



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> : <b>C08F 2/50, 16/32, 26/02, 299/06, C07C 69/347, 69/767</b>		<b>A1</b>	(11) International Publication Number: <b>WO 95/05403</b>
			(43) International Publication Date: 23 February 1995 (23.02.95)
(21) International Application Number: PCT/US94/08203		(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 20 July 1994 (20.07.94)		<b>Published</b> <i>With international search report.</i>	
(30) Priority Data: 08/107,867      18 August 1993 (18.08.93)      US 08/108,212      18 August 1993 (18.08.93)      US			
(71) Applicant: ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US).			
(72) Inventors: PLOTKIN, Jeffrey, S.; 7 Carpenter Court, Monsey, NY 10952 (US). MILLER, Mark, M.; 59 E. Ridgewood Avenue, Ridgewood, NY 07450 (US).			
(74) Agents: MAUE, Marilyn, J. et al.; International Specialty Products, 1361 Alps Road, Wayne, NJ 07470 (US).			
(54) Title: RADIATION CURABLE ALK-1-ENYL ETHER POLYESTER PREPOLYMERS			
$(R_6CH=CHOR_4O-)_2 - [ (COACO-OR_1CHO)_m COACO ] - \quad (I)$ $R_2OCH=CHR_5$			
(57) Abstract			
<p>This invention relates to alk-1-enyl ether-polyester block prepolymers which are curable by cationically initiated radiation and which are defined by formula (I), wherein m has a value of from 1 to 25; A is C<sub>2</sub> to C<sub>12</sub> alkylene, C<sub>6</sub> to C<sub>14</sub> arylene, both groups optionally substituted with lower alkyl, halo lower alkyl, alkyleneoxy, halogen, aryl or NHA'NH wherein A' is the same as A; R<sub>1</sub> is alkylene containing from 1 to 6 carbon atoms; R<sub>2</sub> is a saturated or unsaturated divalent radical containing from 1 to 14 carbon atoms and is selected from the group of alkylene, alkenylene and arylene, each group optionally substituted with oxygen, halogen, lower alkyl and/or hydroxy; R<sub>5</sub> is hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl; R<sub>4</sub> is C<sub>1</sub> to C<sub>6</sub> alkylene, C<sub>6</sub> to C<sub>14</sub> arylene, lower alkyl substituted phenylene or xylylene and R<sub>6</sub> is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl. The invention also relates to the method of preparing and curing the above prepolymer and to the use of the cured prepolymer as a hard, flexible protective coating possessing high density and superior resistance to abrasion and chemical attack.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

RADIATION CURABLE ALK-1-ENYL  
ETHER POLYESTER PREPOLYMERS

In one aspect, the present invention relates to novel prepolymers containing polyurethanyl groups and a plurality of alk-1-enyl ether crosslinking sites. In another aspect the invention relates to the preparation of said prepolymers and in still another aspect the invention relates to cured coatings of said prepolymers.

BACKGROUND OF THE INVENTION

It is known that certain polyester coating materials can be cured thermally or by radiation in the presence of a free radical photoinitiator but these materials do not lend themselves to cationically induced polymerization. It is well recognized that thermal curing is not cost efficient and that radiation curing in free radical systems is oxygen inhibited, thus requiring an inert atmosphere or the minimizing affect of a hydrogen donating component. The later expedient is not completely satisfactory since such hydrogen donating components significantly reduce the rate of reaction. Also, it has been found that polymerization or curing in free radical systems ceases almost immediately upon removing the source of radiation; thus, the cured product often contains significant amounts of unpolymerized components. Accordingly, it is an aim of research to develop monomers or oligomers which provide stable polymerizable formulations with polyester containing materials while incorporating other beneficial properties in the finished cured product. Additionally, it is

- 2 -

desirable that such monomers or their oligomers be amenable to radiation curing at a rapid rate under mild temperature conditions by cationically induced polymerization which is not oxygen inhibited and which permits continued polymerization after removal from the source of radiation exposure.

Accordingly, it is an object of the present invention to overcome the disadvantages of previous polyester prepolymers and to provide a novel polyester prepolymer which is cationically curable at room temperature by radiation.

Another object is to provide a polyester prepolymer containing many crosslinking sites which is rapidly cured to a high density material under mild conditions.

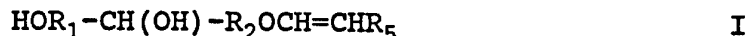
Another object of this invention is to provide a convenient process for the preparation of the present prepolymer.

Still another object of this invention is to provide a protective coating with a cured high density prepolymer having improved hardness, flexibility, resistance to abrasion and chemical attack.

These and other objects will become apparent from the following description and disclosure.

#### THE INVENTION

In accordance with this invention, a polyhydroxylated alk-1-enyl ether having the formula

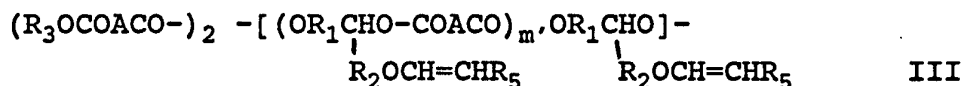


is reacted with a difunctional ester having the structure



- 3 -

or isocyanate having the structure  $O=C=N-A-N=C=O$  to form an intermediate monomer or oligomer defined by the formula



and the corresponding alcohol by-product  $HOR_3$  wherein

$m'$  has a value of from 1 to 25;

A is  $C_2$  to  $C_{12}$  alkylene,  $C_6$  to  $C_{14}$  aryl, both groups optionally substituted with lower alkyl, halo lower alkyl, alkyleneoxy, halogen or aryl;

$R_1$  is alkylene containing from 1 to 6 carbon atoms;

$R_2$  is a saturated or unsaturated divalent radical containing from 1 to 14 carbon atoms and is selected from the group of alkylene, alkenylene and arylene, each group optionally substituted with oxygen, halogen, lower alkyl and/or hydroxy and

$R_3$  is hydrogen or  $C_1$  to  $C_6$  alkyl.

