48 (t,4H, J = 7.5 cps): $-CH_2-CH_2-OH$

4.08 (s,2H)

c) Esterification of 1,3-bis(2-hydroxyethyl)adamantane to give the corresponding diacrylic and dimethacrylic esters

(I), R = H, R' = H,CH_3; A = $-CH_2-CH_2-$

1. Reaction with acrylyl chloride

To 5 g (22.3 mmoles) of 1,3-bis(2-hydroxyethyl)adamantane in

120 ml of dry benzene containing 6.83 ml of triethylamine (49.1 mmoles) was added, at 45°C, 3.97 ml acrylyl chloride (49.1 mmoles). Stirring was continued for 5 hrs at 60°C, and the precipitated triethylamine hydrochloride was filtered off and washed with benzene. The combined filtrate and washings were extracted with water, saturated bicarbonate solution and water and finally dried. Evaporation of the solvent yielded 7.0 g (95%) of diacrylate (I), R = R' = H; A = $-CH_2-CH_2-$. Further purification was achieved by column chromatography on Al_2O_3 using chloroform as the eluent.

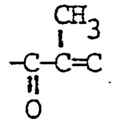
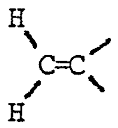
<u>NMR Spectrum</u> (CCl_4 solution, TMS as internal standard, ppm (δ) .

1.17 - 1.83 { (complex m, 12H): adamantane-CH_2-
(t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$
2.05 (m,2H): adamantane $-\overset{|}{\underset{|}{C}}-H$
4.22 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$
5.6 - 6.6 (complex m, 6H): $-CO-CH=CH_2$

2. <u>Reaction with methacrylyl chloride</u>

The same conditions were used as with the previous case but 4.74 ml (49.1 mmoles) of methacrylyl chloride was used instead of the acrylyl chloride. The yield was 7.78 g (97%) of dimethacrylate (I), R = H; R' = CH_3; A = $-CH_2-CH_2-$ Further purification was carried out by column chromatography (Al_2O_3; $CHCl_3$).

<u>NMR Spectrum</u> ($CDCl_3$, TMS as internal standard, ppm (δ) .

1.17 - 1.80 { (Complex m,12H): adamantane-CH_2
(t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$
1.96 (d,6H, J = 1 cps):

$-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=C$
~2. (m,2H): adamantane $-\overset{|}{\underset{|}{C}}-H$
4.23 (t,4H, J = 7.5 cps): $-CH_2-CH_2-O-$
5.58 (m,2H)
6.13 (m,2H) } :


<u>Example 5</u>

Preparation of diacrylate and dimethacrylate esters of 1,3-dimethyl-5,7-bis(p-hydroxyphenyl)adamantane

(I), R = CH_3, R' = H,CH_3, A = 

a) 1,3-dimethyl-5,7-bis(p-hydroxyphenyl)adamantane (IId)

Adamantane bisphenols can be readily made available from the corresponding dibromoderivatives and phenol according to US 3,594,427. Thus, 112 g of 1,3-dimethyl-5,7-dibromoadamantane (III) (0.35 m) (see Example 2a) and 900 g of phenol were heated together at 170°C for 6 hrs. After termination of the evolution of HBr, the mixture was heated to 220°C for a further 2 hrs period and the excess phenol was distilled off. The reaction mixture was poured into warm water and the white precipitate was filtered, washed with warm water and dried at 80°C under vacuum. Yield 117.8 g (97%). The product was recrystallyzed from toluene. MP: 222° - 224°C.

b) Esterification of the 1,3-dimethyl-5,7-bis(p-hydroxyphenyl)adamantane into the corresponding diacrylic and dimethacrylic esters

(I), R = CH_3; R = H, CH_3; A = .

1. Reaction with acrylyl chloride

To 5 g of 1,3-dimethyl-5,7-bis(p-hydroxyphenyl)adamantane (14.3 mmoles) in 120 ml dry tetrahydrofurane containing 4.4 ml triethylamine (31.6 mmoles) was added 2.55 ml acrylyl chloride (31.6 mmoles) during 25 min, while maintaining a reaction temperature of 45-50°C. Stirring was continued for 4 hrs at 60°C and the solvent was evaporated under vacuum. The crude reaction product (7 g) was crystallyzed from ethyl acetate. The yield was 5.2 g (80%) of pure diacrylate (I), R = CH_3; R' = H; A = p-Ph; MP: 145-147°C.

