

Description

The present invention relates to a liquid composition, polymerizable, by means of free-radical polymerization, into organic glasses showing a low water absorption and a high thermal stability (a high heat distortion temperature and a high resistance to yellowing).

The invention relates as well to the organic glasses which can be obtained from said composition.

Among the plastic materials useful as organic glasses, the most interesting ones from a commercial viewpoint are poly(methyl-methacrylate), polycarbonate and polystyrene. Even if they are widely used in the industrial practice for many applications, these materials suffer from some drawbacks, which limit their use as optical elements, e.g., in optical disks, optical papers, wave guides, optical fibres, and optical lenses. A characteristic they share with one another is a poor resistance to abrasion and to the solvents. Furthermore, poly(methyl-methacrylate) shows a high water retention in prolonged-dipping tests, whilst polycarbonate and polystyrene, which do not suffer from this drawback, show a considerably high birefringence.

The thermosetting organic glasses are known to be more resistant to abrasion and to the solvents, and, among these, those organic glasses which derive from the polymerization of polyol allyl-carbonates, in particular, of diethylene-glycol bis(allyl-carbonate), deserve a prominent commercial interest, in view of the peculiar characteristics of clearness, resistance to abrasion, to the solvents and to ageing. See, e.g., F. Strain in "Encyclopaedia of Chemical Processing and Design", 1st Edition, Dekker Inc., New York, Vol. I, pages 799-foll., Interscience Publishers, New York, 1964.

Unfortunately, the products from the polymerization of diethylene glycol bis(allyl-carbonate) suffer from limitations in the above cited application sectors, deriving from the relatively high values of water absorption in tests with prolonged dipping, and of relatively low thermal stability at a high temperature.

US-A-3679727 and US-A-3751374, for example, disclose polymerizable derivatives of cyclohexane in monomeric form but the compounds according to them, totally devoid of oligomeric components, are not suitable for optical articles. Neither US-A-3679727 nor US-A-3751374 solve the problems of high water absorption and low thermal stability.

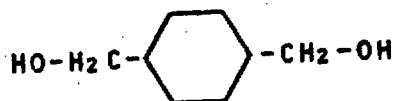
The present Applicant found now that these drawbacks can be overcome, or, at least, considerably reduced, by means of a liquid polymer organic glass composition of the present invention, which can be polymerized by free-radical polymerization, to yield organic glasses endowed with characteristics of low water absorption and high thermal stability (high heat distortion temperature, and high resistance to yellowing), together with good optical and mechanical characteristics.

More particularly the liquid polymer organic glass composition of the present invention, having low water absorption and high thermal stability, comprises a mixture of monomeric and oligomeric bis(allylcarbonates) which are the transesterification reaction product of:

(a) a diallyl-carbonate, and

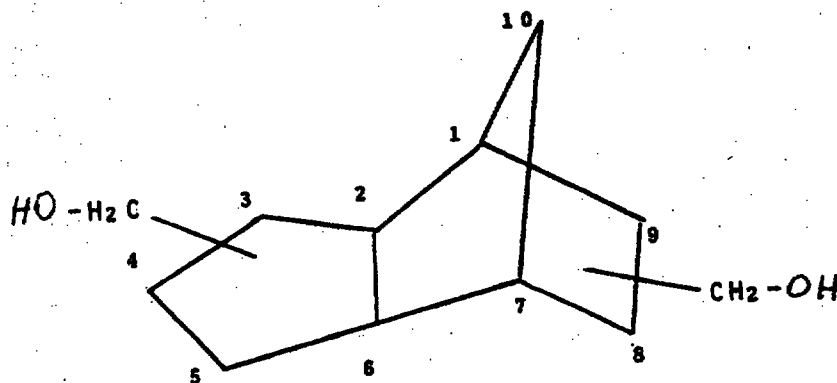
(b) at least one cycloaliphatic diol, with a molar ratio of the diallyl-carbonate to the cycloaliphatic diol of 2:1 to 18:1.

Among the cycloaliphatic diols, 1,4-cyclohexane-dimethanol:



and

3(4),8(9)-bis-(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane:



[hereinafter denominated, in short form, as "bis(hydroxymethyl)tricyclo-decane"), are preferred.

