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Copolymerization Process and Optical Copolymer Produced Therefrom

5 The present invention relates to a copolymerization process for the production of organic copolymers suitable for use in optical elements, the copolymers produced by the process and striation-free optical elements including these copolymers.

10 In the recent past, organic glass lenses have begun to replace inorganic glass lenses. Organic glass possesses several favorable characteristics including lighter weight, better safety, easier processability and good dyeability which offer advantages over inorganic glasses.

15 Attempts have been made to perfect the properties of organic glasses for use in lenses for spectacles. It has been found, for example, that a refractive index of at least 1.55 is needed in order to provide a lens of suitable thickness. Polymers such as polycarbonates and polystyrene having such a high refractive index cannot be processed by
20 casting. Accordingly, in British Patent specification 2 034 721 the solution was proposed to copolymerize specific bifunctional acrylates or dimethacrylates with a radically polymerizable monomer such as styrene, to thereby produce an organic polymer having a refractive index in excess of 1.55.

25 While the foregoing polymer system provided a solution to the refractive index problem, it produced lenses which were highly inhomogeneous when relatively deep molds were employed. These inhomogeneous lenses included flow lines (optical strain) which
30 interfere with the optical transmission of the lenses.

In response to this problem it was suggested to carry out the polymerization in the presence of α -methylstyrene dimer in Japanese patent application J6 1134-701. While this solution reduced the

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5 optical strain in the copolymers it did not entirely solve the problem
as was pointed out in the Japanese patent which states that the
copolymer produced by this method exhibited slight optical strain.

10 This Japanese Patent Application also states, "If other chain transfer
agents or polymerization degree regulators such as various mercaptans,
dialkyl disulfides, thiuram disulfides, chloroform, carbon
tetrachloride and carbon tetrabromide are used, their activity as a
chain transfer agent or polymerization degree regulator is too strong,
15 so that the polymerization degree of a resultant resin is depressed
more than needed. As a result, various physical properties such as
surface hardness, heat resistance, impact resistance, chemical
resistance and processability deteriorate, or optical distortion
increases and discoloration due to these chain transfer agents or
polymerization degree regulators occurs. Thus, plastic lenses for
eyeglasses are not obtained".

20 This statement clearly demonstrates that there is a strong prejudice
among those of skill in the art against using strong chain transfer
agents (i.e. chain transfer agents having a high chain transfer
coefficient) to make particular copolymers for use in optical
25 elements. Therefore, the present invention represents a surprising
step forward in the art since it demonstrates that the prejudice is
not justified and can be overcome by the use of particular amounts of
such strong chain transfer agents.

30 In addition the presently claimed subject matter is novel with respect
to this disclosure since specific amounts of the chain transfer agents
are specified in the claims. The amount of the strong chain transfer
agent referred to in this passage of the Japanese patent application
is not disclosed. Further, the presently claimed amounts could not
have been used since the presently claimed process does not produce

unacceptable adverse effects on the properties of the copolymer, whereas the prior art use of a strong chain transfer agent produced significant adverse effects on the properties of the copolymer. Thus, the present process must be novel since it produces a different result than the prior art process.

Japanese patent application J5 8217-511 also suggests polymerization in the presence of α -methylstyrene dimer in order to produce optically uniform lenses from allyl-group containing monomers. Further, Japanese patent application J5 7104-901 discloses the polymerization of a di(meth)acrylate monomer and an allylic monomer in the presence of a diunsaturated monomer to produce an impact resistant plastic lens.

However, none of the foregoing methods can provide a suitable copolymer composition for lenses which exhibits essentially no optical strain even in thick lens castings.

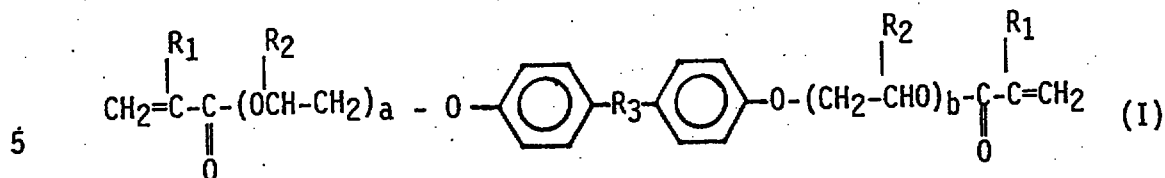
Accordingly, it is the primary object of the present invention to provide a process for making a copolymer for lenses which is homogeneous and exhibits essentially no optical strain.