The polyhydroxylated alk-1-enyl ether reactant (I) may contain an additional OH group in the  $R_2$  group which would result in an intermediate monomer or oligomer of more complex structure, i.e. where  $R_3OOC-A-COOR_3$  reacts with the additional -OH group to provide another  $-OR_1-\underset{\substack{| \\ R_2OCH=CHR_5}}{CHO}-$  group in the side chain of the intermediate

compound. However, the preferred hydroxylated alk-1-enyl ether compounds of this invention are dihydroxylated and most preferred are those wherein  $R_1$  and  $R_2$  are lower alkyl and  $R_3$  is hydrogen, methyl or ethyl. Suitable hydroxylated alk-1-enyl ether reactants include:

- 1,2-dihydroxyethyl ethyl prop-1-enyl ether,
- 1,2-dihydroxypropyl butyl prop-1-enyl ether,
- 1,2-dihydroxypropyl ethyl vinyl ether,
- 1,3-dihydroxybutyl ethyl prop-1-enyl ether,

- 4 -

1,3-dihydroxybutyl octyl vinyl ether,  
1,3-dihydroxyhexyl dodecyl but-1-enyl ether,  
1,2-dihydroxybutenyl ethyl prop-1-enyl ether,  
1,3-dihydroxyoctenyl ethyl vinyl ether,  
1,3-dihydroxydecyl hexyl hex-1-enyl ether,  
1,2-dihydroxyethyl phenyl vinyl ether,  
1,3-dihydroxypropyl bromophenyl vinyl ether,  
1,3-dihydroxyethyl chlorophenyl vinyl ether,  
1,3-dihydroxyethyl tolyl vinyl ether,  
1,3-dihydroxyethyl hydroxyphenyl vinyl ether,  
1,3-dihydroxyethyl oxyphenyl vinyl ether,  
1,3-dihydroxyethyl dibromohexyl vinyl ether,  
1,3-dihydroxyethyl hydroxyoctyl vinyl ether,  
1,2-dihydroxybutyl tolyl prop-1-enyl ether and the like.

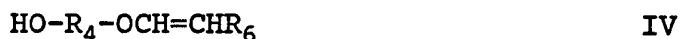
Suitable examples of reactant II include dimethyl terephthalate, dimethyl-amino-terephthalate, dimethyl-amino-isophthalate, dimethyl adipate, dibutyl malonate, diethyl oxalate, dioctyl oxalate, didecyl malonate, diethyl succinate, dimethyl glutarate, dibutyl adipate, dioctyl succinate, didodecyl phthalate, etc.

The transesterification reaction of I and II is carried out in the liquid phase with agitation under a blanket of an inert gas. A temperature of between about 95° and about 210°C., preferably, between about 140° and about 180°C., for a period of from about 1 to about 5 hours. During reaction, the alcohol by-product is continuously removed by distillation; or, when the reaction is conducted in a sealed system, the by-product can be subsequently distilled off at above its vaporization temperature. The mole ratio of the polyhydroxy alk-1-enyl ether (I) to diester (II) is dependent on the number of functional -OH and R<sub>3</sub>COO-groups in the respective reactants. Generally, a -OH to R<sub>3</sub>COO- mole ratio of between about 1:1 and about 1:2.5 can be employed, however, a slight excess of reactant II is preferred. Further, this reaction can be

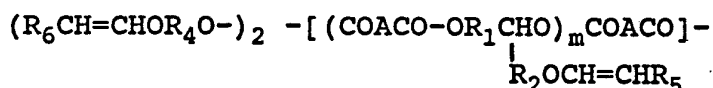
- 5 -

carried out in the presence of from about 0.1 to about 3 wt. %, based on reaction mixture, of a catalyst such as titanium isopropoxide, titanium butoxide, titanium methoxide, sodium hydroxide, potassium hydroxide, sodium methoxide, sodium t-butoxide, potassium methoxide, potassium butoxide, sodium phenoxide, potassium phenoxide, zinc, zinc acetate, manganese acetate, dibutyl tin dioxide or another base catalyst.

The intermediate monomer or oligomer (III) is then reacted with an end capping compound, preferably a monohydroxy alk-1-enyl ether of the formula



wherein  $R_4$  is  $C_1$  to  $C_6$  alkylene,  $C_6$  to  $C_{14}$  arylene, xylylene, each optionally substituted with alkyl, halogen or alkenyl and  $R_6$  is hydrogen or  $C_1$  to  $C_4$  alkyl. The resulting monomer or block oligomer of this invention having the formula



is obtained in quantitative yield.

The monohydroxy alk-1-enyl ether reactants (IV) include hydroxyhexyl prop-1-enyl ether, 1-hydroxy-dimethylene-propylene vinyl ether, hydroxyethyl-prop-1-enyl ether, hydroxycyclohexyl vinyl ether, hydroxybutyl-vinyl ether, hydroxybutyl but-1-enyl ether, hydroxypropyl prop-1-enyl ether,  $\alpha$ -hydroxyoctyl-vinyl ether, 2-hydroxypropyl prop-1-enyl ether, hydroxyphenyl prop-1-enyl ether, hydroxy tolyl but-1-enyl ether, hydroxybutyl but-1-enyl ether, the vinyl ether or prop-1-enyl ether of hydroxymethyl benzyl alcohol, cyclohexane dimethanol mono vinyl ether, etc. The end

- 6 -

capping reaction involving reactant IV is carried out under conditions similar to the reaction between reactants I and II including the presence of the base catalyst.

