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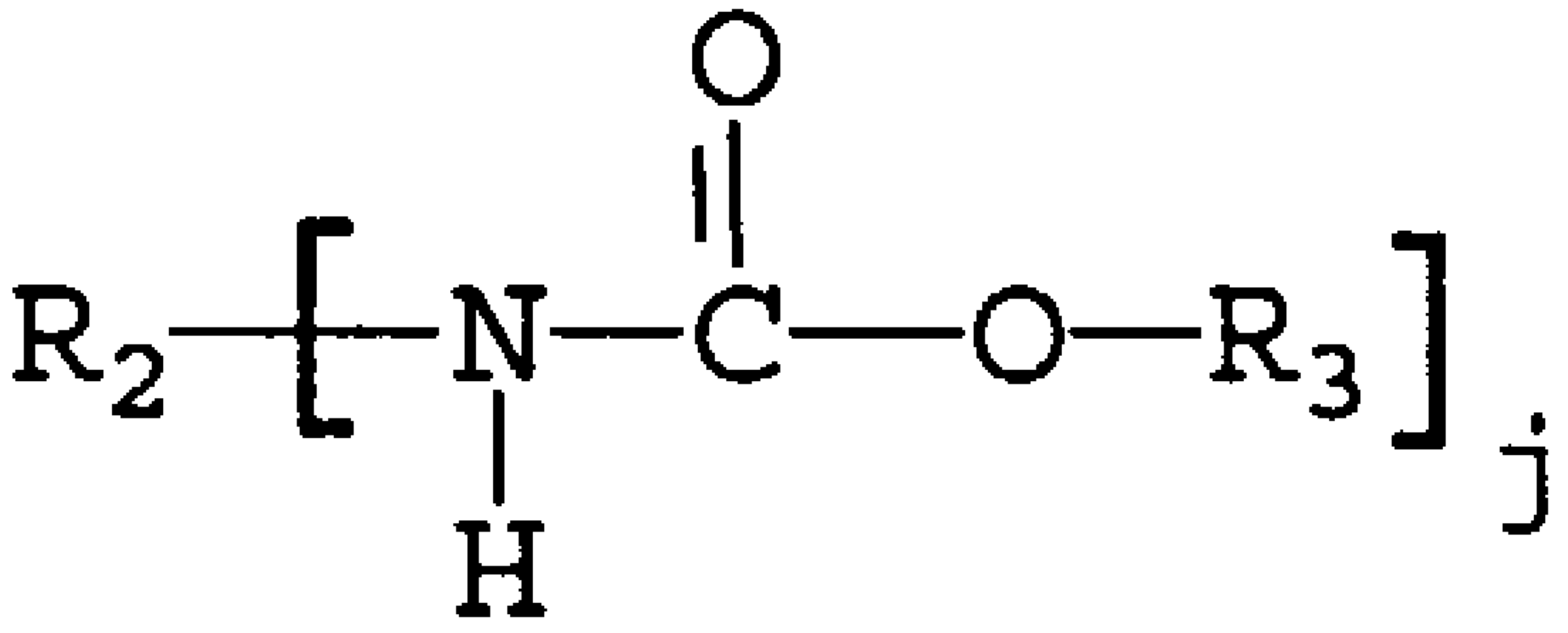
(72) **Inventeur/Inventor**:
NAGPAL, VIDHU J., US
(73) **Propriétaire/Owner**:
PPG INDUSTRIES OHIO, INC., US
(74) **Agent**: BORDEN LADNER GERVAIS LLP

(54) Titre : COMPOSITIONS DE POLYOL(ALLYL CARBONATE) POLYMERISABLES
(54) Title: POLYMERIZABLE POLYOL(ALLYL CARBONATE) COMPOSITIONS



$$R_2 - \left[\underset{\displaystyle H}{\underset{|}{N}} - \overset{\displaystyle O}{\overset{\|}{C}} - O - R_3 \right]_j \qquad (II)$$

(57) **Abrégé/Abstract**:

A polymerizable composition is described, which composition comprises a major amount of a polyol(allyl carbonate) monomer, e.g., diethylene glycol bis(allyl carbonate) monomer, and a minor amount of a radically polymerizable second monomer represented by general formula (II), wherein R^2 is a polyvalent linking group that is free of urethane linkages, e.g., R^2 may be a residue of a polyisocyanate, such as isophorone diisocyanate; R^3 is a residue of a material having a single hydroxy group and at least one allyl group, R^3 being free of urethane linkages, e.g., $R^2$3 may be a residue of a poly(alkylene glycol) allyl ether, such as poly(1,2-propylene glycol) allyl ether; and j is a number from 2 to 4. The second monomer may also be present in the composition in an amount at least sufficient such that a polymerizate, e.g., a plus ophthalmic lens, obtained from the composition is substantially free of tinting defects, e.g., ferns and/or moons.

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(71) Applicant: **PPG INDUSTRIES OHIO, INC.** [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).

(72) Inventor: **NAGPAL, Vidhu, J.**; 5005 Impala Drive, Murrysville, PA 15668 (US).

(74) Agents: **MILLMAN, Dennis, G.**; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 et al. (US).

