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3,784,594

CELLULAR MATERIAL PRODUCED FROM COPOLYMERS OF CYCLIC VINYL ETHERS AND CYCLIC ACETALS

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24 Claims

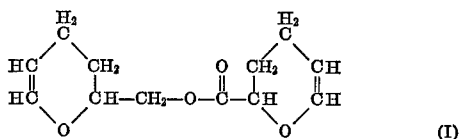
ABSTRACT OF THE DISCLOSURE

Novel copolymerization products are provided by the cationic polymerization of a di-(dihydropyranyl) compound with a substituted 1,3-dioxolane or a substituted 1,3-dioxane. The copolymerization products possess improved abrasion resistance and toughness as compared with the homopolymers of the di-(dihydropyranyl) monomers. Especially useful, particularly in providing foamed polymeric materials of improved friability resistance, are the polymerization reaction products of 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and a bis-dioxolanyl or a bis-dioxanyl carbamate.

This invention relates generally to oxygen-heterocyclic compounds and to polymeric materials obtained therefrom. More particularly, the invention relates to new and improved polymeric compositions, including foamed polymeric materials, obtained by copolymerization of a compound containing a dihydropyranyl cyclic nucleus and a particular class of cyclic acetals.

BACKGROUND OF THE INVENTION

The homopolymerization of cyclic vinyl ethers and copolymerization with certain classes of monomers is known to the art. One such cyclic vinyl ether is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) which is commonly referred to as acrolein tetramer and has the structure:



The polymerization of this compound and its 2,5-dialkyl substituted derivatives is reported in U.S. Pat. No. 2,537,921 wherein the homopolymers are described as having excellent thermostability and resistance to water and solvents. Generally, however, such polymers tend to be brittle compositions. Among the many classes of comonomers which the patentee enumerates are unsaturated ethers and esters such as vinyl alkyl ethers, vinyl esters of carboxylic acids and other compounds containing polymerizable carbon-to-carbon double bonds none of which, however, are oxygen-heterocyclic compounds. Subsequent to the aforesaid patent, it was reported that divinyl ethers, and particularly the aforesaid di-(dihydropyranyl) compound (I) and bis-(dihydropyranyl) compounds, were capable of providing rigid, cellular polymeric products. Such products, which are referred to in the art as pyranyl-based foams, and their preparation, are reported in U.S. Pats. Nos. 3,311,574; 3,311,575; 3,318,824; and British Pat. No. 991,970. Notwithstanding the useful properties which pyranyl-based polymeric compositions possess, one property which detracts from and hinders their widespread commercial application is their poor friability resistance. In particular, Compound I which, from the standpoint of availability and relatively

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low cost, is the most attractive of the dihydropyranyl monomers, provides brittle and highly friable homopolymers and foamed polymeric products, although some improvement in friability is obtained by polymerization thereof in the presence of a phenolic compound such as 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A).

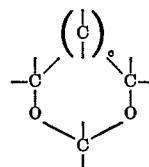
It is an object of this invention, therefore, to provide new and improved polymeric compositions derived from cyclic vinyl ethers and, in particular, polymeric compositions derived from compounds containing a dihydropyranyl ring nucleus.

Another object is to provide new compositions of matter which are copolymerizable with dihydropyranyl compounds to produce products of improved friability resistance.

A further object is to provide improved foam formulations comprising, and improved polymeric foams derived from, 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate).

Various other objects and advantages of this invention will become apparent to those skilled in the art from the accompanying description and disclosure.

In accordance with the present invention, the above objects are generally accomplished by providing polymeric compositions which comprise the polymerization reaction products of a di-(dihydropyranyl) compound and an oxygen-heterocyclic compound comprising at least one cyclic nucleus containing two oxygen atoms and from 3 to 4 carbon atoms arranged to provide a cyclic nucleus represented herein by the symbol "D" which has the following structure:



wherein c has a value of zero or one as in the cyclic acetals, 1,3-dioxolanes and 1,3-dioxanes, respectively. One class of cyclic acetals which are employed in this invention are compounds containing only one of the aforesaid 1,3-dioxolanyl or 1,3-dioxanyl rings (referred to herein as monofunctional compounds) and having a hydroxyl-substituted monovalent organic radical bonded thereto.

A second class of cyclic acetals are the difunctional 1,3-dioxolanes and 1,3-dioxanes (that is, compounds having two 1,3-dioxolanyl or 1,3-dioxanyl rings) and in which the respective dioxolanyl and dioxanyl rings are linked through a bivalent hydrocarbon group or a hydroxyl-substituted bivalent organic radical. A third class of suitable cyclic monomers for use in the present invention are the reaction products obtained by reacting the aforesaid hydroxyl-containing mono- and di-functional cyclic acetals with a dicarboxylic acid or an organic polyisocyanate, the polyisocyanate derivatives constituting new compositions of matter. A fourth class of cyclic acetals for use in the present invention are compounds in which one carbon atom of the aforesaid cyclic nucleus (D) is common to either a second cyclic nucleus (D) or a cycloaliphatic hydrocarbon nucleus, thereby providing spiro compounds containing from one to two 1,3-dioxolanyl or 1,3-dioxanyl rings.

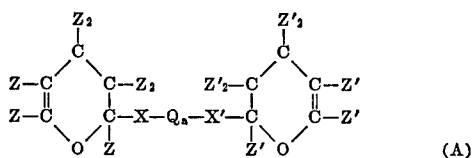
In accordance with one embodiment of the process of the present invention, the aforesaid di-(dihydropyranyl) and cyclic acetals are copolymerized in a reaction medium comprising a cationic polymerization catalyst to provide polymeric products which are useful thermoset resins. In accordance with another embodiment of the process described herein, the aforesaid compounds are

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copolymerized in the presence of a cationic polymerization catalyst under conditions such that polymeric foams are produced.

THE DI-(DIHYDROPYRANYL) MONOMER

The di-(dihydropyranyl) compounds employed in the present invention comprise two 3,4-dihydro-2H-pyran rings which are interconnected by a linking chain bonded at either end to the 2-position of the respective pyran rings. In simplified form, the preferred compounds for use in the present invention have the following general Formula A:



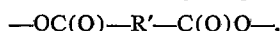
wherein:

Z and Z' each represents hydrogen or an alkyl group having from 1 to 10, and usually no more than 6, carbon atoms;

X and X' are members of the class consisting of a bivalent saturated hydrocarbon group, R, having the structure, $-C_nH_{2n}-$, wherein n is an integer having a value of from 1 to 10; an oxy radical, $-O-$; and a carbonyl group, $-C(O)-$; and, in addition, X' may be a carbonyloxy group, $-O(O)C-$, the carbon atom of which is bonded to the 2-position of the dihydropyranyl ring; X and X' may be the same or different provided that taken together they contain either zero or 2 oxygen atoms;

a has a value of from zero to 1, a being zero only when X' is the aforesaid carbonyloxy group;

Q is a member of the class consisting of the aforesaid R group; a dioxyalkylene group, $-ORO-$, wherein R is as defined above; a dicarboxylate group,

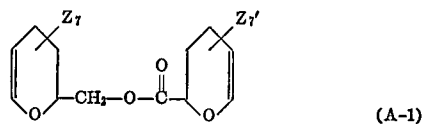


wherein R' is the nucleus of a dicarboxylic acid; and a polycarbamate group such as the dicarbamate group, $-OC(O)NH-R''-NHC(O)O-$, wherein R'', as illustrated, is the nucleus of a diisocyanate; and

X, X' and Q taken together is such that the linking chain, $-X-Q-X'-$, contains an even number of oxygen atoms from two to four, provided that when X and X' are both oxy radicals, the linking chain contains no other oxygen atoms (that is, Q is R), and when X and X' are both carbonyl groups, the linking chain contains four oxygen atoms (that is, Q is $-ORO-$).

Among the suitable di-(dihydropyranyl) compounds which are copolymerized with the cyclic acetals in accordance with the teachings of this invention are the following classes of compounds designated by Formulas A-1 through A-6 below.

(1) 3,4 - dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylates) having the formula:



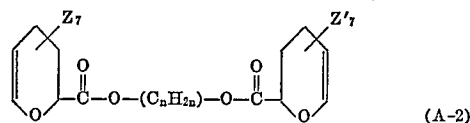
wherein Z and Z' are as above-defined. Preferably, a total of from 5 to 7 of the respective Z and Z' groups are hydrogen and correspondingly, from 2 to zero are alkyl groups. When Z and Z' are alkyl groups, they are usually bonded to the 2- and/or 5-position of the respective rings. Typical examples of this class of reactants are: 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and corresponding alkyl-substituted compounds such as

3,4-dihydro-2,5-dimethyl-2H-pyran-2-methyl(3,4-dihydro-2,5-dimethyl-2H-pyran-2-carboxylate);

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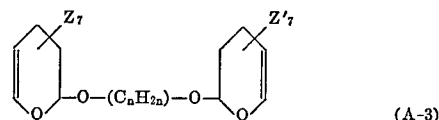
3,4-dihydro-2,5-diisobutyl-2H-pyran-2-methyl(3,4-dihydro-2,5-diisobutyl-2H-pyran-2-carboxylate); 3,4-dihydro-2,5-dihexyl-2H-pyran-2-methyl(3,4-dihydro-2,5-dihexyl-2H-pyran-2-carboxylate); and 3,4-dihydro-2,5-didecyl-2H-pyran-2-methyl(3,4-dihydro-2,5-didecyl-2H-pyran-2-carboxylate).

(2) Alkanedioxy-bis(3',4'-dihydro-2'H-pyran-2'-carbonyl) compounds having the structure:



wherein Z and Z' are as above-discussed, and n is an integer from 1 to 10, preferably from 1 to 4. Typical examples of such compounds which are suitable in the practice of this invention are: 1,2-ethanedioxy-bis-(3',4'-dihydro-2'H-pyran-2'-carbonyl); 1,2-ethanedioxy-bis-(3',4'-dihydro-5'-methyl-2'H-pyran-2'-carbonyl), and corresponding 1,2-isopropanedioxy and 1,4-butanedioxy compounds. Such compounds are prepared by the reaction of an alkylene dihalide, $X''-(C_nH_{2n})-X''$, wherein n is as aforesaid, and X'' is halogen, particularly iodine, chlorine or bromine, with the silver salt of a 3,4-dihydro-2H-pyran-2-carboxylic acid. The latter salts are in turn prepared by the oxidation of 3,4-dihydro-2H-pyran-2-carboxaldehyde in the presence of a silver salt such as silver oxide, preferably in an anhydrous medium containing and organic solvent such as benzene, as described in U.S. Pat. No. 2,514,172

(3) Bis-(3',4'-dihydro-2'H-pyran-2'-oxy)alkanes having the formula:

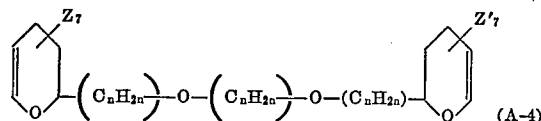


wherein Z, Z' and n have the significance discussed above. Illustrative compounds of this group of di-(dihydropyranyl) compounds are:

1,2-bis-(3',4'-dihydro-2'H-pyran-2'-oxy)ethane;
1,2-bis(3',4'-dihydro-5'-methyl-2'H-pyran-2'-oxy)ethane;
1,3-bis(3',4'-dihydro-5'-methyl-2'H-pyran-2'-oxy)propane; and
1,4-bis(3',4'-dihydro-2'H-pyran-2'-oxy)butane.

Such compounds are prepared by Diels-Alder addition reactions of divinyl bis-ethers such as the divinyl ethers of alkylene glycols, with alpha,beta-unsaturated aldehydes such as acrolein and methacrolein under conditions described, for example, by Curtis W. Smith et al., Journal of The American Chemical Society, vol. 73, 5267 (1951). For example, the reaction between a mole of ethylene glycol divinyl ether and 2 moles of acrolein provides 1,2-bis(3',4'-dihydro-2'H-pyran-2'-oxy)ethane.

