

Description

This invention relates to a composition of matter comprising an aliphatic diol bis(allyl carbonate), an acrylate polymer, a multifunctional acrylate monomer. The invention further comprises the polymeric product of said composition and a method of polymerizing said composition.

US-A-4 217 433 describes copolymers of an acrylic monomer such as methyl methacrylate with an allyl monomer such as allyl methacrylate. These copolymers are crosslinked with diethylene glycol bis(allyl carbonate). The crosslinked materials are characterized as having reduced shrinkage and maintaining optical clarity. The preparation of such crosslinked materials requires at least a two-stage operation with separate steps for the copolymerization and the crosslinking. Castings of diol bis(allyl carbonate) are characterized by hardness, optical clarity and long cure times.

US-A-4 346 197, filed December 22, 1980 and published on August 24, 1982 of John C. Crano et al for Method of Polymerizing Blends of bis(allyl carbonate) monomers with polymers and polymer blends prepared thereby describes how the addition of high molecular weight polymers to the diol bis(allyl carbonate) monomer results in a composition that may be drawn, extruded, injection molded or the like, and is characterized by pseudoplastic rheology, by shorter cure times, and in some cases, an increase in haze.

It has now been found that the addition of a multifunctional acrylate monomer to the monomeric composition of diol bis(allyl carbonate) and dispersed polymer provides a monomeric composition that cures quickly from a pseudoplastic to a substantially non-malleable, substantially non-ductile composition capable of supporting its own weight without deformation, which may be thereafter cured to a hard resin remote from molds.

The addition of the dispersed polymer to the monomeric diol bis(allyl carbonate) causes some degree of haze and some reduction in luminous transmission in the resulting polymer. It has now further been found that certain of the multifunctional acrylates, as will be described more fully hereinbelow, result in a significant reduction of haze and significant increase of luminous transmission in the presence of the dispersed polymer.

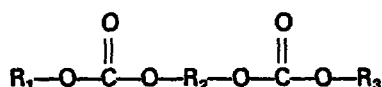
This invention relates therefore to a composition of matter comprising

(a) an aliphatic diol bis(allyl carbonate);

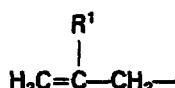
(b) an acrylate polymer; and

(c) a multifunctional acrylate monomer,

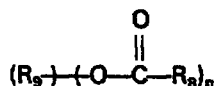
wherein the diol bis(allyl carbonate) monomer (a) is represented by the formula



where R_1 and R_3 are allyl groups independently represented by the formula



where R' is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof, the multifunctional acrylate monomer is represented by the formula



where n is from 2 to 5; R_5 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and R_6-COO- is the residue of an acrylic acid, and wherein said composition contains from 1 part of polymer per hundred parts of diol bis(allyl carbonate) to 100 parts of polymer per hundred parts of diol bis(allyl carbonate); and from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate).

It has been found that the cure of the pseudoplastic material, including liquid pseudoplastic materials, which is formed by the monomeric diol bis(allyl carbonate) and the viscosity increasing acrylate polymer is substantially accelerated by the addition of the multifunctional acrylate monomers to the monomeric composition. Moreover, it has been found that the addition of these monomeric acrylate crosslinking agents, exemplified by diacrylate monomers, to the composition results in reduced haze and increased luminous transmittance in the fully cured polymer relative to that of a fully cured polymer characterized by the substantial absence of polyfunctional cross-linking agents.

As herein contemplated a monomeric composition is prepared containing the specified amounts of (a) the diol bis(allyl carbonate), (b) of the dispersed acrylate polymer which increases the viscosity to form a pseudoplastic composition, which may be a pseudoplastic liquid composition, the monomeric composition becoming pseudoplastic either upon addition and dispersion of the polymer, or subsequent to the addition and dispersion thereof with partial cure, and of (c) the multifunctional acrylate crosslinking agent. The polyfunctional acrylate crosslinking agent is selected so as to serve as an optical compatibilizing agent, reducing the haze and increasing the luminous transmittance of the polymerize prepared therefrom.

Thereafter, the monomeric composition of (a) the diol bis(allyl carbonate) monomer, (b) the viscosity enhancing dispersed acrylate polymer, and (c) the multifunctional acrylate crosslinking agent is polymerized, e.g. by the addition of free-radical polymerization initiator with heating to temperatures sufficient to provide a satisfactory rate of polymerization for initiators present herein.

According to a still further exemplification of this invention, there is provided a polymeric product of a composition of

- (a) an aliphatic diol bis(allyl carbonate);
- (b) an acrylate polymer; and
- (c) a multifunctional acrylate monomer,

wherein the diol bis(allyl carbonate) monomer (a) is represented by the formula



where R_1 and R_3 are allyl groups independently represented by the formula



where R' is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof, the multifunctional acrylate monomer is represented by the formula



where n is from 2 to 5; R_5 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and R_6-COO- is the residue of an acrylic acid, and wherein said composition contains from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 100 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate); and from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate).

The polymeric composition herein contemplated finds utility as an element of optical systems, as an ophthalmic lens, as a fiber optic material, as supporting material for a fiber optic system, and for various other applications where transparency, substantial absence of haze, high luminous transmittance, and hardness are desired in the finished product, pseudoplastic rheology is desired during fabrication, and a rapid rate of initial cure is desired after formation into the desired shape or structure.

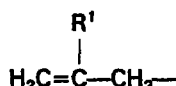
By "haze" is meant the percentage of transmitted light which in passing through the polymerized material deviates from the incident beam by forward scattering by an amount greater than 2.5 degrees, as measured in accordance with ANSI/ASTM D-1003-61 (Reapproved 1977) *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics*.

By "luminous transmittance" is meant the ratio of transmitted light to incident light as determined by the method in the aforementioned American National Standards Institute/American Society for Testing and Materials Standard.

Diol bis(allyl carbonate) monomers which may be utilized to form the monomeric and polymeric compositions of this invention and which may be polymerized by the method of this invention are normally linear, aliphatic liquid allyl carbonates, i.e., glycol bis(allyl carbonate) compounds, in which the allyl groups may be substituted at the 2 position with a halogen, notably chlorine or bromine, or a 1 to 4 carbon alkyl group, generally a methyl or ethyl group, and the glycol group may be an alkylene, alkylene ether, alkylene polyether or alkylene carbonate group having from 2 to 10 carbons and oxygens. These diol bis(allyl carbonate) monomers are represented by the formula:



where R_1 and R_3 are allyl or substituted allyl groups, and R_2 is as defined below. R_1 and R_3 are independently represented by the formula:

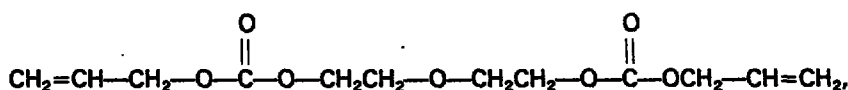
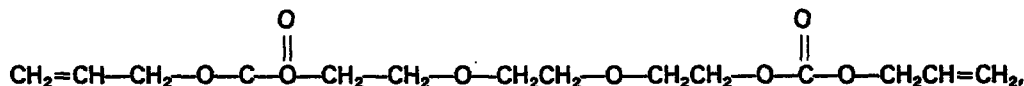


where R' may be hydrogen, halogen, or a 1 to 4 carbon alkyl group. Specific examples of R_1 and R_3 include allyl, 2-chloroallyl, 2-bromoallyl, 2-iodoallyl, 2-fluoroallyl, 2-methallyl, 2-ethylallyl, 2-isopropylallyl, 2-n-propylallyl, and 2-n-butylallyl groups. Most commonly, R_1 and R_3 are allyl groups, $H_2C=CH-CH_2-$. Such compounds and methods for making them are disclosed in U.S. Patents 2,370,567 and 2,403,113.

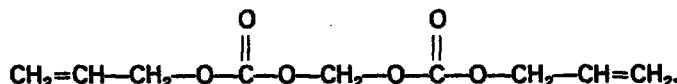
Specific examples of R_2 are alkylene groups such as ethylene, trimethylene, methylethylene, tetramethylene, ethylethylene, pentamethylene, hexamethylene, 2-methylhexamethylene, octamethylene, and decamethylene groups, alkylene ether groups such as $-CH_2-O-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2-O-CH_2-CH_2-$, and $-CH_2CH_2CH_2-O-CH_2CH_2CH_2-$, alkylene polyether groups such as $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$, and $-CH_2-O-CH_2-$ groups, and alkylene carbonate and alkylene polycarbonate groups such as $-CH_2CH_2-O-CO-O-CH_2CH_2-$ and $-CH_2CH_2-O-CH_2CH_2-O-CO-O-CH_2CH_2-O-CH_2CH_2-$ groups. Most commonly, R_2 is $-CH_2CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, or $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$.