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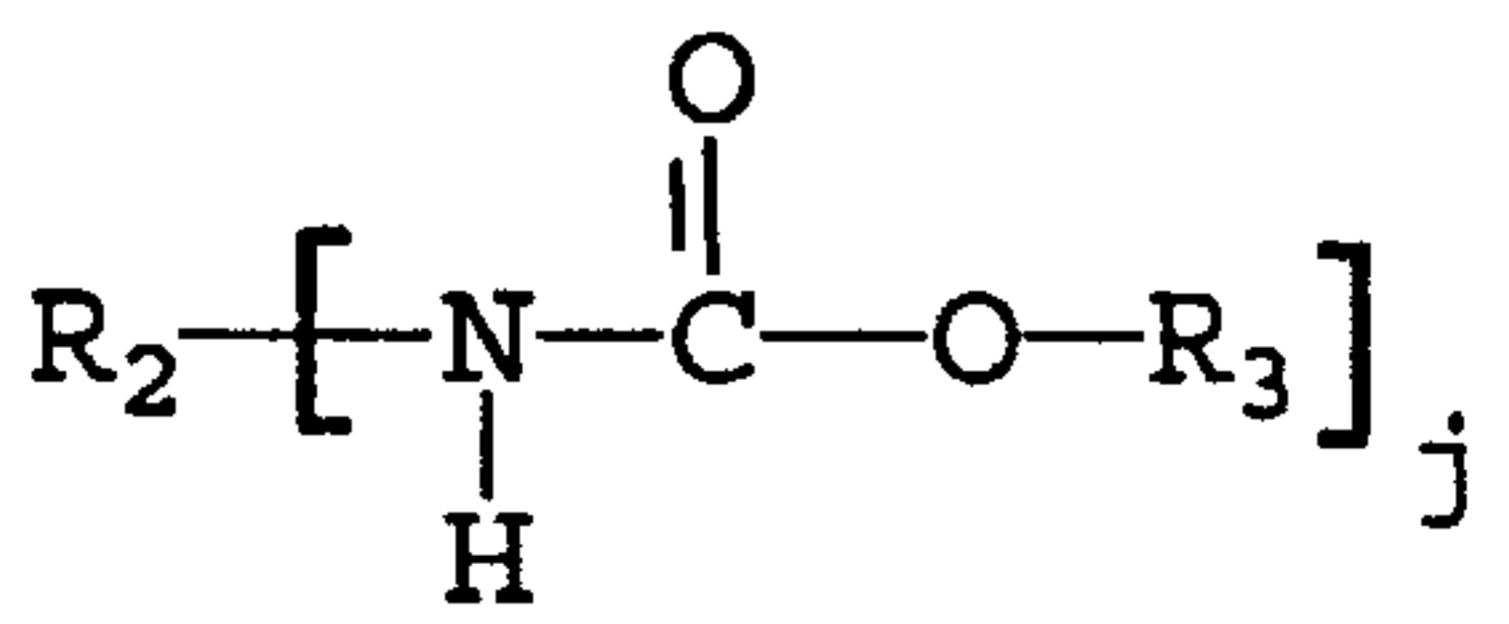

$$R_2\left[\underset{\substack{|\\ H}}{N}-\overset{\overset{O}{\|}}{C}-O-R_3\right]_j$$

(II)

(57) Abstract: A polymerizable composition is described, which composition comprises a major amount of a polyol(allyl carbonate) monomer, e.g., diethylene glycol bis(allyl carbonate) monomer, and a minor amount of a radically polymerizable second monomer represented by general formula (II), wherein R_2 is a polyvalent linking group that is free of urethane linkages, e.g., R_2 may be a residue of a polyisocyanate, such as isophorone diisocyanate; R_3 is a residue of a material having a single hydroxy group and at least one allyl group, R_3 being free of urethane linkages, e.g., R_3 may be a residue of a poly(alkylene glycol) allyl ether, such as poly(1,2-propylene glycol) allyl ether; and j is a number from 2 to 4. The second monomer may also be present in the composition in an amount at least sufficient such that a polymerizate, e.g., a plus ophthalmic lens, obtained from the composition is substantially free of tinting defects, e.g., ferns and/or moons.

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POLYMERIZABLE POLYOL(ALLYL CARBONATE) COMPOSITIONS

DESCRIPTION OF THE INVENTION

The present invention relates to a polymerizable composition. More particularly, the present invention relates to a polymerizable composition comprising polyol(allyl carbonate) monomer and a urethane having at least two allyl or substituted allyl groups. The present invention relates also to polymerizates, e.g., lenses, obtained from the polymerizable compositions.

Polymerizable organic compositions based on polyol(allyl carbonate), particularly diethylene glycol bis(allyl carbonate), and polymerizates obtained therefrom are well known in the art. Polymerizates of polymerizable organic compositions based on homopolymers of diethylene glycol bis(allyl carbonate) possess excellent clarity, good flexibility and abrasion resistance. Examples of applications for which such polymerizates may be used include, ophthalmic lenses, sunglasses, and automotive and aircraft transparencies. It has been observed that tinting of polymerizates prepared from such compositions by surface impregnation of dyes can, in certain instances, result in an uneven tinting of the surface. Such uneven tinting is referred to as tinting failure.

When tinting failure occurs, it is often manifested as visually observable defects on the tinted surface(s) of the polymerizate, which are commonly referred to as "ferns" or "moons." In the case of tinted ophthalmic lenses, such as tinted ophthalmic lenses having a positive diopter, i.e., plus lenses, and non-corrective lenses, e.g., sunglasses, such tinting failure often results in rejection and scrapping of the tinted lens. A solution to tinting failure is desirable in order to avoid the economic loss that results from the scrapping of lenses having tinting defects.