It is another object of the present invention to provide a copolymer for lenses which can be used to cast thick lenses having essentially no optical strain.

These and other objects of the present invention will be apparent from the summary and detailed descriptions which follow.

The present invention relates to a process for preparing a copolymer suitable for use as an optical element which comprises the step of radically polymerizing a composition which comprises at least one first monomer of represented by the formula (I):

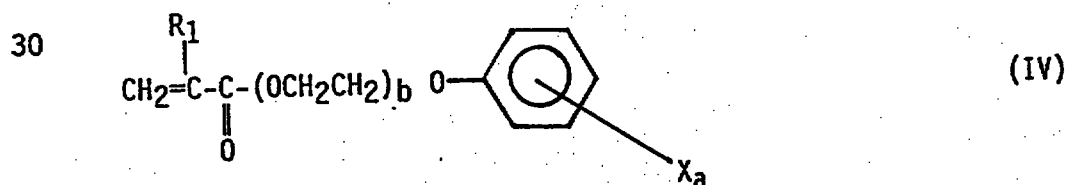
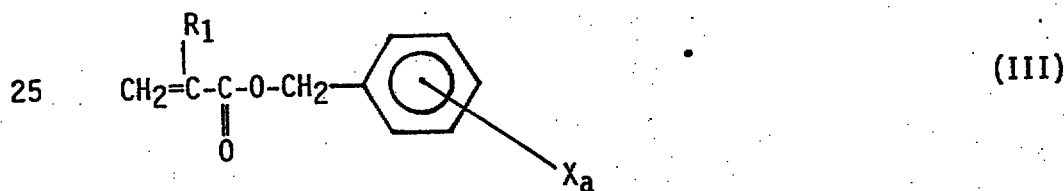




wherein a and b are integers of from 0 to 4,

10 R_1 and R_2 represent H or CH_3 , and R_3 represents $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{CH}_2-$, $-\text{CH}=\text{CH}-$ or $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_3$;

15 5-40 percent by weight, based on the weight of the composition, of at least one second monomer represented by any one of the formulas (II), (III) and (IV):



wherein R_1 represents H or CH_3 , X represents H, lower alkyl or halogen other than fluorine, a represents an integer of from 0 to 5, and b represents an integer of from 0 to 5; and 0.005 to 1.0 weight percent of an organic chain transfer agent having a chain transfer coefficient at 50-60°C of greater than 0.5 with acrylic monomer or styrenic monomer to provide a substantially striation-free copolymer; in the presence of a radical polymerization initiator. The invention also relates to a copolymer suitable for use in an optical element obtained by the radical polymerization process of the present invention and to an optical element which comprises this copolymer.

The first monomer component having the general formula (I) is advantageously used in an amount of about 45 to 95% by weight and more preferably from 65 to 90% by weight of the total composition. The most preferred first monomer component is a compound of the formula (I) wherein R_1 is methyl, R_2 is hydrogen and R_3 is the group:



The second, styrenic monomer component having the general formula (II) is advantageously used in an amount of 5 to 40% by weight, of the total composition, more preferably, 10-30% by weight is employed. Among the second monomer components useful in the present invention, styrene is the most preferred.

The composition of the present invention may also optionally comprise a third component which may be present during the copolymerization process. These optional third components include, for example, naphthylmethacrylates such as α -naphthylmethacrylate, β -naphthylmethacrylate; phenoxyethylacrylate; phenoxyethylmethacrylate;



5 vinylnaphthalenes such as 1-vinylnaphthalene and other monomers such as 4-vinylbiphenyl, divinylbenzene or vinylphenylsulfide. This third monomer component is radically polymerizable and may be used in the copolymerization in an amount of 0 to 50 percent by weight, of the total composition. In addition, to prevent lowering of the impact resistance of the polymer it may be useful to add alkyl(meth)acrylic acid ester such as butylmethacrylate to the copolymerization.

10 As an initiator for the present polymerization process is employed 0.05 to 2.0 wt% of a conventional peroxidic initiator. Suitable initiators include those that decompose at relatively low temperatures such as the peroxydicarbonates.

15 The chain transfer agent used in the present invention is an organic compound having a chain transfer coefficient of at least 0.5 at 50-60°C with acrylic monomer or styrenic monomer. The chain transfer agent is employed in an amount which is effective to provide a substantially striation-free copolymer composition. This amount will depend upon the chain transfer coefficient(s) of the chain transfer agent. In most circumstances, an amount of 0.005 to 1.0 wt% of the total composition is useful, and more preferably an amount of 0.05 to 0.5 wt% of the total composition is used.