In the preferred form of practical embodiment, the composition according to the present invention is the reaction product, under conditions of transesterification, of a diallyl-carbonate and 1,4-cyclohexane-dimethanol in a mutual molar ratio comprised within the range of from 3:1 to 6:1, or of a diallyl-carbonate and bis(hydroxymethyl)-tricyclo-decane in a mutual molar ratio comprised within the range of from 6:1 to 18:1.

In particular, the transesterification reaction is carried out by bringing the reactants into contact, in the above indicated proportions, with the process being out at temperatures comprised within the range of from 80° to 160° C, and preferably of from 90° to 130° C, in the presence of a catalyst of alkaline character, with the allyl alcohol formed in the reaction being continuously removed.

Catalysts suitable for the intended purpose are alkali-metal hydroxides, carbonates and alkoxides, the organic bases and the basic ion-exchange resins. Specific catalyst examples are sodium hydroxide, sodium carbonate and sodium methoxide. The catalyst is advantageously used in an amount of at least 1 ppm (one part per million parts by weight), relatively to the cycloaliphatic diol, and, preferably, in an amount of the order of 0.01-0.3%, by weight relatively to said diol.

The reaction is advantageously carried out under such a pressure, as to bring the system to the boil at the preselected operating temperature, so as to favour the elimination of the allyl alcohol from the reaction mixture. For example, pressure values comprised within the range of from 27 to 1013 mbar (20 to 760 torr), and preferably of from 67.5 to 540 mbar (50 to 400 torr), are suitable for the intended purpose. Under the above stated conditions, the reaction times are generally comprised within the range of from 0.5 to 20 hours, and typically are of the order of from 0.5 to 2 hours.

At the end of the reaction, the mixture is cooled and washed with water in order to remove the small catalyst amounts and, after de-mixing and separation of the aqueous phase, the unconverted diallyl-carbonate is distilled off, by heating the reaction mixture up to temperatures of the order of 120° C, under a reduced pressure down to values of the order of 0.133 - 27 mbar (0.1-20 torr), and preferably of 1.33 - 3.99 mbar (1-3 torr), with the desired composition being obtained as the residue.

If necessary, this composition is submitted to filtration, after a preliminary optional treatment with activated charcoal.

The composition according to the present invention is liquid at room temperature, and shows values of viscosity comprised within the range of from 5 10⁻⁵ to 3 10⁻⁴ m²/s (50 to 300 cst) and of specific gravity, of the order of from 1.10 to 1.20 g/ml. This composition is constituted by either monomer or oligomer bis-(allyl-carbonates) of the cycloaliphatic diol used, with an amount of oligomers which is generally comprised within the range of from 10 to 70% by weight.

More particularly, in the preferred form of practical embodiment, according to which the diallyl-carbonate and 1,4-cyclohexane-dimethanol are reacted with each other in a molar ratio comprised within the range of from 3:1 to 6:1, the resulting composition contains from about 25 to about 50% by weight of oligomers, as a function of the selected ratio between the reactants. Furthermore, in the preferred form of practical embodiment, according to which the diallyl-carbonate and bis(hydroxymethyl)-tricyclo-decane are reacted with each other in a molar ratio comprised within the range of from 6:1 to 18:1, the content of oligomers in the resulting composition is comprised within the range of from about 10 to about 30% by weight.

The composition according to the present invention may contain up to 30% by weight, as referred to the end mixture, of one or more vinylic or acrylic monomers, examples for which are vinyl acetate, butyl (meth)acrylate, 2-ethyl-hexyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, and phenyl (meth)acrylate.

Furthermore, the composition may additionally contain one or more additives, such as stabilizers, lubricants, dyes, pigments, U.V. and I.R. light absorbers, anyway in a total amount not larger than 1 part by weight per each 100 parts by weight of the same composition.

The composition according to the present invention can be transformed into organic glasses by means of free-radical polymerization, with the usual casting technique. For such a purpose, to the composition one or more polymerization initiators, soluble in the same composition, and capable of generating free radicals within a temperature range comprised from about 30 to 120°C are added. Preferred examples of such initiators are di-cyclohexyl-peroxy-dicarbonate, di-isopropyl-peroxy-dicarbonate, di-benzoyl-peroxide, di-sec-butyl-peroxy-dicarbonate, and sec-butyl-cyclohexyl-peroxy-dicarbonate. The amount of the initiator can be generally comprised within the range of from 1 to 6 parts by weight per each 100 parts by weight of the composition.