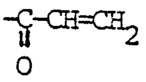
NMR Spectrum

0.95 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$

1.23 (s,2H): adamantane-CH_2-

1.55 (s,8H): adamantane-CH_2-

1.85 (s,2H): adamantane-CH_2-

5.8 - 6.8 (complex m,6H):  $-\underset{\underset{O}{\parallel}}{C}-CH=CH_2$

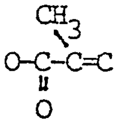
7.05 (d,4H, J = 9 cps) }
7.42 (d,4H, J = 9 cps) } :aromatic C-H

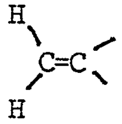
2. Reaction with methacrylyl chloride

This was performed as above but using, instead of the acrylyl chloride, 3.04 ml of methacrylyl chloride (31.6 mmole). The yield of dimethacrylate (I), R = R' = CH_3; A =  was 5.6 g (81%) MP: 159.5 - 161°C (from ethyl acetate).

NMR Spectrum

0.95 (s,6H): $-\overset{|}{\underset{|}{C}}-CH_3$
1.23 (s,2H): adamantane-CH_2-
1.57 (s,8H): adamantane-CH_2-
1.87 (s,2H): adamantane-CH_2-

2.03 (d,6H, J 1 cps) 
$O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{C}=C$

5.73 (m,2H) }
6.37 (m,2H) } : 

7.03 (d,4H, J = 9 cps) }
7.38 (d,4H, J = 9 cps) } : aromatic C-H

While p-phenylene was used in this example, it is expected that alkyl derivatives of phenylene could also be so utilized.

Example 6

Thermal and free radical polymerization of some monomers of LIST I

a) Thermal polymerization of the diacrylates.

The diacrylates (I) were subjected to heating neat at temperature ranging from 150 - 200°C until they had completely hardened. Required heating times were extremely variable, ranging from several minutes to several hours.

The compounds, identified by their substituants, the polymerization conditions and the results on hardness are summarized in Table 1 below.

TABLE 1

Thermal polymerization of adamantane diacrylates (I)

R	R'	A	T.°C	reaction time hr.	Hardness (Knoop)
CH_3	H	$-CH_2-$	150	1	-
CH_3	H	$-CH_2-$	200	0.1	18.33
H	H	$-CH_2-CH_2$	200	0.1	17.49
CH_3	H		150	12	-

b) Free radical catalyzed polymerization of the diacrylates and dimethacrylates.

The diacrylates and dimethacrylates (I) were free radical polymerized using small amounts of standard initiator catalysts and temperatures of 20 to 150°C depending on the kind of initiator. In this manner, very hard, colorless, transparent, highly cross-linked resins were obtained which were infusible and found insoluble in all solvents tried. The solvents tried were 1,1,1-trichloroethane; chloroform; 1,2-dichloroethane; benzene; toulene; xylene; acetone; methyl ethyl ketone; and butyl acetate. Examples are summarized below using lauroyl peroxide as the initiator. Compounds (I) are identified by their substituents R and R'.

TABLE 2

Free radical polymerization of adamantane diacrylates and dimethacrylates (I).

R	R'	A	Initiator (percent)	temp °C	Reaction time hrs	hardness (Knoop)
CH_3	H	$-CH_2$	(0.5)	80	4	22.29
CH_3	CH_3	$-CH_2$	(0.5)	90	4	29.80
H	CH_3	$-CH_2-CH_2$	(0.5)	90	12	25.84

Example 7

Photopolymerization of some monomers of LIST I

The monomers of formula (I) in liquid form, either neat (melted) or dissolved in other liquid olefinic compounds (e.g. acrylic acid, acrylates or acrylamides) were mixed with small amounts of standard photoinitiators (e.g. aromatic ketones) and spread with conventional means (including a doktor knife, painting, spraying and dipping) as thin layers (e.g. 1 to 10 μ) over transparent plates of organic glasses (e.g. polymethacrylates (LUCITE) or polycarbonates (MAKROLON, Bayer). Then, the coated plates were photopolymerized at various temperatures for periods ranging from a few seconds to about a minute using a ultraviolet light source. The organic glasses thus coated were totally inert when immersed into chlorinated solvents (e.g. $CHCl_3$, trichlorethylene, o-dichlorobenzene, etc.) whereas non coated controls will either swell or dissolve under the same conditions. Coatings obtained from conventional monomers such as hexanediol diacrylate, trimethylol-propane triacrylate or pentaerythritol tri- and tetra-acrylates were much less effective in the protection of organic glasses toward outside solvents. Further, the coatings made according to the invention were generally very hard and effectively protected the organic glasses from scratches resulting from accidental contacts with hard objects. Also their adhesive power was excellent and they could not be removed from such substrates by usual mechanical means.