Specific examples of diol bis(allyl carbonate) monomers useful in the practice of the invention herein contemplated include ethylene glycol bis(2-chloroallyl carbonate), diethylene glycol bis(2-methallyl carbonate), triethylene glycol bis(allyl carbonate), propylene glycol bis(2-ethylallyl carbonate), 1,3-propanediol bis(allyl carbonate), 1,3-butanediol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl carbonate), and pentamethylene glycol bis(allyl carbonate).

Commercially important diol bis(allyl carbonate) monomers which may be utilized in the invention herein contemplated are:

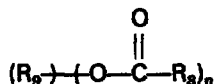


and



The compositions herein contemplated contain bis(allyl carbonate) monomer, a viscosity increasing amount of a viscosity increasing polymer, and a polyfunctional acrylate monomer. For example, the contemplated composition may be a composition of diol bis(allyl carbonate), a viscosity increasing polymer, most commonly poly(methyl methacrylate) or a copolymer of methyl methacrylate and allyl methacrylate, and multifunctional acrylate monomer, most commonly a diacrylate. The polymer is either soluble in the bis(allyl carbonate), swollen by the bis(allyl carbonate), or swollen by and partially soluble in the bis(allyl carbonate).

The multifunctional acrylate monomer



is a cross-linking agent, decreasing the time after commencement of cure that the composition is pseudoplastic, and thereby decreasing the amount of cure that must be carried out in a mold.

Moreover, the multifunctional acrylate monomers useful as cross-linking agents have the further advantage of optically compatibilizing the polymer, i.e., reducing the haze of the polymer and increasing the luminous transmittance thereof.

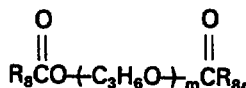
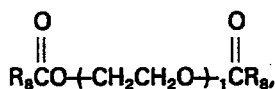
Examples for the acrylic acid moiety in the above formula of the multifunctional acrylate monomer are acrylic acid, methacrylic acid and ethylacrylic acid.

The polyol residue is derived from a polyol corresponding to the formula $R_9(OH)_n$ wherein n is from 2 to 5 and may therefore be a diol, a triol, a tetra carbanol, or a penta carbanol. Most commonly $R_9(OH)_n$ is a diol or triol. Typical diols useful providing the terminal diacrylate esters include alpha, omega glycols such as

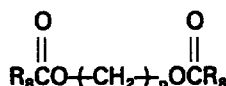
ethylene glycol, trimethylene glycol, 1,4-butanediol, 1,5-pentane diol and 1,6-hexanediol, other 1,2 glycols, such as propylene glycol, the hydrated ethylene oxide and propylene oxide condensation products, such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol. Exemplary diacrylates include ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, trimethylene glycol diacrylate, trimethylene glycol dimethacrylate, butane diol diacrylate, butane diol dimethacrylate, pentane diol diacrylate, pentane diol dimethacrylate, hexane diol diacrylate, hexane diol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, dipropylene glycol diacrylate, dipropylene glycol dimethacrylate, tripropylene glycol diacrylate, tetrapropylene glycol diacrylate, and tetrapropylene glycol.

Suitable triacrylates include trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, glycerol triacrylate, glycerol trimethacrylate, pentaerythritol triacrylate, and pentaerythritol dimethacrylate. Suitable tetra acrylates include pentaerythritol tetra acrylate and pentaerythritol tetramethacrylate.

Difunctional monomers, i.e., diacrylates and dimethacrylates, are preferred as optical compatibilizing agents. Preferred compatibilizing agents are the diacrylates and dimethacrylates of aliphatic diols. Especially preferred diol diacrylates and dimethacrylates are those having from about 4 to about 15 atoms, i.e., carbon atoms or carbon and oxygen atoms, between the carboxyl carbon atoms. Exemplary diacrylates and dimethacrylates have the structures represented by



and



where 1 is from 1 to 4, m is from 1 to 4 when (C₃H₆O) is chosen from



and mixtures thereof, m is from 1 to 3 when (C₃H₆O) is $\text{-(CH}_2\text{CH}_2\text{CH}_2\text{O)-}$, and p is from 1 to 13.

The amount of multifunctional acrylate monomer in the composition is within the stated range a function of the desired cure rate of the monomeric composition and the desired degree of clarity, i.e., transmittance and haze, of the polymer.

By an acrylate polymer is meant an acrylate polymer which, at the concentrations of polymer and polymer molecular weight herein contemplated, provides a composition of diol(allyl carbonate) and polymer having a viscosity high enough to provide pseudoplastic rheology. By a "pseudoplastic rheology" is meant a viscosity that decreases with increasing shear stress a shear rate. The composition may be liquid or a gum, gel, or the like. The monomeric compositions herein contemplated have a shear stress that increases from about 10³ to 10⁶ Pascal (10⁴ to about 10⁷ dynes per square centimeter) at shear rates increasing from 10¹ to 10⁴ per second, and viscosities decreasing from about 10⁵ centipoise at low shear rates to about 10⁴ centipoise at high shear rates.

For the applications herein contemplated, e.g., ophthalmic lenses, photographic lenses, fiber optics, fiber optic fittings, and the like, the polymer should be optically compatible with the bis(allyl carbonate). That is, it should not form haze in the bis(allyl carbonate) polymerizate. The tendency of the polymer to form a haze is reduced by the addition of the multifunctional acrylate monomer, as is described hereinabove.

Moreover, the polymer should be resistant to destruction by the peroxy initiators used to polymerize the bis(allyl carbonate), and not interfere therewith.

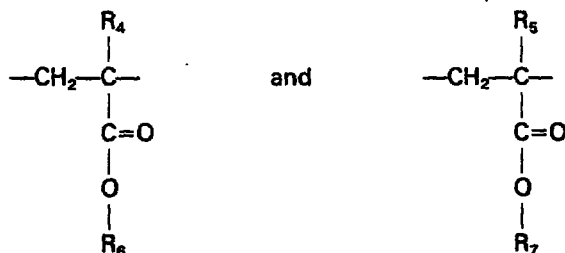
The amount of dispersed polymer in the bis(allyl carbonate) monomer is an amount sufficient to provide the desired characteristics and properties in the monomeric composition, or during casting, or in the partially cured polymerizate, or in the finally cured polymerizate, or in any combination thereof. This is an amount from 1 to about 100 parts of dispersed polymer per 100 parts of diol bis(allyl carbonate), and preferably from about 1 to about 35 parts of dispersed polymer per 100 parts of diol bis(allyl carbonate).

As herein contemplated, the polymer may be the polymer of a monofunctional homomonomer or a

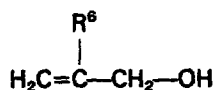
copolymer of monofunctional monomers, or a copolymer of a monofunctional monomer and a difunctional monomer. Preferably the difunctional monomer has functional groups of high and low reactivity, e.g., an acrylic group and an allyl group, and the monofunctional monomer is an acrylic monomer.

The dispersed, viscosity enhancing polymer may be chosen from the group consisting of homopolymers of acrylic acids, homopolymers of lower alkyl alcohol esters of acrylic acids, copolymers of allyl alcohol esters of acrylic acids with lower alkyl alcohol esters of acrylic acids, where acrylic acids, allyl alcohols, alcohols, and lower alkyl alcohols are as defined herein.

Preferably the copolymer is a copolymer of (a) an acrylate, i.e., an acrylate ester or an acrylic acid, and (b) an ester of an acrylic acid and an allyl alcohol or substituted allyl alcohol. Suitable acrylic acids are acrylic acid, methacrylic acid, ethyl acrylic acid, butyl acrylic acid, propyl acrylic acid, and higher acrylic acids. Such copolymers comprise the recurring units



where R_4 and R_5 are independently hydrogen or an alkyl group, R_6 is the residue of an allyl alcohol, and R_7 is chosen from the group consisting of H, and C_1 to C_4 alkyl groups. The residue of the allyl alcohol can be derived from an allyl alcohol or a substituted allyl alcohol, having the formula



where R^6 is chosen from the group consisting of hydrogen, halogen, and C_1 to C_4 alkyls. Most frequently R_6OH is allyl alcohol, $H_2C=CH-CH_2OH$.

