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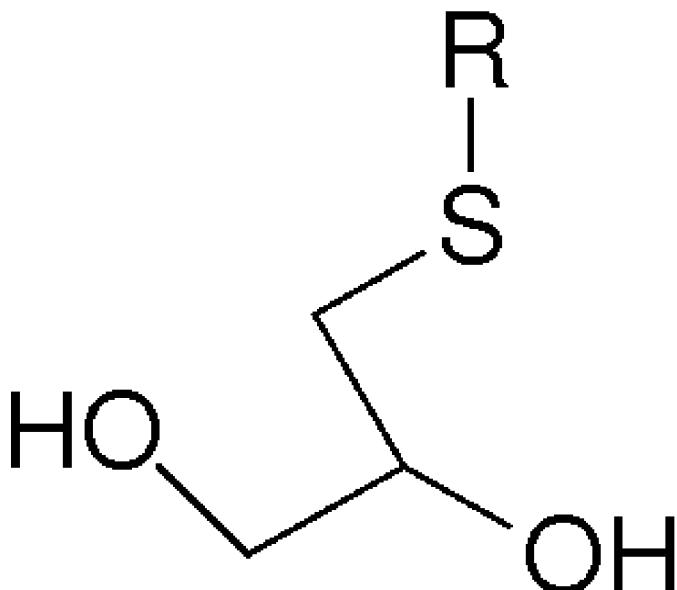
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[Continued on nextpage]

(54) Title: POLYURETHANE (METH) ACRYLATES USING MODIFIED HYDROXYTHIOLS



(57) Abstract: The invention provides intermediates of the formula: (I) as well as a method of their preparation by reacting a thiol having at least two hydroxyl groups with a mono-unsaturated organic compound in the presence of a base catalyst. A polymerizable urethane acrylate oligomer or urethane methacrylate oligomer is formed by reacting a polyisocyanate with the intermediate. The polymerizable urethane acrylate oligomer or urethane methacrylate is blended with a polymerization initiator to form a composition which is useful in such applications as adhesives.

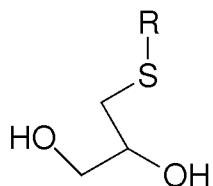
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POLYURETHANE (METH) ACRYLATES USING MODIFIED
HYDROXYTHIOLSBACKGROUND OF THE INVENTION10 Field of the Invention

The invention pertains to intermediates of the formula:



as well as a method of their preparation by reacting a thiol having at least two hydroxyl groups with a mono-unsaturated organic compound in the presence of a 15 base catalyst. A polymerizable urethane acrylate oligomer or urethane methacrylate oligomer is formed by reacting a polyisocyanate with the intermediate. The polymerizable urethane acrylate oligomer or urethane methacrylate is blended with a polymerization initiator to form a composition which is useful in such applications as adhesives.

20

Description of the Related Art

Curable adhesive compositions are well-known in the art. In the past, many adhesives particularly anaerobic adhesives, have been rendered resistant to 25 degradation at elevated temperatures by the inclusion of certain additives. For instance, U.S. Pat. No. 3,988,299 teaches a heat curable composition having

improved thermal properties, which includes certain acrylate monomers and maleimide compounds.

While the addition to curable adhesive compositions of such compounds to render them resistant to thermal degradation provides reaction products with acceptable performance, it would be desirable to find alternative compounds to include in such formulations. Thus, there is an on-going search for additives to improve the thermal performance of reaction products of curable adhesives. In addition, it would be desirable from a commercial, economic, environmental, supply and regulatory standpoint to provide alternatives and/or replacements for maleimide-type materials for improving the resistance to thermal degradation of reaction products of radical-curable adhesive compositions.

It has been unexpectedly found that improved adhesive formulations can be prepared by preparing intermediates by reacting a thiol having at least two hydroxyl groups with a mono-unsaturated organic compound in the presence of a base catalyst. When this intermediate is reacted with a polyisocyanate reactive acrylate or methacrylate a polymerizable urethane acrylate oligomer or urethane methacrylate oligomer is formed. When blended with a polymerization initiator a curable adhesive is formed. When applied to a substrate or carrier and cured by heating or actinic radiation, the adhesive results in a product having improved impact toughness and/or impact resistance useful in a wide variety of applications.

A composition of the invention includes polyurethane (meth)acrylate oligomers (prepolymers), and formulations thereof, which contain residues of modified hydroxythiols in the oligomeric chain. Within the context of this invention, the term (meth)acrylate means either an acrylate or a methacrylate. These polyurethane (meth)acrylate oligomers will have a wide range of properties

beneficial to industrial adhesive and coating applications due to the presence of both thioether functionality, which improve chemical and thermal resistance, and other functionalities that are incorporated through the hydroxythiol modification. Examples of such functionalities are carboxylic acids or other highly hydrophilic

5 groups for water reduction/dilution, anti-fog coatings, and adhesion; hydrophobic groups for water resistance, adhesion to plastics and high refractive index groups for optical applications; silicone bearing groups for decreased surface tension, improved impact resistance, and anti-graffiti coatings; and (meth)acrylate groups for increased crosslink density, strength, and hardness. Other functionalities

10 added to the oligomers change their pigment dispersion characteristics and therefore make them useful in inks. The ability to add pendant functionalities without compromising the physical properties such as tensile strength, scratch and chemical resistance, is especially important for commercial applications. For example in antifog coatings, having a high scratch and solvent resistance while

15 keeping the antifog properties are contradictory and challenging. Prior techniques require expansive nanoparticles to obtain the necessary properties. With the present method it is possible to obtain scratch and solvent resistant coatings with very good antifog properties.

20 The preparation of the inventive oligomers is by a two stage process with the first stage being the modification of the hydroxythiol with the desired functionality. This is carried out through Michael Addition reaction of the hydroxythiol with a composition containing both the functionality and units of unsaturation, particularly acrylate. The product will be a (poly)ol with the number of thioether

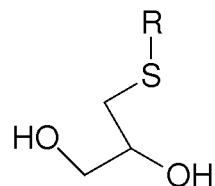
25 and functional groups equal to the starting number of thiol groups. This product, alone or with other polyols, is then reacted by standard methods with polyisocyanates and hydroxy (meth)acrylates or with monoisocyanate-

(meth)acrylates to produce the polyurethane (meth)acrylate oligomer bearing the thioether and desired functionality.

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SUMMARY OF THE INVENTION

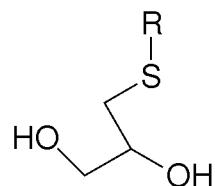
The invention provides an intermediate of the formula



wherein R is a linear or branched C₁ to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxy silane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative.