25 Particular chain transfer agents which have been found suitable for use in the present invention include α -bromomethylstyrene, ethyl-2-bromomethylpropenoate, tetrabromomethane and trichlorobromomethane.

30 It has been found that by employing the particular chain transfer agents in the process of the present invention, one obtains a substantially striation-free copolymer having substantially less optical strain than similar polymers prepared in the absence of chain



transfer agent or prepared with other chain transfer agents. This provides the ability to make optical elements from polymers with better optical transmission properties than was previously possible and also allows the casting of thicker lenses since the optical strain in such lenses can be essentially eliminated by the present process.

It has also been found that the use of chain transfer agents in the process of the present invention does not adversely effect other properties of the resultant copolymer. Thus, for example, the surface hardness, impact resistance and coloration of the copolymers produced by the present process, are all suitable for the fabrication of optical elements, including thick lenses for glasses.

To carry out the process of the present invention, one or more of the first monomer, one or more of the second monomer, the chain transfer agent and an initiator are mixed, if desired, together with a third monomer, to prepare a liquid casting mixture. The liquid is then poured into a casting mold and is cured by means of heating over a prescribed heating program. The particular heating program will depend upon the specific composition of the liquid mixture. The most advantageous manner for copolymerizing the liquid mixture is directly in a casting mold for a lens. In this way, one carries out the copolymerization and the lens fabrication in the same step.

The organic glass copolymer of the present invention has high strength, high refractive index, good solvent resistance, good surface hardness and is striation-free, thereby having essentially no optical strain. Thus, this material is suitable for all sorts of lenses including extremely thick lenses.



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5 The primary use for the lens of the present invention is in ophthalmic
glasses but it is possible to use this lens for other purposes such as
in cameras or other optical elements, or non-corrective optical
elements such as sunglasses.

10 The following examples will further illustrate the present invention.

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Examples 1-10

5 80 parts by weight of tetra-ethoxylated bisphenol A dimethacrylate was mixed with 20 parts by weight of styrene, 0.5 wt% of bis(4-t-butylcyclohexyl) peroxydicarbonate and various amounts of chain transfer agents as detailed in table 1. These mixtures were placed in glass molds having an 18 mm thick molding cavity and were
10 polymerized in a water bath using the following temperature program: 6 hours at 35°C, a linear temperature rise program over 14 hours from 35°C to 90°C and 2 hours at 90°C. After this cycle, the water bath was cooled to 60°C and the lenses were removed from the mold.

15 The lenses were checked for the presence of striations (optical strain) by visual inspection with the unaided eye and by employing polarized light. The presence of striations was graded as follows:

- = reference standard without chain transfer agent, significant
20 striations visible with the unaided eye; + = improvement but some striations remain visible to the unaided eye; ++ = no striations visible with unaided eye but some striations visible with polarized light; and +++ = no striations visible with either the unaided eye or polarized light. The results of the tests are listed in table I.

25

Comparative Example A

The procedure of example 1 was repeated except that no chain transfer agent was employed. The results are given in table 1.

30 Comparative Examples B,C,D,E,F and G

The procedure of example 1 was repeated except that α -methylstyrene dimer was employed as the chain transfer agent. The amount of α -methylstyrene employed and the test results are given in table I.



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TABLE I

5	<u>Chain Transfer Agent</u>	<u>Example</u>	<u>Amount Used</u>	<u>Rating</u>
	ethyl-2-bromomethyl propenoate	1	500ppm	+++
	ethyl-2-bromomethyl propenoate	2	1000ppm	+++
10	bromomethylstyrene	3	500ppm	++
	bromomethylstyrene	4	1000ppm	++
	trichlorobromomethane	5	500ppm	+++
	trichlorobromomethane	6	1000ppm	+++
15	trichlorobromomethane	7	2000ppm	+++
	tetrabromomethane	8	500ppm	+++
	tetrabromomethane	9	1000ppm	+++
	tetrabromomethane	10	5000ppm	+++
20	-----	A	-----	-
	α -methylstyrene dimer	B	500ppm	+
	α -methylstyrene dimer	C	1000ppm	+
25	α -methylstyrene dimer	D	3000ppm	+
	carbon tetrachloride	E	500ppm	-
	carbon tetrachloride	F	1000ppm	-
	carbon tetrachloride	G	5000ppm	-

30

The chain transfer coefficients (C_x) for the materials used in the examples were measured on styrene and methylmethacrylate (MMA) and are given in table II.