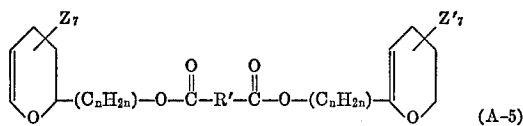
(4) Bis-(3',4'-dihydro-2'H-pyran-2'-alkoxy) - alkanes having the formula:



wherein Z, Z' and n are as defined hereinabove. Typical examples of this type of reactant are: 1,1-bis(3',4'-dihydro-2'H-pyran-2'-methoxy)ethane; 1,1-bis(3',4'-dihydro-5'-methyl-2'H-pyran-2'-methoxy)ethane; and 1,2-bis(3',4'-dihydro-2'H-pyran-2'-methoxy)ethane. Such compounds are prepared by the addition of alpha,beta-unsaturated aldehydes (such as, for example, acrolein and methacrolein) to the corresponding bisunsaturated ethers.

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(5) Bis-(3',4'-dihydro-2'H-pyran-2'-alkyl)-carboxylates having the general formula:



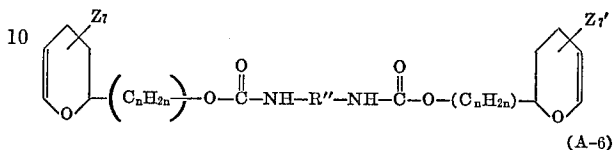
wherein Z, Z' and n are as above-defined; and R' is the nucleus of a dicarboxylic acid and may be a bivalent aliphatic, cycloaliphatic or aromatic nucleus including corresponding halogen-substituted nuclei. Thus, R' may be: a bivalent alkylene group, $-(C_n^o H_{2n}^o)-$, wherein n^o is an integer of from 1 to 10 as in the saturated acyclic dibasic acid series, $HOOC-(CH_2)_n^o-COOH$; an alkenylene group having from 2 to 10 carbon atoms as in maleic acid and itaconic acid; an arylene group as in phthalic, isophthalic and terephthalic acids; an aralkylene nucleus as in homophthalic acid; cycloaliphatic nuclei as in the hydrophthalic acids including di-, tetra-, and hexa-hydrophthalic acids, and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid; and corresponding halogenated nuclei as in chloromaleic acid, tetrachloro- and tetrabromophthalic acids and chlorobicyclo-[2.2.1]-hept-5-ene-2,3-dicarboxylic acids such as chlорендид acid. Specific examples of this class of compounds are: bis-(3,4-dihydro-2H-pyran-2-methyl)-succinate, -adipate, -azelate, -sebacate, -tetrachloro-phthalate, -tetrabromophthalate and -chlорендидate. This type of reactant is prepared by the condensation of 3,4-dihydro-2H-pyran-2-alkanols with the dibasic acid or acid halide of the dibasic acid.

(6) Poly-(3',4'-dihydro-2'H-pyran-2'-alkyl) carbamates which comprise the reaction products formed by condensation of 3,4-dihydro-2H-pyran-2-carbinols and an organic polyisocyanate such as those described below. Among the suitable polyisocyanates which may be used in the preparation of such monomers for use in the present invention are those having the formula, $R''(NCO)_i$, wherein i is an integer of two or more and R'' is an organic radical having the valence of i . R'' can be an aliphatic, cycloaliphatic or aromatic radical which may be unsubstituted hydrocarbon groups or hydrocarbon groups substituted, for example, with halogen or alkoxy groups. Thus, when i is two, for example, R'' is a bivalent substituted or unsubstituted hydrocarbon group such as alkylene, cycloalkylene, arylene, alkyl-substituted cycloalkylene, alkarylene, aralkylene and like groups. Typical examples of such polyisocyanates are: 1,6-hexamethylene diisocyanate; 1,4-tetramethylene diisocyanate; 1-methyl-2,4-diisocyanatocyclohexane; bis(4-isocyanatophenyl) methane; phenylene diisocyanates such as 4-methoxy-1,3-phenylene-diisocyanate, 5,6-dimethyl-1,3-phenylene-diisocyanate, 2,4- and 2,6-tolylene diisocyanates, crude tolylene diisocyanate, 6-isopropyl-1,3-phenylenediisocyanate, durylene diisocyanate, triphenylmethane-4,4',4''-triisocyanate, and many other organic polyisocyanates that are known in the art such as those disclosed in an article by Siefkin, Ann. 565, 75 (1949). Also included as useful in the preparation of the carbamate monomers employed in this invention are the polyisocyanates of the aniline-formaldehyde polyaromatic type which are produced by phosgenation of the polyamine obtained by acid-catalyzed condensation of aniline with formaldehyde. Polyphenylmethylenepolyisocyanates of this type are available commercially under such trade names as PAPI, AFPI, Mondur MR, Isonate 390P, NCO-120 and NCO-20. The products are low viscosity (50-500 centipoises at 25° C.) liquids having average isocyanato functionalities in the range of about 2.25 to about 3.2 or higher, depending upon the specific aniline-to-formaldehyde molar ratio used in the polyamine preparation. Other useful polyisocyanates are combinations of diisocyanates with polymeric isocyanates containing more than two isocyanate groups per molecule. Illustrative of such combinations are: a mixture of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and the aforesaid

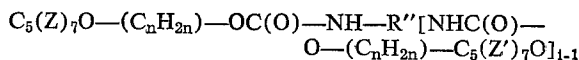
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polyphenylmethylenepolyisocyanates; and a mixture of isomeric tolylene diisocyanates with polymeric tolylene diisocyanates obtained as residues from the manufacture of the diisocyanates.

When the isocyanate which is reacted with the 3,4-dihydro-2H-pyran-2-carbinol contains two isocyanato functions, bis-(3',4'-dihydro-2'H-pyran-2-alkyl) dicarbamates are formed having the general formula:



wherein Z, Z' and n are as defined hereinabove; and R'' corresponds to the R'' nucleus of the isocyanate reactant, $R''(NCO)_i$ when i is two. It is to be understood that when the isocyanate has an isocyanato function greater than two, the pyran-2-alkyl monomer will have a corresponding average number of carbamate groups and the general formula:



wherein $C_5(Z)_7O$ and $C_5(Z')_7O$ are the respective 3,4-dihydro-2H-pyran rings. Typical examples of this class of di-(dihydropyran-2-alkyl) compounds are toluene-2,4-(or 2,6)-(bis-3',4'-dihydro-2'H-pyran-2'-methyl) carbamate and the reaction products of 3,4-dihydro-2'H-pyran-2-carbinol with the aforesaid polymeric liquids having an average isocyanato function of about 2.25 to about 3.2.

THE CYCLIC ACETAL MONOMERS

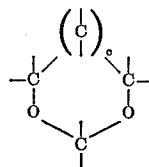
The 1,3-dioxolanes and 1,3-dioxanes employed in the process of this invention and which are copolymerized with the above-described pyran-2-alkyl compounds, have the following general Formula B:



wherein:

e and f represent numbers having a value of from zero to one, the sum $e+f$ being one;

D represents the aforesaid cyclic nucleus,



where c is a number having a value of from zero to one, D being a 1,3-dioxolanyl ring when c is zero and a 1,3-dioxanyl ring when c is one;

D' represents a cyclic nucleus having from five to seven members and is of the class consisting of a cyclic hydrocarbon nucleus and an oxygen-heterocyclic nucleus corresponding to the aforesaid 1,3-dioxolanyl or 1,3-dioxanyl nucleus (D), one carbon atom of D' being common to cyclic nucleus D of general Formula B and forming a spiro compound therewith; and

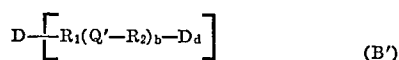
S designates a monovalent radical as defined in detail below with respect to general Formula B' and, when present, is bonded to a carbon atom of cyclic nucleus D.

In the aforesaid general Formula B, when e is one (and thus f is zero), all but one of the valences of the carbon atoms of the 1,3-dioxolanyl or 1,3-dioxanyl ring (D) are satisfied by monovalent substituents (S') of the class consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, haloalkyl, cycloalkyl, alkenyl, cycloalkenyl, bicycloalkenyl, alkoxy, aryloxy and carbalkoxy. The unsatisfied valence is the valence through which the cyclic nucleus (D) is linked to the remainder of the compound, that is, to the monovalent radical, S. On the other hand, when f of general Formula B is one (and thus e is zero), all but two va-

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lences of a single carbon atom of the cyclic nucleus (D) are satisfied by one of the aforesaid monovalent substituents (S') and the remaining two unsatisfied valences of said single carbon atom form a spiro compound with the cyclic nucleus, D'. The remaining valences of D' may also be satisfied by the aforesaid monovalent substituents, S'. When S' is one of the aforesaid organic radicals, it may contain from 1 to 16 carbon atoms per radical, and preferably has not more than 10 carbon atoms. When two organic radicals (S') are bonded to the same carbon atom, they are usually lower alkyl, lower haloalkyl, or lower alkoxy (that is, radicals having from 1 to 4 carbon atoms), or lower alkenyl groups (that is, radicals having from 2 to 4 carbon atoms).

When *f* of the general Formula B is zero, the cyclic acetal monomers employed in this invention have the formula, D—S, wherein S is a monovalent radical having the structure shown within brackets in the following Formula B':



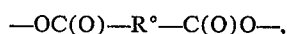
wherein:

D represents a 1,3-dioxolanyl or 1,3-dioxanyl ring all but one of the carbon atoms of which are bonded to the aforesaid S' radicals, as described above;

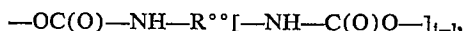
b and *d* each represents a number having a value from zero to one, *b* being one only when *d* is one;

R₁ is either a monovalent or divalent group depending upon the value of *d*; thus, when *d* is zero (and thus *b* is also zero), R₁ is the monovalent hydroxyalkyl group, —C_mH_{2m}(OH), wherein the —OH group may be a primary, secondary or tertiary hydroxyl; and, when *d* is one and *b* is either zero or one, R₁ is a bivalent alkylene group having the formula, —C_mH_{2m-w}Y_w—, wherein *w* has a value of zero to one and the definition of Y, when present (that is, when *w* is one), depends upon the value of *b*; thus, when *b* is zero, Y is a hydroxyl group, and, when *b* is one, Y is the cyclic nucleus, D; in each instance, *m* represents an integer having a value of from 1 to 16 and is preferably from 1 to 10;

Q' represents the dicarboxylate group,



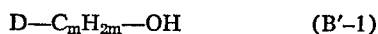
or the polycarbamate group,



wherein R[°] and R^{°°} are, respectively, the nucleus of a dicarboxylic acid and the nucleus of an organic polyisocyanate having *i* number of isocyanato groups, *i* being at least two;

R₂ is the same as R₁ when *d* is one and, of course, when *b* is one; that is, R₂ has the formula, —C_mH_{2m-w}Y_w—, wherein *m* and *w* are as above-defined and Y, when present, is the cyclic nucleus D. Among the suitable 1,3-dioxolanes and 1,3-dioxanes encompassed by the above general Formula B and which are employed in the present invention are the following sub-classes designated as Compound B'-1 through B'-8.

(1) Hydroxyalkyl-mono-1,3-dioxolanes and -1,3-dioxanes, that is, compounds wherein *d* of the general Formula B' is zero (and thus *b* is also zero) and R₁ is, therefore, a hydroxyalkyl group. This particular class of compounds has the formula:

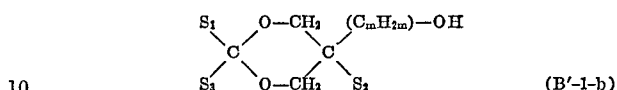
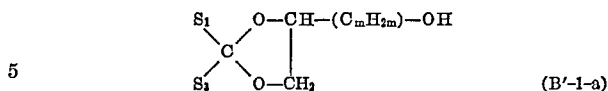


wherein a carbon atom of the —C_mH_{2m}— group is bonded to either the 2-, 4-, or 5-position of cyclic nucleus D, and the remaining carbon atoms of D are bonded to one of the aforesaid substituents, S', including hydrogen.