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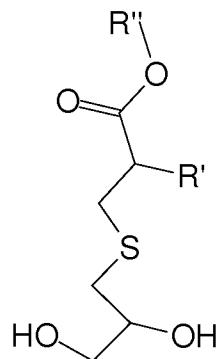
The invention also provides a method for forming an intermediate of the formula



wherein R is a linear or branched C₁ to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, alkoxy silane containing group, Si(OCH₃)₃ containing group, a fluorinated

alkyl group, a brominated alkyl group, or a benzene derivative, which comprises reacting a thiol having at least two hydroxyl groups with a mono-unsaturated organic compound in the presence of a base catalyst.

5 The invention further provides a method of forming a urethane acrylate or urethane methacrylate oligomer which comprises reacting a polyisocyanate with an intermediate of the formula



wherein

10 $R' = -H, -CH_3;$
 R'' is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxy silane containing group, $Si(OCH_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative.

15

The invention still further provides a polymerizable urethane acrylate oligomer or urethane methacrylate oligomer having one of the formulae (I), (II) or (III):

20

(I): $C-D-(I-D)_m-(P^2-D)_n-(I-D)_k-C,$

wherein:

C is a capping agent which is a monoalcohol acrylate having from 1 to 5 acrylate functionalities or a monoalcohol methacrylate having from 1 to 5 methacrylate functionalities;

D is a diisocyanate,

5 P² is a diol,

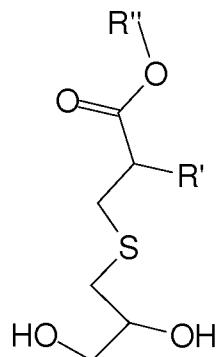
n is from 0 to 10;

m is from 1 to 5;

k is from 0 to 5;

I is an intermediate having the structure:

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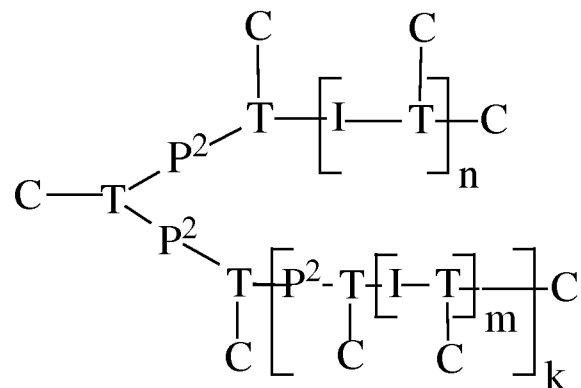
wherein

R' = -H, -CH₃;

15 R'' is a linear or branched C₁ to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative;

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(II):



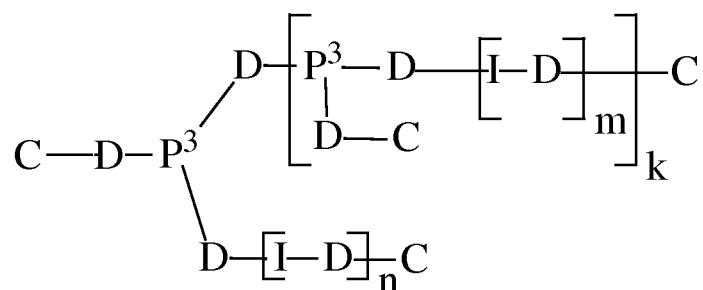
T is a triisocyanate;

n is from 1 to 10;

m is from 0 to 5;

5 k is from 1 to 10;

(III)



10 wherein P³ is a triol;

n is from 0 to 10;

m is from 1 to 5;

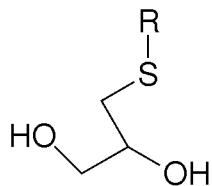
k is from 1 to 10.

15 The above polymerizable urethane acrylate oligomer or urethane methacrylate oligomer may further comprise a polymerization initiator.

DESCRIPTION OF THE INVENTION

In embodiment of the invention pertains to an intermediate compound of the formula

5



wherein R is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxy silane containing group, $Si(OCH_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative.

This intermediate compound may be prepared by reacting a thiol having at least two hydroxyl groups with a mono-unsaturated organic compound in the presence

15 of a base catalyst. Examples of a thiol having at least two hydroxyl groups non-exclusively include at least one of 1-thioglycerol, 1-thiobutane-2,3-diol, 2-thio-1,4-butanediol, 2,2 -bis(3-hydroxypropanoyloxymethyl)butyl-3-sulfanylpropionate, and 4-thio-1,16-hexanediol, 1-thiohexadecane-5,8-diol.

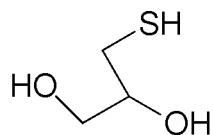
20 Non-exclusive examples of the mono-unsaturated organic compound comprises at least one of a monoacrylate, a mono (meth)acrylate, a mono allyl ether, a mono vinyl ether, maleic anhydride, a maleic anhydride ester and a maleic anhydride imide. More particularly, non-exclusive examples of the mono-unsaturated organic compound comprises at least one of a methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl

(meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, ethylene glycol phenyl ether acrylate, phenylthioethyl acrylate, ethylene glycol methyl ether (meth)acrylate, diethylene glycol methyl ether (meth)acrylate, poly(ethyleneglycol) methyl ether 5 (meth)acrylate, poly(propyleneglycol) methyl ether (meth)acrylate, silicone acrylate, 3-(trimethoxysilyl)propyl (meth)acrylate, 3-(triethoxysilyl)propyl (meth)acrylate, 3-trimethoxysilylpropyl (meth)acrylate, trifluoroethyl acrylate, tetrafluoropropyl acrylate, pentafluoropropyl acrylate, heptafluorobutyl acrylate, dodecafluoroheptyl acrylate, pentabromophenyl acrylate, allyl butyl ether, allyl propyl ether, allyl ethyl 10 ether, allyl methyl ether, allyl tetrafluoroethyl ether, allyl 1,1,2,3,3,3-hexafluoropropyl ether, allyl 2,4,6-tribromophenyl ether, cyclohexyl vinyl ether, dodecyl vinyl ether, ethylene glycol butyl vinyl ether, isobutyl vinyl ether, methyl vinyl ether, or propyl vinyl ether.

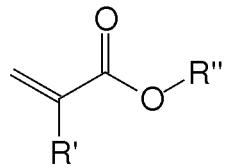
15 Useful examples of the base catalyst non-exclusively include diethyl ethanol amine, tri-n-butylamine, triethyl amine, 1,4-diazobicyclo[2.2.2]octane, triethanol amine, triisopropanol amine, dimethyl phenyl phosphine, and trioctyl phosphine.