Such acrylate copolymers are obtained by copolymerizing an acrylate ester of an acrylic acid with an ester of an acrylic acid and of an allyl alcohol.

For example, the difunctional monomer may be allyl acrylate, or allyl methacrylate, and the monofunctional monomer may be methyl acrylate, methyl methacrylate, ethyl acrylate, or ethyl methacrylate. In this way there is provided a linear, minimally cross linked, soluble, swellable polymer, with polymerization predominantly through the vinyl groups.

One particularly desirable copolymer is a copolymer of methyl methacrylate and allyl methacrylate. In a preferred exemplification the copolymer contains from about 80 to about 99 weight percent methyl methacrylate and balance allyl methacrylate. It should be recognized, however, that as the degree of saturation in the dispersed polymer increases, the tendency for haze formation increases, necessitating greater amounts of the multifunctional acrylate monomer for haze reduction. Especially preferred is a copolymer containing up to 97 weight percent methyl methacrylate, balance allyl methacrylate, and an apparent molecular weight of 100,000 and preferably above about 250,000 to above about 600,000 or even above about 800,000 determined by inherent viscosity versus poly(methyl methacrylate).

Especially preferred copolymers with olefinic unsaturation, i.e., copolymers of an acrylate and an allyl acrylate, are those having a macromolecule molecular weight above about 100,000, and especially from about 250,000 to above about 800,000. These copolymers are characterized by a low rate of solubilization and swelling by the polyol(allyl carbonate) monomer. As a consequence, in order to obtain high levels thereof in the final polymerizate, they are usually first solubilized in or swollen by a suitable solvent, e.g., methylene chloride, and thereafter admixed with polyol(allyl carbonate) and the solvent subsequently recovered therefrom.

Alternatively, the polymer may be a homopolymer of a monomer having mono-olefinic unsaturation, poly(acrylic acid), poly(methacrylic acid), poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate) and copolymers thereof.

The polymer may be added directly to the diol bis(allyl carbonate) monomer. Alternatively, the polymer may be added to an organic solvent, e.g., methylene chloride, whereby to form a solution. When the polymer is added to an organic solvent, the diol bis(allyl carbonate) monomer is added to the solution, and the solvent driven off, e.g., by distillation, evaporation, boiling, or the like.

According to another exemplification the polymer is first added to a solvent, and the diol bis(allyl carbonate) is added to the resulting solvent. The especially preferred solvents are those solvents having a solubility parameter of about 9.0 to about 10.0 (calories/cubic centimeter)^{-0.5}, where the solubility parameter is the square root of the cohesive energy density, as described in F. Rodriguez, *Principles of*

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Polymer Systems, McGraw-Hill Book Co., New York, N.Y. (1970), and Beerbower, Kaye, and Pattison, *Chem. Engr.*, December 18, 1967, page 118.

Exemplary solvents include halogenated hydrocarbons, such as methylene chloride, chloroform, dichloroethylene, ethylene dichloride, tetrachloroethane, tetrachloroethylene, trichloroethane, trichloroethylene, aromatics, such as benzene, nitrobenzene, orthodichlorobenzene, styrene, and chlorobenzene, and hydrocarbons. Alternatively, other solvents such as benzaldehyde, carbon disulfide, chlorobromomethane, cyclohexanone, ethyl chloroformate, diethylene glycol, diphenyl, turpentine, cyclohexane, isooctane, and the like may be used.

The polymerization of the polyol(allyl carbonate) composition is initiated by the creation of active centers, e.g., free radicals, carbanions, and carbonium ions. Useful free radical initiators are peroxy initiators. The peroxy initiators include: isobutyryl peroxide; di(2-ethylhexyl) peroxydicarbonate; acetyl cyclohexane sulfonyl peroxide; di(sec-butyl) peroxydicarbonate; diisopropyl peroxydicarbonate; 2,4-dichlorobenzoyl peroxide, t-butyl peroxyvalerate; decanoyl peroxide; lauroyl peroxide, propionyl peroxide; 2,5-dimethyl-2,5-bis(2-ethyl hexylperoxy) hexane; acetyl peroxide; succinic acid peroxide; t-butyl peroxyoctoate; benzoyl peroxide; p-chlorobenzoyl peroxide; t-butyl peroxyisobutyrate; t-butyl peroxy maleic acid; bis(1-hydroxycyclohexyl) peroxide, 1-hydroxy-1'-hydroperoxy dicyclohexyl peroxide; t-butyl peroxyisopropyl carbonate; 2,5-dimethyl-2,5-bis(benzoylperoxy) hexane; t-butyl peroxyacetate; methyl ethyl ketone peroxides; di-t-butyl diperoxyphthalate and t-butyl peroxybenzoate.

Especially preferred peroxy initiators are those that do not discolor, char, or burn the resulting polymerizate. Exemplary are diisopropyl peroxydicarbonate and benzoyl peroxide.

The fully cured polymerizates herein contemplated are nonelastomeric, rigid, hard resins formed by the polymerization of polar monomers in the presence of a polymer of polar monomers. For certain applications the polymerizates herein contemplated may be characterized by a 0—15 second Barcol hardness above about 25—20, e.g., preferably above about 35—30. The polymerizates herein contemplated are further characterized by a luminous transmission of above about 90 percent and a haze below about 10 percent, both determined by ANSI/ASTM Standard D-1003-61 (Reapproved 1977), *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics*.

According to one exemplification herein contemplated, a liquid composition is prepared containing (a) diethylene glycol bis(allyl carbonate), (b) from about 2 to about 10 parts per hundred (basis diethylene glycol bis(allyl carbonate)) of either a copolymer containing above about 90 weight percent methyl methacrylate balance allyl methacrylate, or a homopolymer of methyl methacrylate, the polymer having a viscosity average molecular weight of from about 100,000 to about 800,000, and (c) from about 2 to about 10 parts per hundred (basis diethylene glycol bis(allyl carbonate)) of tripropylene glycol diacrylate. The polymer and diacrylate monomer are dispersed in the diethylene glycol bis(allyl carbonate) monomer by mechanical mixing whereby to yield a substantially clear, liquid composition having a viscosity above about 100 poise. Thereafter, initiator, for example, isopropylperoxydicarbonate is added thereto at about 1.5 to about 3.5 parts per hundred parts of diethylene glycol bis(allyl carbonate) and dispersed therein. Thereafter the material may be heated over a period of about 10 to 24 hours whereby to yield a hard resin. The curing may be effectuated in ophthalmic molds, between molds, cathode ray tube covers, or other means so as to form a flat sheet or plate, or a shaped or curved sheet or plate. Alternatively, prior to curing, the composition may be extruded or drawn down to form a fiber optic, surrounded with a high refractive index or reflective material, and cured.

The following examples are illustrative of this invention.

Example I

A series of tests were conducted to determine the effect of the addition of various multifunctional acrylate monomers on polymers prepared from a composition of diethylene glycol bis(allyl carbonate) with poly(methyl methacrylate) dispersed therethrough.

For each test 78.4 grams of PPG Industries, Inc. CR-39® brand diethylene glycol bis(allyl carbonate) was weighed into a 400 milliliter beaker, to which was added 20 grams of poly(methyl methacrylate) having a viscosity average molecular weight of about 500,000, and 200 milliliters of CH_2Cl_2 . The composition of monomer, polymer, and solvent was stirred with a magnetic stirrer until all of the solids appeared to be dispersed. Thereafter, 1.6 grams of benzoyl peroxide was added to the composition, and stirring was continued until the benzoyl peroxide appeared to be dispersed. Thereafter, 4 grams of the multifunctional acrylate shown in Table I was added dropwise, and 2 grams of a solution of 0.4 gram of isopropyl peroxy dicarbonate in diethylene glycol bis(allyl carbonate) was added to each sample.

Each sample was then evaporated in a rotary vacuum evaporator for two hours, and thereafter stored at 40°F (5°C) until the polymerization tests were conducted.

The first series of polymerization tests were carried out by placing a portion of each sample between two four inch by seven inch glass plates separated by a one-eighth inch rubber gasket, clamping the two glass sheets together, maintaining the samples at 27 to 30 degrees Centigrade for 16 hours, removing the samples from between the glass sheets, and heating portions of each sample to 100 degrees Centigrade for six minutes. The results shown in Table I, below, were obtained.