A preferred class of hydroxyalkyl-1,3-dioxolanes and hydroxyalkyl-1,3-dioxanes for use in the practice of this

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invention are compounds having the following formulas, respectively:



wherein the value of *m* is preferably from 1 to 10; the substituents, S₁ and S₂, may be the same or different and are members of the class consisting of hydrogen and an alkyl group preferably having from 1 to 10, and most preferably from 1 to 4 carbon atoms; and the substituent, S₃, is a member of the class consisting of S₁ (or S₂), an alkenyl group preferably having from 2 to 10 carbon atoms and a dihaloalkyl group preferably having from 2 to 10 carbon atoms. Of these, the particularly preferred monomers are those wherein S₃ is an alkenyl group of 2 to 4 carbon atoms such as a vinyl or isopropenyl group.

Typical examples of monomers encompassed by general Formula B' are:

2,2-dimethyl- and 2,2-diethyl-4-hydroxymethyl-1,3-dioxolanes;

2,2-dimethyl- and 2,2-dipropyl-4-(4-hydroxybutyl)-1,3-dioxolanes;

2-vinyl-4-hydroxymethyl-1,3-dioxolane;

2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane;

2-vinyl-4-(omega-hydroxyoctyl)-5-octyl-1,3-dioxolane;

2-isopropenyl-4-(4-hydroxybutyl)-1,3-dioxolane;

2-(1,2-dichloroethyl)-4-(4-hydroxybutyl)-1,3-dioxolane;

2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane;

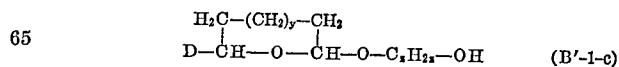
2-isopropenyl-4-ethyl-4-(omega-hydroxypentyl)-1,3-dioxane;

2-vinyl-4-(omega-pentylhydroxy)-1,3-dioxane; and

2-phenyl-4-hydroxymethyl-1,3-dioxolane.

This class of reactants are obtained by the reaction of ketones or aldehydes with triols by conventional acid-catalyzed reactions. For example, in producing the 2,2-dialkyl-substituted hydroxymethyl-1,3-dioxolanes, ketones such as acetone, diethyl ketone, dipropyl ketone and the like are condensed with the triol, glycerol, in the presence of an acid catalyst such as para-toluenesulfonic acid. In producing the 1,3-dioxolanes containing a 4-hydroxybutyl substituent in the four position of the ring, the ketone or aldehyde is reacted with 1,2,6-hexanetriol. When an unsaturated aldehyde such as acrolein or methacrolein are reacted with the triol, an alkenyl substituent such as vinyl and isopropenyl groups are introduced to the cyclic nucleus. For example, 2-vinyl-5-hydroxymethyl-5-ethyl-1,3-dioxane is readily prepared by the acid-catalyzed condensation reaction of acrolein and trimethylolpropane. The alkenyl substituent is readily converted to corresponding dihaloalkyl radicals by the addition thereto of molecular halogen such as chlorine or bromine.

Also included within the scope of suitable hydroxyalkyl-mono-1,3-dioxolanes and -1,3-dioxanes are compounds in which a carbon atom of the respective 1,3-dioxolanyl and 1,3-dioxanyl rings is linked to the hydroxyalkyl group through an oxy-substituted cyclic monoether as shown by the following general formula B'-1-c:



wherein D has the aforesaid significance, *y* has a value of from 0 to 2 and *z* is an integer of from 2 to 12, the sum *y*+*z* being no greater than 12. The preparation of these compounds is discussed hereinbelow in connection with the following class of monomers.

(2) Hydroxy-bis-(1,3-dioxolanyl or -1,3-dioxanyl) alkanes, that is, compounds having the general Formula B' above wherein *b* is zero, *d* is one, R₁ is the bivalent hydroxyalkylene group, —C_mH_{2m-1}(OH)—, wherein OH

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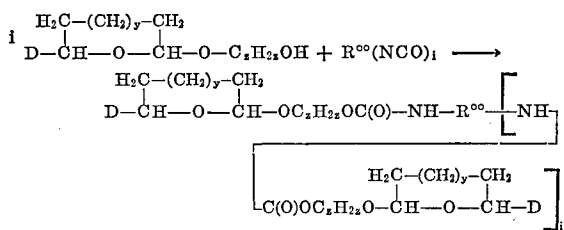
phenylenediisocyanate, 4-chloro-1,3-phenylenediisocyanate, 4-bromo-1,3-phenylenediisocyanate, 5,6-dimethyl-1,3-phenylenediisocyanate, 2,4- and 2,6-tolylene diisocyanates, crude tolylene diisocyanate, 6-isopropyl-1,3-phenylene diisocyanate, durylene diisocyanate, triphenylmethane-4,4',4''-triisocyanate, and many other organic polyisocyanates that are known in the art such as those disclosed in the aforesaid article by Siefkin.

Also included as useful in the preparation of the poly-carbamate cyclic acetals employed in this invention are the polyisocyanates of the anilineformaldehyde polyaromatic type which are produced by phosgenation of the polyamine obtained by acid-catalyzed condensation of aniline with formaldehyde. Polyphenylmethylenepolyisocyanates of this type are available commercially under such trade names as PAPI, AFPI, Mondur MR, Isonate 390P, NCO-120 and NCO-20. These products are low viscosity (50-500 centipoises at 25° C.) liquids having average isocyanato functionalities in the range of about 2.25 to about 3.2 or higher, depending upon the specific aniline-to-formaldehyde molar ratio used in the polyamine preparation. Other useful polyisocyanates are combinations of diisocyanates with polymeric isocyanates containing more than two isocyanate groups per molecule. Illustrative of such combinations are: a mixture of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and the aforesaid polyphenylmethylenepolyisocyanates; and a mixture of isomeric tolylene diisocyanates with polymeric tolylene diisocyanates obtained as residues from the manufacture of the diisocyanates.

Typical examples of the cyclic acetal carbamates are: the reaction product of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and 2,4- (or 2,6)-tolylene diisocyanate; the reaction product of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane and the aforesaid polyphenylmethylenepolyisocyanate having an average isocyanato functionality of about 2.7; the reaction product of 2-(1,2-dichloroethyl)-4-hydroxybutyl-1,3-dioxolane and 2,4- (or 2,6)-tolylene diisocyanate; and the reaction product of 2-vinyl-5-methyl-5-hydroxymethyl-1,3-dioxane and 2,4- (or 2,6)-tolylene diisocyanate.

Also included within this class of cyclic monomers for use in the present invention are the reaction products of any one of the aforesaid organic polyisocyanates and the hydroxyalkyl-1,3-dioxolanes and hydroxyalkyl-1,3-dioxanes represented above by general Formulas B'-1-a and B'-1-b wherein substituent S_3 is an alkenyl group to which an alpha,beta-unsaturated carboxylic acid such as acrylic acid has been added. For example, the reaction of 2-vinyl-4-(hydroxyalkyl)-1,3-dioxolanes and acrylic acid in the presence of p-toluenesulfonic acid provides 2-ethyl acrylate-4-(hydroxyalkyl)-1,3-dioxolanes. Reaction of i number of moles of the latter compound per mole of one of the aforesaid organic polyisocyanates, $R^{\circ\circ}(\text{NCO})_i$, provides the corresponding bis[(2-ethylacrylate-1,3-dioxolan-4-yl)alkyl]carbamates.

Also included within the scope of the cyclic acetal monomers are the reaction products of one of the aforesaid organic polyisocyanates and the cyclic acetals having general Formula B'-1-c above, as shown by the following equation:



wherein D, i , $R^{\circ\circ}$, y and z have the aforesaid significance.

(7) Bis-(1,3-dioxolanyl or 1,3-dioxanyl)alkanes, that is, compounds of the general Formula B' above wherein d is one, b is zero, and R_1 is the divalent alkylene group,

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$-\text{C}_m\text{H}_{2m}-$. Such compounds have the following general formula:

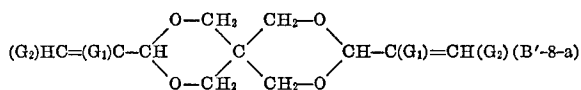


wherein the alkylene group is bonded to either the 2-, 4- or 5-position of the 1,3-dioxolanyl or 1,3-dioxanyl cyclic nucleus (D). Preferably, m has a value of from 1 to 10, and the carbon atoms of D are substituted with S_1 and S_2 radicals as shown for Compounds B'-2-a and B'-2-b above. Such compounds are prepared by the acid-catalyzed condensation reaction of a diol and dialdehyde, and are typically illustrated by: bis-(1,3-dioxolan-2-yl or 1,3-dioxan-2-yl)propane; bis-(4-alkyl-1,3-dioxolane-2-yl)butanes; and bis-(5-alkenyl-1,3-dioxan-2-yl)propanes.

(8) Spiro compounds comprising from one to two 1,3-dioxolanyl or 1,3-dioxanyl rings, and correspondingly from one to zero hydrocarbon cycloaliphatic nuclei, that is, compounds having the general Formula B above wherein f is one (and thus e is zero). This class of monomers have the formula:

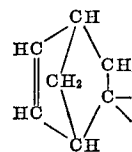


wherein D and D' share a common carbon atom and D' may or may not be the same cyclic nucleus as D. Typical examples of compounds in which D' is the same as D are the 3,9-dialkenylspirobi(meta-dioxanes) having the formula:

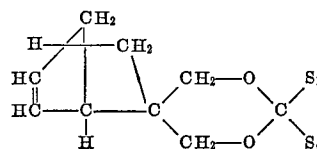


wherein G_1 is hydrogen, methyl or chlorine, and G_2 is hydrogen or methyl. Such compounds are prepared as described in U.S. Pat. No. 3,110,703, granted Nov. 12, 1963, and any of the unsaturated spirobi(meta-dioxanes) described therein are suitable monomers for use in the present invention. Specific examples of suitable spirobi(meta-dioxanes) for use in the present invention are: 3,9-divinylspirobi(meta-dioxane), 3,9-diisopropenylspirobi(meta-dioxane) and 3,9-di-(1-chlorovinyl)spirobi(meta-dioxane).

Examples of compounds in which D' is different from D are the norbornenyl-containing dioxanes in which a carbon atom of the D nucleus is common to a bicyclo[2.2.1]-5-heptenylene nucleus,



This type of monomer is obtained by the reaction of bicyclo[2.2.1]-5-heptene-2,2-diols and an aldehyde. Such compounds have the structure:



wherein S_1 is hydrogen or a lower alkyl group, and S_4 is S_1 or a bicyclo[2.2.1]-5-heptenyl radical, the nature of S_1 and S_4 depending upon the type of aldehyde reactant employed in preparing the spiro compound.

THE COPOLYMERIZATION REACTION

In accordance with the process of this invention, the aforesaid di-(dihydropyranyl) compounds and cyclic acetals are copolymerized in a reaction medium comprising

a cationic polymerization catalyst under conditions such that either thermoset resins or foamed polymeric products are produced. The relative proportions of monomers employed may vary over a relatively wide range without departing from the scope of this invention. Generally, the mole ratio of di-(dihydropyranyl) monomer to the cyclic acetal monomer ranges from about 0.2:1 to about 10:1. It is to be understood that included within the scope of the present invention is the copolymerization of one or more of the di-(dihydropyranyl) compounds with more than one of either the above-described 1,3-dioxolanes or 1,3-dioxanes, or the di-(dihydropyranyl) monomer may be copolymerized with a combination of the dioxolane and dioxane monomers.

In accordance with the teachings of this invention, the polymerization catalyst is cationic by which latter term is meant any strongly acid catalyst including strong proton-donating acids and Lewis acids. Typical examples of suitable cationic polymerization catalysts for use in the present invention are p-toluene-sulfonic acid, phosphoric acid, perchloric acid, trifluoroacetic acid, trichloroacetic acid, fluoroboric acid, fluosilicic acid, hydrogen fluoride, hexafluorophosphoric acid, silicotungstic acid, boron trifluoride, trimethoxy boroxine, ferric chloride, stannic chloride, phosphorus pentachloride, antimony pentafluoride, zinc chloride and aluminum chloride.