An example of this method comprises reacting 1-thioglycerol of the formula

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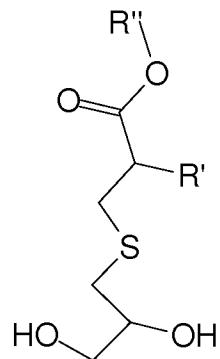


with a mono-acrylate or mono-methacrylate of the formula:



wherein $\text{R}' = -\text{H}, -\text{CH}_3$;

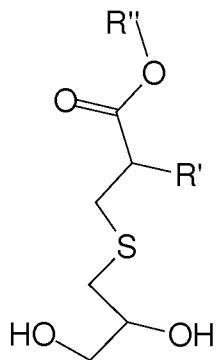
5 R'' is linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, $\text{Si}(\text{OCH}_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative, to
10 thereby form an intermediate of the formula:



15 The reaction may be conducted under the following general conditions:
Reagents such as 1-thioglycerol and mono (meth)acrylate, are blended in the molar ratio of thioglycerol : mono (meth)acrylate of 1 to about 3, or, preferably 1 to about 2, or more preferably 1 to about 1. When (meth)acrylate is taken in a ratio more than 1:1, the excess of non-reacted (meth)acrylate present in the

intermediate serves as a reactive diluent. A reaction vessel with 1-thioglycerol and mono (meth)acrylate is thermostatted at a temperature of from about 20 °C to about 100 °C, or preferably from about 30 °C to about 80 °C, or more preferably from about 55 °C to about 65 °C. A catalyst is added in a concentration of from 5 about 600 to about 1800 ppm, or, preferably from about 800 to about 1400 ppm, or more preferably from about 800 to about 1200 ppm. Useful examples of the base catalyst non-exclusively include diethyl ethanol amine, tri-n-butylamine, triethyl amine, 1,4-diazobicyclo[2.2.2]octane, triethanol amine, triisopropanol amine, dimethyl phenyl phosphine, and trioctyl phosphine. Typical reaction time 10 at 65 °C with a concentration of catalyst of from about 800 to about 1200 ppm is from about 2 to about 3 hours. An increase (decrease) of the temperature leads to acceleration (deceleration) of a reaction of the intermediate (I) formation.

Another embodiment of the invention is a method of forming a urethane oligomer 15 (prepolymer) which comprises reacting a polyisocyanate with an intermediate of the formula



wherein

R' = -H, -CH₃;

20 R'' is a linear or branched C₁ to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene

glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, $\text{Si}(\text{OCH}_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative. The polyisocyanate is preferably a diisocyanate, but may be a triisocyanate.

5 Reagents, intermediate (I) with a structure presented above, is blended with polyisocyanate in the equivalent ratio of OH-groups of I : NCO-groups of polyisocyanate of 1 to about 10, or, preferably 1 to about 5, or more preferably 1 to about 3. Polyisocyanate is taken in the equivalent ratio of more than 1:1, non-reacted NCO groups present as chemically bound to I or as free isocyanate. Non-reacted NCO groups can participate in further urethane formation reactions.

10 Reaction vessel with I and polyisocyanate is thermostatted at a temperature of from about 20 °C to about 100 °C, or, preferably from about 30 °C to about 80 °C, or more preferably from about 60 °C to about 70 °C. A catalyst should be added in the concentrations of from about 10 to about 1000 ppm, or, preferably from about 20 to about 700 ppm, or more preferably from about 50 to about 100 ppm.

15 Useful examples of the urethane links formation catalysts non-exclusively include dibutyltin dilaurate (DBTDL), stannous octoate, diazobicyclo[2.2.2]octane, bismuth catalysts of urethane formation. Typical reaction time at 65 °C with a concentration of catalyst 100 ppm was from about 3 to about 4 hours. An increase

20 (decrease) of the temperature leads to acceleration (deceleration) of a reaction of the intermediate formation.

Another embodiment of the invention is a polymerizable urethane acrylate oligomer or urethane methacrylate oligomer having one of the formulae (I), (II) or

25 (III):

(I): $\text{C-D-(I-D)}_m\text{-(P}^2\text{-D)}_n\text{-(I-D)}_k\text{-C,}$
wherein:

C is a capping agent which is a monoalcohol acrylate having from 1 to 5 acrylate functionalities or a monoalcohol methacrylate having from 1 to 5 methacrylate functionalities;

D is a diisocyanate,

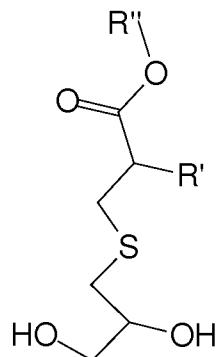
5 P² is a diol,

n is from 0 to about 10; preferably from 0 to about 6, and more preferably from 0 to about 3,

m is from 1 to about 5; preferably from 1 to about 2, more preferably 1 to about 2,

k is from 0 to 5; preferably from 0 to about 3, more preferably from 0 to about 1

10 I is an intermediate having the structure:



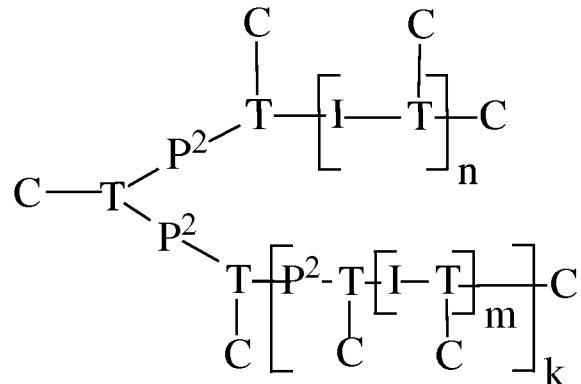
15 wherein

R' = -H, -CH₃;

R'' is a linear or branched C₁ to C₃ alkyl group, a linear or branched C₃ to C₃ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene

20 glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative;

(II):



T is a triisocyanate;

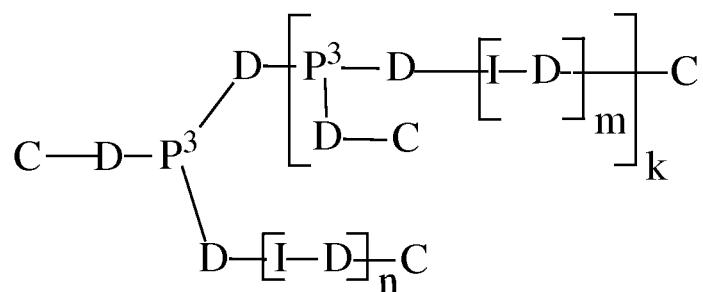
5 n is from 1 to about 10; preferably from 1 to about 6, and more preferably from 1 to about 2;

m is from 0 to about 5; preferably from 0 to about 3, and more preferably from 0 to 1;

k is from 1 to 10; preferably from 1 to about 6, and more preferably from 1 to about 2;

10

(III)



15 wherein P³ is a triol;