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TABLE II

5	<u>Chain Transfer Agent</u>	<u>C_x-Styrene</u>	<u>Temp.</u>	<u>C_x-MMA</u>	<u>Temp.</u>
	ethyl-2-bromomethyl				
	propenoate	1.45	60°C	0.87	60°C
	bromomethylstyrene	2.93	60°C	2.27	60°C
10	trichlorobromomethane	65	60-80°C	1.2	30°C
	tetrabromomethane	1.78	60°C	0.27	60°C
	α -methylstyrene dimer	0.15	50°C	0.12	60°C
	carbon tetrachloride	0.0069	60°C	0.0005	60°C

15 The foregoing examples serve merely to illustrate the present invention and are not to be construed as limiting the invention in any way. The scope of the invention is to be determined by the claims appended hereto.

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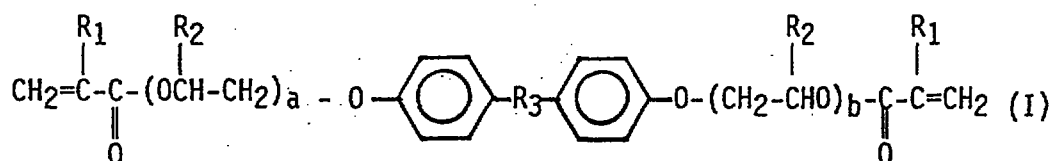
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Claims

1. A process for preparing a copolymer suitable for use in an optical element which comprises the step of radically polymerizing a composition which comprises at least one first monomer of represented by the formula (I):

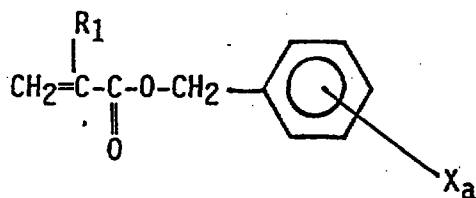
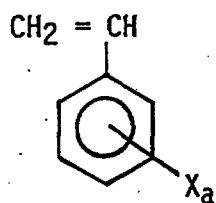


wherein a and b are integers of from 0 to 4,

R₁ and R₂ represent H or CH₃, and R₃ represents -O-, -S-, -CO-,

-SO₂-, -CH₂-, -CH=CH- or CH₃-C-CH₃;

5-40 weight percent, based on the total weight of the polymerizable composition, of at least one second monomer represented by any one of the formulas (II), (III) and (IV):



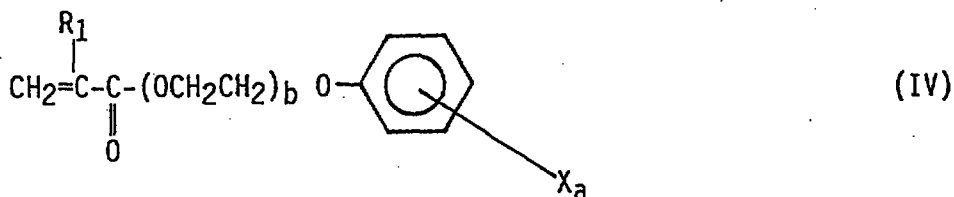
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wherein R_1 represents H, lower alkyl or CH_3 , X represents H or halogen other than fluorine, a represents an integer of from 0 to 5, and b represents an integer of from 0 to 5; and 0.005 to 1.0 weight percent of said polymerizable composition, of an organic chain transfer agent having a chain transfer coefficient at 50-60°C greater than 0.5 with acrylic monomer or styrenic monomer; in the presence of a radical polymerization initiator.

- 15
2. A process in accordance with claim 1 wherein said chain transfer agent is employed in an amount of 0.05 to 0.5 wt% of said polymerizable composition.
- 20
3. A process in accordance with any one of claims 1-2 wherein said polymerization step comprises at least 4 hours at 35°C, at least 12 hours in a linear temperature rise program from 35°C to 90°C and at least one hour at 90°C.
- 25
4. A process in accordance with any one of claims 1-3 wherein said chain transfer agent is selected from α -bromomethylstyrene, ethyl-2-bromomethylpropenoate, tetrabromomethane and trichlorobromomethane.
- 30
5. A copolymer suitable for use in an optical element obtained by the radical polymerization of a composition which comprises at least one first monomer represented by the formula (I):