United States Patent No.'s 4,994,208, 5,084,529, 5,110,881, 5,221,721, 5,236,978 and 5,246,630 describe polymerizable compositions composed of polyol(allyl carbonate) monomer and at least 10 weight percent of aliphatic polyurethanes, the terminal portions of which contain allyl functional groups. United States Patent No. 5,200,483 describes organic resin compositions containing polyol(allyl carbonate) monomer and a mixture of aliphatic urethanes, the terminal portions of which contain allyl or acrylyl functional groups.

It has now been discovered that cured polymerizates prepared from the polymerizable compositions of the present invention are substantially free of tinting defects, for example, tinting defects referred to in the art as ferns or moons. In accordance with the present invention there is provided a polymerizable composition comprising:

(a) a major amount of a radically polymerizable first monomer represented by the following general formula I,

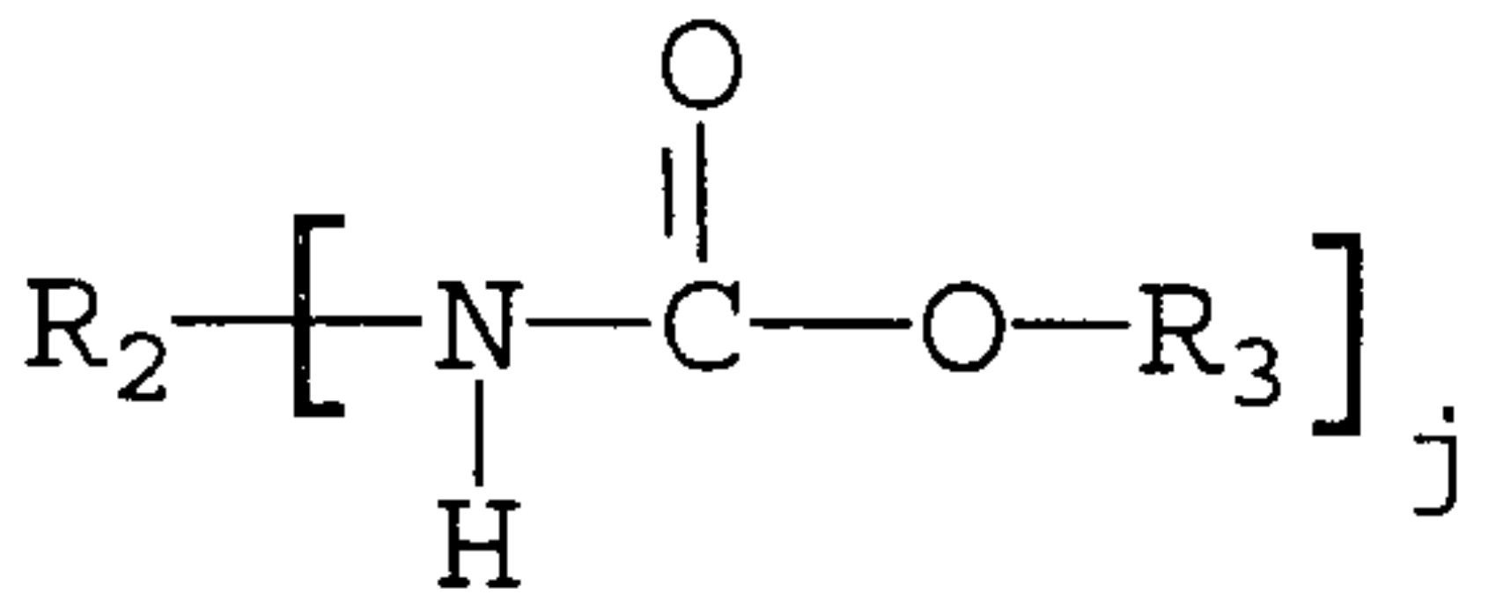
I

$$R\text{-}[\text{-}O\text{-}C(O)\text{-}O\text{-}R_1]_i$$

wherein R is a polyvalent residue of a polyol having at least two hydroxy groups, R_1 is an allyl or substituted allyl group, and i is a whole number from 2 to 4; and

(b) a minor amount of a radically polymerizable second monomer represented by the following general formula II,

II



$$R_2\!-\!\left[\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_3\right]_j$$

wherein R_2 is a polyvalent linking group that is free of urethane linkages; R_3 is a residue of a material having a single hydroxy group and at least one allyl group, R_3 being free of urethane linkages, acryloyl groups and methacryloyl groups; and j is a number from 2 to 4, e.g., 2, 3 or 4.

In an embodiment of the present invention, said second monomer (b) is present in said composition in an amount at least sufficient such that a polymerizate of said composition is substantially free of tinting defects.

The features that characterize the present invention are pointed out with particularity in the claims, which are annexed to and form a part of this disclosure. These and other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully understood from the following detailed description and the accompanying illustrative drawing.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term "about."

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a representation of a negative image of a tinted lens having tinting defects.

DETAILED DESCRIPTION OF THE INVENTION

In an embodiment of the present invention, the second monomer described with reference to general formula II is present in the polymerizable compositions in an amount at least sufficient such that polymerizates prepared from such compositions are substantially free of tinting defects. As used herein and in the claims, the term "tinting defects" and similar terms refer generally to a visually observable uneven distribution of dye over the surface of a tinted polymerizate, such as a tinted lens. More particularly, tinting defects are often visually observable as lighter colored or untinted surface patterns, sometimes in the form of ferns or moons.