Table 3, below, summarizes some results obtained from various compounds (I) identified again by the nature of their substituents R, R' and A which were photopolymerized in the presence of 1% of benzophenone as films about 5.8 μ thick deposited on substrates of either aluminum, polyester (MYLAR), polymethacrylate (LUCITE) or polycarbonate (MACROLON) and placed for 1 min at 25 cm from a PHILIPS HOK 1KW ultraviolet lamp, at the temperatures indicated in the table. Mixtures of monomers (I) and conventional monomers as well as controls obtained from conventional monomers and two of the bare substrate are also included in the table.

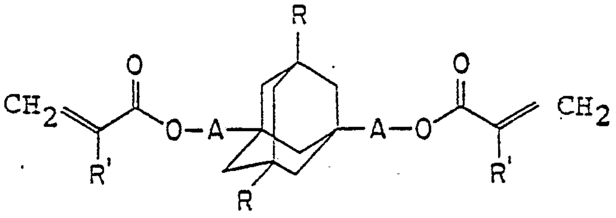
TABLE 3

Monomer (I)			Other monomer (M) (weight ratio(I) (M)	Substrate	Pol. temp. (°C)	Hardness (Knoop)	% weight loss at 450°C heating rate 6°C/ min in air	temperature of highest decompo- sition rate	Resistance to CHCl
R'	R	A							
H	CH_3		---	all	50	---	---	---	good
H	CH_3	CH_2	---	all	50	---	27.1	480	good
H	H	C_2H_4	---	all	20	---	64.7	420	good
H	CH_3		---	all	150	---	24.9	550	excellent
CH_3	CH_3		---	all	150	---	29.6	540	excellent
CH_3	CH_3	CH_2	---	all	20	28	---	---	good
CH_3	CH_3	C_2H_4	---	all	20	21	---	---	good
H	CH_3	CH_2	acrylic acid (2/1)	all	20	---	27.3	470	good
---	---	---	Hexane diol diacrylate (HDD)	all	20	---	77.8	420	poor
---	---	---	HDD + acrylic acid (2/1)	all	20	---	74.9	430	poor
---	---	---	none	MAKROLON (M)	---	13	---	---	no resistance
---	---	---	none	PLEXIGLASS	---	22	---	---	no resistance

Although the examples have been limited to methylene and ethylene, the propylene and butylene are additional homologs that one skilled in the art would expect to form similar compounds with but only a slight loss in hardness and strength properties.

CLAIMS

1. A compound having the formula



wherein R is a radical selected from the group consisting of hydrogen or methyl; R' is a radical selected from the group consisting of hydrogen or methyl; and A is either a sigma ( ) bond; or a radical satisfying the formula $(CH_2)n$ where n is an integer of from 1 through 4; or phenylene; or an alkyl derivative of phenylene.

2. Compounds according to claim 1, where

R = H or CH_3

R' = H or CH_3

A is a sigma (σ) bond

3. Compounds according to claim 1, where

R = H or CH_3

R' = H or CH_3

A = $-CH_2$ or $-CH_2-CH_2-$

4. A composite material which will withstand more than 24 hours immersion in chlorinated solvents without significant damage, comprising:

(a) a clear substrate of organic glass; and

(b) a very fine coating of cross-linked polymers resulting from the polymerization of monomers described in claims 1, 2, or 3.

5. A composite material as described in claim 4 where the thickness of the coating is in the range of 2 to 8 microns.

6. Cross-linked polymers obtained by the polymerization of the compounds of claim 1, 2, or 3, or the copolymerization of mixtures thereof.

7. Cross-linked resins obtained by copolymerizing the compounds

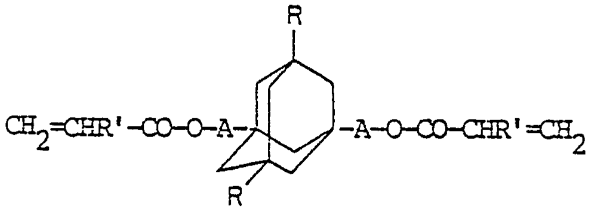
of claim 1, 2, or 3 in admixture with other copolymerizable acrylic monomers.