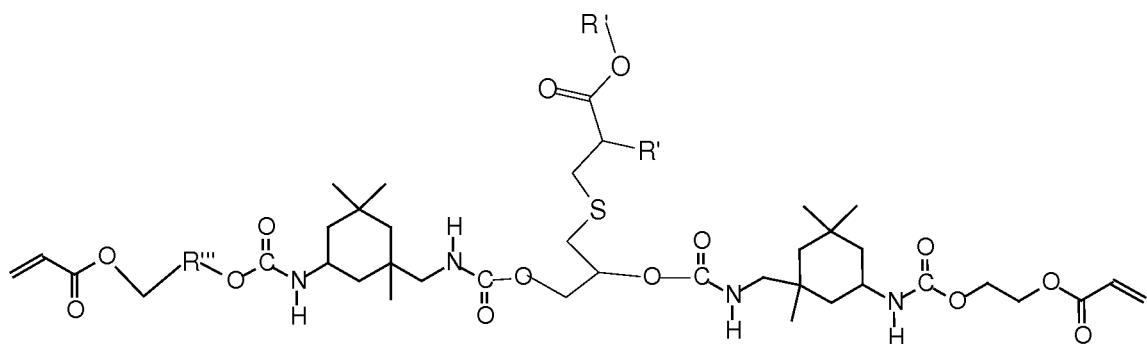
n is from 0 to about 10; preferably from 0 to about 6, more preferably from 0 to about 3,

m is from 1 to about 5; preferably from 1 to about 3, more preferably from 1 to about 2,

5 k is from 1 to about 10, preferably from 1 to about 6, more preferably from 1 to about 2.

In a preferred embodiment, the polymerizable composition comprises a urethane acrylate oligomer or urethane methacrylate oligomer of the formula:

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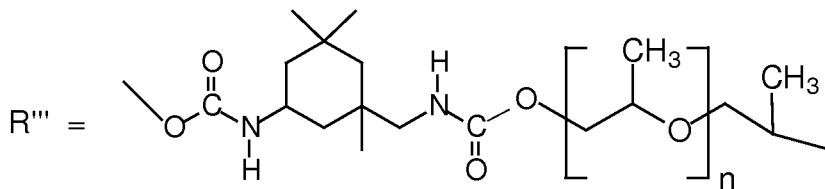


wherein n is 1 to 50,

15 R' = -H, -CH3;

R" = is a linear or branched C1 to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing

20 group, an alkoxy silane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative,



This reaction is a typical reaction of urethane (meth)acrylate formation with a suggested intermediate I as given about, or an intermediate with -NCO excess 5 described above. A suggested reaction of urethane (meth)acrylate formation is as follows. Reagents, polyol of OH-functionality 2 or 3, is blended with an excess of polyisocyanate of NCO-functionality 2 or 3 in the equivalent ratio of OH-groups of polyols : NCO-groups of polyisocyanate as 1 to about 7, or preferably 1 to about 5, or more preferably 1 to about 4. A reaction vessel with polyol and 10 polyisocyanate is themostatted at a temperature of from about 20 °C to about 100 °C, or, preferably from about 30 °C to about 80 °C, or more preferably from about 60 °C to about 70 °C. A catalyst should be added in the concentrations of from about 10 to about 1000 ppm, or, preferably from about 20 to about 700 ppm, or more preferably from about 50 to about 100 ppm. Useful examples of the 15 urethane links formation catalysts non-exclusively include dibutyltin dilaurate (DBTDL), stannous octoate, diazobicyclo[2.2.2]octane, bismuth catalysts of urethane formation. Typical reaction time at 65 °C with a concentration of catalyst 100 ppm is from about 3 to about 4 hours. An increase (decrease) of the temperature leads to acceleration (deceleration) of a reaction of urethane 20 prepolymer formation. Upon completion of a reaction indicated by termination of disappearance of NCO characteristic absorption in the IR spectrum, an intermediate I is added to the mixture which has non-reacted NCO. It is a stage of chain extension. I is added to the mixture the way that the ratio of equivalents of non-reacted NCO : equivalents OH of I is about 8:1, or, preferably about 5:1, or 25 more preferably from about 2:1. Reaction is continued at the same temperature as

the first reaction of a prepolymer formation. Typical reaction time at 65 °C with a concentration of catalyst 100 ppm is from about 5 to about 6 hours. Upon completion of a reaction indicated by termination of disappearance of NCO characteristic absorption in the IR spectrum, a capping agent - hydroxyl substituted acrylate or methacrylate is added to the mixture which has residual non-reacted NCO. Upon completion of a capping reaction indicated by complete disappearance of NCO characteristic absorption in the IR spectrum the final urethane (meth)acrylate is formed. Typical reaction time at 65 °C with a concentration of catalyst 100 ppm is from about 8 to about 10 hours. A concentration of a capping agent is selected the way that a number of OH-equivalents of the capping agent is equal to a number of residual non-reacted NCO.

Another embodiment of the invention is a polymerizable composition comprising the above polymerizable urethane acrylate oligomer or urethane methacrylate oligomer and a polymerization initiator. Useful polymerization initiators non-exclusively include at least one of a peroxide, an azo compound, an organic, free radical polymerizable monomer, oligomer or polymer having at least one olefinically unsaturated double bonds. Examples of useful polymerization initiator comprises at least one of benzoyl peroxide, cumyl peroxide, 2,2'-azobis(2-methylpropionitrile) (AIBN), *tert*-butyl hydroperoxide, diethyl ether peroxide, bis(2-tertiary-butylcyclohexyl)peroxydicarbonate, cumyl hydroperoxide and aliphatic hydroperoxides.

Other polymerization initiators comprise the least one free radical polymerizable component which is present in an amount sufficient to polymerize the urethane acrylate or methacrylate oligomer upon exposure to sufficient actinic radiation.

Suitable polymerization initiators comprises a free radical polymerization initiator component which preferably photolytically generates free radicals. Examples of free radical generating components include photoinitiators which themselves photolytically generate free radicals by a fragmentation. Suitable initiators include 5 aromatic ketones. Preferred examples thereof include benzophenone, benzoin, acetoin, acyloin, diketone, xanthone, thioxanthone, and ketocoumarin derivatives. Specific examples include benzophenone (CAS 119-61-9); Michler's ketone (CAS 90-94-1); benzoin methyl ether (CAS 3524-62-7); benzoin ethyl ether (CAS 574-09-4); 2-hydroxy-2-methylpropiophenone (CAS 7473-98-5); 1- 10 hydroxycyclohexyl phenyl ketone (CAS 947-19-3); 2,2-diethoxyacetophenone (CAS 6175-45-7); camphorquinone (CAS 10373-78-1); 2-ethylanthraquinone (CAS 84-51-5);; 2-tert-butylanthraquinone (CAS 84-47-9; 2,3-dichloro-1,4- naphthoquinone (CAS 117-80-6) 2-hydroxy-4'-(2-hydroxyethoxy)-2- 15 methylpropiophenone (CAS 106797-53-9); methyl benzoylformate (CAS 15206- 55-0); 2,2-dimethoxy-2-phenylacetophenone (CAS 24650-42-8); 2-ethylhexy-4- (dimethylamino)benzoate (CAS 21245-02-3); 2-ethyl-4-(dimethylamino)benzoate (CAS 10287-53-3); 2-isopropylthioxanthone (CAS 5495-84-1); 4- phenylbenzophenone (CAS 2128-93-0); and 2-benzyl-2-(dimethylamino)-4'- 20 morpholinobutyrophenone (CAS 119313-12-1). In addition, suitable photoinitiators include phosphine oxides, such as diphenyl(2,4,6- trimethylbenzoyl)phosphine oxide (CAS 75980-60-8); and phenylbis(2,4,6- trimethylbenzoyl)phosphine oxide (CAS 162881-26-7).