Tinting defects in the form of ferns can be further described with reference to Figure 1. The tinted polymerizate 4 of Figure 1 is a tinted plus lens 11, prepared from diethylene glycol bis(allyl carbonate) monomer, and having tinting defects 15 thereon. For purposes of illustration, the tinting defects 15 of Figure 1 are shown as a negative image. As used herein, by "plus lens" is meant a lens having a positive (+) diopter, i.e., a lens having a positive focal length or real focal point. The tinting defects shown in the lens depicted in Figure 1 were observed in a lens having a plus five (+5) diopter.

Tinting defects in the form of moons (not shown in Figure 1) are typically observed as a series of concentric circles of varying tint strength on the surface of the tinted lens. In some instances a tinted lens will exhibit a combination of both moon and fern type tinting defects.

The occurrence of tinting defects with polymerizates prepared from polyol(allyl carbonate) monomers is a largely statistical phenomenon. Accordingly, in order to determine if a polymerizable composition can be used to prepare polymerizates that are "substantially free of tinting defects," more than one polymerizate, e.g., several lenses, should be prepared. Optionally, a set of comparative polymerizates may also be prepared under similar conditions, e.g., using the same cure cycle, from a composition that is known to result in tinting defects. The specific number of polymerizates that must be prepared is often determined by trial and error. In the case of ophthalmic lenses, typically between 10 and 100 lenses are prepared to determine if they are substantially free of tinting defects. Such a determination is described in further detail in the Examples herein. Typically, a set of polymerizates, e.g., 100 ophthalmic plus lenses, prepared from a polymerizable composition according to the present inention, is considered to be substantially free of tinting defects if 10 percent or less, preferably 5 percent or less, and more preferably 0 percent of the tinted polymerizates have tinting defects, such as ferns.

Second monomer (b) is present in the polymerizable composition of the present invention in a minor amount (e.g., from 0.1 percent by weight to 49 percent by weight, based on the total weight of the composition). Typically, second monomer (b) is present in the composition of the instant invention in an amount of at least 0.1 percent by weight, preferably at least 0.2 percent by weight, and more preferably at least 0.3 percent by weight, based on the total weight of the composition. Second monomer (b) is also typically present in the composition of the present invention in an amount of less than 10 percent by weight, preferably less than 5 percent by weight and more preferably less than 3 percent by weight, based on the total weight of the composition. The amount of second monomer (b) present in the composition of the present invention may range between any combination of these values, inclusive of the recited values, e.g., from 0.1 percent by weight to 10 percent by weight or from 0.3 percent by weight to 3 percent by weight, based on the total weight of the composition.

With reference to general formula II, second monomer (b) is distinguishable from polyurethanes having terminal allyl functional groups as described in, for example, United States Patent No.'s 4,994,208, 5,084,529, 5,110,881, 5,221,721, 5,236,978 and 5,246,630. In general formula II, R_2 and R_3 are each free of urethane linkages, more particularly, R_2 and R_3 are each free of internal urethane linkages. As used herein and in the claims, the term "urethane linkage" is meant to refer to the following structural linkage, -N(H)-C(O)-O-. In the case when R_2 is a residue of a polyisocyanate, second monomer (b) can be described as a polyisocyanate that is capped with the mono-hydroxy functional material of which R_3 is a residue.

Depending on the method by which second monomer (b) is prepared, R_2 may be a residue of, for example, a polyisocyanate, i.e., a material having at least two isocyanate groups, or a polyamine, i.e., a material having at least two primary amine groups. When the second monomer is prepared by capping a polyisocyanate with the mono-hydroxy functional material of which R_3 is a residue, R_2 is a residue of a polyisocyanate. The second monomer may also be prepared by first reacting the mono-hydroxy functional material of which R_3 is a residue with phosgene to form the corresponding chloroformate, which is then reacted with a polyamine, in which case R_2 is a residue of a polyamine.

In an embodiment of the present invention, R_2 is a residue of a polyisocyanate having at least two isocyanate groups, and the polyisocyanate may be selected from aromatic polyisocyanates, aliphatic polyisocyanates, cycloaliphatic polyisocyanates and mixtures thereof. As used herein and in the claims, the term "polyisocyanate" is meant to be inclusive of dimers and trimers of polyisocyanates, for example, trimers of diisocyanates containing a core isocyanurate ring.

Classes of aromatic polyisocyanates of which R_2 may be a residue include, for example, aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring, e.g., α,α'-xylene diisocyanate; and aromatic polyisocyanates wherein the isocyanate groups are bonded directly to the aromatic ring, e.g., benzene diisocyanate.

Examples of aromatic polyisocyanates having isocyanate groups bonded directly to the aromatic ring, of which R_2 may be a residue include, but are not limited to, phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzene triisocyanate, benzene triisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, ortho-tolidine diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, triphenylmethane triisocyanate, polymeric 4,4'-diphenylmethane diisocyanate, naphthalene triisocyanate, diphenylmethane-2,4,4'-triisocyanate, 4-methyldiphenylmethane-3,5,2',4',6'-pentaisocyanate, diphenylether diisocyanate, bis(isocyanatophenylether)ethyleneglycol, bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate and dichlorocarbazole diisocyanate. Examples of aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring, of which R_2 may be a residue include, but are not limited to, bis(isocyanatoethyl)benzene, α,α,α',α'-tetramethylxylene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl)phthalate, mesitylene triisocyanate and 2,5-di(isocyanatomethyl)furan.