In the reaction between intermediate compound III and the end capping monohydroxy alk-1-enyl ether, a mole ratio of  $-COOR_3$  to  $-OCH=CHR_5$  between about 4:1 and about 1:4, preferably between about 1:1.5 and about 1:2 is employed. The Brookfield viscosity of the liquid prepolymeric product, which ranges from about 5,000 to about 500,000 cps, is inversely affected by the amount of end capping diluent added.

The above reactions can be effected in a single stage or in a two-stage process. In the single stage, the polyhydroxylated alk-1-enyl ether, the difunctional ester and the end capping component diluent are contacted with constant agitation under a pressure of from about atmospheric to about 20 psig.

The cationically curable prepolymer of this invention exhibits many advantages over the polyester prepolymers of the art in that the present prepolymer offers an increased number of crosslinking sites, which, when polymerized, provides a coating of extremely high density having excellent resistance to abrasion and chemical attack. The present prepolymer, obtained in a liquid state, allows for improved uniform coating applications on a substrate of metal, plastic, ceramic, wood, paper, glass, etc. The cured prepolymer also maintains flexibility resulting from their many unsaturated sites where polymer units are extended by addition to double bonds. Further, coatings of the present cured polymer preserve the finish of a painted surface, e.g. as automotive, aircraft and ship coatings. The present prepolymers III are prepared for curing by the addition of a cationic initiator and between about 10 and about 80 wt. % of a diluent.



- 7 -

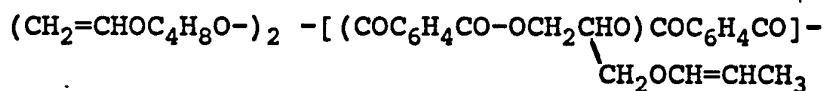
The present prepolymers which are useful as high density curable molding resins and highly solvent resistant adhesive coatings. The product can be diluted with a suitable solvent, applied to a surface in a thickness of between about 0.1 to about 5 mils and cured by exposure to a source of radiation such as UV light, electron beam, laser emission, X-rays, gamma-rays, etc. in the presence of an onium photoinitiator such as, for example a diaryl iodonium salt, a polyphenyl sulphonium fluoride, a triaryl sulphonium salt and the like. Curing by UV light exposure is generally effected at between about 300 and about 3,000 milli joules/cm<sup>2</sup>. Radiation curing of the prepolymer is extremely rapid, so that a coated substrate can be processed at a rate of up to 700 feet/sec and; whereas curing by heat requires a longer treatment up to about 2 hours. Examples of the reactive diluents employed in formulations of the present curable products are divinyl ether of triethylene glycol (DVE) and cyclohexane dimethanol divinyl ether (CHVE), the propenyl propylene ether of propylene carbonate (PEPC), tetrahydrofurfuryl vinyl ether and epoxides, e.g. 3,4-epoxycyclohexyl-3,4-epoxycyclohexane. The present coatings are clear, colorless, flexible films which find many applications as indicated above.

Having thus generally described the invention, reference is now had to the accompanying examples which illustrate comparative examples and preferred embodiments which are not construed as limiting to the scope of the invention as more broadly set forth above and in the appended claims.

- 8 -

EXAMPLE 1Aromatic Polyester Resin (Prepolymer) Synthesis

Into a 500 cc round bottom flask, equipped with an agitator, temperature control, nitrogen sparge and a distillation head, was added 65.05 grams (0.50 moles) of 3-(1-propeneoxy)-1,2-propanediol; 194.19 grams (1.0 moles) or dimethyl terphthalate; 0.56 grams (0.0018 moles) of titanium (IV) isopropoxide; and 116.1 grams of 4-hydroxy butyl vinyl ether. The reaction was heated to 90°C. at which point methanol began to distill overhead. The reaction temperature was increased incrementally over a period of 16 hours to a temperature of 180°C. after which 95.0% of the stoichiometric methanol by-product was distilled overhead, and the reaction was terminated. The product,



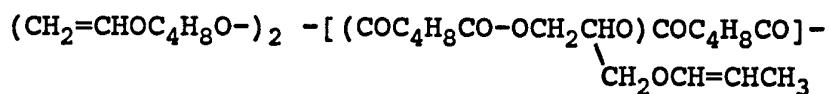
(305.2 grams) was recovered and its structure identified by  $\text{H}^1\text{NMR}$  and FTIR analysis. The product obtained in 97.9% yield was of high purity.

EXAMPLE 2Aliphatic Polyester Resin (Prepolymer) Synthesis

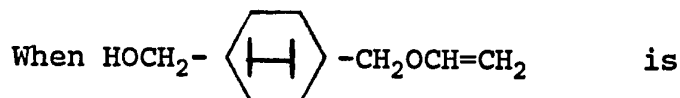
Into a 500 cc round bottom flask, equipped with an agitator, temperature control, nitrogen sparge and a distillation head, was added 65.05 grams (0.50 moles) of 3-(1-propeneoxy)-1,2-propanediol; 174.19 grams (1.0 moles) or dimethyl adipate; 0.56 grams (0.0018 moles) of titanium (IV) isopropoxide; and 116.1 grams of 4-hydroxy butyl vinyl ether. The reaction was heated to 90°C. at

- 9 -

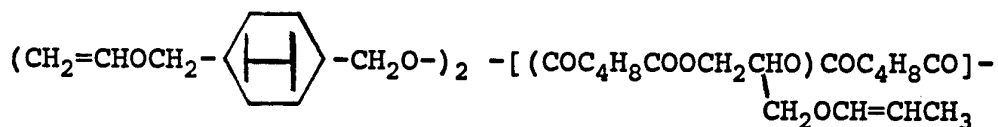
which point methanol began to distill overhead. The reaction temperature was increased incrementally over a period of 16 hours to a temperature of 180°C. after which 95.0% of the stoichiometric methanol by-product was distilled overhead, and the reaction was terminated. The product,



(285.2 grams) was recovered and its structure identified by  $^1\text{H}$ NMR and FTIR analysis. The product obtained in a yield of 97.9% was of high purity.