It is to be understood that the catalyst system may comprise a combination of any of the aforesaid polymerization catalysts and that the catalyst may be used in the form of a coordination complex with an organic compound wherein the donor atom is oxygen, sulfur or fluorine. Typical examples of such complexing agents are ethers, alcohols including mono-ols and polyols, carboxylic acids, alkyl sulfides, mercaptans and hydrogen fluoride. Such complexes may be added to the polymerization reaction system in a preformed state or they may be formed in the reaction system. The catalyst may also be used in the form of a solution in non complexing solvents such as the normally liquid hydrocarbons (e.g., heptane, toluene, xylene and the like). A preferred class of catalysts are those comprising boron such as, in particular, boron trifluoride which is usually added to the polymerization reaction system as a solution in a complexing solvent such as the saturated aliphatic or aromatically unsaturated ethers and glycols including glycols which also contain an ether linkage. Typical examples of such solvents are diethyl ether, dibutyl ether, ethyl alcohol, benzyl alcohol, propylene glycol, diethylene glycol, and dipropylene glycol. Solutions of boron trifluoride etherates are especially suitable.

The catalyst is present in the polymerization reaction system in an amount which is, of course, at least sufficient to initiate the polymerization reaction. Generally, the mole ratio of catalyst to total monomers varies from about 0.0001:1 to about 0.5:1, and is preferably at least 0.001:1. This ratio expresses the total concentration of active cationic initiator (e.g., boron trifluoride) and, when present, the complexing agent (e.g., ether as in the boron trifluoride etherates).

The polymerization reactions described herein are exothermic and occur over a relatively wide range of temperatures such as from about 0° C. up to the peak exotherm of any particular reaction mixture. Usually, the copolymerization reactions commence at temperatures from about 15° C. to about 25° C. and peak exotherms up to about 200° C. may be reached relatively rapidly. The temperature at which a particular reaction begins and the exothermicity thereof depends on a number of factors such as the particular mixture of monomers, the catalyst, the presence or absence of complexing agents, solvents or diluents and the like. As desired, initial reaction temperatures may be controlled in any suitable manner such as by cooling, adding the catalyst at a controlled rate or effecting the reaction in dilute phase. When the initial liberation of heat has subsided, the reaction mixture may

be heated from an external source to maximize the extent of copolymerization.

In accordance with a preferred embodiment of the process described herein, the polymerization is carried out in the presence of a phenolic compound, that is, a compound in which at least one hydrogen atom of an aromatic nucleus has been replaced by a hydroxyl group. Typical examples of suitable phenolic compounds which may be used as an ingredient of the polymerization reaction mixture are: the mono- and polyhydric unsubstituted phenols such as phenol, naphthol, catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol; alkyl-substituted phenolic compounds in which the alkyl group contains from 1 to 12 carbon atoms and usually not more than 6 carbon atoms such as the cresols, xylenols, ethylphenols, 2,4,5-trimethylphenol, durenol, thymol, 2,4,6-tritert-butylphenol, 4-tert-amylphenol, and o-cyclohexylphenol; aryl- and halogen-substituted phenols such as m-phenylphenol, 4,4'-dihydroxybiphenyl, m-chlorophenol, 2,4,5-trichlorophenol, 2,4,6-tribromophenol; hydroxyphenyl-substituted alkanes such as bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A), 2,2-bis(4-hydroxyphenyl)butane and 2,2-bis(4-hydroxy-3-methylphenyl)propane; low molecular weight phenol-terminated polycarbonates; condensation products of phenols with aldehydes and ketones such as resoles and novolaks; and any combination of such phenolic compounds.

When used, the phenolic compound constitutes from about 2 to about 30, and preferably from about 5 to about 20, weight percent of the combined total weight of the di-(dihydropyranyl) and cyclic acetal monomers.

In accordance with one embodiment of the process of this invention, the polymerization reaction is carried out under the aforesaid conditions to provide copolymers ranging from viscous liquid resins, useful as plasticizers, to tough resinous solids, useful as surface coatings.

In accordance with another embodiment of the process of this invention, the polymerization reaction is carried out under the aforesaid conditions and such that foamed polymeric products are provided. In accordance with this embodiment, the polymerization reaction medium comprises the monomer mixture, one or more of the above-described cationic polymerization catalysts, a blowing agent, usually a foam stabilizer to reduce any tendency of the foam to collapse until the foamed product has developed sufficient gel strength to become self-supporting, and preferably one or more of the aforesaid phenolic compounds.

The blowing agents which can be employed in the process of this invention include liquefied gases which vaporize at or below the temperature of the exothermic polymerization reaction such as saturated or non polymerizable halogenated hydrocarbons, or other inert gases such as nitrogen, carbon dioxide, methane, helium and argon. Halocarbon blowing agents suitable for use in the process of this invention are: trichloromonofluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, dibromodifluoromethane, 1,1-dichloro-1-fluoroethane, 1-chloro-1,1-difluoro-2,2-dichloroethane, dichlorotetrafluoroethane, trichlorotrifluoroethane, 1,1,1-trifluoro-2-fluoro-3,3-difluoro-4,4,4-trifluorobutane, dichlorohexafluorocyclobutane, methylene chloride, chloroform, trichloroethylene, carbon tetrachloride and perchloroethylene.

The foam stabilizer, when used, is usually a siloxane-oxyalkylene block copolymer and may be any of such copolymers described in the prior art. Generally, the block copolymers comprise (1) siloxy units having the formula, Z_2SiO , (2) polyether-substituted siloxy units having the formula, $Z^o(C_nH_{2n}O)_x C_m H_{2m} Si(Z)O$, and (3) siloxy units having the formula, $Z_3SiO_{1/2}$, where: Z in each instance is a monovalent hydrocarbon group having from 1 to 12 carbon atoms such as alkyl and aryl groups, in particular methyl; Z^o is either Z, Z—C(O)

or hydrogen where Z is as aforesaid; $-C_nH_{2n}-$ is a bivalent hydrocarbon radical, usually of 2 to 5 carbon atoms, that links the respective silicon atoms of the polyether-substituted siloxy units to the polyether block, $Z^{\circ}O(C_nH_{2n}O)_x$, in which n has a value of from 2 to 4 and the average value of x is such that the average molecular weight of the polyether block is from about 200 to about 6000. Illustrative block copolymers for use as foam stabilizers in the foaming reaction of this invention are, for example, the copolymers described in U.S. Pats. Nos. 2,834,748; 2,917,480; 3,505,377; 3,507,815; and in U.S. patent applications Ser. No. 718,920, filed Apr. 4, 1968, and Ser. No. 109,587, filed Jan. 25, 1971, now abandoned. Such copolymer compositions are incorporated herein by reference to the aforesaid patents and applications.

The relative amounts of the various components used in the foaming formulation are not narrowly critical. The di-(dihydropyranyl) and cyclic acetal monomers, taken together, usually comprise the major percent by weight of the foam formulation (exclusive of solvents or diluents). The catalyst, blowing agent and foam stabilizer, when used, are each present in a minor amount sufficient to perform their respective functions. The blowing agent usually comprises from about 5 to about 40 weight percent of the total weight of monomers, the particular amount of blowing agent employed depending primarily on the desired density of the foamed product. The foam stabilizer, when used, is usually present in an amount of from about 0.1 to about 5 weight percent of the total weight of the monomer mixture. The cationic polymerization catalyst and the phenolic compound, when used, are present in the respective concentrations stated above.

If desired, other additional ingredients can be employed in minor amounts and for specific purposes in producing the polymeric products of this invention including the foamed products. For example, one type of additive is an organic flame-retardant which preferably contains phosphorus or halogen or both phosphorus and halogen. Among the suitable flame-retardants which may be incorporated in the polymeric compositions of this invention are: tri(2-chloroethyl)phosphate; 2,2-bis(3',5'-dibromo-4'-hydroxyphenyl)propane; 2,2-di(bromomethyl)-1,3-propanediol; chlorendic acid; brominated phthalate ester diols (e.g., from tetrabromophthalic anhydride and propylene oxide); tetrabromobisphenol-A; tetrabromophthalic anhydride; 2,4,6-tribromophenol; bis(2,3-dibromopropyl)phosphoric acid or salts thereof; tris(1-bromo-3-chloroisopropyl)phosphate; tris(2,3-dibromopropyl)phosphate; and other flame-retardants known in the art.

When used, the flame retardant is usually present in an amount between about 2 and about 20 weight percent of the weight of the monomers to be polymerized. Other additives which may be present during the polymerization process described herein and incorporated into the polymeric products are dyes, fillers, stabilizers, anti-oxidants, plasticizers and the like.

The polymeric foams produced in accordance with this invention are useful as insulation materials. In view of their good thermal insulating and mechanical strength properties, they find particular application in refrigeration equipment, trailer trucks and in the building industry.

EXAMPLES I-XXII

These examples illustrate copolymerization of 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and various monofunctional and difunctional 1,3-dioxolanes and 1,3-dioxanes.

(1) Monomers employed

In these examples, the di-(dihydropyranyl)-monomer employed was 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) having a boiling point of 115°-119° C. at 0.50 mm. mercury pressure and prepared

by the self-condensation of 2-formyl-3,4-dihydro-2H-pyran in the presence of aluminum isopropoxide catalyst. This monomer is designated as Monomer M₁.

The 1,3-dioxolanes and 1,3-dioxanes employed are identified in Table I below and, for convenience, are designated generally as Monomer M₂ and individually as Comonomers A through K. Comonomers A, B, C and K of Table I are known compounds and were used as available commercially from Aldrich Chemical Company (Comonomer A) and Union Carbide Corporation (Comonomers B, C and K). Comonomers D-J of Table I were prepared as described under the following Examples 2(i)-(vii).

(2) Preparation of comonomers D-J of Table I

(i) Comonomer D.—2-(1,2-dichloroethyl)-4-(4-hydroxybutyl)-1,3-dioxolane:

Liquid chlorine (228 ml.; 5 moles) was added to a solution of Comonomer B (860 grams; 5 moles), that is, 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane, in 3600 ml. of carbon tetrachloride over a period of 4.5 hours while maintaining the temperature at 20-30° C. by means of intermittent cooling with an ice-bath. When the addition of chlorine was complete, the mixture was stirred at ambient temperature overnight. After removal of solvent by heating the mixture at 51° C. and 1 mm. mercury pressure for one hour, the product was obtained as a colorless viscous material.

(ii) Comonomer E.—1,3-bis(1,3-dioxolan-2-yl)propane:

A reaction flask containing 1001 grams of a 50 weight percent aqueous solution of glutaraldehyde (5 moles), ethylene glycol (621 grams; 10 moles), toluene (800 ml.) and p-toluene sulfonic acid (0.56 gram) was heated slowly to refluxing temperatures (90°-125° C.). During a seven hour period, water (665 grams; 98 percent recovery) was collected by means of a Dean-Stark trap. The reaction mixture was then distilled through a 10-inch Vigreux column thereby providing 803 grams (85 weight percent yield) of colorless product having a boiling point of 133°-137° C. at 1.66 mm. pressure. Upon analysis, the product was found to contain 57.16 and 8.72 weight percent carbon and hydrogen, respectively; the corresponding values calculated for the empirical formula, C₉H₁₆O₄, of Comonomer E are 57.43 and 8.57.

(iii) Comonomer F.—Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]isophthalate:

Into a five-liter capacity, four-necked flask equipped with a thermometer, stirrer, nitrogen inlet and a 10-inch helix packed column were placed 1322 grams (10 moles) of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (Comonomer A herein), 971 grams (5 moles) of dimethyl isophthalate, 1700 grams of dry toluene and 7 grams of sodium methoxide. The reaction mixture was heated to reflux. During 5 hours, a binary mixture (927 grams) of toluene-methanol was collected at a head temperature of 95°-106° C. by maintaining a flask temperature of 137°-145° C. After cooling to 25° C., 500 ml. of dichloromethane was dissolved in the reaction mixture. The resulting mixture was washed with four 1000 ml. portions of 5 percent aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to give a crude amber-colored oil. Distillation of the oil afforded 999.5 grams (51 percent yield) of substantially pure white product having a boiling point of 205°-212° C. (at 0.50-0.60 mm. pressure). Analysis of the product showed carbon and hydrogen contents of 60.74 and 6.83 weight percent, respectively. The calculated carbon and hydrogen contents (basis, C₂₀H₂₆O₈) are 60.91 and 6.59 respectively.