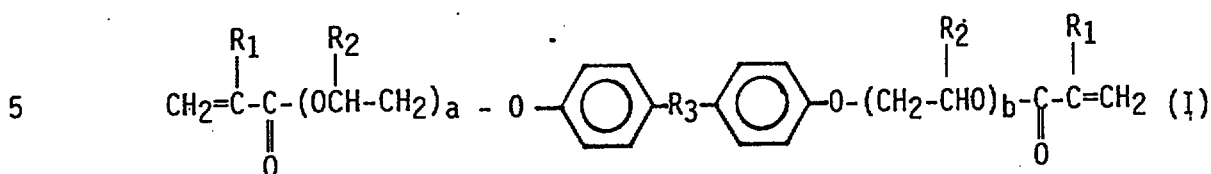
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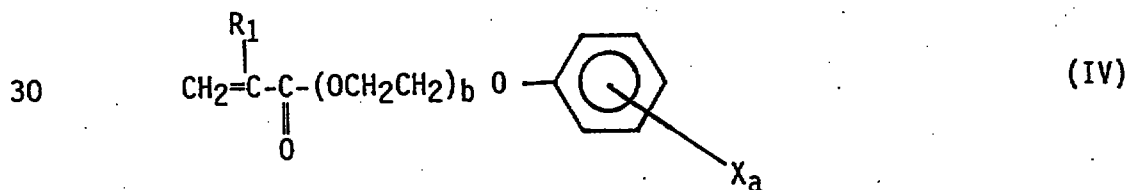
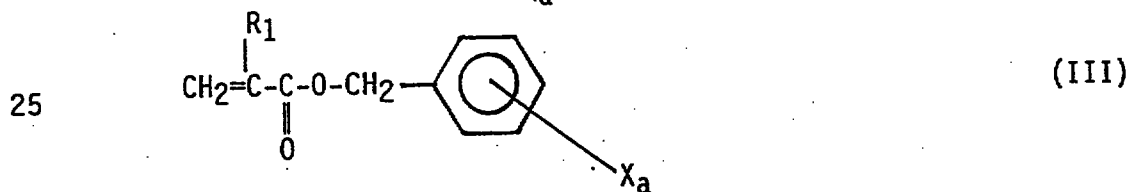
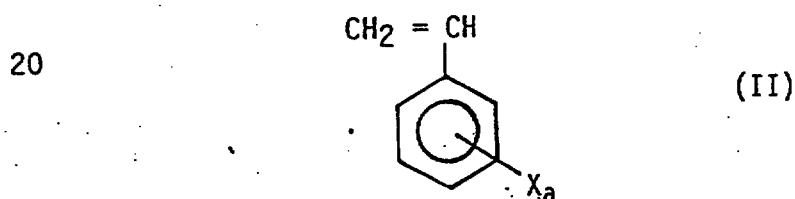


wherein a and b are integers of from 0 to 4,

10 R_1 and R_2 represent H or CH_3 , and R_3 represents -O-, -S-, -CO-,

-SO₂-, -CH₂-, -CH=CH- or $\text{CH}_3-\text{C}-\text{CH}_3$;

15 5-40 weight percent, based on the weight of the polymerizable composition, of at least one second monomer represented by any one of the formulas (II), (III) and (IV):



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5 wherein R_1 represents H or CH_3 , X represents H, lower alkyl or halogen
other than fluorine, a represents an integer of from 0 to 5, and b
represents an integer of from 0 to 5; and 0.005 to 1.0 weight percent
of the polymerizable composition of an organic chain transfer agent
having a chain transfer coefficient at 50-60°C greater than 0.5 with
10 acrylic monomer or styrenic monomer; in the presence of a radical
polymerization initiator.

6. A copolymer in accordance with claim 5 wherein said chain transfer agent is employed in an amount of 0.05 to 0.5 wt%.
- 15 7. A copolymer in accordance with any one of claims 5-6 wherein said polymerization step comprises at least four hours at 35°C, at least 12 hours in a linear temperature rise program from 35°C to 90°C and at least one hour at 90°C.
- 20 8. A copolymer in accordance with any one of claims 5-7 wherein said chain transfer agent is selected from α -bromomethylstyrene, ethyl-2-bromomethylpropenoate, tetrabromomethane and trichlorobromomethane.
- 25 9. An optical element which comprises a copolymer as claimed in any one of claims 5-8.

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