The free radical generating component is preferably present in an amount 25 sufficient to effect polymerization of the urethane acrylate or methacrylate oligomer compound upon exposure to sufficient actinic radiation, especially in the visible and/or ultraviolet region of the electromagnetic spectrum. The polymerization initiator may comprise from about 0.1 wt. % to about 50 wt. % of

the non-solvent parts of the overall polymerizable composition, more preferably from about 0.1 wt. % to about 10 wt. %.

5 The overall polymerizable composition of the invention finds use as an adhesive or a coating composition. Although the radiation curable composition may comprise a compatible solvent, preferably the composition is substantially free of solvents, such as organic, nonreactive solvents.

10 The polymerizable composition may be prepared by admixing the composition components until a substantially homogenous fluid is formed. In one use, the polymerizable composition is formed and then exposed to sufficient actinic radiation to initiate the polymerization of the polymerizable urethane acrylate or methacrylate component. In another embodiment, the polymerizable composition is applied as a coating onto a surface and then exposed to sufficient 15 actinic radiation to initiate the polymerization of the urethane acrylate or methacrylate component. In another embodiment, the polymerizable composition in the form of an adhesive is applied to a first surface and then contacting a second surface to the radiation curable composition, and then exposing the radiation curable adhesive composition to sufficient actinic radiation to initiate the 20 polymerization of said polymerizable component while maintaining contact of the radiation curable adhesive composition with the first surface and the second surface. The polymerization of the polymerizable component may be initiated by exposure to visible and/or ultraviolet. In one embodiment, the polymerization of said polymerizable component may be initiated by exposure to radiation having a 25 wavelength of from about 300 nm to about 465 nm, preferably about 360 nm to about 410 nm. In another embodiment, the polymerization of the polymerizable component may be initiated by exposure to ultraviolet radiation, visible radiation, or combinations thereof, by means of a light emitting diode such as those having

an emission wavelength of from about 360 nm to about 465 nm, preferably about 380 nm to about 410 nm.

The length of time for exposure is easily determined by those skilled in the art and
5 depends on the selection of the particular components of the radiation curable
composition. Typically exposure ranges from about 1 second to about 60
seconds, preferably from about 2 seconds to about 30 seconds, and more
preferably from about 2 seconds to about 15 seconds. Typical exposure intensities
range from about 5 mW/cm² to about 600 W/cm², preferably from about 10
10 mW/cm² to about 450 W/cm², and more preferably from about 50 mW/cm² to
about 300 W/cm².

Polymerizable composition which are Adhesive compositions according to the
present invention may also contain other common adjuvants and additives, such
15 as plasticizers, reactive and/or non-reactive diluents, flow auxiliaries, wetting
agents, tackifiers, flame retardants, thixotropic and/or rheology control agents,
ageing and/or corrosion inhibitors, stabilizers and/or coloring pigments.
Depending on the requirements made of the adhesive application with respect to
its processing properties, its flexibility, the required rigidifying action and the
20 adhesive bond to the substrates, the relative proportions of the individual
components may vary within comparatively wide limits which are easily
determinable by those skilled in the art.

The following non-limiting examples serve to illustrate the invention.

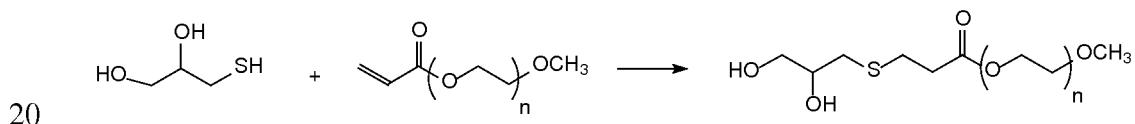
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EXAMPLE 1

Stage 1 - Hydroxythiol Modification

5 An amount of methoxypolyethyleneglycol monoacrylate (with 12 ethylene glycol repeating units) was added to a reaction vessel together with small amounts of methyldiethanolamine, as catalyst, and hydroquinone methyl ether, As an inhibitor of free-radical polymerization. Stirring was started and the batch warmed to 40 °C. 2-Thioglycerol was added incrementally to control exothermic activity. The equivalent ratio of methoxypolyethyleneglycol monoacrylate and thioglycerol was 1:1. After exothermic activity ceased the batch was warmed to 10 65 °C and cooked for 2 hours. The reaction yielded >98% yield as determined by GPC with no free thioglycerol. This was confirmed by FTIR with no -SH being detected. The -OH equivalent weight of the product was calculated by dividing 15 the total weight of the batch by the number of thioglycerol equivalents added.

The Stage 1 reaction scheme is given below.



Stage 2 - Urethane Acrylate Synthesis

An amount of isophorone diisocyanate was added to a reaction vessel at room temperature. Heating jacket temperature was adjusted to 45 °C suspended in a room temperature water bath and stirred. When the reaction batch temperature was 45 °C, dibutyltin dilaurate (DBTDL), as catalyst, and 4-methoxy phenol (MEHQ), as free-radical polymerization inhibitor, were also added. Pentaerytritol

triacrylate was added incrementally to control exothermic activity. When the exothermic activity ceased, the result of Stage 1 was added and batch temperature was adjusted to 60 °C. The batch was kept at 60 °C until no free isocyanate was detected by FTIR. Reaction scheme is given below. Viscosity of the product was 5 13,000 cP at 25 °C. and it readily mixes with water. When the product was diluted with equal amount (by weight) of water viscosity was 50 cP at 25 °C.

EXAMPLE 2

10 Stage 1 - Hydroxythiol Modification

An amount of methoxypolyethyleneglycol monoacrylate (with 23 ethylene glycol repeating units) was added to a reaction vessel together with small amounts of methyldiethanolamine, as catalyst, and hydroquinone methyl ether, as an inhibitor of free-radical polymerization. Stirring was started and the batch warmed to 40 15 °C. 2-Thioglycerol was added incrementally to control exothermic activity. The equivalent ratio of methoxypolyethyleneglycol monoacrylate and thioglycerol was 1:1. After exothermic activity ceased the batch was warmed to 65 °C and cooked for 2 hours. The reaction yielded >98% yield as determined by GPC with no free thioglycerol. This was confirmed by FTIR with no -SH being detected. 20 The -OH equivalent weight of the product was calculated by dividing the total weight of the batch by the number of thioglycerol equivalents added.