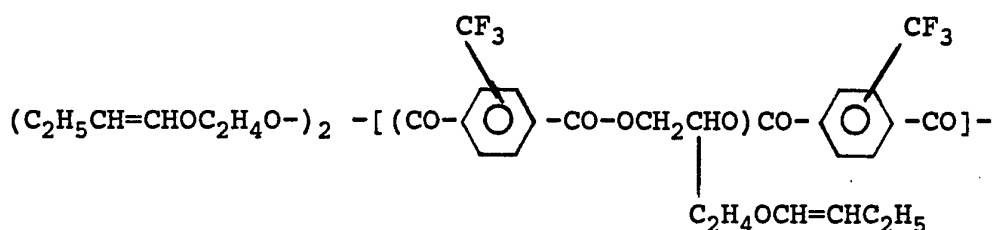
substituted in the same molar amount in the above Example 2 for 4-hydroxybutyl vinyl ether, the product has the structure



- 10 -

EXAMPLE 3Halo-Aromatic Polyester Resin (Prepolymer) Synthesis

Into a 500 cc round bottom flask, equipped with agitation, temperature control, nitrogen sparge and a simple distillation head, was added 80.05 grams (0.50 moles) of 4-(1-buteneoxy)-1,2-butanediol; 262.2 grams (1.0 moles) of 2-(trifluoromethyl)-1,4-dimethylterphthalate; 0.56 grams (0.0018 moles) of titanium (IV) isopropoxide; and 116.1 grams (1.0 moles) of 2-(1-buteneoxy)-1-ethanol. The reaction was heated to 90°C. after which methanol began to distill overhead. The reaction temperature was increased incrementally over a period of 16 hours to 180°C. At this point 95.0% of the stoichiometric methanol was distilled overhead, and the reaction was terminated. 385.9 grams product having the formula



was recovered.  $\text{H}^1\text{NMR}$  and FTIR analysis confirmed the structure and high purity of the product. An overall yield of 97.9% was obtained.

EXAMPLE 4

The products of Examples 1-3 were tested as radiation curable formulations containing 49% of the respective products, 49% of divinyl ether of triethylene glycol and 2% of triphenyl sulfonium salt initiator (FX-512). The resulting formulations were each coated on an aluminum panel and subjected to curing using a 400 mJ/cm<sup>2</sup> PPG model QC-1202A/N U.V. processor. The coating performance of each of these formulations was compared and the results summarized in the following Table.

TABLE

PRODUCT OF	PENCIL HARDNESS	ADHESION %	MANDRELL BEND	MEK RUBS	TENSILE PROPERTIES		
					YOUNG'S MODULUS	TENSILE STRENGTH	ELONGATION %
EXAMPLE 1	H	100	1/8	>200	64	880	6.4
EXAMPLE 2	HB	80	1/8	>200	50	700	5.3
EXAMPLE 3	F	70	1/8	>200	50	650	5.1

- 12 -

Merely by increasing the mole ratio of the intermediate with respect to the end capping hydroxy alk-1-enyl ether in the above examples, a product where  $m$  has a value greater than 1 can be obtained. Accordingly, a 25-fold increase in the intermediate concentration produces a product where  $m$  is 25.

#### EXAMPLE 4

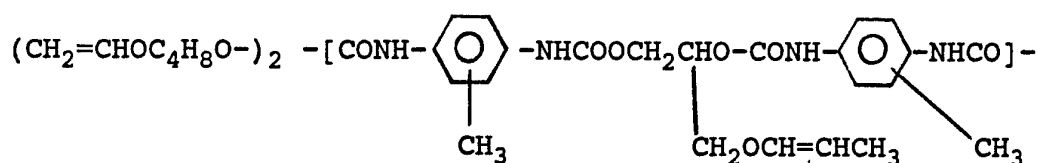
##### Preparation of Dihydroxy Alk-1-Enyl Ether

Into a 1500 cc stainless steel reaction vessel, equipped with a mechanical stirrer, high pressure gas feed lines, internal cooling, and temperature control, was added 1140.6 grams (10 moles) of propenyl glycidyl ether (PGE), 198.0 grams (11 moles) of water, 5.7 grams of tetrabutyl ammonium bromide, and 3.0 grams of sodium bicarbonate. The mixture was heated to 100°C. under a CO<sub>2</sub> pressure of 200 psig for 6 hours, with continuous CO<sub>2</sub> feed. Analysis by gas chromatography showed quantitative conversion of PGE. This material was then flash distilled at a temperature of 120°C. at 5.0 mm Hg, to remove water and separate the product from the catalyst. 1-Propenyloxy-2,3-propanediol 1250 grams of 98.5% purity was recovered, and its structure was confirmed by FTIR and H<sup>1</sup>NMR spectroscopic methods.

- 13 -

EXAMPLE 5Preparation of Uncured Prepolymer

Into a 250 cc round bottom flask equipped with agitation, reflux condenser, nitrogen sparge, and temperature control was added 87.08 grams (0.5 moles) of toluene diisocyanate. To this was added 87.08 grams (0.75 moles) of 4-hydroxybutyl vinyl ether, 16.53 grams (0.125 moles) of 1-propenyloxy propanediol from Example 4 and 0.2 grams of dibutyl tin dilaurate at a controlled rate so as to maintain a temperature of 60-80°C. The reaction was monitored by volumetric isocyanate analysis, and proceeded to completion after 4 hours. The viscous product,



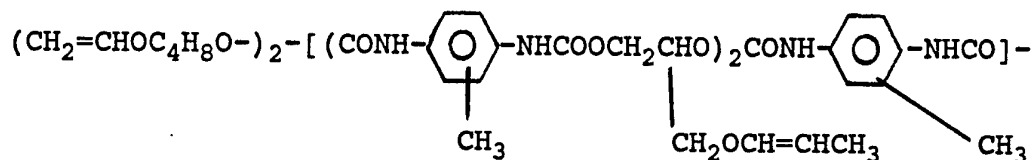
was recovered, and the above structure was confirmed by  $^1\text{H}$ -NMR and FTIR spectroscopy.