(iv) Comonomer G.—Bis[(2-vinyl-1,3-dioxolan-4-yl)-4-butyl]isophthalate:

A five-liter, four necked flask equipped with a thermometer, stirrer, nitrogen inlet and a 10-inch helix packed

column containing a solution of 1720 grams (10 moles) of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (Comonomer B herein, 791 grams (5 moles) of dimethyl isophthalate, 1700 grams of dry toluene and 7 grams of sodium methoxide was heated to reflux. During 5 hours, 700 grams of a toluene-methanol binary mixture was collected at a temperature of 63° to 105° C. The remaining toluene was distilled from the reaction mixture at atmospheric pressure and the residue was washed four times with 1000 ml. portions of a 5 percent sodium chloride solution, adding 500 grams of dichloromethane to break the emulsion. After drying the non aqueous layer over magnesium sulfate and removing the solvent under reduced pressure, the product was found to be an oil which was nondistillable at temperatures up to 235° C. at 0.7 mm. mercury pressure.

(v) Comonomer H.—2,4-bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]-N,N'-tolyl carbamate:

To a one-liter, four-necked flask equipped with a stirrer, thermometer, nitrogen inlet and dropping funnel was placed 396.5 grams (3 moles) of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (Comonomer A herein). Toluene diisocyanate (261 grams; 1.5 moles) was added dropwise during 10 minutes while maintaining the temperature at 25° C. There was no immediate exotherm but on continued stirring after the addition was complete, the temperature of the reaction mixture rose to 35° C. The mixture was then stirred for 6 hours at 30° C. The product was isolated as a residue and purified by heating at 150° C. and 0.20 mm. pressure in a falling film still. The purified product had a viscosity of 392,000 centipoises at 25° C.

(vi) Comonomer I.—2,4-bis[(2-vinyl-1,3-dioxolan-4-yl)-4-butyl]-N,N'-tolyl carbamate:

Toluene diisocyanate (870 grams; 5 moles) was added to 1720 grams (10 moles) of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (Comonomer B herein) with stirring, under an atmosphere of nitrogen, during 3.24 hours. The reaction was slightly exothermic and the temperature was adjusted between 25°-45° C. during the addition. The carbamate was isolated as a residue product. Purification was effected by heating at 150° C. and 0.20 mm. pressure in a falling film still. The purified product had a viscosity of 260,000 centipoises at 25° C.

(vii) Comonomer J.—2,4-bis[(2-vinyl-5-methyl-1,3-dioxan-5-yl)methyl]-N,N'-tolyl carbamate:

Toluene diisocyanate (696 grams; 4 moles) was added dropwise during 4 hours while maintaining the temperature at 20°-25° C. to 1264 grams (8 moles) of 2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane (Comonomer C herein). The reaction was exothermic and an ice bath was employed for cooling purposes. When the addition was complete the mixture was stirred overnight at 25° C. The product crystallized to a glassy solid and was used without further purification.

(3) The copolymerization reactions

In each of the copolymerization reactions of Examples I-XXII, the catalyst was rapidly and thoroughly mixed into an undiluted solution of the di(dihydropyranyl) monomer (M₁) and the respective, aforesaid cyclic acetal monomers, designated as Comonomers A-K, at about 25° C. during a period of 20 seconds. The catalyst employed was a 10 weight percent solution of boron trifluoride etherate, BF₃·O(C₂H₅)₂ in diethylene glycol. The respective polymerization mixtures were then poured into a three-inch diameter aluminum mold. The polymerization induction time was taken as the first noticeable deflection of the pyrometer needle and the peak exotherm (i.e., the temperature-time profile) was recorded. The structure of Comonomers A-K, the relative molar proportions of monomers and catalyst used and the results obtained are indicated in the following Table I.

TABLE I

Example number	Number	Name and structure	Cyclic acetal monomer (M ₂)		Monomer concentration, moles X 10		Initiator (I) concentration	Mole X 10 ⁴	M ₁ -M ₂ /I	Induction, time, sec.	Peak exotherm		Description of product
			M ₁	M ₂	° C.	Time, sec.							
I.....	A	2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane..... 	1.11	1.88	0.5	3.53	848	50	100	180	155	Do.	
II.....	A	2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane..... 	1.11	1.88	1.0	7.05	425	45	96	155	Do.	Do.	
III.....	B	2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane..... 	1.11	1.45	0.5	3.53	725	160	147	412.5	400	Do.	
IV.....	B	2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane..... 	1.11	1.45	1.0	7.05	363	80	159	400	Do.	Do.	
V.....	C	2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane..... 	1.11	1.58	0.5	3.53	762	60	139	225	150	Do.	
VI.....	C	2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane..... 	1.11	1.58	1.0	7.05	382	30	153	150	Do.	Do.	
VII.....	D	2-(1,2-dichloroethyl)-4-(4-hydroxybutyl)-1,3-dioxolane..... 	1.11	1.32	0.5	3.53	688	68	96	260	150	Do.	

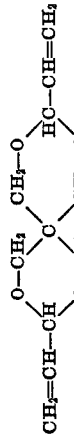
See footnotes at end of table.

TABLE I—Continued

Example number	Number Name and structure	Cyclic acetal monomer (M ₂)	Monomer concentration, moles×10		Initiator (I) ³ concentration	Polymerization		Description of product			
			M ₁ ¹	M ₂		Gms. ² Mole×10 ⁴ M ₁ +M ₂ /I	Induction, time, sec.		Peak exotherm ° C.	Time, sec.	
											M ₁ ¹
VIII..... D			1.11	1.32	1.0	7.05	345	35	93	160	Hard, plaque (slightly tacky surface).
IX..... E		1,3-bis(1,3-dioxolan-2-yl)-propane.....	1.11	1.33	0.5	3.53	691	90	110	420	Hard, tough plaque (slight shrinkage).
X..... E			1.11	1.33	1.0	7.05	346	45	140	240	Hard, tough plaque (high gloss).
XI..... F		bis[4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]isophthalate.....	1.11	0.630	0.5	3.53	493	75	92	180	Hard, tough, clear plaque.
XII..... F			1.11	0.630	1.0	7.05	247	40	97	180	Hard, tough, brown plaque.
XIII..... G		bis[2-vinyl-1,3-dioxolan-4-yl]-4-butyl]isophthalate.....	0.223	0.106	0.35	2.47	133	57	95	90	Hard, tough, clear amber plaque.
XIV..... G			0.134	0.143	0.35	2.47	114	64	120	110	Do.
XV..... H		2,4-bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]-N,N'-tolyl carbamate.....	1.11	0.568	0.5	3.53	475	50	79	250	Hard, brittle, clear plaque.
XVI..... H			1.11	0.568	1.0	7.05	238	30	90	150	Hard, brittle, amber plaque.
XVII..... I		2,4-bis[(2-vinyl-1,3-dioxolan-4-yl)-4-butyl]-N,N'-tolyl carbamate.....	1.11	0.481	0.5	3.53	451	40	47	28	Soft, rubbery (polymerization incomplete). ⁴
XVIII..... I			1.11	0.481	1.0	7.05	226	30	152	160	Hard, tough plaque (high gloss).
XIX..... J		2,4-bis[(2-vinyl-5-methyl-1,3-dioxan-5-yl)methyl]-N,N'-tolyl carbamate.....	1.11	0.510	0.5	3.53	459	30	93	160	Hard, tough plaque.
XX..... J			1.11	0.510	1.0	7.05	230	32	109	100	Hard, tough, light brown plaque.

See footnotes at end of table.

TABLE I—Continued

Example number	Cyclic acetal monomer (M ₂)	Monomer concentration, Moles X 10		Initiator (D) ² concentration	Polymerization			Description of product
		M ₁ ¹	M ₂		Gms. ³ Mole X 10 ⁴	Induction time, sec.	Peak exotherm ° C.	
XXI..... K	3,9-divinylisprobi(m-dioxane)	1.03	2.21	0.70	4.94	50	143	210 Hard, tough, clear tan plaque (high gloss).
XXII..... K		0.625	2.64	0.70	4.94	60	92	220 Hard (tacky) plaque. ⁴

¹ Monomer M₁ was 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate).

² The initiator designated I was BF₃·O(C₂H₅)₂ employed as a 10 weight percent solution in diethylene glycol.

³ Weight of solution referred to in footnote 2, containing the indicated number of moles of BF₃·O(C₂H₅)₂.

⁴ Minutes.

⁵ At the combination of relatively low comonomer and catalyst concentrations employed in this example, the exothermicity of the reaction was low indicating a more severe condition is required to complete the reaction such as longer reaction time or higher catalyst concentration (as used in Example XVIII).

⁶ After reaction mixture was allowed to stand 2 days to provide more complete copolymerization.

The results of Table I show that, with the exception of Comonomer A employed in Examples I and II, copolymerization of the di(-dihydropyranyl) monomer and cyclic acetal Comonomers B-K provided hard, and in most instances, tough plaques. The term "tough" as used in Table I indicates that the respective surfaces of the copolymer products did not crack or break when scraped with a knife edge and that such products are useful as ingredients of coating compositions (e.g., paints) which require satisfactory abrasion resistance. The viscous resinous products produced in accordance with Examples I and II in which Comonomer A was used, are useful as plasticizers. The brittle nature of the products provided in Examples XV and XVI is believed attributable to the relatively low concentration of Comonomer H which was used, and may be improved by carrying out the copolymerization at higher concentrations of this particular comonomer such as, for example, about 0.7 mole per mole of the di-(hydropyranyl) compound.

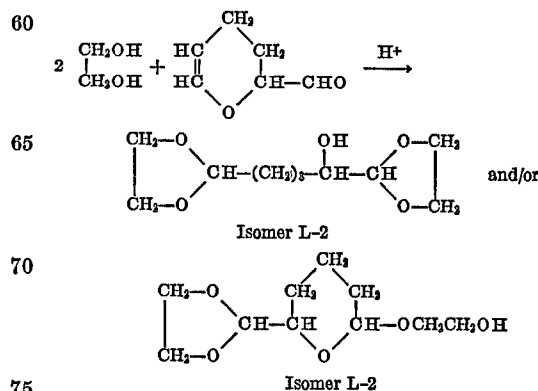
EXAMPLES XXIII-XXVI

In these examples, the cyclic acetals employed are designated Comonomer L (the product obtained by reacting acrolein dimer with ethylene glycol) and Comonomer N (the product obtained by reaction of Comonomer L and toluene diisocyanate).

(1) Preparation of Comonomer L.—1-hydroxy-1,4-bis(1,3-dioxolan-2-yl)butane and/or 2-(2-hydroxyethoxy)-6-(1,3-dioxolan-2-yl)pyran

Freshly distilled acrolein dimer (560.6 grams; 5.0 moles) was added dropwise to a solution of 620.1 grams (10.0 moles) of ethylene glycol and 13 drops of concentrated hydrochloric acid in 1500 ml. of benzene at 80° C. during 2 hours and 15 minutes. Water which formed was collected by means of a Dean-Stark trap. During the addition of acrolein dimer, the reaction maintained itself at 80° C. and 21.0 grams of water was collected. When the addition of the dimer was complete, the mixture was heated for 2.5 hours during which time an additional 65.0 grams of water was collected. The total yield of water was 86.0 grams or 96 weight percent. The reaction mixture was concentrated by distillation of 968 grams of the benzene at atmospheric pressure, followed by the addition of calcium oxide (2.0 grams). After standing for several days, the remainder of the solvent was stripped at 60° C. and 0.6 mm. mercury pressure. Distillation of the remaining material provided 393.4 grams of colorless product having a boiling point of 125°-129° C. at 0.47-0.48 mm. pressure. Analysis of the reaction product by infrared absorption revealed bands at 2.89 microns attributable to OH and at 3.45, 8.64, 9.15 and 9.40 microns attributable to ether (O—CH₂, C—O, C—O—C) linkages; no peaks due to C=C absorption were revealed. This acid-catalyzed condensation reaction of acrolein dimer and ethylene glycol may proceed in accordance with the following Equation 1 to provide Isomer L-1 or Isomer L-2 or a mixture thereof.