TABLE I

	Multifunctional acrylate	Appearance of polymer
5	Trimethylolpropane trimethacrylate	opaque
	Trimethylolpropane triacrylate	opaque
10	Pentaerythritol triacrylate	opaque
	Tripropylene glycol diacrylate	clear
	Tetraethylene glycol diacrylate	clear
15	Hexanediol diacrylate	clear

Example II

20 A second series of polymerization tests were conducted using the monomer compositions prepared in Example I. This series of polymerization tests were carried out by placing portions of each sample between two four inch by seven inch glass plates separated by a one-eighth inch thick rubber gasket, clamping the two glass sheets together, maintaining the samples at 27 to 30 degrees Centigrade for sixteen hours, removing the samples from between the glass sheets, and heating portions of each sample according to the cure cycle shown in Table II below:

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TABLE II
Time-temperature sequence for benzoyl peroxide cure

	Cumulative time (hours)	Temperature, °C
30	2	63
	4	65
35	6	67
	8	77
	10	80
40	12	85
	14	88
45	16	92
	18	100

The results shown in Table III, below, were obtained:

TABLE III

	Multifunctional acrylate	Appearance of polymer
50	Trimethylolpropane trimethacrylate	opaque
55	Trimethylolpropane triacrylate	opaque
	Pentaerythritol triacrylate	opaque
60	Tripropylene glycol diacrylate	slight haze
	Tetraethylene glycol diacrylate	"
65	Hexanediol diacrylate	"

Example III

The procedure of Example II was repeated, except that the samples were maintained between the glass sheets during the eighteen hour benzoyl peroxide cure. The resulting one-eighth inch thick polymer sheets were tested according to ANSI/ASTM D-1003-61 (Reapproved), Haze and Luminous Transmittance of Transparent Plastics, and for fifteen second Barcol hardness. The results shown in Table IV, below, were obtained:

TABLE IV

Multifunctional acrylate	Luminous transmittance	Haze	Barcol hardness (15 second)
Tripropylene glycol diacrylate	88.2%	5.3%	46—36
Tetraethylene glycol diacrylate	85.1%	13.4%	42—32
Trimethylolpropane trimethacrylate	68.4%	43.5%	47—39
Trimethylolpropane triacylate	61.3%	70%	42—33

Example IV

A series of tests were conducted to determine the effect of the levels of tripropylene glycol diacrylate and poly(methyl methacrylate) in benzoyl peroxide cured diethylene glycol bis(allyl carbonate) polymerizates.

In each test 100 grams of PPG Industries, Inc. CR-39® diethylene glycol bis(allyl carbonate) was weighed into a beaker, to which was added a measured quantity of poly(methyl methacrylate) having a viscosity average molecular weight of above 500,000, and 200 milliliters of CH_2Cl_2 . The compositions were stirred on a magnetic stirrer. Thereafter tripropylene glycol diacrylate and 3 grams of benzoyl peroxide were added to each of the compositions with continued stirring until the solids had dissolved.

Each composition was then poured into a crystallizing dish and a stream of air was passed over the crystallizing dish to drive off the solvent. Thereafter each composition was maintained in a vacuum at 25 to 30 degrees Centigrade for about sixteen hours to drive off the solvent.

Each composition was then poured between two four inch by eight inch sheets of glass separated by a one-eighth inch rubber gasket and cured according to the eighteen hour cure cycle shown in Table II of Sample II. After cure, each sample was tested for luminous transmission, haze, and fifteen second Barcol hardness. The results are shown in Table V below:

TABLE V
Haze, luminous transmission, and barcol hardness versus
tripropylene glycol diacrylate and polymethylmethacrylate concentrations

Tripropylene glycol diacrylate		0	5	10
parts per hundred				
polymethyl methacrylate				
parts per hundred				
5 parts per hundred				
Haze		48.8%	22.3%	14.1%
Luminous transmission		85.3%	89.9%	89.9%
Barcol hardness		41—33	34—25	40—31
10 parts per hundred				
Haze		35.2%	17.4%	14.8%
Luminous transmission		88.9%	89%	89.3%
Barcol hardness		39—30	40—31	42—32%
20 parts per hundred				
Haze			9.4%	3.8%
Luminous transmission			87.1%	88.1%
Barcol hardness			42—33	16—0

Example V

A series of tests were conducted to determine the effect of levels of tripropylene glycol diacrylate on polymers prepared by the isopropyl peroxydicarbonate initiated polymerization of diethylene glycol bis(allyl carbonate) having poly(methyl methacrylate) dispersed therethrough.

In each test 86 grams of PPG Industries, Inc. CR-39® diethylene glycol bis(allyl carbonate) was weighed into a beaker with 5 grams of poly(methyl methacrylate) having a viscosity average molecular weight above 500,000, and 100 milliliters of CH_2Cl_2 . The amount of tripropylene glycol diacrylate shown in Table VII, below, was then added to the composition. The composition was stirred on a magnetic stirrer until all of the solid appeared to be dispersed. Thereafter 17.5 grams of a solution prepared from 14 grams of the diethylene glycol bis(allyl carbonate) monomer and 3.5 grams of diisopropyl peroxy dicarbonate was added to the composition, with continued stirring.

Each composition was then poured onto a crystallizing dish and a stream of air was passed over the crystallizing dish to drive off the CH_2Cl_2 solvent. Thereafter each composition was maintained in a vacuum at 25 to 30 degrees Centigrade for about sixteen hours to drive off remaining solvent.

Each composition was then poured between two four inch by eight inch sheets of glass separated by a one-eighth inch thick rubber gasket, and cured according to the cure cycle in Table VI, below:

TABLE VI
Time-temperature sequence for diisopropyl peroxydicarbonate cure

(18)

	Cumulative time (hours)	Temperature, °C
5	0	42
	4	44
10	6	45
	8	47
	10	48
15	12	50
	14	52
20	16	54.5
	18	57
	20	61
25	22	69
	23	79
30	23.6	84
	24	98
35	24.1	100

After cure each sample was tested for haze, luminous transmission, and Barcol hardness as described in Example III, above. The following results were obtained:

TABLE VII
Haze, luminous transmission, and barcol hardness versus
tripropylene glycol diacrylate concentration

		Tripropylene glycol diacrylate	
		(parts per hundred parts of diethylene glycol bis(allyl carbonate) at 5 parts of poly (methyl methacrylate) per hundred parts of diethylene glycol bis (allyl carbonate).)	
		0	5
45	Haze	15.6%	5.8%
50	Luminous transmission	90.7%	92.2%
55	Barcol hardness (15 second)	15—2	27—16
60			

Example VI

The procedure of Example V, above, was followed except that the addition, use and evaporation of the CH_2Cl_2 was not performed. The resulting compositions were cured and tested as described in Example V, above, and the results shown in Table VIII, below, were obtained:

TABLE VIII
Haze, luminous transmission, and barcol hardness versus
tripropylene glycol diacrylate concentration

	Tripropylene glycol diacrylate		
	(parts per hundred parts of diethylene glycol bis(allyl carbonate) at 5 parts of poly (methyl methacrylate) per hundred parts of diethylene glycol bis (allyl carbonate).)		
	0	5	10
Haze	36.2%	12.2%	5.3%
Luminous transmission	88.4%	91.5%	91.2%
Barcol hardness (15 second)	37—30	38—29	34—25

Example VII

A series of tests were conducted to determine the effect of various levels of tripropylene glycol diacrylate on polymers prepared from diethylene glycol bis(allyl carbonate) having a copolymer of allyl methacrylate and methyl methacrylate dispersed therethrough.

A copolymer of allyl methacrylate and methylmethacrylate was prepared. The copolymer contained about 1 weight percent allyl methacrylate, balance methyl methacrylate, and had a viscosity average molecular weight above about 500,000.

One composition was prepared containing 95.2 grams of PPG Industries, Inc. CR-39® diethylene glycol bis(allyl carbonate), 4.8 grams of the allyl methacrylate-methyl methacrylate copolymer, and 3.3 grams of neat diisopropyl peroxy dicarbonate.

A second composition was prepared containing 101.9 grams of PPG Industries, Inc. CR-39® diethylene glycol bis(allyl carbonate), 5.1 grams of the allyl methacrylate-methyl methacrylate copolymer, 3.6 grams of neat isopropyl peroxy dicarbonate, and 5.1 grams of tripropylene glycol diacrylate.