The conversion of the initiator-containing composition into the organic glass takes place at temperatures comprised within the range of from about 35 to about 120°C, with polymerization times which may generally be comprised within the range of from 1 to 100 hours.

During the polymerization, phenomena of reduced volume shrinkage occur, and the so obtained organic glasses are endowed with characteristics of low water absorption, and high thermal stability (a high heat distortion temperature, and a high resistance to yellowing), and that, together with good general optical and mechanical characteristics.

The following experimental examples are given for merely exemplifying purposes, and it should be understood that in no way is the invention limited to them, or by them. In these examples, the liquid, polymerizable composition is prepared by reacting, under transesterification conditions, diallyl-carbonate and 1,4-cyclohexane-dimethanol or bis(hydroxymethyl)tricyclo-decane. To the so obtained liquid composition, di-cyclohexyl-peroxy-dicarbonate is added as the initiator, in the amount of 5% by weight, as referred to the weight of the mixture. The composition which contains the initiator is converted by polymerization into flat sheets of 3 mm of thickness by means of the conventional casting technique. According to this technique, the composition is poured into the hollow of a mould obtained by assembling two sheets of FLOAT glass, with a spacer gasket of plasticized poly(vinyl chloride).

The whole is then submitted to polymerization, by being heated for 72 hours inside a forced air circulation oven, at the temperature of 48°C. At the end of this time, the moulds are opened, and the polymerized sheets are recovered and are maintained for 2 hours at 110°C, in order to decompose any possible initiator residues.

On the so-obtained sheets, the following characteristics are determined:

a) Optical Characteristics:

- Refractive index (n_D^{20}): measured by means of the Abbe's refractometer (ASTM D-542).
- Haze and transmittance within the visible range (%): measured by using the Gardner's Hazegard XL-211 (ASTM D-1003).
- Yellow index (YI), defined as:

$$YI = \frac{100}{Y} (1.277 X - 1.06 Z)$$

as determined by means of the Gardner's colorimeter XL-805 (ASTM D-1925).

b) Physical and Mechanical Characteristics

- Specific gravity:
As determined by means of the hydrostatic balance at the temperature of 25°C (ASTM D-792).
- Volume shrinkage during polymerization ("shrinkage"):
As computed by means of the following formula:

(polymer density - monomer density)

$$\text{shrinkage \%} = \frac{\text{-----}}{\text{(polymer density)}} \times 100$$

- Rockwell hardness (M):

Measured by means of the Rockwell durometer (ASTM D-785).

- Ultimate strength and elastic modulus at bending (ASTM D-790).

- Water absorption:

As measured by dipping a specimen of 27x34x3 mm of dimensions in water, and determining the weight increase with time (ASTM D-543, modified).

c) Thermal characteristics:

- Heat Distorsion Temperature under a load of 1.82 mPa (HDT) (ASTM D-648).

- Thermal stability:

As measured by determining the change in Yellow Index after a thermal treatment of 5 hours at the respective temperatures of 150°C, 170°C, and 190°C.

Example 1

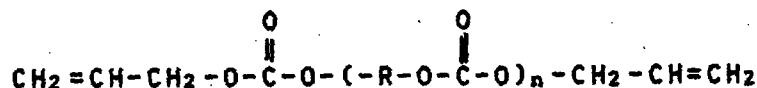
To a jacketed, three-necked flask equipped with thermometer and stirring means, and with an overhanging distillation column with 20 perforated trays, 201.6 g (1.4 mol) of 1,4-cyclohexane-dimethanol, 759 g (5.6 mol) of diallyl-carbonate and 0.30 ml of a solution at 30% by weight of sodium methoxide in methanol are charged.

The reaction is allowed to proceed for 1 hour and 15 minutes under a pressure of 199 mbar (150 torr), with the allyl alcohol formed during the reaction being distilled off (163 g in total; purity 99.6%). After cooling, the reaction mixture is washed twice, each time with 500 ml of distilled water. The excess of diallyl-carbonate is distilled off from the reaction mixture by operating under 1 torr, and up to an end temperature of 120°C. The obtained product is decolorized by being brought into contact with 2% by weight of activated charcoal, for 4 hours at 80°C, and is subsequently filtered.