Aliphatic polyisocyanates of which R_2 may be a residue may be selected from, for example, ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, nonamethylene diisocyanate, 2,2′-dimethylpentane diisocyanate, 2,2,4-trimethylhexane diisocyanate, decamethylene diisocyanate, 2,4,4,-trimethylhexamethylene diisocyanate, 1,6,11-undecanetriisocyanate, 1,3,6-hexamethylene triisocyanate, 1,8-diisocyanato-4-(isocyanatomethyl)octane, 2,5,7-trimethyl-1,8-diisocyanato-5-(isocyanatomethyl)octane, bis(isocyanatoethyl)-carbonate, bis(isocyanatoethyl)ether, 2-isocyanatopropyl-2,6-diisocyanatohexanoate, lysinediisocyanate methyl ester and lysinetriisocyanate methyl ester.

In an embodiment of the present invention, R_2 of general formula II is a residue of a cycloaliphatic polyisocyanate. Examples of cycloaliphatic polyisocyanates of which R_2 may be a residue include, but are not limited to, isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane. In a preferred embodiment of the present invention, R_2 is a residue of a cycloalphatic diisocyanate selected from, for example, isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, and mixtures thereof. When R_2 is a residue of a diisocyanate, such as a cycloaliphatic diisocyanate, j of general formula II is 2.

Classes of polyamines of which R_2 may be a residue, include, aromatic polyamines, aliphatic polyamines, cycloaliphatic polyamines, each having at least two primary amines, and mixtures thereof. As is known to the skilled artisan, polyisocyanates are typically prepared from the corresponding polyamine precursors having two or more primary amine groups. Accordingly, specific examples of polyamines within these recited classes include, but are not limited to, polyamine precursors corresponding to those polyisocyanates as recited previously herein.

With further reference to general formula II, R_3 is a residue of a material having a single hydroxy group and one or more allyl groups. The mono-hydroxy functional material of which R_3 is a residue is free of acryloyl groups and methacryloyl groups. The allyl group may be an unsubstituted allyl group or a substituted allyl group, as represented by the following general formula III,

III

$$H_2C{=}C(R_4)\text{-}CH_2\text{-}$$

wherein R_4 is hydrogen, halogen or a C_1 to C_4 alkyl group. More typically, R_4 is hydrogen and consequently general formula III represents the unsubstituted allyl group, $H_2C{=}CH\text{-}CH_2\text{-}$. More specifically, the allyl group of the material having a single hydroxy group, of which R_3 is a residue, may be an allyl ether, an allyl carbonate or an allyl ester group. The material of which R_3 is a residue typically has at least one allyl ether group.

The mono-hydroxy functional material of which R_3 is a residue may be selected from aromatic alcohols, aliphatic alcohols, cycloaliphatic alcohols, poly(alkylene glycols), each having at least one allyl group, and combinations thereof. Examples of aromatic alcohols having at least one allyl group include, but are not limited to, allyloxy phenol, e.g., 4-allyloxy phenol, allyloxybenzyl alcohol, e.g., 4-allyloxybenzyl alcohol, and 4-allyl-2,6-dimethoxyphenol. Cycloaliphatic alcohols having at least one allyl group of which R_3 may be a residue include, for example, allyloxymethyl cyclohexylmethanols, e.g., 4-allyloxymethyl cyclohexylmethanol.

Examples of aliphatic alcohols having at least one allyl group, of which R_3 may be a residue include, but are not limited to, allyl alcohol, substituted allyl alcohols, e.g., methallyl alcohol, allyl ethers of alkylene glycols, e.g., C_2-C_4 alkylene glycols, such as, ethylene glycol allyl ether and 1,2- or 1,3-propylene glycol allyl ether. A preferred class of aliphatic alcohols, of which R_3 may be a residue, are poly(allyl ethers) of aliphatic polyols, e.g., trimethylol propane di(allyl ether), trimethylol ethane di(allyl ether), pentaerythritol tri(allyl ether), and di-trimethylolpropane tri(allyl ether).

Poly(alkylene glycols) of which R_3 may be a residue include, for example, homopolymeric, block copolymeric, e.g., diblock and triblock copolymeric, and random copolymeric poly(alkylene glycols), such as poly(C_2-C_4 alkylene glycols), having a single allyl ether group and a single hydroxy group. Examples of poly(alkylene glycol) allyl ethers of which R_3 may be a residue include, for example, poly(ethylene glycol) allyl ether, poly(1,2-propylene glycol) allyl ether, poly(1,2-

butylene glycol) allyl ether, poly(ethylene glycol)-b-poly(1,2-propylene glycol) allyl ether, poly(1,2-propylene glycol)-b-poly(ethylene glycol) allyl ether, poly(1,2-butylene glycol)-b-poly(ethylene glycol) allyl ether, poly(ethylene glycol)-b-poly(1,2-butylene glycol) allyl ether and poly(ethylene glycol)-b-poly(1,2-propylene glycol)-b-poly(1,2-butylene) allyl ether.