Both solutions were poured between four inch by eight inch glass plates separated by one-eighth inch rubber gaskets, and cured according to the isopropyl peroxy dicarbonate cure cycle in Table VI of Example V, above. The polymerized products were then tested for luminous transmission and haze as described in Example III, above. The following results were obtained:

TABLE IX
Haze and luminous transmission versus tripropylene glycol diacrylate concentration

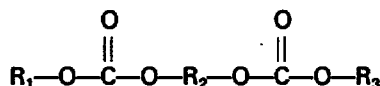
	Tripropylene glycol diacrylate	
	(parts per hundred parts of diethylene glycol bis(allyl carbonate) at 5 parts of poly (methyl methacrylate) per hundred parts of diethylene glycol bis (allyl carbonate).)	
	0	5
Haze	14.0%	1.3%
Luminous transmission	91.4%	92.4%

While the invention has been described with respect to certain exemplifications and embodiments, such description is only illustrative, the scope of the invention being defined by the claims appended hereto.

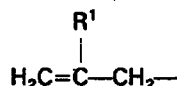


Claims

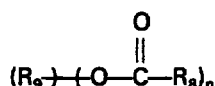
1. A composition of matter comprising:
 (a) an aliphatic diol bis(allyl carbonate);
 (b) an acrylate polymer; and
 (c) a multifunctional acrylate monomer,
 wherein the diol bis(allyl carbonate) monomer (a) is represented by the formula



where R_1 and R_3 are allyl groups independently represented by the formula



where R^1 is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof, the multifunctional acrylate monomer is represented by the formula

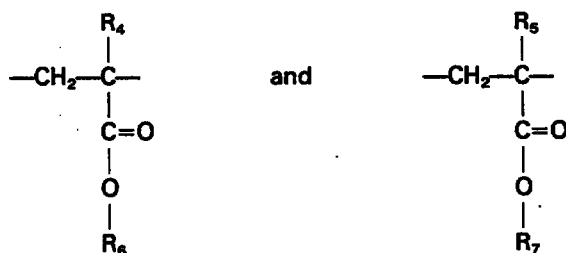


where n is from 2 to 5; R_9 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and R_8-COO- is the residue of an acrylic acid, and wherein said composition contains from 1 part of polymer per hundred parts of diol bis(allyl carbonate) to 100 parts of polymer per hundred parts of diol bis(allyl carbonate); and from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate).

2. The composition of claim 1 wherein said composition contains: (a) from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 35 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate); and (b) from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate); said composition having a pseudoplastic rheology with a shear stress of from 10^3 to 10^6 Pascal (10^4 to 10^7 dynes per square centimeter) at shear rates of from 10^1 to 10^4 per second.

3. The composition of claim 1 wherein the acrylate polymer is a copolymer of
 (a) an allyl alcohol ester of an acrylic acid; with
 (b) a mono-unsaturated acrylic component chosen from the group consisting of acrylic acids and low alkyl alcohol esters thereof.

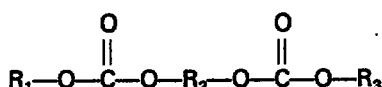
4. The composition of claim 3 wherein the copolymer comprises the recurring units of the formulas



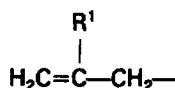
where R_4 and R_5 are independently hydrogen or an alkyl group, R_6 is the residue of an allyl alcohol, and R_7 is chosen from the group consisting of H, and C_1 to C_4 alkyl groups.

5. The composition of claim 1 wherein

(a) the diol bis(allyl carbonate) monomer is represented by the formula

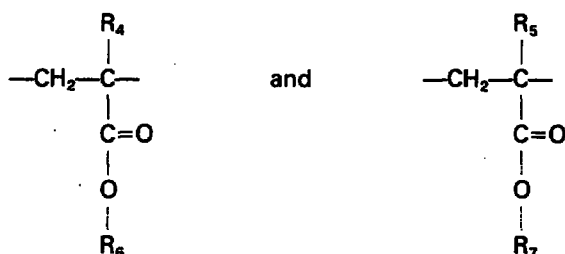


where R_1 and R_3 are allyl groups represented by the formula



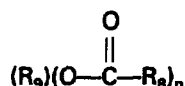
where R^1 is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups, and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof;

(b) the acrylate polymer is a copolymer consisting of the recurring units of the formulas



wherein R_4 and R_5 are independently hydrogen or an alkyl group, R_6 is the residue of an allyl alcohol, and R_7 is chosen from the group consisting of H, and C_1 to C_4 alkyl groups;

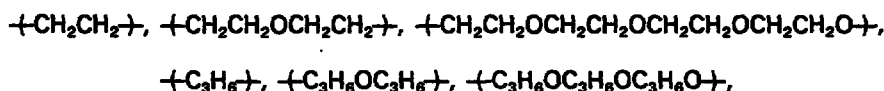
(c) the multifunctional acrylate monomer is represented by the formula



where n is from 2 to 5; R_9 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and R_8-COO- is the residue of an acrylic acid;

(d) R_1OH , R_3OH , and R_6OH are allyl alcohol;

(e) R_2 and R_9 are independently chosen from the group consisting of



and mixtures thereof;

(f) R_4 and R_5 are independently chosen from the group consisting of hydrogen or a methyl group, and mixtures thereof; and

(g) the composition contains: (i) from 1 part of copolymer per hundred parts of diol bis(allyl carbonate) to 35 parts of the acrylate polymer per hundred parts of diol bis(allyl carbonate) and (ii) from 1 part of the multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of the acrylate monomer per hundred parts of diol bis(allyl carbonate); said composition having a pseudoplastic rheology with a shear stress of from 10^3 to 10^6 Pascal (10^4 to 10^7 dynes per square centimeter) at shear rates of from 10^1 to 10^4 per second.

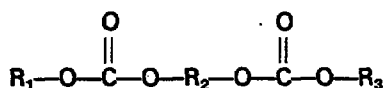
6. The polymeric product of a composition of

(a) an aliphatic diol bis(allyl carbonate);

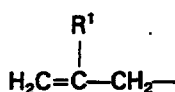
(b) an acrylate polymer; and

(c) a multifunctional acrylate monomer,

wherein the diol bis(allyl carbonate) monomer (a) is represented by the formula



where R_1 and R_3 are allyl groups independently represented by the formula

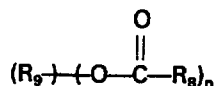


where R^1 is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof,



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the multifunctional acrylate monomer is represented by the formula

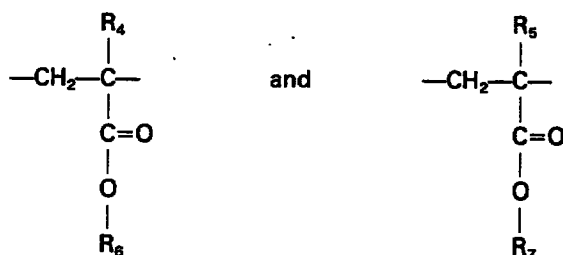


where n is from 2 to 5; R_9 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and $R_9 - COO -$ is the residue of an acrylic acid, and wherein said composition contains from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 100 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate); and from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate).

7. The polymeric product of claim 6 wherein the acrylate polymer is a copolymer comprising:

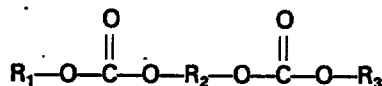
- (a) an allyl alcohol ester of an acrylic acid; with
- (b) a mono-unsaturated acrylic component chosen from the group consisting of acrylic acids and low alkyl alcohol esters thereof.

8. The polymeric product of claim 7 wherein the polymer is a copolymer consisting of the recurring units of the formulas

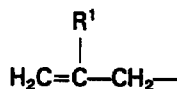


where R_4 and R_5 are independently hydrogen or an alkyl group, R_6 is the residue of an allyl alcohol, and R_7 is chosen from the group consisting of H, and C_1 to C_4 alkyl groups.

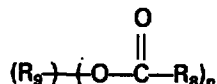
9. In a method of polymerizing a monomeric composition of a diol bis(allyl carbonate) having an acrylate polymer dispersed therethrough, wherein the diol bis(allyl carbonate) monomer is represented by the formula



where R_1 and R_3 are allyl groups independently represented by the formula



where R^1 is chosen from the group consisting of hydrogen, fluorine, chlorine, bromine, and C_1 to C_4 alkyl groups and R_2 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof, and wherein said composition contains from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 100 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate); and from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate), characterised by providing a multifunctional acrylate monomer represented by the formula



where n is from 2 to 5; R_9 is chosen from the group consisting of alkylene groups, alkylene ether groups, alkylene polyether groups, alkylene carbonate groups, and mixtures thereof and $R_9 - COO -$ is the residue of an acrylic acid, in the monomeric composition.