Equation 1:



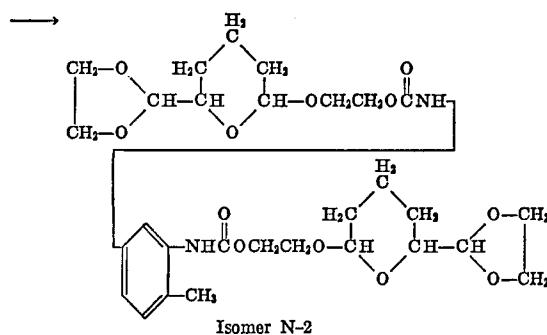
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The empirical formula for each of these isomeric compounds is $C_{10}H_{18}O_5$, representing calculated weight percentages of carbon, hydrogen and oxygen of 55.03; 8.31 and 36.66, respectively. Upon analysis of the aforesaid colorless product, it was found to contain 55.14 and 8.42 weight percent carbon and hydrogen, respectively (another analysis showed 55.17 and 8.16, respectively). In an attempt to identify Monomer L as having the structure of Isomer L-1 or Isomer L-2 or a mixture thereof, the NMR spectrum of the reaction product was taken. This analysis exhibited signals centered at delta 4.78 (two protons, a triplet, attributed to protons at C_2 of the dioxolane rings); 3.77 (ten protons, a multiplet due to ethylene glycol, methine and hydroxy protons) and 1.67 p.p.m. (six methylene protons). This spectrum fits the structures of both isomers of Comonomer L but cannot differentiate between them.

(2) Preparation of Comonomer N.—2,4 - bis{1-[1,4-bis(1,3-dioxolan-2-yl)butyl]}-N,N'-tolyl carbamate and/or 2,4 - bis[beta-[2 - ethoxy-6-(1,3-dioxolan-2-yl)-pyran-yl]H-N,N'-tolyl carbamate

To Comonomer L above (60 grams; 0.275 mole) there was added 2,4-toluene diisocyanate (23.95 grams; 0.1375

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(3) Copolymerization of Comonomers L and N

Each of the above-described cyclic acetals, designated as Comonomers L and N, were copolymerized at room temperature (about 25° C.) with 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) in accordance with the procedure described above with respect to Examples I-XXII using 25 grams of each monomer. The reaction conditions employed and the results obtained are given in the following Table II.

TABLE II

Example No.	Cyclic acetal comonomer, M_2	Concentration of monomers mole $\times 10^4$		Initiator (I) ² concentration		Polymerization induction time, seconds	Polymerization peak exotherm		Description of product	
		M_1^1	M_2	Gram ³	Mole $\times 10^4$		Temp., °C.	Time, seconds		
XXIII	L	1.11	1.15	0.5	3.53	640	180	88	15.54	Hard plaque (tacky surface).
XXIV	L	1.11	1.15	1.0	7.05	321	90	91	330	Do.
XXV	N	1.11	0.410	0.5	3.53	430	40	103	260	Hard, tough, brown plaque.
XXVI	N	1.11	0.410	1.0	7.05	216	45	111	270	Do.

¹ Monomer M_1 was 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate).

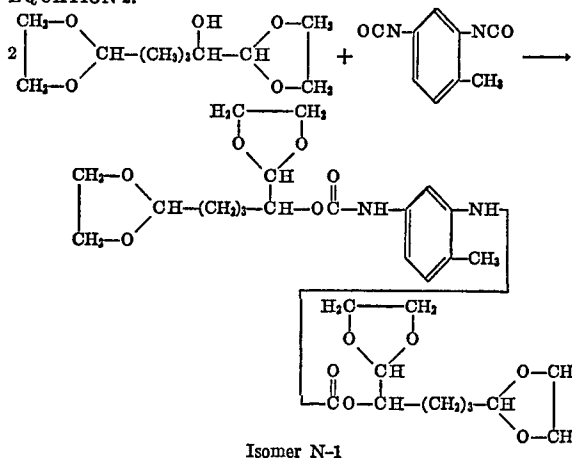
² The initiator (I) was $BF_3 \cdot O(C_2H_5)_2$ employed as a 10 weight percent solution in diethylene glycol.

³ Weight of solution referred to in footnote (2), containing the indicated number of moles of $BF_3 \cdot O(C_2H_5)_2$.

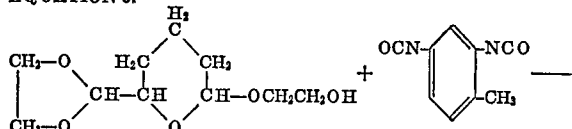
⁴ Minutes.

mole) during 30 minutes while maintaining the reaction temperature at 25°-30° C. The reaction tended to be exothermic and cooling of the reaction flask was necessary throughout the addition. The reaction mixture was stirred overnight at ambient conditions and, after standing three days, the viscous, colorless product crystallized to a glassy solid. Depending upon whether Comonomer L has the structure of Isomer L-1 or Isomer L-2, Comonomer N has the structure of Isomer N-1 or Isomer N-2, respectively, or is a mixture thereof, as shown by the following Equations 2 and 3:

EQUATION 2:



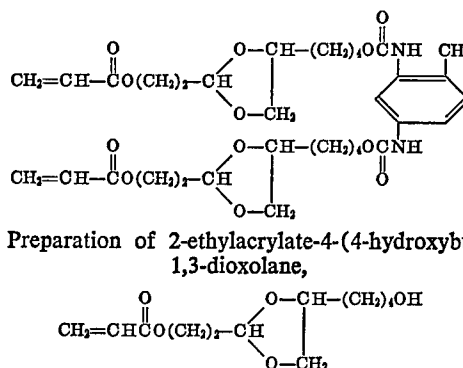
EQUATION 3:



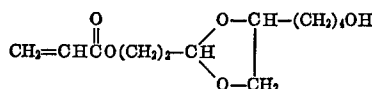
The results of Table II further demonstrate that the cyclic acetals described herein including those of a relatively complex nature such as Comonomer N, are capable of providing thermosetting resins. Although the general procedure of Examples III-XXVI was such to provide solid polymeric products in the form of a molded plaque, the reactions may also be carried out by spreading or casting the respective reaction mixtures on glass with a doctor knife in accordance with conventional procedure, to form films having essentially the same physical characteristics as the molded plaques.

EXAMPLE XXVII

Preparation and copolymerization of Comonomer O.—2,4 bis[2 - ethylacrylate - 1,3 - dioxolan - 4 - yl] - 4 - butyl]-N,N'-tolyl carbamate



(1) Preparation of 2-ethylacrylate-4-(4-hydroxybutyl)-1,3-dioxolane,



A solution of 172.2 grams (1 mole) of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (Comonomer B herein), 72.1 grams (1 mole) of acrylic acid and 0.1 gram of p-toluenesulfonic acid in 5 ml. of 1,2-dimethoxyethane was heated for 10 hours at 50-60° C. After adding water (150 ml.) and dichloromethane (200 ml.), the nonaqueous layer

was washed successively with 100 ml. of 5 percent sodium bicarbonate and two 100-ml. portions of water, and was then dried over magnesium sulfate. Hydroquinone (0.5 gram) stabilizer was added, the magnesium sulfate removed by filtration and the solvent evaporated under reduced pressure. The resulting oil was distilled through a 6-inch Vigreux column to give 46.2 grams (19 weight percent yield) of colorless product having a boiling point of 83°–87° C. at 1 mm. pressure. Upon analysis, the product was found to contain 62.28 and 9.12 weight percent of carbon and hydrogen, respectively. The corresponding calculated values, based on the empirical formula, $C_{12}H_{20}O_5$, are 59.00 and 8.25.

(2) Preparation of Comonomer O

Toluene diisocyanate (7.14 grams; 0.041 mole) was added to the above-described addition product (20 grams; 0.082 mole) of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and acrylic acid, over a period of 30 minutes at 25°–30° C. The reaction was slightly exothermic and there was a slight increase in solution viscosity when the addition was complete. The viscous yellow liquid was employed as the residue product.

(3) Copolymerization of Comonomer O

A mixture containing 25 grams of Comonomer O and 25 grams of 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) was copolymerized in the presence of 0.5 gram of a 10 weight percent solution of boron trifluoride complexed with diethyl ether in diethylene glycol, at about 25° C. following the procedure described above with respect to Examples I–XXII. The polymerization induction time was 50 seconds and the polymerization peak exotherm was 115° C. reached in 280 seconds. The copolymer product was a hard, tough, transparent plaque which did not break or crack when scratched with a knife edge indicating good abrasion resistance.

EXAMPLE XXVIII

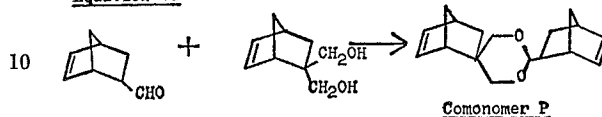
This example illustrates the preparation and copolymerization of a norbornenyl-substituted spiro compound of 1,3-dioxane.

(1) Preparation of Comonomer P.—2-(2-bicyclo[2.2.1]-5-heptene)-5-(2-spirobicyclo[2.2.1]-5-heptene)-1,3-dioxane

A solution of 190.2 grams (1.56 moles) of bicyclo[2.2.1]-5-heptene-2-carboxaldehyde, 240 grams (1.56 moles) of bicyclo[2.2.1]-5-heptene-2,2-dimethanol, 0.47

gram of p-toluenesulfonic acid and 468 ml. of benzene, was heated under reflux for 4 hours during which time 28 grams (100 percent yield) of water was collected in a Dean-Stark trap. This acid-catalyzed condensation reaction provides Comonomer P as shown by the following Equation 4.

Equation 4:



The reaction mixture was washed successively with 1 liter of a 1 percent sodium bisulfite solution and water and dried over anhydrous sodium sulfate. After filtering the sodium sulfate, the mixture was subjected to reduced pressure (40 mm.) at 50° C. to remove the benzene. The remaining crude solid residue (377 grams; 94 percent yield) melted at 144°–156° C. Recrystallization from methanol afforded a 56 percent yield of a substantially pure white product having a melting point of 165°–168° C. The calculated carbon and hydrogen contents for the assigned structure of Comonomer P ($C_{17}H_{22}O_2$) are C, 79.03 and H, 8.58, weight percent. Upon analysis, the carbon and hydrogen contents were found to be: C, 78.82 and H, 8.41 weight percent.

(2) Copolymerization of Copolymer P

A mixture containing 4.0 grams (0.155 mol) of Comonomer P and 4.0 grams (0.179 mole) of 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) was copolymerized at about 25° C. in the presence of 1.9 grams of a 10 weight percent solution of $BF_3 \cdot O(C_2H_5)_2$ ($13.40 \text{ moles} \times 10^4$) dissolved in diethylene glycol following the procedure described above with respect to Examples I–XXII. The polymerization induction time was 30 seconds and the polymerization peak exotherm was 145° C. reached in 360 seconds. The copolymer product was a hard, tough plaque which exhibited good abrasion resistance when scraped with a knife edge.