The poly(alkylene glycol) allyl ethers of which R_3 may be a residue have at least 2 alkylene ether units. For example, diethylene glycol allyl ether has two (2) ethylene ether units, i.e., $H_2C{=}CHCH_2O\text{-}(\text{-}CH_2CH_2\text{-}O\text{-})_2\text{-}H$. Typically, the poly(alkylene glycol) allyl ether has less than 100 alkylene ether units, e.g., less than 50, less than 20 or less than 15 alkylene ether units. The poly(alkylene glycol) allyl ether may have a number of alkylene ether units ranging between any combination of these values, inclusive of the recited values, e.g., from 2 to 100, 2 to 50, 2 to 20 or 2 to 15 alkylene ether units.

In an embodiment of the present invention, the material of which R_3 is a residue is selected from a C_2-C_4 alkylene glycol allyl ether, a poly(C_2-C_4 alkylene glycol) allyl ether, trimethylol propane di(allyl ether), trimethylol ethane di(allyl ether), pentaerythritol tri(allyl ether), di-trimethylolpropane tri(allyl ether) and mixtures thereof. In a preferred embodiment of the present invention, the material of which R_3 is a residue is selected from poly(ethylene glycol) allyl ether, poly(1,2-propylene glycol) allyl ether and mixtures thereof.

The polymerizable organic composition of the present invention includes also a radically polymerizable first monomer as described above with reference to general formula I, which may be further described as a polyol(allyl carbonate) monomer. Polyol(allyl carbonate) monomers that may be used in the aforedescribed polymerizable organic composition are allyl carbonates of, for example, linear or branched aliphatic polyols, e.g., aliphatic glycol bis(allyl carbonate) compounds, and cycloaliphatic polyols. The scope of the present invention also includes allyl carbonates of aromatic polyols, e.g., 4,4′-isopropylidenediphenol bis(allyl carbonate). These monomers may further be described as unsaturated polycarbonates of polyols, e.g., glycols. The polyol(allyl carbonate) monomer may be prepared by procedures well known in the art, e.g., as described in U.S. Patents 2,370,567 and 2,403,113.

In reference to general formula I, R_1 is an allyl group, which may be described with reference to general formula III. The allyl group R_1 of general formula I may be substituted at the 2-position with a halogen, most notably chlorine or bromine, or an alkyl group containing from 1 or 4, e.g., 1 to 2, carbon atoms, in which case R_1 is a substituted allyl group. More commonly, and with reference to general formula III, R_4 is hydrogen and consequently R_1 of general formula I is the unsubstituted allyl group, $H_2C=CH-CH_2-$.

With reference to general formula I, R is a polyvalent residue of a polyol, which can, for example, be an aliphatic or cycloaliphatic polyol, containing 2, 3 or 4 hydroxy groups. Typically, the polyol contains 2 hydroxy groups, i.e., a glycol. When the polyol is an aliphatic polyol, it may be linear or branched and contain from 2 to 10 carbon atoms. Commonly, the aliphatic polyol is an alkylene glycol having from 2 to 4 carbons atoms, e.g., ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, or a poly(C_2-C_4 alkylene glycol), e.g., diethylene glycol, triethylene glycol, etc.

Specific examples of polyol(allyl carbonate) monomers that may be used in the present invention include, but are not limited to, ethylene glycol bis(2-chloroallyl carbonate), ethylene glycol bis(allyl carbonate), diethylene glycol bis(2-methylallyl carbonate), diethylene glycol bis(allyl 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), pentamethylene glycol bis(allyl carbonate), 1,4-cyclohexanediol bis(allyl carbonate) and 4,4'-isopropylidenebiscyclohexanol bis(allyl carbonate).

A preferred polyol(allyl carbonate) monomer in the composition of the present invention is diethylene glycol bis(allyl carbonate). Commercially available examples of diethylene glycol bis(allyl carbonate) monomers include CR-39® monomer and HIGH ADC CR-39® monomer, Chemical Abstracts (CAS) No. 142-22-3, available from PPG Industries, Inc.

A detailed description of polyol(allyl carbonate) monomers that may be used in the polymerizable organic compositions of the present invention may be found in U.S. Patent No. 4,637,698 at column 3, line 33 through column 5, line 61.

As used in the present description with reference to the radically polymerizable monomer represented by general formula I, the term "polyol(allyl carbonate) monomer" and like names, e.g., diethylene glycol bis(allyl carbonate), is intended to mean and include the named monomers or prepolymers thereof and any related monomer or oligomer species contained therein.

The polyol(allyl carbonate) monomer is present in the polymerizable composition of the present invention in a major amount, e.g., from 51 percent by weight to 99.9 percent by weight, based on the total weight of the polymerizable composition. Typically, the polyol(allyl carbonate) monomer is present in the polymerizable composition of the present invention in an amount of at least 90 percent by weight, preferably at least 95 percent by weight, and more preferably at least 97 percent by weight, based on the total weight of the polymerizable composition. Also, the polyol(allyl carbonate) monomer is typically present in the composition in an amount of not greater than 99.9 percent by weight, preferably not greater than 99.8 percent by weight, and more preferably not greater than 99.7 percent by weight, based on the total weight of the polymerizable composition. The polyol(allyl carbonate) monomer may be present in the composition of the present invention in an amount ranging between any combination of these values, inclusive of the recited values.