10. The method of claim 9 wherein said monomeric composition contains from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 35 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate).



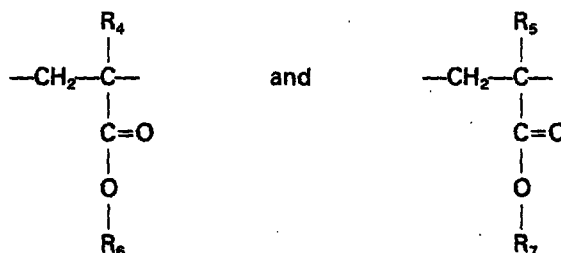
11. The method of claim 9 wherein said monomeric composition contains from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate).

12. The method of claim 9 wherein said monomeric composition contains: (a) from 1 part of acrylate polymer per hundred parts of diol bis(allyl carbonate) to 35 parts of acrylate polymer per hundred parts of diol bis(allyl carbonate); and (b) from 1 part of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate) to 20 parts of multifunctional acrylate monomer per hundred parts of diol bis(allyl carbonate); said composition having a pseudoplastic rheology with a shear stress of from 10^5 to 10^6 Pascal (10^4 to 10^7 dynes per square centimeter) at shear rates of from 10^1 to 10^4 per second.

13. The method of claim 9 wherein the acrylate polymer is a copolymer comprising:

(a) an allyl alcohol ester of an acrylic acid; with
(b) a mono-unsaturated acrylic component chosen from the group consisting of acrylic acids and low alkyl alcohol esters thereof.

14. The method of claim 13 wherein the acrylate polymer is a copolymer consisting of the recurring units of the formulas



where R_4 and R_5 are independently hydrogen or an alkyl group, R_6 is the residue of an allyl alcohol, and R_7 is chosen from the group consisting of H, and C_1 to C_4 alkyl groups.

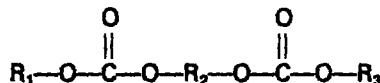
30 Patentansprüche

1. Zusammensetzung enthaltend

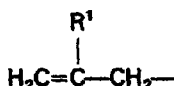
(a) ein aliphatisches Diol-bis(allylcarbonat),

(b) ein Acrylatpolymer und

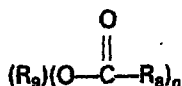
(c) ein multifunktionelles Acrylatmonomer,
in der das Diol-bis(allylcarbonat)monomer (a) die Formel



aufweist, in der R_1 und R_3 unabhängig voneinander Allylgruppen der Formel



sind, in der R^1 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Fluor, Chlor, Brom und C_1 — C_4 Alkylgruppen, R_2 ausgewählt ist aus der Gruppe bestehend aus Alkylgruppen, Alkylenergruppen, Alkylpolyethergruppen, Alkylcarbonatgruppen und Mischungen derselben, das multifunktionelle Acrylatmonomer die Formel



aufweist, in der n von 2 bis 5 ist, R_9 ausgewählt ist aus der Gruppe bestehend aus Alkylgruppen, Alkylenergruppen, Alkylpolyethergruppen, Alkylcarbonatgruppen und Mischungen derselben, und $R_8\text{---COO}$ — der Acrylsäurerest ist, und die Zusammensetzung ein Teil Polymer pro 100 Teile Diol-bis(allylcarbonat) bis 100 Teile Polymer pro 100 Teile Diol-bis(allylcarbonat) und 1 Teil multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) enthält.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß diese Zusammensetzung enthält:

(a) von 1 Teil Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) bis 35 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) und



(b) von 1 Teil multifunktionellem Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat), und die Zusammensetzung ein quasilastisches Fließverhalten bei Schubspannungen von 10^3 bis 10^6 Pascal (10^4 bis 10^7 dyn pro cm^2) und Schergeschwindigkeiten von 10^1 bis 10^4 pro Sekunde aufweist.

3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Acrylatpolymer ein Copolymer ist aus

(a) einem Allylalkoholester einer Acrylsäure mit

(b) einer einfach ungesättigten Acrylkomponente ausgewählt aus der Gruppe Acrylsäuren und Estern derselben mit niederen Alkylalkoholen.

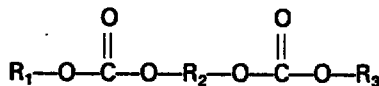
4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß das Copolymer wiederkehrende Einheiten der Formeln



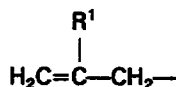
enthält, in denen R_4 und R_5 unabhängig voneinander Wasserstoff oder eine Alkylgruppe sind, R_6 der Rest eines Allylalkohols ist und R_7 ausgewählt ist aus der Gruppe Wasserstoff und C_1 — C_4 Alkylgruppen.

5. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß

(a) das Diol-bis(allylcarbonat)monomer die Formel

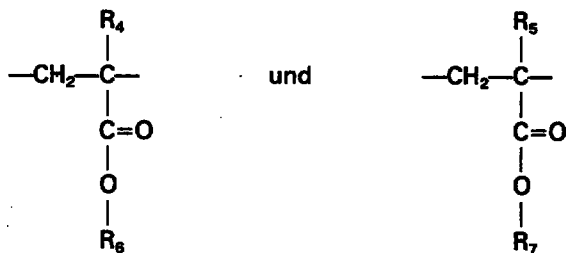


aufweist, in der R_1 und R_2 Allylgruppen der Formel



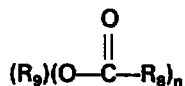
sind, in der R_1 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Fluor, Chlor, Brom und C_1 — C_4 Alkylgruppen, R_2 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenergruppen, Alkylpolyethergruppen, Alkylcarbonatgruppen und Mischungen derselben,

(b) das Acrylatpolymer ein Copolymer ist, bestehend aus wiederkehrenden Einheiten der Formeln



in denen R_4 und R_5 unabhängig voneinander Wasserstoff oder eine Alkylgruppe sind und R_6 der Rest eines Allylalkohols ist und R_7 ausgewählt ist aus der Gruppe Wasserstoff und C_1 bis C_4 Alkylgruppen,

(c) das multifunktionelle Acrylatmonomer die Formel



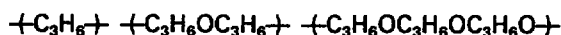
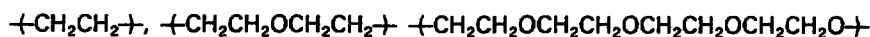
aufweist, in der n von 2 bis 5 ist, R_9 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenergruppen, Alkylpolyethergruppen, Alkylcarbonatgruppen und Mischungen derselben und $\text{R}_9-\text{COO}-$ der Acrylsäurerest ist,

(d) R_1OH , R_2OH und R_6OH Allylalkohol sind,

(e) R_2 und R_9 unabhängig voneinander ausgewählt sind aus der Gruppe bestehend aus



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und Mischungen derselben,

(f) R_4 und R_5 unabhängig voneinander ausgewählt sind aus der Gruppe bestehend aus Wasserstoff oder einer Methylgruppe oder Mischungen derselben und

(g) die Zusammensetzung enthält:

- 10 (i) von 1 Teil Copolymer pro 100 Teile Diol-bis(allylcarbonat) bis 35 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) und
(ii) von 1 Teil multifunktionellem Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat), und

- 15 die Zusammensetzung ein quasilastisches Fließverhalten bei Schubspannungen von 10^3 bis 10^6 Pascal (10^4 bis 10^7 dyn pro cm^2) und Schergeschwindigkeiten von 10^1 bis 10^4 pro Sekunde aufweist.