EXAMPLES XXIX–XXXVII

In accordance with these examples, 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate), designated herein as Monomer M₁, was polymerized with the 2:1 adduct of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and toluene diisocyanate, designated and described hereinabove as Comonomer I, under conditions such that

TABLE III

Foamed products of Di-(dihydropyran)l monomer and 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane/toluene diisocyanate adduct

Example No.	M-1	M-2	XXIX	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI	XXXVII
Foam formulation, parts by weight:											
Di-(dihydropyran)l monomer											
M ₁ ¹	76	76	36.8	33.8	37.5	47.4	38	33	42	40	30
1,3-dioxolane, comonomer I ²			39	66.2	62.5	52.6	57	57	33	40	50
Bisphenol A	24	24	24.4				5	10	25	20	20
10 weight percent solution of $BF_3 \cdot O(C_2H_5)_2$ in diethylene glycol											
	1.05	0.80	0.81	2.98	2.25	1.58	1.33	1.33	0.48	1.13	1.67
Trichloromonofluoromethane	17	17	18.86	17.25	16.28	13.71	15.95	15.95	14.95	15.67	15.85
Silicone surfactant A ³	1.00	1.00	0.78	0.159	0.150		0.80	0.80	0.80	0.80	0.80
Silicone surfactant B ⁴						3.98					
Foaming properties:											
Cream time, seconds	25	50	<10	37	37	45	40	28	17	20	10
Rise time, seconds	45	80	100	263	234	420	180	135	100	90	80
Tack free time, seconds			100	139	224	325	177	250	167	81	85
Foam properties:											
Core density pounds/cubic foot	2.11	2.03	2.33	1.88	1.79	2.05	2.06	2.11	2.33	2.18	2.42
Closed cells, percent	90	89	91	85	85	84	90	88	92	88	86
Compressive strength, p.s.i.:											
Parallel to direction of rise	35	33	35	19	25	24	30	30	39	33	26
Perpendicular to direction of rise	8	14	12	7	8	11	10	9	14	10	11
Friability:											
Density, pounds/cubic foot	1.97	1.87	2.14	1.80	1.98	1.97	1.88	1.74	2.18	1.78	1.95
Weight loss, percent:											
After 2 minutes	15	18	0.30	2.64	2.25	9.19	1.52	1.09	0.87	0.34	0.00
After 10 minutes	71	77	2.23	15.49	12.20	48.06	7.94	4.93	3.34	2.68	0.65
After 20 minutes	100	100	4.16	31.51	24.88	78.71	16.88	8.03	6.40	4.46	1.30

¹ 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate).
² 2:1 adduct of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and toluene diisocyanate.

³ The foam stabilizer was a nonhydrolyzable polyoxyethylene-poly-methylsiloxane block copolymer containing an average number of about

7 oxyethylene units per polyoxyethylene block each such block being hydroxyl-terminated.

⁴ Same type as Surfactant A except that the average number of oxyethylene units per polyoxyethylene block is about 16 and the latter blocks are methoxy-capped.

foamed polymeric products were produced. In producing the foams of these examples, the monomers, trichloromonofluoromethane (blowing agent), silicone surfactant (foam stabilizer) and, when used, a phenolic compound were first preblended at ambient temperature in a one quart cardboard container for 30 seconds. The catalyst solution was then added and the mixture vigorously stirred for 20 seconds and quickly poured into a metal mold (8" x 8" x 6") whereupon the respective reaction mixtures foamed and the cream, rise and tack-free times were recorded. The foams were then cured at room temperature for three days followed by testing according to standard ASTM procedures. The friability resistance of the foamed products was measured using a combination of ASTM C367 and C421 tumbling tests, that is, the test specimens were conditioned at room temperature in red oak cubes in accordance with ASTM C367, and the test time intervals (after 2- and 8-minute periods for a total of 10 minutes) were in compliance with ASTM C421. In most instances, friability resistance was also reported after a total test time of 20 minutes. Compressive strengths were determined using ASTM test method D1621. The relative proportions of Monomer M₁, Comonomer I, catalyst and other ingredients of the foam formulation, and the results obtained are set forth in the foregoing Table III. For the purpose of comparison, runs M-1 and M-2 are also included in Table III in accordance with which Monomer M₁ was homopolymerized under the indicated foaming conditions. In order to provide comparative data based on the preferred method for producing rigid foam from Monomer M₁, runs M-1 and M-2 were carried out using the phenolic compound, Bisphenol A, the presence of the phenolic compound providing foams having better friability properties than foams which are produced in the absence thereof.

Inspection of the results shown in Table III above shows that the foamed copolymeric products produced in accordance with Examples XXIX-XXXVII exhibited improved friability resistance as compared with the foamed product obtained by the polymerization of the di-(dihydropyranil) compound in the absence of the cyclic acetal comonomer. The improvement in friability resistance of the polymer products of this invention was obtained in the absence of the added phenolic compound, Bisphenol A (as in Examples XXX-XXXII), although friability was at a particularly low level in Examples XXIX and XXXIII-XXXVII in which the phenolic compound was present. It is noted that the excellent and markedly improved friability resistance of the rigid foams

or less than the amount present in comparative runs M-1 and M-2.

In another run presented for the purpose of comparison, Comonomer I, that is the 2:1 adduct of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and toluene diisocyanate, was homopolymerized using the procedure employed in carrying out the runs of Table III in a reaction mixture containing 20 parts of Comonomer I, 2 parts of a ten weight percent solution of BF₃·O(C₂H₅)₂ in diethylene glycol, 5 parts of trichloromonofluoromethane as blowing agent, and 0.2 part of Surfactant A identified in Table III above. Although as demonstrated by the examples of Table III cyclic acetal Comonomer I provided a foamed product when copolymerized with the di-(dihydropyranil) monomer, under the aforesaid conditions homopolymerization of Comonomer I did not provide a foamed product but rather a soft, tacky resin after standing for one day.

EXAMPLES XXXVIII-XLVIII

In accordance with these examples, the general procedure described above with reference to the examples of Table III was followed except that 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) was copolymerized with the reaction product of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and polyphenylmethylenepolyisocyanate, designated herein as Comonomer Q which was prepared as described below. In Examples XLIII-XLVIII, the monomer mixture also contained the 2:1 adduct of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and toluene diisocyanate (Comonomer I herein).

Preparation of Comonomer Q

To 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (688 grams; 4.0 moles) dissolved in trichloromonofluoromethane (308 grams), there was added 540 grams (4.0 moles) of a polyphenylmethylenepolyisocyanate having the following properties:

Free NCO, percent by weight	30.5-32.3
Isocyanato functionality (average)	2.70
Viscosity, centipoises at 25° C. (maximum)	500
Apparent specific gravity, 20/20° C.	1.242
Total acidity, percent by weight as HCl (maximum)	0.50
Flash point, ° F. (Cleveland Open Cup)	440
Vapor pressure, mm. Hg at 20° C.	<0.01

The relative proportions of monomers and the ingredients of the foam formulation, and the results obtained in carrying out these examples are given in the following Table IV.

TABLE IV

Foamed products of Di-(dihydropyranil) compound and 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane/polyisocyanate adducts

Example No.	XXXVIII	XXXIX	XL	XLI	XLII	XLIII	XLIV	XLV	XLVI	XLVII	XLVIII
Foam formulation, parts by weight:											
Di-(dihydropyranil) monomer M ₁	45	37.5	30	45	45	45	45	45	30	41.7	26.7
1,3-dioxolane, comonomer Q ²	55	62.5	70	45	35	25	35	30	35	21.7	31.7
1,3-dioxolane, comonomer I ³						30	20	25	35	26.7	31.7
Bisphenol A				10	20					10	10
10 weight percent solution in BF ₃ ·O(C ₂ H ₅) ₂ in diethylene glycol											
Trichloromonofluoromethane	4.00	4.50	5.00	4.00	3.33	4.00	3.33	4.00	4.00	4.00	4.00
Silicone surfactant ⁴	17.7	16	17.7	15	15	15	15	15	17	15	16
	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Foaming properties:											
Cream time, seconds	54	88	48	27	16	45	57	50	55	21	25
Rise time, seconds	110	190	135	70	37	105	160	130	135	45	75
Tack free time, seconds	75	118	130	44	25	60	80	65	95	26	50
Foam properties:											
Core density, pounds/cubic foot		2.20		2.00	2.05	1.80		1.93	2.05	2.03	2.30
Closed cells, percent		87		89	84	83		84	87	80	84
Compressive strength, p.s.i.:											
Parallel to direction of rise		26		27	19	16		17	20	15	20
Perpendicular to direction of rise		7		8	10	5		7	7	7	10
Friability:											
Density, pounds/cubic foot	1.72	2.00	1.69	1.82	1.82	1.56	1.93	2.15	2.15	1.93	2.50
After 2 minutes	1	0.2	0.4	0.5	0.7	0.0	1.32	0.0	0.0	0.0	0.3
After 10 minutes	12	8	8	8	7	10	10.86	3	3	4	0.4
After 28 minutes	19	19	19	16	16	25	24.01	7	7	10	0.4

¹ 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate).

² Adducts of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane and toluene

diisocyanate (comonomer I and polyphenylmethylenepolyisocyanate (comonomer Q).

⁴ Same as surfactant A of Table II herein.

of these latter examples was obtained at a content of phenolic compound which was at about the same level

The results of Table IV further demonstrate that the friability resistance of the rigid foams produced by polym-

erization of the di-(dihydropyranyl) compound with cyclic acetal Comonomer Q or with a combination of Comonomer Q and Comonomer I in the presence as well as the absence of a phenolic compound, was significantly greater than that of the rigid foams produced by homo-

EXAMPLES XLIX-LIV

In accordance with these examples, a series of foams were produced using 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran - 2 - carboxylate) as the di-(dihydropyranyl) monomer, designated Monomer M₁, and the 2:1 adduct of 2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane and toluene diisocyanate, described and designated hereinabove as Comonomer J. The foam formulation employed in these examples had the composition of Formulation A of the following Table V, no phenolic compound having been added.

TABLE V

Foam Formulation A	
Component:	Parts by weight
Monomer M ₁	Varied (120-210).
Comonomer J	Varied (180-90).
10 weight percent solution of BF ₃ ·O(C ₂ H ₅) ₂ in diethylene glycol	90.
Trichloromonofluoro- methane	50.
Silicone Surfactant (same as Surfactant A of Table III) ..	2.4.

In producing the foams of these examples, the general procedure followed was that described above with reference to the examples of Table III. The relative proportions of Monomer M₁ and Comonomer J and the results obtained are presented in Table VI below.

TABLE VI

Foamed products of Di-(dihydropyranyl) monomer and substituted 1,3-dioxane

Example No.	XLIX	L	LI	LII	LIII	LIV
Monomers, parts by weight:						
Di-(dihydropyranyl) monomer M ₁	210	180	165	150	135	120
1,3-dioxane, comonomer J ²	90	120	135	150	165	180
Weight percent ratio, M ₁ :J	70:30	60:40	55:45	50:50	45:55	40:60
Foaming properties:						
Cream time, seconds	45	38	28	22	22	30
Rise time, seconds	65	70	65	60	80	65
Tack free time, seconds	52	50	35	35	38	50
Foam properties:						
Core density, pounds/cubic foot	1.71	1.63	1.71	1.65	1.73	1.85
Closed cells, percent	90	91	91	92	92	93
Compressive strength, p.s.i.:						
Parallel to direction of rise	27	29	32	32	34	33
Perpendicular to direction of rise	12	12	11	10	11	13
Friability:						
Density, pounds/cubic foot	1.70	1.59	1.65	1.59	1.65	1.81
Weight loss, percent:						
After 2 minutes	16	9	6	8	4	0.7
After 10 minutes	79	62	46	44	28	18

¹ 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-carboxylate).

² 2/1 adduct of 2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane and toluene diisocyanate.

amples XLIX-LIV, in which no phenolic compound was used was about the same as, or significantly better than, the friability resistance of the homopolymeric di-(dihydropyranyl) product formed in runs M-1 and M-2 of Table III in which latter runs, however, a phenolic compound was used. The results of Table VI also indicate that the friability resistance of the foamed copolymeric products improved significantly as the concentration of the 1,3 - dioxanyl monomer increased from 30 to 60 weight percent of the monomer mixture.

EXAMPLES LV-LIX

In accordance with these examples, the general procedure described above with reference to the examples of Table III was followed except that 3,4 - dihydro - 2H-pyran - 2 - methyl(3,4 - dihydro - 2H - pyran - 2 - carboxylate) was copolymerized with isocyanate derivatives of 2,2 - dimethyl - 4 - hydroxymethyl - 1,3 - dioxolane. In Examples LV-LVIII, the isocyanate derivative employed, designated herein as Comonomer R, was prepared by the reaction of polyphenylmethylenepolyisocyanate and the aforesaid dimethylhydroxymethyl - 1,3 - dioxolane, as described below. In Examples LIX-LXI, the monomer mixture also contained the 2:1 adduct of the aforesaid dioxolane and toluene diisocyanate, designated and described hereinabove as Comonomer H.