EXAMPLE 6Prepolymer Preparation

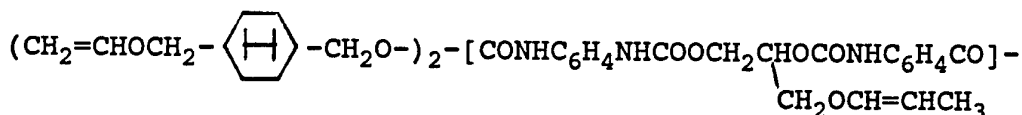
Into a 250 cc round bottom flask equipped with agitation, reflux condenser, nitrogen sparge, and temperature control was added 87.98 g (0.5 moles) of toluene diisocyanate. To this was added 58.05 grams (0.50 moles) of 4-hydroxybutyl vinyl ether 33.05 grams (0.25 moles) of 1-propenyloxy propanediol from Example 4 and 0.2 grams of dibutyl tin dilaurate at a controlled rate so as to maintain a temperature of 60-80°C. The reaction was monitored by volumetric isocyanate analysis, and proceeded to completion after 4 hours. The same viscous product as obtained in Example 5 was recovered,

- 14 -

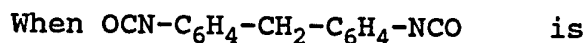
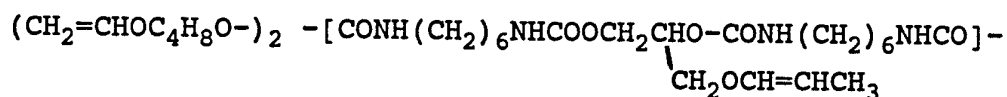
and the structure was confirmed by  $H^1$ NMR and FTIR spectroscopy



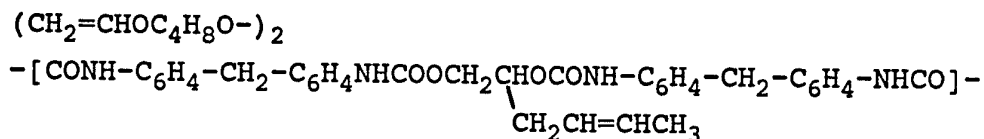
is substituted in the same molar amount in the above Example 6 for 4-hydroxybutyl vinyl ether, the product has the structure



When  $OCN(CH_2)_6CNO$  is substituted in the same molar amount in the above Example 6 for toluene diisocyanate, the product has the structure



substituted in the same molar amount in the above Example 6 for toluene diisocyanate, the product has the structure

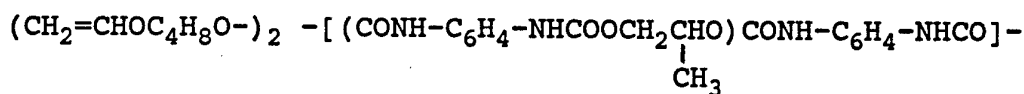




- 15 -

EXAMPLE 7

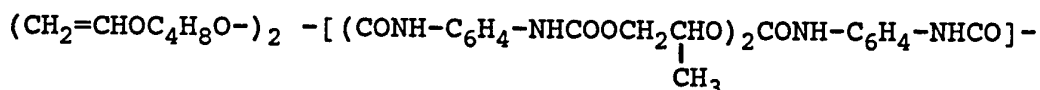
The procedure of Example 5 was repeated using 7.8 grams of 1,2-propanediol in place of 1-propenyloxy propanediol. The product of this example was identified as having the formula



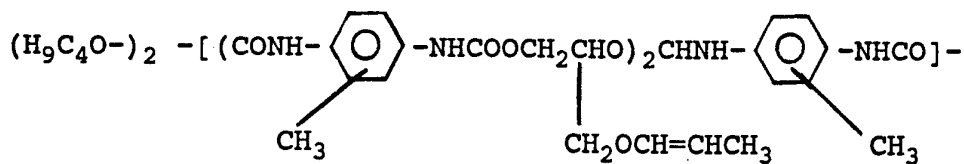
and is useful as a non-reactive chain extender resin.

EXAMPLE 8

The procedure of Example 6 was repeated using 15.5 grams of 1,2-propanediol in place of 1-propenyloxy propanediol. The product of this example is identical to that obtained in Example 7

COMPARATIVE EXAMPLE 9

The procedure of Example 6 was repeated using 37.06 grams of n-butanol in place of hydroxybutyl vinyl ether. The product of this example



- 16 -

possesses a non-reactive end-capping group but would retain internal cross-linking properties because of the reactive-chain extender. However, this product exhibits poor pencil hardness, little or no adhesive properties and low tensile properties.

#### EXAMPLE 10

The products of Examples 5-9 were tested as radiation curable formulations containing 49% of the respective products, 49% of divinyl ether of triethylene glycol and 2% of triphenyl sulfonium salt initiator (FX-512). The resulting formulations were each coated on an aluminum panel and subjected to curing using a 400 mJ/cm<sup>2</sup> PPG model QC-1202A/N U.V. processor. The coating performance of each of these formulations was compared and the results summarized in the following Table.