Stage 2 - Urethane Acrylate Synthesis

25 An amount of dicyclohexylmethane-4,4'-diisocyanate ($H_{12}MDI$) was added to a reaction vessel at room temperature. Heating jacket temperature was adjusted to 45 °C suspended in a room temperature water bath and stirred. When the reaction batch temperature was 45 °C, dibutyltindilaurate, as catalyst, and hydroquinone

methyl ether, as free-radical polymerization inhibitor, were also added.

Pentaerytritol triacrylate was added incrementally to control exothermic activity.

When the exothermic activity ceased the result of Stage 1 was added and batch temperature was adjusted to 60 °C. The batch was kept at 60 °C until no free

5 isocyanate was detected by FTIR. Viscosity of the result was 11,750 cP at 25 °C and it readily mixes with water. When the result was diluted with equal amount (by weight) of water viscosity was 150cP at 25°C.

EXAMPLE 3

10

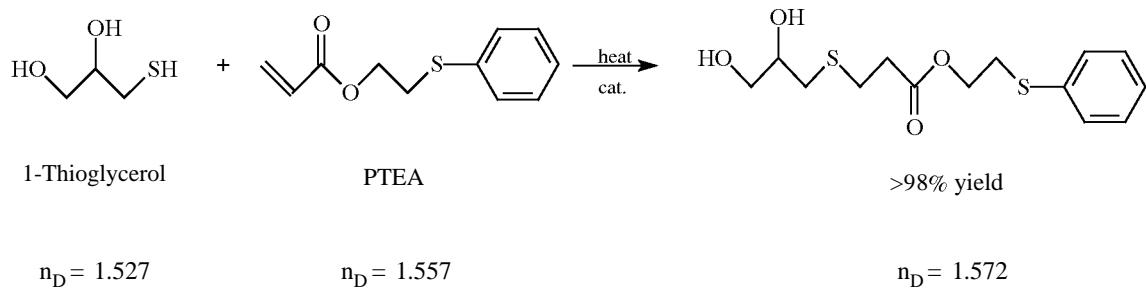
Stage 1 - Hydroxythiol Modification

An amount of phenylthioethylacrylate (PTEA) was added to a reaction vessel together with small amounts of methyldiethanolamine, as catalyst, and hydroquinone methyl ether, as an inhibitor of free-radical polymerization.

15 Stirring was started and the batch warmed to 40 °C. 1-Thioglycerol was added incrementally to control exothermic activity. The equivalent ratio of PTEA_{acrylate}:ThioglycerolH was 1:1. After exothermic activity ceased the batch was warmed to 65 °C and cooked for 2 hours. The reaction yielded >98% yield as determined by GPC with no free thioglycerol. This was confirmed by FTIR
20 with no -SH being detected. The -OH equivalent weight of the product was calculated by dividing the total weight of the batch by the number of thioglycerolH equivalents added.

The Stage 1 reaction scheme is given below.

25



5

Stage 2 - Urethane Acrylate Synthesis

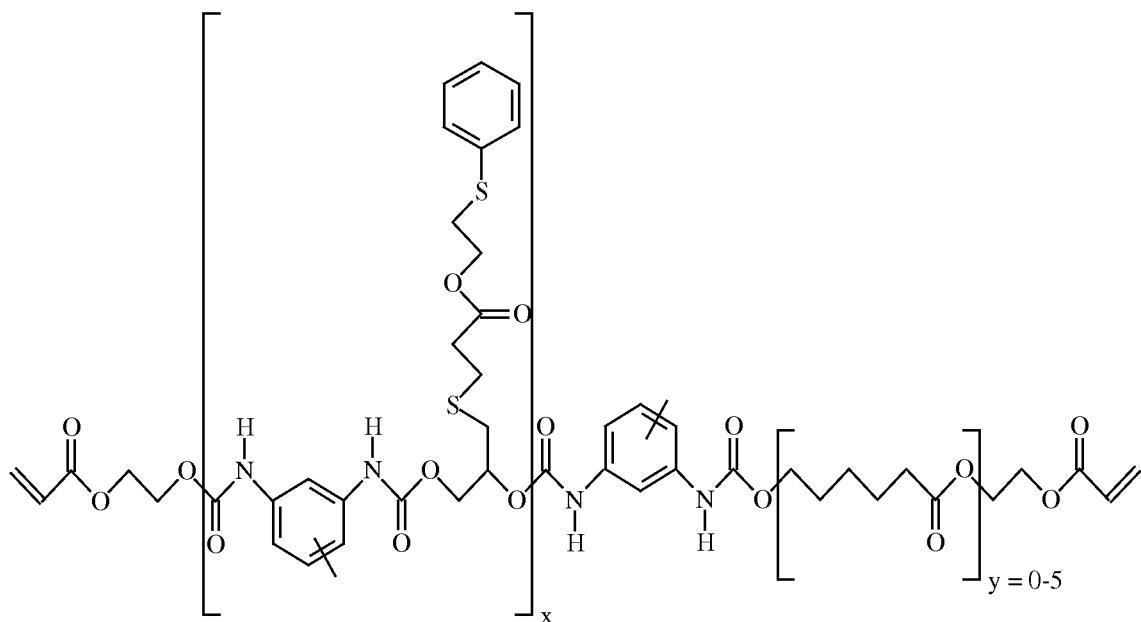
An amount of toluene diisocyanate was added to a reaction vessel suspended in a room temperature water bath and stirred. The above product from Stage 1 was added incrementally to control exothermic activity. When the exothermic activity

10 ceased the batch was heated to 82 °C and cooked for 1 hour. After the one hour cook the batch was cooled to 70 °C and polycaprolactone acrylate was added followed by an addition of hydroxyethylacrylate (HEA). A small amount of dibutyltindilaurate, a urethane catalyst, was also added to aid bringing the reaction to completion. The batch was cooked at 82 °C until no free isocyanate was

15 detected by FTIR. The equivalent ratio of TDLStage 1 product:polycaprolactone acrylate:HEA was 2.0:1.0:0.5:0.5.

The theoretical structure of the urethane acrylate product is given below. Its n_D was measured at 1.555.

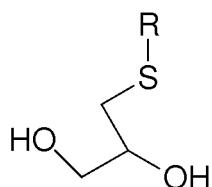
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While the present invention has been particularly shown and described with reference to preferred embodiments, it will be readily appreciated by those of ordinary skill in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. It is intended that the claims be interpreted to cover the disclosed embodiment, those alternatives which have been discussed above and all equivalents thereto.

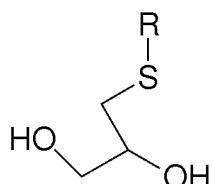
What is claimed is:

1. An intermediate of the formula



5 wherein R is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxy silane containing group, $Si(OCH_3)_3$ containing group, a 10 fluorinated alkyl group, a brominated alkyl group, or a benzene derivative.

2. A method for forming an intermediate of the formula



wherein R is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, alkoxy silane containing group, $Si(OCH_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative, which comprises 15 reacting a thiol having at least two hydroxyl groups with a mono-unsaturated 20 organic compound in the presence of a base catalyst.