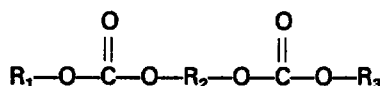
6. Polymeres Produkt einer Zusammensetzung aus

(a) einem aliphatischen Diol-bis(allylcarbonat),

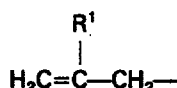
(b) einem Acrylatpolymer und

- 20 (c) einem multifunktionellen Acrylatmonomer,

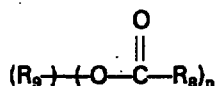
in der das Diol-bis(allylcarbonat)monomer (a) die Formel



aufweist, in der R_1 und R_3 unabhängig voneinander Allylgruppen der Formel



sind, in der R^1 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Fluor, Chlor, Brom und C_1 - C_4 Alkylgruppen, R_2 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenerethergruppen, Alkylpolyethergruppen, Alkylencarbonatgruppen und Mischungen derselben, das multifunktionelle Acrylatmonomer die Formel



aufweist, in der n von 2 bis 5 ist, R_9 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenerethergruppen, Alkylpolyethergruppen, Alkylencarbonatgruppen und Mischungen derselben, und $\text{R}_9-\text{COO}-$ der Acrylsäurerest ist, und

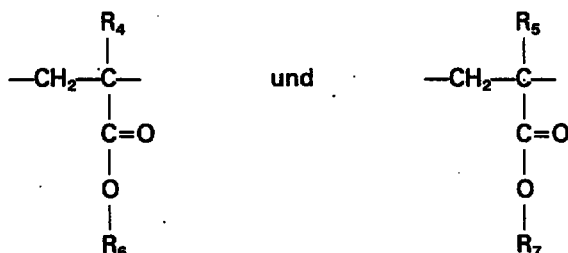
- 45 die Zusammensetzung ein Teil Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) bis 100 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) und 1 Teil multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) enthält.

- 50 7. Polymeres Produkt nach Anspruch 6, dadurch gekennzeichnet, daß das Acrylatpolymer ein Copolymer ist aus

(a) einem Allylalkoholester einer Acrylsäure mit

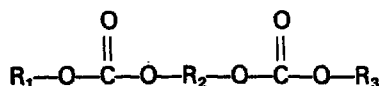
(b) einer einfach ungesättigten Acrylkomponente ausgewählt aus der Gruppe Acrylsäuren und Estern derselben mit niederen Alkylalkoholen.

- 55 8. Polymeres Produkt nach Anspruch 7, dadurch gekennzeichnet, daß das Polymer ein Copolymer ist, bestehend aus wiederkehrenden Einheiten der Formeln

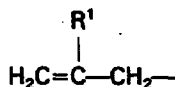


in denen R_4 und R_5 unabhängig voneinander Wasserstoff oder eine Alkylgruppe sind, R_6 der Rest eines Allylalkohols ist und R_7 ausgewählt ist aus der Gruppe Wasserstoff und C_1-C_4 Alkylgruppen.

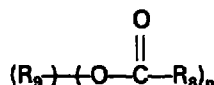
9. Verfahren zum Polymerisieren einer Monomierzusammensetzung eines Diol-bis(allylcarbonats) in dem ein Acrylpolymer dispergiert ist, wobei das Diol-bis(allylcarbonat)monomer die Formel



aufweist, in der R_1 und R_3 unabhängig voneinander Allylgruppen der Formel

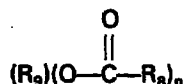


in der R^1 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Fluor, Chlor, Brom und C_1-C_4 Alkylgruppen, R_2 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenethergruppen, Alkylpolyethergruppen, Alkylencarbonatgruppen und Mischungen derselben, das multifunktionelle Acrylatmonomer die Formel



aufweist, in der n von 2 bis 5 ist, R_9 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenethergruppen, Alkylpolyethergruppen, Alkylencarbonatgruppen und Mischungen derselben, und wobei die Zusammensetzung ein Teil Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) bis 100 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) und von 1 Teil multifunktionellem Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teilen multifunktionellem Acrylatmonomer pro 100 Teilen Diol-bis(allylcarbonat) enthält,

gekennzeichnet durch Verwenden eines multifunktionellen Acrylatmonomers der Formel



in der n von 2 bis 5 ist, R_9 ausgewählt ist aus der Gruppe bestehend aus Alkylengruppen, Alkylenethergruppen, Alkylpolyethergruppen, Alkylencarbonatgruppen und Mischungen derselben, R_9-COO- der Acrylsäurerest ist, in der monomeren Zusammensetzung.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die monomere Zusammensetzung 1 Teil Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) bis 35 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) enthält.

11. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die monomere Zusammensetzung 1 Teil multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) enthält.

12. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die monomere Zusammensetzung enthält

(a) von 1 Teil Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) bis 35 Teile Acrylatpolymer pro 100 Teile Diol-bis(allylcarbonat) und

(b) ein Teil multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat) bis 20 Teile multifunktionelles Acrylatmonomer pro 100 Teile Diol-bis(allylcarbonat), und die Zusammensetzung ein quasiplastisches Fließverhalten bei Schubspannungen von 10^3 bis 10^6 Pascal (10^4 bis 10^7 dyn pro cm^2) und Schergeschwindigkeiten von 10^1 bis 10^4 pro Sekunde aufweist.

13. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Acrylatpolymer ein Copolymer ist, enthaltend

(a) einen Allylalkoholester einer Acrylsäure mit

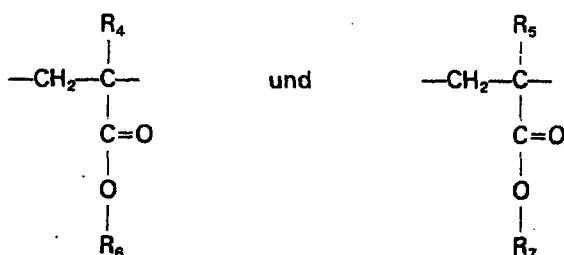
(b) einer einfach ungesättigten Acrylkomponente, ausgewählt aus der Gruppe bestehend aus Acrylsäuren und Estern derselben mit niederen Alkylalkoholen.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Acrylatpolymer ein Copolymer ist, bestehend aus wiederkehrenden Einheiten der Formel





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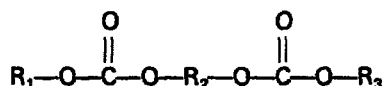


enthält, in denen R_4 und R_5 unabhängig voneinander Wasserstoff oder eine Alkylgruppe sind, R_6 der Rest eines Allylalkohols ist und R_7 ausgewählt ist aus der Gruppe Wasserstoff und C_1-C_4 Alkylgruppen.

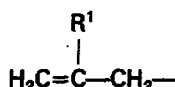
Revendications

1. Composition de matière comprenant:
 - (a) un bis(allyl carbonate) de diol aliphatique;
 - (b) un polymère d'acrylate; et
 - (c) un monomère acrylate polyfonctionnel,

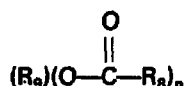
dans laquelle le monomère bis(allyl carbonate) de diol (a) est représenté par la formule:



où R_1 et R_3 sont des groupes allyle représentés indépendamment par la formule:



où R' est choisi dans le groupe constitué par un hydrogène, un fluor, un chlore, un brome et les groupes alkyle en C_1 à C_4 et R_2 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges, le monomère acrylate polyfonctionnel est représenté par la formule:



où n est 2 à 5; R_9 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges, et R_8-COO- est le reste d'un acide acrylique, et dans laquelle ladite composition contient de 1 partie de polymère pour 100 parties de bis(allyl carbonate) de diol à 100 parties de polymère pour 100 parties de bis(allyl carbonate) de diol; et de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol.

2. Composition selon la revendication 1, dans laquelle la composition contient (a) de 1 partie de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol à 35 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol; et (b) de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol; ladite composition ayant une rhéologie pseudoplastique avec une contrainte tangentielle au cisaillement de 10^5 à 10^6 Pascal (10^4 à 10^7 dynes/cm²) pour des gradients de cisaillement de 10^1 à 10^4 par seconde.

3. Composition selon la revendication 1, dans laquelle le polymère d'acrylate est un copolymère de:

- (a) un ester d'alcool allylique d'un acide acrylique; avec
- (b) un composant acrylique mono-insaturé choisi dans le groupe constitué par les acides acryliques et les esters d'alcanols inférieurs de ces acides.

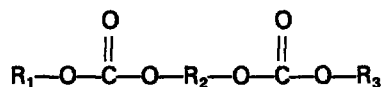
4. Composition selon la revendication 3, dans laquelle le copolymère comprend les motifs récurrents de formules:



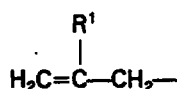
dans lesquelles R_4 et R_5 représentent indépendamment un hydrogène ou un groupe alkyle, R_6 est le reste d'un alcool allylique et R_7 est choisi dans le groupe constitué par H et les groupes alkyle en C_1 à C_4 .