In this way, 385 g is obtained of a liquid product, which has the following characteristics:

- viscosity (25°C)	9.06 10 ⁻⁵ m ² /s (90.6 cst)
- specific gravity (20°C)	1.107 g/ml
- refractive index (n _D ²⁰)	1.4735
- colour (APHA)	10

The product consists of monomer and oligomer 1,4-cyclohexane-dimethanol bis(allyl carbonates), with the following hypothesized distribution:



wherein: R =



- monomer	n = 1	64 % by weight
- dimer	n = 2	25 % by weight
- trimer	n = 3	8 % by weight
- tetramer	n = 4	3 % by weight

Example 2

The reaction product from Example 1, after the addition of dicyclohexyl-peroxy-dicarbonate in an amount of 5% by weight, as referred to the weight of the same mixture, is submitted to polymerization under the same condition as reported in the disclosure, and on the hardened compositions, the characteristics are determined, which are reported in Table 1, under the "Test 1" heading.

In the same Table, under the "Test 2" heading, the corresponding values are reported, of the product obtained by hardening diethylene glycol bis(allyl carbonate), according to the prior art.

Table 1

	Test 1	Test 2
- Specific gravity (g/ml)	1.2093	1.3111
- Shrinkage (%)	8.5	12.3
- n_D^{20}	1.5053	1.5010
- Haze (%)	0.35	0.16
- Transmittance in the visible range (%)	92.5	93.3
- Yellow Index	1.18	1.20
- Ultimate strength at bending (MPa)	32	79
- Elastic modulus at bending (MPa)	2330	2300
- Rockwell hardness (M)	106	97
- IZOD impact strength without notch (kJ/m ²)	5.8	17.2
- HDT (°C)	173	66

In Table 2, the water absorption values are reported, which are determined in the prolonged dipping tests on the hardened products from Test 1 and Test 2, together with the corresponding values as determined on poly(methyl methacrylate) (Test 3).

Table 2

	Absorbed water (% weight change)		
	1 day	7 days	15 days
Test 1	0.11	0.38	0.38
Test 2	0.27	0.67	0.96
Test 3	0.34	0.81	1.14

In Table 3, the yellow index values are reported, which are measured on the hardened products of Test 1 and Test 2, after a thermal treatment of 5 hours at the respective temperatures of 150°C, 170°C, and 190°C.

Table 3

	Change in yellow index		
	150 °C	170 °C	190 °C
Test 1	-0.29	+0.45	+3.74
Test 2	+2.95	+6.11	+14.23

Example 3

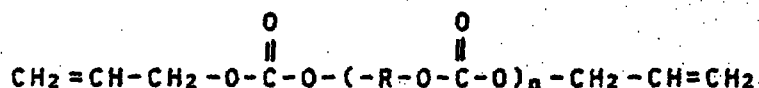
To the same equipment as disclosed in Example 1, 196.3 g (1.0 mol) of bis(hydroxymethyl)-tricyclo-decane, 1704 g (12.0 mol) of diallyl-carbonate and 0.8 ml of a solution at 30% by weight of sodium methoxide in methanol are charged.

The reaction is allowed to proceed for 30 minutes at a temperature of 105-120 °C and under a pressure of 199 mbar (150 torr), with the allyl alcohol formed during the reaction being distilled off (116 g). After cooling, the reaction mixture is washed twice, each time with 500 ml of distilled water, in order to bring it to a neutral pH. The excess of diallyl-carbonate is distilled off under a reduced pressure of 1.33 mbar (1 torr), and up to an end temperature of 120 °C. The reaction product is decolorized by being brought into contact with 2% by weight of activated charcoal, for 4 hours at 80 °C, and is subsequently filtered.

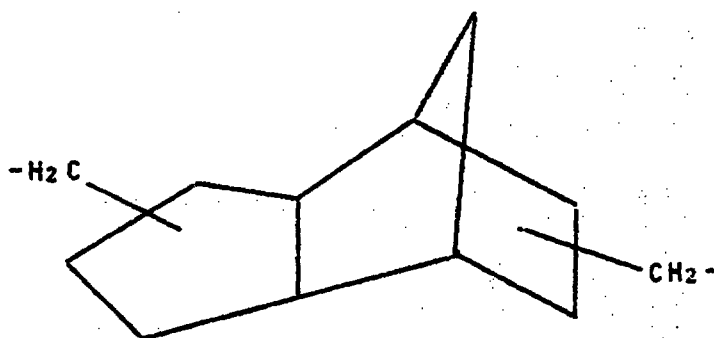
In this way, 370 g is obtained of a liquid product, which has the following characteristics:

- viscosity (25 °C)	1.95 10 ⁻⁴ m ² /s (195 cst)
- specific gravity (25 °C)	1.14 g/ml
- refractive index (n _D ²⁰)	1.4935
- colour (APHA)	30

The product consists of monomer and oligomer bis-(hydroxymethyl)-tricyclo-decane bis(allyl carbonates), with the following hypothesized distribution:



wherein: R =



- monomer	n = 1	87.6 % by weight
- dimer	n = 2	11.2 % by weight
- trimer	n = 3	1.2 % by weight

Example 4

The reaction product from Example 3, after the addition of dicyclohexyl-peroxy-dicarbonate (5% by weight, as referred to the weight of the same mixture), is submitted to polymerization under the same conditions as of Example 2, and on the hardened compositions, the characteristics are determined, which are reported in Table 4.

Table 4

- Specific gravity (g/ml)	1.2257
- Shrinkage (%)	7.6
- n_D^{20}	1.5215
- Haze (%)	0.22
- Transmittance in the visible range (%)	91.6
- Yellow index	2.27
- Ultimate strength at bending (MPa)	96
- Elastic modulus at bending (MPa)	3300
- Rockwell hardness	112
- IZOD impact strength without notch (kJ/m ²)	13.1
- HDT (°C)	90.1
- Absorbed water (% weight change)	
- after 1 day	0.08
- after 7 days	0.19
- after 15 days	0.25

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. A liquid polymer organic glass composition having low water absorption and high thermal stability, comprising a mixture of monomeric and oligomeric bis(allylcarbonates) which are the transesterification reaction product of:
 - (a) a diallyl-carbonate, and
 - (b) at least one cycloaliphatic diol, with a molar ratio of the diallyl-carbonate to the cycloaliphatic diol of 2:1 to 18:1.
2. Composition according to Claim 1, wherein the cycloaliphatic diol is 1,4-cyclohexane dimethanol and the molar ratio of the diallyl carbonate to 1,4-cyclohexane dimethanol is from 3:1 to 6:1.
3. Composition according to Claim 1, wherein the cycloaliphatic diol is 3(4),8(9)-bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,8})-decane and the molar ratio of the diallyl carbonate to 3(4),8(9)-bis(hydroxymethyl)-tricyclo(5.2.1.0^{2,8})-decane is from 6:1 to 18:1.
4. Composition according to Claim 1, further comprising up to 30% by weight, relative to the composition, of at least one vinylic or acrylic monomer selected from vinyl acetate, butyl methacrylate, 2-ethyl-hexyl methacrylate, cyclohexyl methacrylate and phenyl methacrylate.
5. Composition according to Claim 1, further comprising at least one additive selected from stabilizers, lubricants, dyes, UV- and IR-light absorbers, in an amount not larger than 1% by weight relative to the weight of the composition.
6. Composition according to Claim 1, further comprising an amount of from 1 part to 6 parts by weight per 100 parts of the composition of at least one polymerization initiator soluble in the composition and capable of generating free radicals at a temperature of from 30°C to 120°C.

Example 4

The reaction product from Example 3, after the addition of dicyclohexyl-peroxy-dicarbonate (5% by weight, as referred to the weight of the same mixture), is submitted to polymerization under the same conditions as of Example 2, and on the hardened compositions, the characteristics are determined, which are reported in Table 4.

Table 4

- Specific gravity (g/ml)	1.2257
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- after 15 days	0.25

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. A liquid polymer organic glass composition having low water absorption and high thermal stability, comprising a mixture of monomeric and oligomeric bis(allylcarbonates) which are the transesterification reaction product of:

(a) a diallyl-carbonate, and

(b) at least one cycloaliphatic diol, with a molar ratio of the diallyl-carbonate to the cycloaliphatic diol of 2:1 to 18:1.

2. Composition according to Claim 1, wherein the cycloaliphatic diol is 1,4-cyclohexane dimethanol and the molar ratio of the diallyl carbonate to 1,4-cyclohexane dimethanol is from 3:1 to 6:1.

3. Composition according to Claim 1, wherein the cycloaliphatic diol is 3(4),8(9)-bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,8})-decane and the molar ratio of the diallyl carbonate to 3(4),8(9)-bis(hydroxymethyl)-tricyclo(5.2.1.0^{2,8})-decane is from 6:1 to 18:1

4. Composition according to Claim 1, further comprising up to 30% by weight, relative to the composition, of at least one vinylic or acrylic monomer selected from vinyl acetate, butyl methacrylate, 2-ethyl-hexyl methacrylate, cyclohexyl methacrylate and phenyl methacrylate.