3. The method of claim 2 wherein the thiol comprises at least one of 1-thioglycerol, 1-thiobutane-2,3-diol, 2-thio-1,4-butanediol, 2,2 -bis(3-hydroxypropanoyloxymethyl)butyl-3-sulfanylpropionate, and 4-thio- 1,16-hexanediol, 1-thiohexadecane-5,8-diol.

5

4. The method of claim 2 wherein the mono-unsaturated organic compound comprises at least one of a monoacrylate, a mono (meth)acrylate, a mono allyl ether, a mono vinyl ether, maleic anhydride, a maleic anhydride ester and a maleic anhydride imide.

10

5. The method of claim 2 wherein the mono-unsaturated organic compound comprises at least one of a methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate,

15

tetrahydrofurfuryl (meth)acrylate, ethylene glycol phenyl ether acrylate, phenylthioethyl acrylate, ethylene glycol methyl ether (meth)acrylate, diethylene glycol methyl ether (meth)acrylate, poly(ethyleneglycol) methyl ether

(meth)acrylate, poly(propyleneglycol) methyl ether (meth)acrylate, silicone acrylate, 3-(trimethoxysilyl)propyl (meth)acrylate, 3-(triethoxysilyl)propyl (meth)acrylate, 3-

20

ftrimethoxysilylethyl (meth)acrylate, trifluoroethyl acrylate, tetrafluoropropyl acrylate, pentafluoropropyl acrylate, heptafluorobutyl acrylate, dodecafluoroheptyl acrylate, pentabromophenyl acrylate, allyl butyl ether, allyl propyl ether, allyl ethyl ether, allyl methyl ether, allyl tetrafluoroethyl ether, allyl 1,1,2,3,3,3-

hexafluoropropyl ether, allyl 2,4,6-tribromophenyl ether, cyclohexyl vinyl ether,

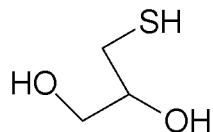
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dodecyl vinyl ether, ethylene glycol butyl vinyl ether, isobutyl vinyl ether, methyl vinyl ether, or propyl vinyl ether.

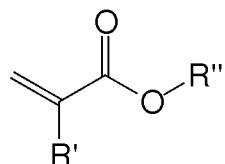
6. The method of claim 2 wherein the base catalyst comprises at least one of diethyl ethanol amine, tri-n-butylamine, triethyl amine, 1,4-diazobicyclo[2.2.2]octane, triethanol amine, triisopropanol amine, dimethyl phenyl phosphine, trioctyl phosphine.

5

7. The method of claim 2 which comprises reacting 1-thioglycerol of the formula

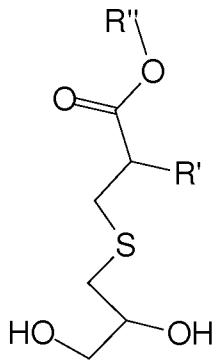


10 with a mono-acrylate or mono-methacrylate of the formula:

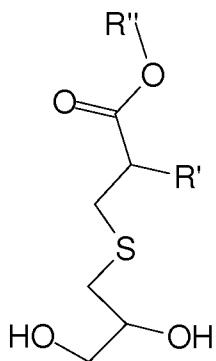


wherein R' = -H, -CH₃;

15 R'' is linear or branched C₁ to C₃₀ alkyl group, a linear or branched C₃ to C₃₀ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, Si(OCH₃)₃ containing group, a
20 fluorinated alkyl group, a brominated alkyl group, or a benzene derivative, to thereby form an intermediate of the formula:



8. A method of forming a urethane acrylate or urethane methacrylate oligomer
 5 which comprises reacting a polyisocyanate with an intermediate of the formula



wherein

$R' = -H, -CH_3;$

R'' is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30}
 10 alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a
 (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene
 glycol mono ethyl ether containing group, a lauryl group, a silicone containing
 group, an alkoxysilane containing group, $Si(OCH_3)_3$ containing group, a
 fluorinated alkyl group, a brominated alkyl group, or a benzene derivative.

15

9. The method of claim 8 wherein the polyisocyanate comprises a diisocyanate.

10. A polymerizable urethane acrylate oligomer or urethane methacrylate oligomer having one of the formulae (I), (II) or (III):

5 (I): $C-D-(I-D)_m-(P^2-D)_n-(I-D)_k-C$,

wherein:

C is a capping agent which is a monoalcohol acrylate having from 1 to 5 acrylate functionalities or a monoalcohol methacrylate having from 1 to 5 methacrylate functionalities;

10 D is a diisocyanate,

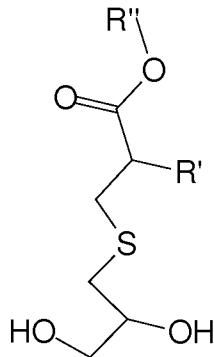
P^2 is a diol,

n is from 0 to 10;

m is from 1 to 5;

k is from 0 to 5;

15 I is an intermediate having the structure:



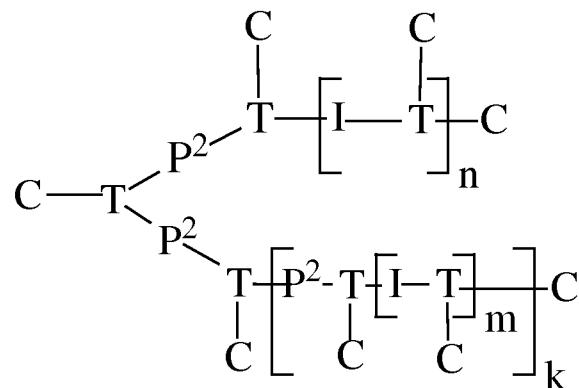
wherein

$R' = -H, -CH_3$;

20 R'' is a linear or branched C_1 to C_{30} alkyl group, a linear or branched C_3 to C_{30} alkenyl group, a C_6 to C_{22} aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene

glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxy silane containing group, $\text{Si}(\text{OCH}_3)_3$ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative;

5 (II):



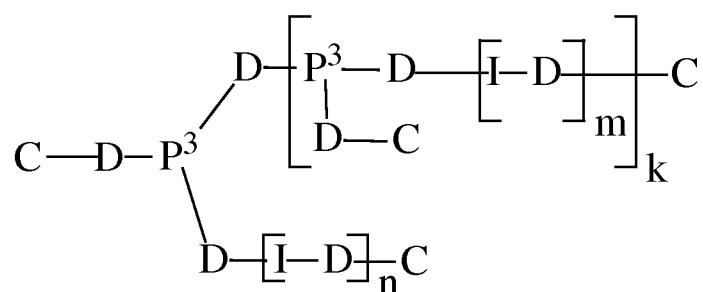
T is a triisocyanate;

n is from 1 to 10;

m is from 0 to 5;

10 k is from 1 to 10;

(III)



15 wherein P^3 is a triol;

n is from 0 to 10;

m is from 1 to 5;

k is from 1 to 10.