Preparation of Comonomer R

To 2,2 - dimethyl - 4 - hydroxymethyl - 1,3 - dioxolane (500 grams; 3.79 moles) in 253 grams of trichloromonofluoromethane there were added 512 grams (3.79 moles) of polyphenylmethylenepolyisocyanate (having the properties given above with respect to the preparation of Comonomer Q), at 25° C. during a period of 40 minutes. When the addition was complete, the reaction mixture commenced to exotherm but the temperature was maintained at 25°-30° C. by means of a cooling bath, and was

As shown by the results of Table VI above, stable, rigid foams were produced by the copolymerization of the di-(dihydropyranyl) compound and the 1,3-dioxanyl carbamate in the absence of any added phenolic compound. The friability resistance of the foamed products of Ex-

stirred at 25°-30° C. for 5 hours. The reaction product was used as such, without purification. The composition of the foam formulation, relative proportions of monomers employed, and the results of these examples are set forth in the following Table VII.

TABLE VII

Foamed products of di-(dihydropyranyl) compound and isocyanate reaction products of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane

Example No.	LV	LVI	LVII	LVIII	LIX	LX	LXI
Foam formulation, parts by weight:							
Di-(dihydropyranyl) monomer M ¹	50	50	50	50	50	50	50
1,3-dioxolane, comonomer R ²	50	40	40	30	12.5	25	15
1,3-dioxolane, comonomer H ³					37.5	25	15
Bisphenol A		10	10	20			20
10 weight percent solution of BF ₃ ·O(C ₂ H ₅) ₂ in diethylene glycol:							
Trichloromonofluoromethane	3.67	3.00	2.67	3.67	2.50	2.67	3.00
Silicone surfactant ⁵	16.7	16.7	15.7	7	15.8	15	7
Foaming properties:							
Cream time, seconds	67	25	28	84	58	61	81
Rise time, seconds	120	60	57	120		150	150
Tack free time, seconds	77	37	37	94	88	87	100
Foam properties:							
Core density, pounds/cubic foot	2.23	2.03	2.26		2.60	2.56	
Closed cells, percent	94	93	95		92	92	
Compressive strength, p.s.i.:							
Parallel to direction of rise	33	37	44		38	26	
Perpendicular to direction of rise	18	11	18		21	22	
Friability:							
Density, pounds/cubic foot	2.32	2.10	2.34	1.95	2.33	2.53	1.81
Weight loss, percent:							
After 2 minutes	8	3	3	2	2	12	2
After 10 minutes	54	25	22	19	74	61	12
After 20 minutes	88	45	43	39	99	92	26

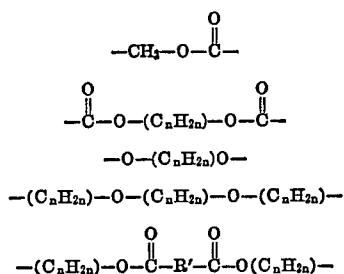
¹ 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate).² Adduct of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane and polyphenylmethylene polyisocyanate.³ 2:1 adduct of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane and toluene diisocyanate.⁴ In place of Bisphenol A, the phenolic compound employed was a phenolic resole resin.⁵ Same as surfactant A of Table III herein.

Comparison of the results of Table VII with comparative runs M-1 and M-2 of Table III shows that the friability resistance of the foamed products of Examples LV, LIX and LX in which no phenolic compound was used, was about the same as or somewhat better than that of the foamed products of comparative runs M-1 and M-2 in which, however, a phenolic compound was used. On the other hand, in Examples LVI-LVIII and LXI in which a phenolic compound was also used, the friability resistance of the respective copolymeric and terpolymeric products was improved at least two-fold.

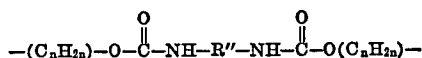
What is claimed is:

1. A cellular polymeric composition which comprises the product formed by polymerization of:

(A) a di(3,4-dihydro-2H-pyran) compound in which the two pyran rings are linked through a bivalent organic radical selected from the group consisting of



and



wherein:

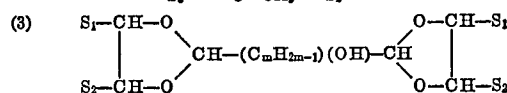
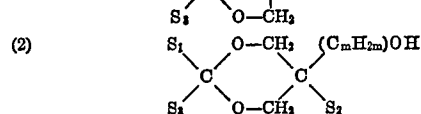
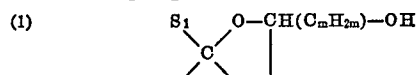
n has a value from 1 to 4,

R' is the nucleus of a dicarboxylic acid, and

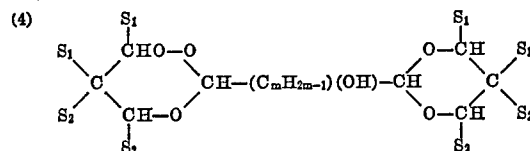
R'' is the nucleus of an organic diisocyanate, the two valences of said bivalent organic radical being satisfied by respective bonds to the 2-position of the respective pyran rings; in the presence of a blowing agent and a cationic polymerization catalyst, with

(B) a polycarbamate produced by the reaction of an organic polyisocyanate and a 1,3-cyclic acetal in an amount of at least one mole of 1,3-cyclic acetal per isocyanato group contained in said organic polyiso-

30 cyanate, said 1,3-cyclic acetal having a formula selected from the group consisting of:



and



50 wherein m is an integer having a value from 1 to 10; S_1 and S_2 are selected from the group consisting of hydrogen and an alkyl group having from 1 to 4 carbon atoms, and S_3 is a member of the group consisting of S_1 , an alkyl group having from 2 to 4 carbon atoms, and a dihaloalkyl group having from 2 to 4 carbon atoms; the mole ratio of (A):(B) ranging from about 0.2:1 to about 10:1.

2. A polymeric composition as defined in claim 1 wherein the polyisocyanate reacted with said cyclic acetal is an aromatic diisocyanate.

3. A polymeric composition as defined in claim 1 wherein the polyisocyanate is a tolylene diisocyanate.

4. A polymeric composition as defined in claim 1 wherein the polyisocyanate reacted with said cyclic acetal has an average isocyanato functionality of at least 2.25.

5. A polymeric composition as defined in claim 1 wherein the polyisocyanate is the phosgenation reaction product of the polyamine produced by aniline-formaldehyde condensation.

6. A polymeric composition as defined in claim 1 wherein the polyisocyanate reacted with said cyclic acetal is an aliphatic diisocyanate.

7. A polymeric composition as defined in claim 1 wherein (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-

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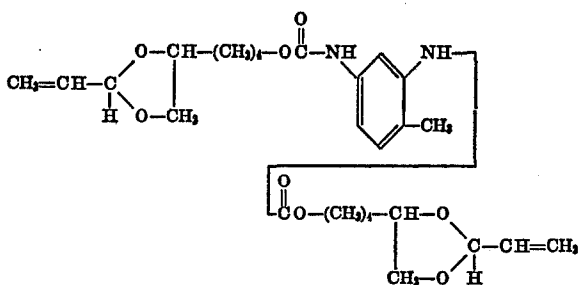
pyran-2-carboxylate) and said cyclic acetal is a 1,3-dioxolane having said Formula 1 in which the S_1 group is hydrogen and S_3 is a vinyl group.

8. A polymeric composition as defined in claim 1 wherein (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and said cyclic acetal is a 1,3-dioxolane having said Formula 1 in which said S_1 and S_3 groups are both lower alkyl groups.

9. A polymeric composition as defined in claim 1 wherein (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and said cyclic acetal is a 1,3-dioxolane having said Formula 1 in which S_1 is hydrogen and S_3 is a dichloroalkyl group.

10. The polymeric composition of claim 7 wherein said 1,3-dioxolane is 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane.

11. A foamed polymeric composition which comprises the product formed by polymerizing (1) 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate), and (2) a polycarbamate having the formula:



in the presence of a blowing agent and a cationic polymerization catalyst selected from the group consisting of a strong proton-donating acid and a Lewis acid, the mole ratio of (1):(2) being between about 0.2:1 and about 10:1.

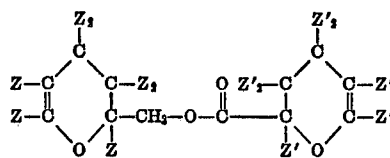
12. A foamed polymeric composition which comprises the product formed by polymerizing (1) 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) in the presence of a cationic polymerization catalyst and a blowing agent, with (2) a polycarbamate, the mole ratio of (1):(2) being between about 0.2:1 and about 10:1, said polycarbamate comprising the reaction product of an organic polyisocyanate having an average isocyanato functionality of from about 2.25 to about 3.2 with 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane in an amount at least sufficient to convert the isocyanato functions of said polyisocyanate to carbamate groups.

13. A foamed polymeric composition which comprises the product formed by polymerizing (1) 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate), in the presence of a cationic polymerization catalyst and a blowing agent, with (2) a polycarbamate comprising the reaction product of an organic polyisocyanate and the 1,3-dioxolane produced by reacting ethylene glycol and acrolein dimer in a mole ratio of about 2:1, said polycarbamate being formed by the reaction of one mole of said 1,3-dioxolane per isocyanato group in said organic polyisocyanate, the mole ratio of (1):(2) being between about 0.2:1 and about 10:1.

14. A polymeric composition as defined in claim 1 wherein (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and said cyclic acetal is a 1,3-dioxane having said formula (2) in which S_3 is a vinyl group.

15. A cellular polymeric composition as defined in claim 1 in which (A) is a 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) having the formula:

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wherein Z and Z' are selected from the group consisting of hydrogen and an alkyl group having from 1 to 10 carbon atoms.

16. A cellular polymeric composition as defined in claim 15 in which said cationic polymerization catalyst is boron trifluoride complexed with diethyl ether.

17. The cellular polymeric composition as defined in claim 15 in which said reaction of (A) and (B) is carried out in the presence of a phenolic compound.

18. The cellular polymeric composition as defined in claim 17 in which said phenolic compound is 2,2-bis(4-hydroxyphenyl)propane.

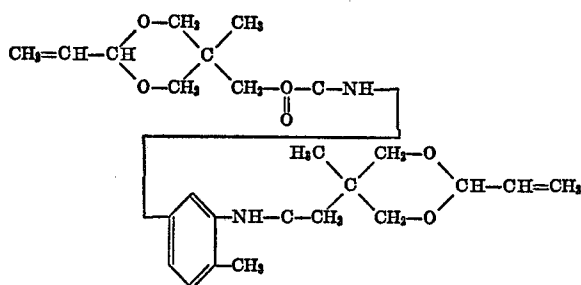
19. The cellular polymeric composition as defined in claim 15 in which said blowing agent comprises a halocarbon.

20. A cellular polymeric composition as defined in claim 15 wherein each of said Z and Z' radicals is hydrogen.

21. A cellular polymeric composition as defined in claim 1 in which (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and said cyclic acetal is of said Formula 3.

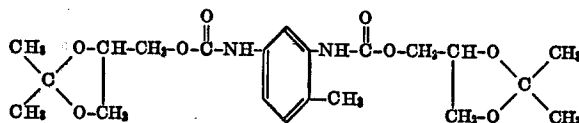
22. A cellular polymeric composition as defined in claim 1 in which (A) is 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) and said cyclic acetal is of said Formula 4.

23. A foamed polymeric composition which comprises the product formed by polymerizing (1) 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate), and (2) a polycarbamate having the formula,



in the presence of a blowing agent and a cationic polymerization catalyst selected from the group consisting of a strong proton-donating acid and a Lewis acid, the mole ratio of (1):(2) being between about 0.2:1 and about 10:1.

24. A foamed polymeric composition which comprises the product formed by polymerizing (1) 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate), and (2) a polycarbamate having the formula,



in the presence of a blowing agent and a cationic polymerization catalyst selected from the group consisting of a strong proton-donating acid and a Lewis acid, the mole

ratio of (1):(2) being between about 0.2:1 and about 10:1.

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