5. Composition according to Claim 1, further comprising at least one additive selected from stabilizers, lubricants, dyes, UV- and IR-light absorbers, in an amount not larger than 1% by weight relative to the weight of the composition.

6. Composition according to Claim 1, further comprising an amount of from 1 part to 6 parts by weight per 100 parts of the composition of at least one polymerization initiator soluble in the composition and capable of generating free radicals at a temperature of from 30°C to 120°C.



7. Process for producing organic glasses, comprising the step of polymerizing by casting a liquid polymer organic glass composition having low water absorption and high thermal stability, comprising a mixture of monomeric and oligomeric bis(allylcarbonates) which are the transesterification reaction product of:
 - (a) a diallyl-carbonate, and
 - (b) at least one cycloaliphatic diol, with a molar ratio of the diallyl-carbonate to the cycloaliphatic diol of 2:1 to 18:1, at a temperature of from 35° C to 120° C and for a time of from 1 hour to 100 hours.
8. Organic glasses whenever obtained by the process as defined in Claim 7.

Claims for the following Contracting State : ES

1. Process for producing organic glasses, comprising the step of polymerizing by casting a liquid polymer organic glass composition having low water absorption and high thermal stability, comprising a mixture of monomeric and oligomeric bis(allylcarbonates) which are the transesterification reaction product of:
 - (a) a diallyl-carbonate, and
 - (b) at least one cycloaliphatic diol, with a molar ratio of the diallyl-carbonate to the cycloaliphatic diol of 2:1 to 18:1, at a temperature of from 35° C to 120° C and for a time of from 1 hour to 100 hours.
2. Process according to Claim 1, characterized in that the cycloaliphatic diol is 1,4-cyclohexane dimethanol and the molar ratio of the diallyl carbonate to 1,4-cyclohexane dimethanol is from 3:1 to 6:1.
3. Process according to Claim 1, characterized in that the cycloaliphatic diol is 3(4),8(9)-bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decane and the molar ratio of the diallyl carbonate to 3(4),8(9)-bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decane is from 6:1 to 18:1.
4. Process according to Claim 1, characterized in that the composition further comprises up to 30% relative to the weight of the composition, of at least one vinylic or acrylic monomer selected from vinyl acetate, butyl methacrylate, 2-ethyl-hexyl methacrylate, cyclohexyl methacrylate and phenyl methacrylate.
5. Process according to Claim 1, characterized in that the composition further comprises at least one additive selected from stabilizers, lubricants, dyes, UV- and IR-light absorbers, in an amount not larger than 1% by weight relative to the weight of the composition.
6. Process according to Claim 1, characterized in that the composition further comprises an amount of from 1 part to 6 parts by weight per 100 parts of the composition of at least one polymerization initiator soluble in the composition and capable of generating free radicals at a temperature of from 30° C to 120° C.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. Flüssige, polymere Zusammensetzung für organisches Glas mit niedriger Wasserabsorption und hoher Wärmestabilität, umfassend ein Gemisch aus monomeren und oligomeren Bis(allylcarbonaten), die das Umesterungsreaktionsprodukt von
 - (a) einem Diallylcarbonat und
 - (b) wenigstens einem cycloaliphatischen Diol darstellen, mit einem Molverhältnis von Diallylcarbonat zu cycloaliphatischem Diol von 2:1 bis 18:1.
2. Zusammensetzung nach Anspruch 1, worin das cycloaliphatische Diol 1,4-Cyklohexandimethanol ist, und das Molverhältnis des Diallylcarbonats zu dem 1,4-Cyklohexandimethanol von 3:1 bis 6:1 beträgt.
3. Zusammensetzung nach Anspruch 1, worin das cycloaliphatische Diol 3(4),8(9)-Bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decan ist und das Molverhältnis von Diallylcarbonat zu 3(4),8(9)-Bis(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decan von 6:1 bis 18:1 beträgt.
4. Zusammensetzung nach Anspruch 1, mit einem weiteren Gehalt an bis zu 30 Gew.-%, bezogen auf die Zusammensetzung, wenigstens eines Vinyl- oder Acrylmonomers, ausgewählt unter Vinylacetat, Butyl-



methacrylat, 2-Ethylhexylmethacrylat, Cyclohexylmethacrylat und Phenylmethacrylat.