5. Composition selon la revendication 1 dans laquelle:

(a) le monomère bis(allyl carbonate) de diol est représenté par la formule:

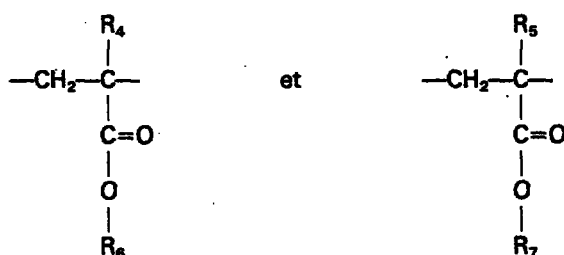


où R_1 et R_3 sont des groupes allyle représentés par la formule:



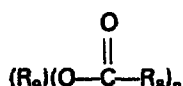
où R' est choisi dans le groupe constitué par un hydrogène, un fluor, un chlore, un brome et les groupes alkyle en C_1 à C_4 , et R_2 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges;

(b) le polymère d'acrylate est un copolymère constitué par les motifs récurrents de formules:



où R_4 et R_5 sont indépendamment un hydrogène ou un groupe alkyle, R_6 est le reste d'un alcool allylique et R_7 est choisi dans le groupe constitué par H et les groupes alkyle en C_1 à C_4 ;

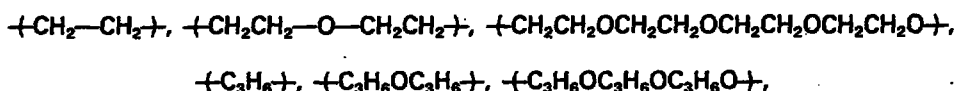
(c) l'acrylate polyfonctionnel monomère est représenté par la formule:



où n est de 2 à 5; R_9 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène, et leurs mélanges, et R_9-COO- est le reste d'un acide acrylique;

(d) R_1OH , R_3OH et R_6OH sont des alcools allyliques;

(e) R_2 et R_9 sont choisis indépendamment dans le groupe constitué par:



et leurs mélanges;

(f) R_4 et R_5 sont choisis indépendamment dans le groupe constitué par l'hydrogène en une groupe méthyle et leurs mélanges et;

(g) la composition contient (i) de 1 partie de copolymère pour 100 parties de bis(allyl carbonate) de diol à 35 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol; et (ii) de 1 partie d'un monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate pour 100 parties de bis(allyl carbonate) de diol; ladite composition ayant une rhéologie



pseudoplastique avec une contrainte de cisaillement de 10^3 à 10^6 Pascal (10^4 à 10^7 dynes par cm^2) à des gradients de cisaillement de 10^1 à 10^4 par seconde.

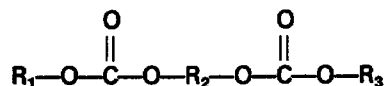
6. Produit polymère d'une composition de:

(a) un bis(allyl carbonate) de diol aliphatique;

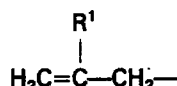
(b) un polymère d'acrylate; et

(c) un monomère acrylate polyfonctionnel,

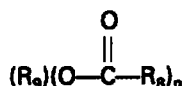
dans lequel le le monomère bis(allyl carbonate) de diol (a) est représenté par la formule:



où R_1 et R_3 sont des groupes allyle représentés indépendamment par la formule:



où R' est choisi dans le groupe constitué par un hydrogène, un fluor, un chlore, un brome et les groupes alkyle en C_1 à C_4 , et R_2 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges, le monomère acrylate polyfonctionnel est représenté par la formule:



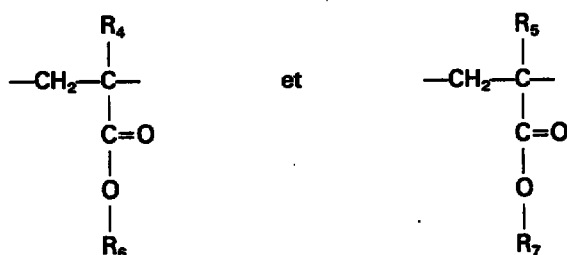
où n est de 2 à 5, R_9 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges et $\text{R}_9-\text{COO}-$ est le reste d'un acide acrylique, et dans lequel ladite composition contient de 1 partie de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol à 100 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol; et de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol.

7. Produit polymère selon la revendication 6, dans lequel le polymère d'acrylate est un copolymère comprenant:

(a) un ester d'alcool allylique d'un acide acrylique; avec

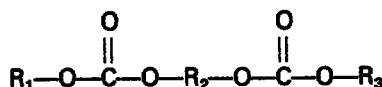
(b) un composant acrylique mono-insaturé choisi dans le groupe constitué par les acides acryliques et leurs esters d'alkanols inférieurs.

8. Produit polymère selon la revendication 7, dans lequel le polymère est un copolymère constitué par les motifs récurrents de formules:

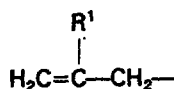


où R_4 et R_5 sont indépendamment un hydrogène ou un groupe alkyle, R_6 est le reste d'un alcool allylique et R_7 est choisi dans le groupe constitué par H et les groupes alkyle en C_1 à C_4 .

9. Procédé de polymérisation d'une composition monomère d'un bis(allyl carbonate) de diol dans laquelle est dispersé un polymère d'acrylate dans lequel le bis(allyl carbonate) de diol monomère est représenté par la formule:



où R_1 et R_3 sont des groupes allyle indépendamment représentés par la formule:



- 5 où R^1 est choisi dans le groupe constitué par un hydrogène, un fluor, un chlore, un brome et les groupes alkyle en C_1 à C_4 , et R_2 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate d'alkylène et leurs mélanges, et dans lequel cette composition contient de 1 partie de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol à 100 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol et de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol, caractérisé en ce qu'on apporte dans la composition monomère, un monomère acrylate polyfonctionnel représenté par la formule:



- 15 dans laquelle n est de 2 à 5; R_9 est choisi dans le groupe constitué par les groupes alkylène, les groupes éther d'alkylène, les groupes polyéther d'alkylène, les groupes carbonate, d'alkylène et leurs mélanges, et $\text{R}_8-\text{COO}-$ est le reste d'un acide acrylique.

- 20 10. Procédé selon la revendication 9 dans lequel ladite composition monomère contient de 1 partie de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol à 35 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol.

- 25 11. Procédé selon la revendication 9, dans lequel ladite composition monomère contient de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol.

12. Procédé selon la revendication 9 dans lequel la dite composition monomère contient:

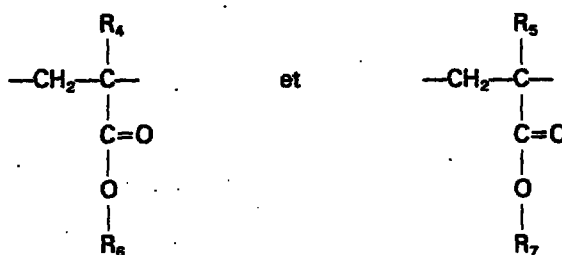
- 30 (a) de 1 partie de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol à 35 parties de polymère d'acrylate pour 100 parties de bis(allyl carbonate) de diol; et
(b) de 1 partie de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol à 20 parties de monomère acrylate polyfonctionnel pour 100 parties de bis(allyl carbonate) de diol; ladite composition ayant une rhéologie pseudoplastique avec une sollicitation au cisaillement de 10^2 à 10^6 Pascal (10^4 à 10^7 dynes/cm²) à des gradients de cisaillement de 10^1 à 10^4 par seconde.

- 35 13. Procédé selon la revendication 9, dans lequel le polymère d'acrylate est un copolymère comprenant:

- (a) un ester d'alcool allylique d'un acide acrylique; avec

- (b) un composant acrylique mono-insaturé choisi dans le groupe constitué par les acides acryliques et leurs esters d'alkanols inférieurs.

- 40 14. Procédé selon la revendication 13 dans lequel le polymère acrylate est un copolymère constitué par les motifs récurrents de formules



où R_4 et R_5 sont indépendamment un hydrogène ou un groupe alkyle, R_6 est le reste d'un alcool allylique et R_7 est choisi dans le groupe constitué par H et les groupes alkyle en C_1 à C_4 .