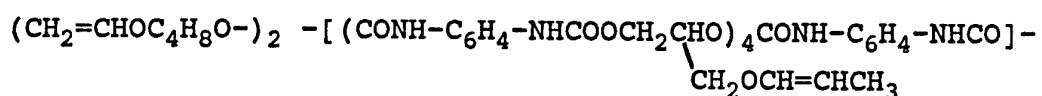
TABLE

OLIGOMER	PENCIL HARDNESS	ADHESION %	MANDRELL BEND	MEK RUBS	TENSILE PROPERTIES		
					YOUNGS MODULUS	TENSILE STRENGTH	ELONGATION %
EXAMPLE 5	2H	100	1/8	>200	89	1250	7.6
EXAMPLE 6	3H	70	1/8	>200	76	1150	8.4
EXAMPLE 7	H	70	1/8	>200	65	1000	5.1
EXAMPLE 8	H	50	1/8	>200	55	800	4.8
EXAMPLE 9	B	0	1/8	>200	10	600	8.5

- 18 -

EXAMPLE 11

Example 5 is repeated, except that 3 moles of 4-hydroxybutyl vinyl ether, 2 moles of toluene diisocyanate and 0.8 grams of dibutyl tin dilaurate are substituted for the amounts shown therein (a 4-fold excess). The product of this reaction has the formula

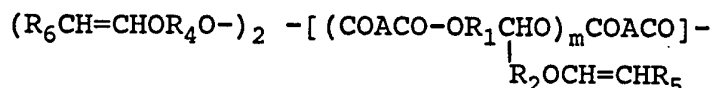


Merely by increasing the mole ratio of the intermediate with respect to the end capping hydroxy alk-1-enyl ether, a product where m has a value greater than 1 can be obtained. Accordingly, a 25-fold increase in the intermediate concentration produces a product where m is 25.

- 19 -

WHAT IS CLAIMED IS:

1. A polyalk-1-enyl polyester prepolymer having the formula



wherein

m has a value of from 1 to 25;

A is C<sub>2</sub> to C<sub>12</sub> alkylene, C<sub>6</sub> to C<sub>14</sub> arylene, both groups optionally substituted with lower alkyl, halo lower alkyl, alkyleneoxy, halogen, aryl or NHA'NH wherein A' is the same as A;

R<sub>1</sub> is alkylene containing from 1 to 6 carbon atoms;

R<sub>2</sub> is a saturated or unsaturated divalent radical containing from 1 to 14 carbon atoms and is selected from the group of alkylene, alkenylene and arylene, each group optionally substituted with oxygen, halogen, lower alkyl and/or hydroxy;

R<sub>5</sub> is hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl;

R<sub>4</sub> is C<sub>1</sub> to C<sub>6</sub> alkylene, C<sub>6</sub> to C<sub>14</sub> arylene, lower alkyl substituted phenylene or xylylene and

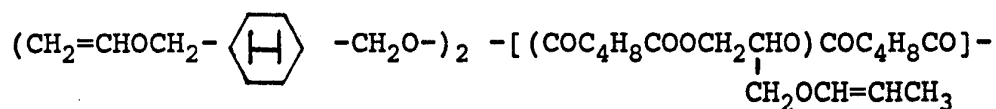
R<sub>6</sub> is hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl.

2. The prepolymer of Claim 1 wherein A is arylene and m has a value of 2.

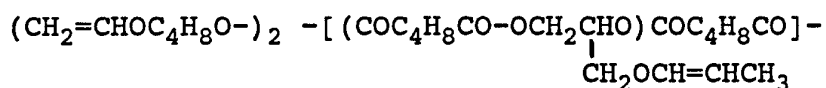
3. The prepolymer of Claim 1 wherein A is an aliphatic radical and m has a value of 2.

- 20 -

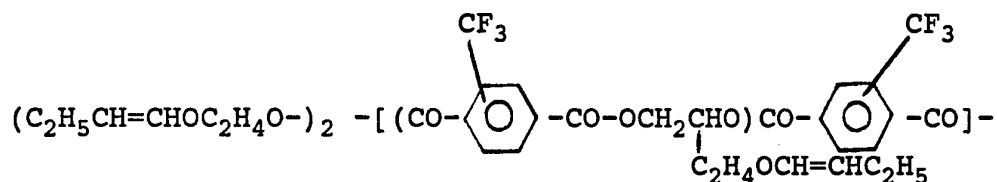
4. The prepolymer of Claim 1 having the formula:



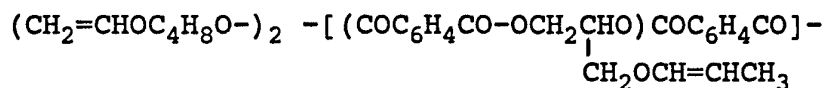
5. The prepolymer of Claim 1 having the formula:



6. The prepolymer of Claim 1 having the formula:



7. The prepolymer of Claim 1 having the formula:



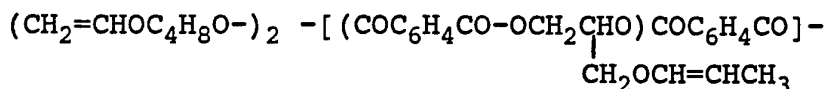
8. A radiation curable composition containing the prepolymer of Claim 1 and an effective amount of a cationic polymerization initiator.

- 21 -

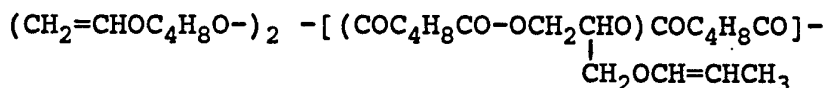
9. The composition of Claim 8 wherein said initiator is an onium salt initiator.