8. The cross-linked resins of claim 7, as obtained by thermal, free-radical, or photo-initialed polymerization methods.

9. The cross-linked resins of claim 7 having outstanding thermal resistance, up to the range of 400-450°C.

10. The cross-linked resins of claim 7 having knoop hardness exceeding 25.

11. Compounds of the formula



(I),

Wherein R and R' are hydrogen or methyl and A is a bond, a methylene, an ethylene or a phenylene group.

12. Compounds according to claim 11, selected from the group consisting of the following diesters:

Adamantane-diol acrylate and methacrylate;

dimethyl-adamantane-diol acrylate and methacrylate;

adamantane-dimethylol acrylate and methacrylate;

dimethyl-adamantane-dimethylol acrylate and methacrylate;

di-(hydroxyethyl)-adamantane acrylate and methacrylate;

dimethyl-di(hydroxyethyl)-adamantane acrylate and methacrylate; di-(hydroxyphenyl)-adamantane acrylate and methacrylate;

dimethyl-di-(hydroxyphenyl)-adamantane acrylate and methacrylate.

13. Cross-linked polymers obtained by the polymerization of the compounds of claim 11 or 12 or the copolymerization of mixtures thereof.

14. Cross-linked resins obtained by copolymerizing the compounds of claim 12 in admixture with other copolymerizable acrylic monomers.

15. The cross-linked resins of claim 14, as obtained by thermal-, radical- or photo-initiated polymerization methods.

16. The cross-linked resins of claim 14 having outstanding ther-

mal resistance, i.e. up to 400 - 450°C.

17. The cross-linked resins of claim 14 having KNOOP hardness better than 25.

18. Clear substrates made of organic glasses coated with a 2 to 8 µm layer of cross-linked polymer resulting from the polymerization of monomers according to claim 1, which will withstand more than 24 hrs immersion in chlorimated solvents without significant damage.

19. The compound of claim 1 wherein A is a sigma bond.

20. The compound of claim 1 wherein A is $-CH_2-$ or $-CH_2-CH_2-$.

21. The compound of claim 1 wherein A is a phenylene group.

22. The compound of claim 19, 20, or 21 wherein R and R' both are hydrogen.

23. The compound of claim 19, 20, or 21 wherein R and R' both are methyl groups.

24. The compound of claim 19, 20 or 21 wherein R is hydrogen and R' is a methyl group.

25. The compound of claim 19, 20 or 21 wherein R is a methyl group and R' is hydrogen.

INTERNATIONAL SEARCH REPOR -2-

International Application No PCT/EP 81/00066

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.^{3}: C 07 C 69/753; C 07 C 31/27; C 07 C 69/608;
C 07 C 39/17

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
International Searching Authority [1] EUROPEAN PATENT OFFICE Branch at The Hague P.O.Box 5818 Patentlaan ,2 2280 HV RIJSWIJK (ZH) The Netherlands	Signature of Authorized Officer [20] G.L.M. Kruydenberg

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 81/00066

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.^{3}: C 07 C 69/54; C 08 F 20/20; C 08 J 7/04;
//C 07 C 35/37; C 07 C 23/38; C 07 C 61/135 ./.

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int.Cl.^{3}	C 07 C 69/54

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	US, A, 3398165, published August 20, 1968, see the whole patent, I.N. Duling	1-3,11,12, 19-25
	US, A, 3518241, published June 30, 1970, see the whole patent, I.N. Duling	1-25
	US, A, 3342880, published September 19, 1967, see the whole patent, H.F. Reinhardt cited in the application	1-25
	Chemical Abstracts, volume 89, No. 14, published October 2, 1978, (Columbus, Ohio, US), S.S. Novikon et al. "Synthesis and polymerization of unsaturated adamantane derivatives", see page 1, the abstract No. 110434q, Izv. Akad. Nauk SSSR, Ser. Khim. 1977 (12), 2765-7 cited in the application	1-25

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
August 17, 1981	September 3, 1981
International Searching Authority [1]	**Signature of Authorized Officer [20]**
EUROPEAN PATENT OFFICE Branch at The Hague P.O.Box 5818 Patentlaan ,2 2280 HV RIJSWIJK (ZH) The Netherlands	G.L.M. Kruydenberg

Form PCT/ISA/210 (second sheet) (October 1977)