5. Zusammensetzung nach Anspruch 1, mit einem weiteren Gehalt an wenigstens einem unter Stabilisatoren, Gleitmitteln, Farbstoffen, UV- und IR-Lichtabsorbern ausgewählten Additiv, in einer Menge von nicht größer als 1 Gew.-%, bezogen auf das Gewicht der Zusammensetzung.
6. Zusammensetzung nach Anspruch 1 mit einem weiteren Gehalt an 1 bis 6 Gew.-Teilen je 100 Gew.-Teile der Zusammensetzung an wenigstens einem in der Zusammensetzung löslichen Initiator, der zur Bildung freier Radikale bei einer Temperatur von 30 °C bis 120 °C befähigt ist.
7. Verfahren zur Herstellung von organischen Gläsern, umfassend die Stufe des Gießpolymerisierens einer flüssigen, polymeren Zusammensetzung für organisches Glas mit niedriger Wasserabsorption und hoher Wärmestabilität, die ein Gemisch aus monomeren und oligomeren Bis(allylcarbonaten) umfaßt, die das Umesterungsreaktionsprodukt von
 - (a) einem Diallylcarbonat und
 - (b) wenigstens einem cykloaliphatischen Diol
 darstellen, mit einem Molverhältnis von Diallylcarbonat zu cykloaliphatischem Diol von 2:1 bis zu 18:1, bei einer Temperatur von 35 °C bis 120 °C und während einer Zeitdauer von 1 Stunde bis 100 Stunden.
8. Organische Gläser, erhalten nach dem Verfahren gemäß Anspruch 7.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung von organischen Gläsern, umfassend die Stufe des Gießpolymerisierens einer flüssigen, polymeren Zusammensetzung für organisches Glas mit niedriger Wasserabsorption und hoher Wärmestabilität, die ein Gemisch aus monomeren und oligomeren Bis(allylcarbonaten) umfaßt, die das Umesterungsreaktionsprodukt von
 - (a) einem Diallylcarbonat und
 - (b) wenigstens einem cykloaliphatischen Diol
 darstellen, mit einem Molverhältnis von Diallylcarbonat zu cykloaliphatischem Diol von 2:1 bis zu 18:1, bei einer Temperatur von 35 °C bis 120 °C und während einer Zeitdauer von 1 Stunde bis 100 Stunden.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das cykloaliphatische Diol 1,4-Cyklohexandimethanol ist und das Molverhältnis von Diallylcarbonat zu 1,4-Cyklohexandimethanol von 3:1 bis 6:1 beträgt.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das cykloaliphatische Diol 3(4),8(9)-Bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decan ist und das Molverhältnis von Diallylcarbonat zu 3(4),8(9)-Bis-(hydroxymethyl)-tricyclo(5.2.1.0^{2,6})-decan von 6:1 bis 18:1 beträgt.
4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich bis zu 30 %, bezogen auf das Gewicht der Zusammensetzung, wenigstens eines Vinyl- oder Acrylmonomers, ausgewählt unter Vinylacetat, Butylmethacrylat, 2-Ethylhexylmethacrylat, Cyclohexylmethacrylat und Phenylmethacrylat, umfaßt.
5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich wenigstens ein unter Stabilisatoren, Gleitmitteln, Farbstoffen, UV- und IR-Lichtabsorbern ausgewähltes Additiv in einer Menge von nicht größer als 1 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, umfaßt.
6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich eine Menge von 1 bis 6 Gew.-Teilen je 100 Gew.-Teil der Zusammensetzung an wenigstens einem Polymerisationsinitiator umfaßt, der in der Zusammensetzung löslich ist und zur Bildung von freien Radikalen bei einer Temperatur von 30 °C bis 120 °C befähigt ist.



Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. Composition liquide pour verre organique polymère, présentant un faible taux d'absorption d'eau et une stabilité thermique élevée, et comprenant un mélange de bis(allylcarbonate) monomères et oligomères qui sont les produits de la réaction de transestérification de :
 - a) un carbonate de diallyle et
 - b) au moins un diol cycloaliphatique,
 le rapport molaire du carbonate de diallyle au diol cycloaliphatique valant de 2/1 à 18/1.
2. Composition selon la revendication 1, dans laquelle le diol cycloaliphatique est du 1,4-cyclohexane-diméthanol et le rapport molaire du carbonate de diallyle au 1,4-cyclohexane-diméthanol vaut de 3/1 à 6/1.
3. Composition selon la revendication 1, dans laquelle le diol cycloaliphatique est du 3(4),8(9)-bis-(hydroxyméthyl)-tricyclo-(5.2.1.0^{2.6})-décane et le rapport molaire du carbonate de diallyle au 3(4),8(9)-bis(hydroxyméthyl)-tricyclo-(5.2.1.0^{2.6})-décane vaut de 6/1 à 18/1.
4. Composition selon la revendication 1, comprenant en outre au plus 30 % en poids, par rapport à la composition, d'au moins un monomère vinylique ou acrylique choisi parmi l'acétate de vinyle, le méthacrylate de butyle, le méthacrylate de 2-éthyl-hexyle, le méthacrylate de cyclohexyle et le méthacrylate de phényle.
5. Composition selon la revendication 1, comprenant en outre au moins un adjuvant choisi parmi les stabilisants, lubrifiants, colorants et absorbeurs de lumière UV ou IR, en une proportion ne dépassant pas 1 % en poids par rapport au poids de la composition.
6. Composition selon la revendication 1, comprenant en outre une quantité de 1 à 6 parties en poids, pour 100 parties de composition, d'au moins un amorceur de polymérisation, soluble dans la composition et capable d'engendrer des radicaux libres à une température de 30 ° C à 120 ° C.
7. Procédé de production de verres organiques, comprenant l'étape de polymérisation par coulée d'une composition liquide pour verre organique polymère, présentant un faible taux d'absorption d'eau et une stabilité thermique élevée, et comprenant un mélange de bis(allylcarbonate) monomères et oligomères qui sont les produits de la réaction de transestérification de :
 - a) un carbonate de diallyle et
 - b) au moins un diol cycloaliphatique,
 le rapport molaire du carbonate de diallyle au diol cycloaliphatique valant de 2/1 à 18/1, à une température de 35 ° C à 120 ° C et pendant une durée d'une heure à cent heures.
8. Verres organiques obtenus selon le procédé défini dans la revendication 7.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de production de verres organiques, comprenant l'étape de polymérisation par coulée d'une composition liquide pour verre organique polymère, présentant un faible taux d'absorption d'eau et une stabilité thermique élevée, et comprenant un mélange de bis(allylcarbonate) monomères et oligomères qui sont les produits de la réaction de transestérification de :
 - a) un carbonate de diallyle et
 - b) au moins un diol cycloaliphatique,
 le rapport molaire du carbonate de diallyle au diol cycloaliphatique valant de 2/1 à 18/1, à une température de 35 ° C à 120 ° C et pendant une durée d'une heure à cent heures.
2. Procédé selon la revendication 1, caractérisé en ce que le diol cycloaliphatique est du 1,4-cyclohexane-diméthanol et le rapport molaire du carbonate de diallyle au 1,4-cyclohexane-diméthanol vaut de 3/1 à 6/1.



3. Procédé selon la revendication 1, caractérisé en ce que le diol cycloaliphatique est du 3(4),8(9)-bis-(hydroxyméthyl)-tricyclo-(5.2.1.0^{2,6})-décane et le rapport molaire du carbonate de diallyle au 3(4),8(9)-bis(hydroxyméthyl)-tricyclo-(5.2.1.0^{2,6})-décane vaut de 6/1 à 18/1.

4. Procédé selon la revendication 1, caractérisé en ce que la composition comprend en outre au plus 30 % en poids, par rapport à la composition, d'au moins un monomère vinylique ou acrylique choisi parmi l'acétate de vinyle, le méthacrylate de butyle, le méthacrylate de 2-éthyl-hexyle, le méthacrylate de cyclohexyle et le méthacrylate de phényle.

5. Procédé selon la revendication 1, caractérisé en ce que la composition comprend en outre au moins un adjuvant choisi parmi les stabilisants, lubrifiants, colorants et absorbeurs de lumière UV ou IR, en une proportion ne dépassant pas 1 % en poids par rapport au poids de la composition.

6. Procédé selon la revendication 1, caractérisé en ce que la composition comprend en outre une quantité de 1 à 6 parties en poids, pour 100 parties de composition, d'au moins un amorceur de polymérisation, soluble dans la composition et capable d'engendrer des radicaux libres à une température de 30 °C à 120 °C.