10. The composition of Claim 9 wherein said initiator is the triphenylsulfonium salt of hexafluorophosphate.

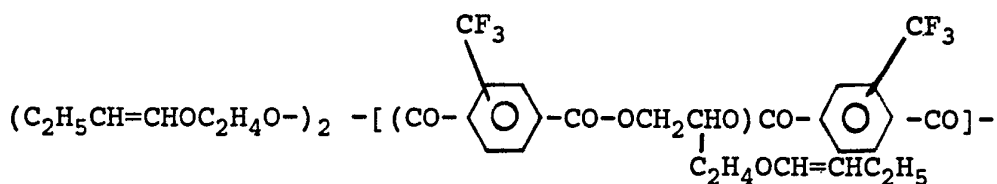
11. The composition of Claim 9 wherein said prepolymer has the formula:



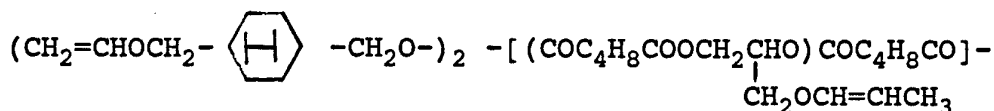
12. The composition of Claim 9 wherein said prepolymer has the formula:



13. The composition of Claim 9 wherein said prepolymer has the formula:



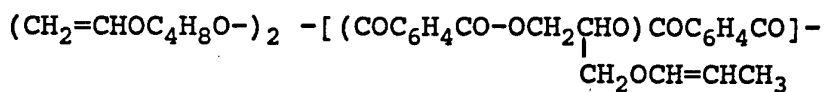
14. The composition of Claim 9 wherein said prepolymer has the formula:



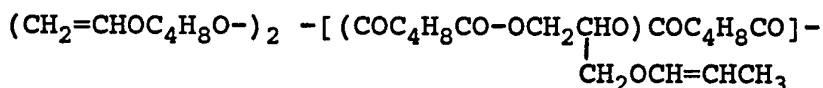
- 22 -

15. A substrate having a hard, durable and flexible coating of the cured prepolymer of Claim 1.

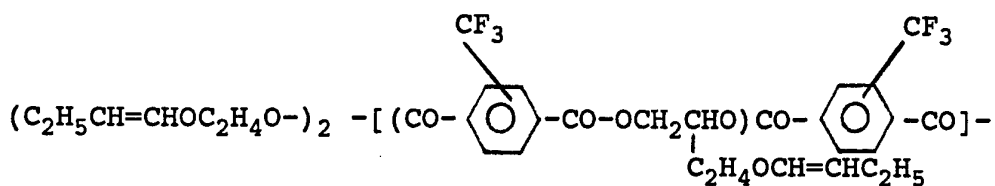
16. The substrate of Claim 15 which is coated with the cured prepolymer having the formula:



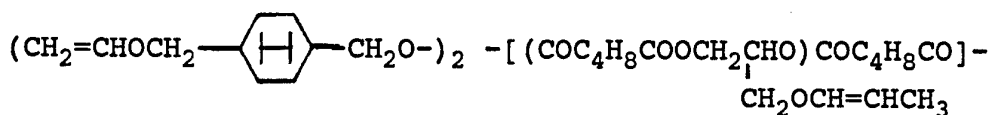
17. The substrate of Claim 15 which is coated with the cured prepolymer having the formula:



18. The substrate of Claim 15 which is coated with the cured prepolymer having the formula:



19. The substrate of Claim 15 which is coated with the cured prepolymer having the formula:



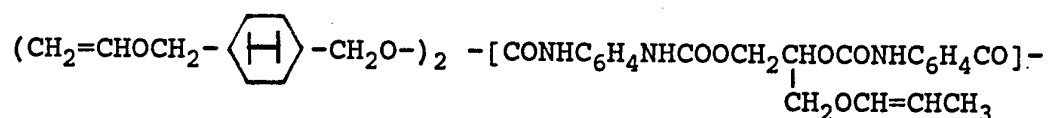


- 23 -

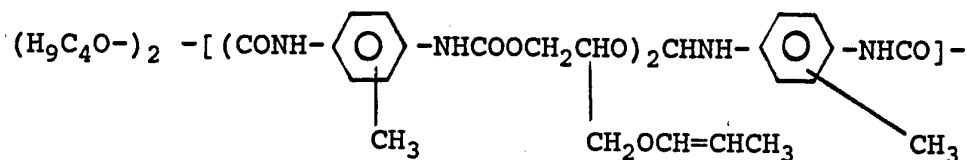
20. The prepolymer of Claim 1 wherein A is NHA'NH; m has a value of from 1 to 4, A' is alkylene, R<sub>5</sub> is lower alkyl, R<sub>4</sub> is alkylene and R<sub>6</sub> is hydrogen or methyl.

21. The prepolymer of Claim 1 wherein A is NHA'NH; m has a value of from 1 to 4, A' is arylene, R<sub>5</sub> is lower alkyl, R<sub>4</sub> is alkylene and R<sub>6</sub> is hydrogen or methyl.

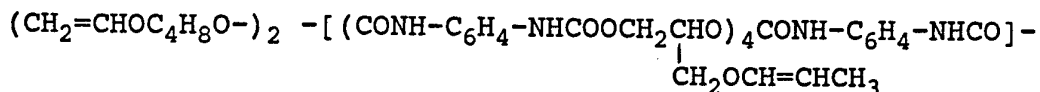
22. The prepolymer of claim 1 having the formula



23. The prepolymer of Claim 1 having the formula

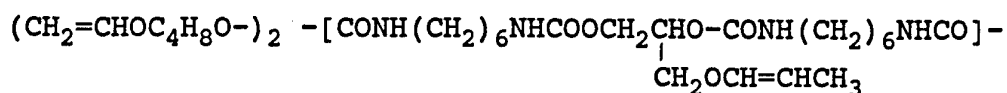


24. The prepolymer of Claim 1 having the formula



- 24 -

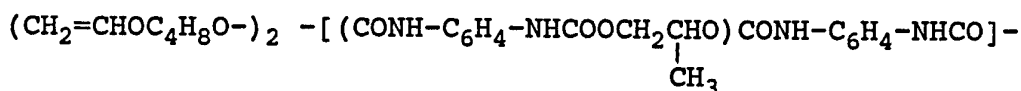
25. The prepolymer of Claim 1 having the formula