5 11. The polymerizable urethane acrylate oligomer or urethane methacrylate oligomer of claim 10 having the formula:

(I): $C-D-(I-D)_m-(P^2-D)_n-(I-D)_k-C$,

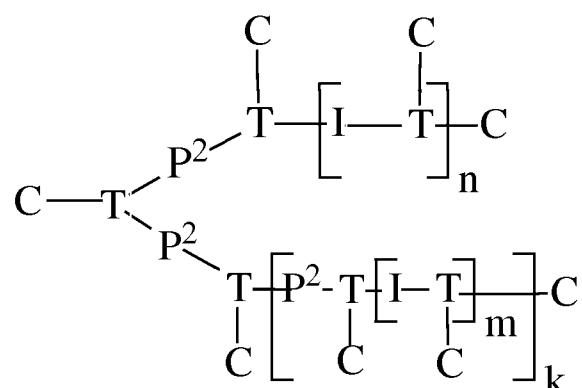
wherein:

10 n is from 0 to 10;

m is from 1 to 5;

k is from 0 to 5.

15 12. The polymerizable urethane acrylate oligomer or urethane methacrylate oligomer of claim 10 having the formula:



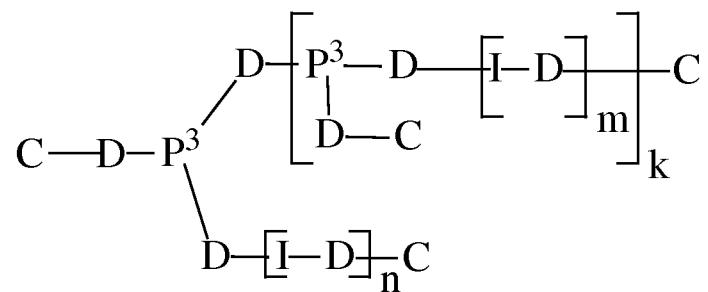
20 wherein:

n is from 1 to 10;

m is from 0 to 5;

k is from 1 to 10.

13. The polymerizable urethane acrylate oligomer or urethane methacrylate
5 oligomer of claim 10 having the formula:



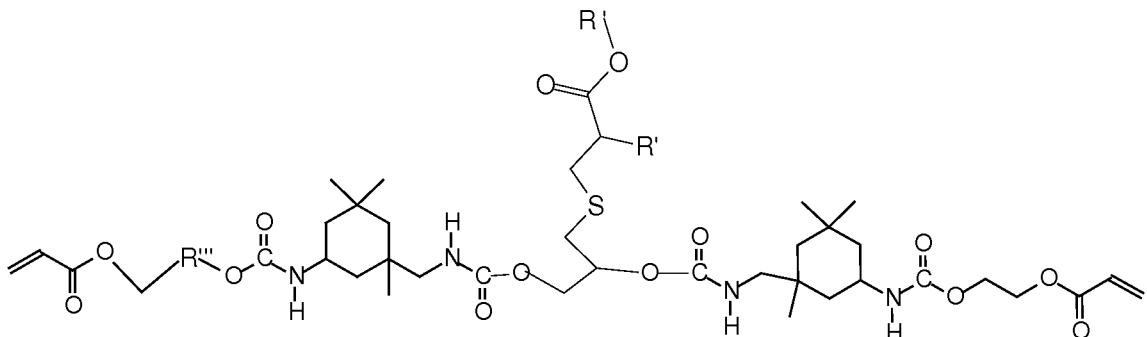
wherein:

10 n is from 0 to 10;

m is from 1 to 5;

k is from 1 to 10.

14. The polymerizable composition of claim 10 which comprises a urethane
15 acrylate oligomer or urethane methacrylate oligomer of the formula:

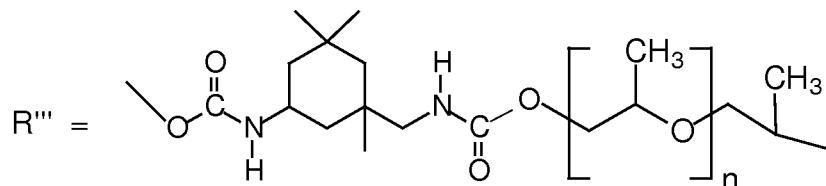


wherein n is 1 to 50

5 R' = -H, -CH₃;

R'' = is a linear or branched C₁ to C₃ alkyl group, a linear or branched C₃ to C₃ alkenyl group, a C₆ to C₂₂ aryl group, a polyethylene glycol containing group, a (poly)ethylene glycol mono methyl ether containing group, a (poly)ethylene glycol mono ethyl ether containing group, a lauryl group, a silicone containing group, an alkoxysilane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative,

10 group, an alkoxysilane containing group, Si(OCH₃)₃ containing group, a fluorinated alkyl group, a brominated alkyl group, or a benzene derivative,



15 15. A polymerizable composition comprising the polymerizable urethane acrylate oligomer or urethane methacrylate oligomer of claim 10, and a polymerization initiator.

16. The polymerizable composition of claim 15 wherein the polymerization initiator comprises at least one of a peroxide, an azo compound, an organic, free radical polymerizable monomer, oligomer or polymer having at least one olefinically unsaturated double bonds.

5

17. The polymerizable composition of claim 15 wherein the polymerization initiator comprises at least one of benzoyl peroxide, cumyl peroxide, 2,2'-azobis(2-methylpropionitrile) (AIBN), *tert*-butyl hydroperoxide, diethyl ether peroxide, bis(tertiary-butyldicyclohexyl)peroxydicarbonate, cumyl hydroperoxide and aliphatic hydroperoxides.

18. The polymerizable composition of claim 15 wherein the polymerization initiator comprises the least one free radical polymerizable component which is present in an amount sufficient to polymerize the urethane acrylate or methacrylate oligomer upon exposure to sufficient actinic radiation.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/29961

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G03C 1/00; G03F 7/00 (201 1.01)
USPC - 430/281 .1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 USPC: 430/281 .1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 USPC: 525/535; 528/360; 528/373 (see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 Electronic Database Searched: PUBWEST (PGPUB, EPAB, JPAB, USPT), Google. Search Terms Used urethane acrylate, urethane methacrylate, polyisocyanate, diisocyanate, hydroxy thiol, hydroxythiol, 1-thiobutane, 1-thioglycerol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- A	US 3,065,21 1 A (Miford et al.) 20 November 1962 (20.1 1.1962) especially col 2, In 7	1 --- 2-18
A	US 2010/0056722 A 1 (Thomas et al.) 04 March 2010 (04.03.2010) especially para [0023]-[0026]	2-18
A	US 6,596,786 B2 (Purvis et al.) 22 July 2003 (22.07.2003) especially abstract; col 4, In 11-40	2-18

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published 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
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 2011 (17.05.2011)	07 JUN 2011
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774