Polymerization of the polymerizable composition of the present invention may be accomplished by adding to the composition an initiating amount of material capable of generating free radicals, such as organic peroxy compounds, i.e., an initiator. Methods for polymerizing polyol(allyl carbonate) compositions are well known to the skilled artisan and any of those well known techniques may be used to polymerize the aforedescribed polymerizable compositions.

Suitable examples of organic peroxy compounds, that may be used as initiators include: peroxymonocarbonate esters, such as tertiarybutylperoxy isopropyl carbonate; peroxydicarbonate esters, such as di(2-ethylhexyl) peroxydicarbonate, di(secondary butyl) peroxydicarbonate and diisopropylperoxydicarbonate; diacylperoxides, such as 2,4-dichlorobenzoyl peroxide, isobutyryl peroxide, decanoyl peroxide, lauroyl peroxide, propionyl peroxide, acetyl peroxide, benzoyl peroxide, p-chlorobenzoyl peroxide; peroxyesters such as t-butylperoxy pivalate, t-butylperoxy octylate, and t-butylperoxyisobutyrate; methylethylketone peroxide, acetylcyclohexane sulfonyl peroxide, and azobisisobutyronitrile. Preferred initiators are those that do not discolor the resulting polymerizate. A preferred initiator is diisopropyl peroxydicarbonate.

The amount of initiator used to initiate and polymerize the polymerizable compositions of the present invention may vary and will depend on the particular initiator used. Only that amount that is required to initiate and sustain the polymerization reaction is required, i.e., an initiating amount. With respect to the preferred peroxy compound, diisopropyl peroxydicarbonate, typically between 2.0 and 5.0 parts of that initiator per 100 parts of the polymerizable organic composition (phm) may be used. More usually, between 2.5 and 4.0 phm is used to initiate the polymerization. The amount of initiator and the consequent cure cycle should be adequate to produce a polymerizate having a 15 second Barcol hardness of at least 1, preferably, at least 4, e.g., from 4 to 35. Typically, the cure cycle involves heating the polymerizable organic composition in the presence of the initiator from room temperature to 85°C over a period of from 15 hours to 30 hours.

Various conventional additives may be incorporated into the polymerizable composition of the present invention. Such conventional additives may include light stabilizers, heat stabilizers, ultraviolet light absorbers, mold release agents, pigments and flexibilizing additives that are not radically polymerizable, e.g., alkoxylated phenol benzoates and poly(alkylene glycol) dibenzoates. Conventional additives are typically present in the compositions of the present invention in amounts totaling less than 10 percent by weight, more typically less than 5 percent by weight, and commonly less than 3 percent by weight, based on the total weight of the polymerizable composition.

Polymerizates obtained from polymerization of polymerizable organic compositions of the present invention will be solid, transparent and substantially free of tinting defects. Solid articles that may be prepared from the polymerizable compositions of the present invention include, but are not limited to, optical lenses, such as plano and ophthalmic lenses, sun lenses or sunglasses, windows, automotive transparencies, e.g., windshields, sidelights and backlights, and aircraft transparencies, etc.

The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight.

Casting Composition Examples

The following summarizes polymerizable casting compositions that are comparative and compositions that are in accordance with the present invention. Casting composition A is a comparative composition, and Casting compositions B and C represent compositions according to the present invention.

Casting Compositions

Ingredients	Casting Composition A	Casting Composition B	Casting Composition C
CR-39® monomer (a)	100.0	99.0	99.0
diisopropyl peroxydicarbonate (b)	2.6	3.0	3.2
Second monomer (c)	0	1.0	0
Second monomer (d)	0	0	1.0

(a) CR-39® diethylene glycol bis(allyl carbonate) monomer available commercially from PPG Industries, Inc.

(b) In each of casting compositions B and C, the level of diisopropyl peroxydicarbonate initiator was adjusted such that tinted polymerizates obtained from these compositions had substantially the same percent transmission as tinted polymerizates obtained (under the same tinting conditions) from composition A, e.g., having about 35 percent transmission. The percent transmittance was determined using a HunterLab Model ColorQuest II colorimeter employing the CIE Tristimulus XYZ scale, illuminant D65 and 10°C observer.

(c) Diallyl urethane monomer obtained from Sartomer Company, Inc. and having the designation NTX-4434.

(d) Tetraallyl urethane monomer obtained from Sartomer Company, Inc. and having the designation NTX-4439.

Cast Lens Examples

The casting compositions A - C were each mixed at room temperature and injected separately into glass lens molds used to prepare circular lenses having a +5 diopter and an outer rim diameter of 6.5 cm. Twenty (20) lens molds were filled at a time and their contents polymerized using the same cure cycle. The cure cycle used involved heating the molds in an electric forced air oven in stages from 48°C to 85 °C over a period of 18 hours, followed by cooling to and holding at 60°C until demolding of the lenses.

The cast lenses were then tinted by imbibing them with a black dye. An aqueous tinting solution of 1 part BPI® Molecular Catalytic™ Black Dye, commercially available from Brain Power Incorporated, and 10 parts deionized water was heated to and held at a temperature of 94°C - 95°C. The lenses cast from casting compositions A - C were fully immersed in the heated dye solution for a period of 5 minutes, after which they were thoroughly rinsed with deionized water. The tinted lenses were evaluated for tinting defects, the results of which are summarized in Table 1.