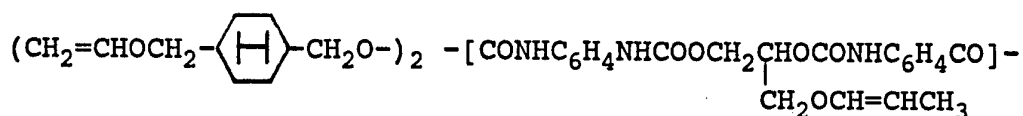
26. The composition of Claim 8 wherein A is NHA'NH and the initiator is diphenyl-4-thiophenoxy phenyl sulfonium salt.

27. The composition of Claim 8 containing the prepolymer wherein m has a value of 2, A' is aryl, R<sub>5</sub> and R<sub>4</sub> are each lower alkyl and R<sub>6</sub> is hydrogen or methyl.

28. The composition of Claim 27 which additionally contains a diluent having the formula

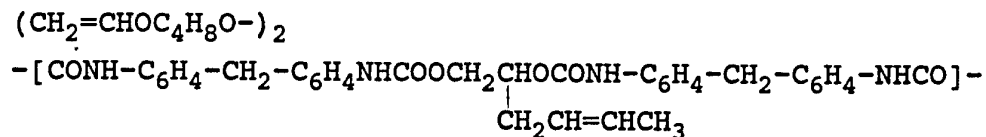


29. The composition of Claim 27 wherein said prepolymer is

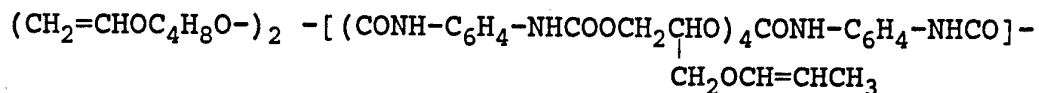


- 25 -

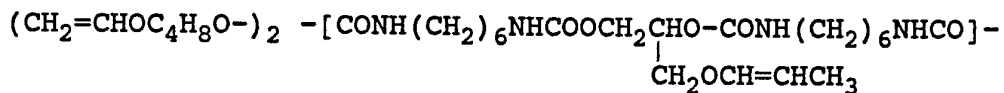
30. The composition of Claim 27 wherein said prepolymer is



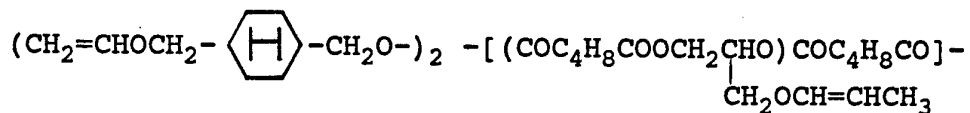
31. The composition of Claim 27 wherein said prepolymer is



32. The composition of Claim 27 wherein said prepolymer is



33. The substrate of Claim 15 wherein said coating is the cured poly(alk-1-enyl)/urethanyl prepolymer having the formula



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/08203**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : C08F 2/50, 16/32, 26/02, 299/06; C07C 69/347, 69/767

US CL : Please See Extra Sheet.

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)

U.S. : 428/421, 458, 462; 522/31, 96, 97, 98, 104, 107, 181; 526/292.3, 301, 309, 320; 525/ 445; 560/ 95, 193, 210

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: vinyl ether, alkenyloxy

CAS ONLINE: vinyl ether, alkenyloxy

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,845,265 (LAPIN ET AL) 04 July 1989, Abstract, columns 3-4 and Examples 1-2.	1-33
Y	US, A, 4,749,807 (LAPIN ET AL) 07 June 1988, Abstract, column 2 and Examples 1-7.	1-33
Y	US, A, 5,019,636 (LAPIN ET AL) 28 May 1991, Summary of the Invention, column 3, lines 66-68, and column 4.	1-33
Y	US, A, 3,485,733 (D'ALELIO) 23 December 1969, Abstract.	1-33
Y	US, A, 5,139,872 (LAPIN ET AL) 18 August 1992, Abstract; column 2, line 50, to column 3, line 49; column 4, line 23, to column 6, line 6.	1-33

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be part of particular relevance	"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
"E" earlier document published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"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

21 SEPTEMBER 1994

Date of mailing of the international search report

14 NOV 1994

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SUSAN BERMAN

Telephone No. (703) 308-2351

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/08203

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,153,237 (PLOTKIN ET AL) 06 October 1992, Abstract, column 2, lines 1-43, column 3, lines 13-17, column 3, line 58, to column 4, line 18.	1-33
Y	US, A, 5,140,054 (MILLER ET AL) 18 August 1992, Abstract; column 1, line 56, to column 2, line 20; column 2, line 66, to column 3, line 2; column 3, line 35, to column 4, line 2.	1-33
Y	US, A, 5,045,572 (PLOTKIN ET AL) 03 September 1991, Abstract.	1-33
Y	US, A, 4,751,273 (LAPIN ET AL) 14 June 1988, Abstract, column 2, lines 12-27, column 6, lines 3-38.	1, 8, 27, 28
A	US, A, 4,091,141 (HARRIS) 23 May 1978, Abstract, column 2, lines 58-65, column 4, lines 15-37.	1-33

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/08203

## A CLASSIFICATION OF SUBJECT MATTER:

US CL :

428/421, 458, 462; 522/31, 96, 97, 98, 104, 107, 181; 526/292.3, 301, 309, 320; 525/ 445; 560/ 95, 193, 210