TABLE 1

Evaluation of Tinted Lenses

Casting Composition	Number of Tinted Lenses Evaluated	Number of Tinted Lenses Having Tinting Defects (e)	Percent of Tinted Lenses Having Tinting Defects (f)
A	228	57	25
B	529	30	5.7
C	436	23	5.3

(e) The lenses were evaluated for tinting defects by means of visual naked eye inspection. Tinting defects were observed as having a lighter colored vein or fern-like appearance relative to the rest of the tinted lens.

(f) 100 x (the number of tinted lenses observed to have tinting defects / the number of tinted lenses evaluated). For example, with casting composition A: 100 x (57/228) = 25 percent (%).

The results summarized in Table 1 show that articles, e.g., lenses, cast from polymerizable compositions according to the present invention, such as Compositions B and C, have fewer tinting defects than lenses cast from comparative compositions, such as Composition A.

The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

What is claimed is:

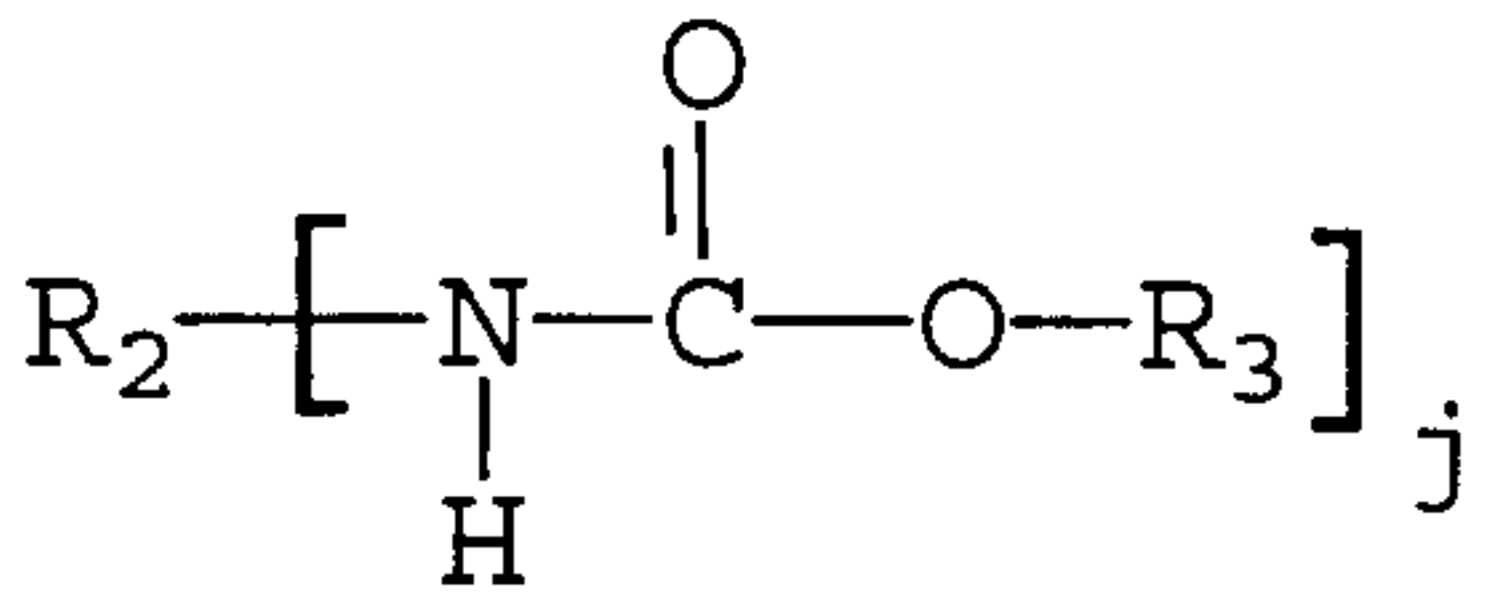
1. A polymerizable composition comprising:

(a) a major amount of a radically polymerizable first monomer represented by the following general formula,

$$R\text{-}[\text{-}O\text{-}C(O)\text{-}O\text{-}R_1]_i$$

wherein R is a polyvalent residue of a polyol having at least two hydroxy groups, R_1 is an allyl group, and i is a whole number from 2 to 4; and

(b) a minor amount of a radically polymerizable second monomer represented by the following general formula,



$$R_2\!-\!\left[-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_3\right]_j$$

wherein R_2 is a polyvalent linking group that is free of urethane linkages; R_3 is a residue of a material having a single hydroxy group and at least one allyl group, R_3 being free of urethane linkages; and j is a number from 2 to 4.

2. The polymerizable composition of claim 1 wherein second monomer (b) is present in said composition in an amount at least sufficient such that a polymerizate of said composition is substantially free of tinting defects.

3. The polymerizable composition of claim 2 wherein said second monomer (b) is present in said composition in an amount of from 0.1 percent by weight to 10 percent by weight, based on the total weight of said polymerizable composition.

4. The polymerizable composition of claim 1 wherein R_2 is a residue of a polyisocyanate selected from aromatic polyisocyanates, aliphatic polyisocyanates, cycloaliphatic polyisocyanates and mixtures thereof; and the material of

which R_3 is a residue is selected from, aromatic alcohols, aliphatic alcohols, cycloaliphatic alcohols, poly(alkylene glycols), each having at least one allyl group, and mixtures thereof.

5. The polymerizable composition of claim 4 wherein R_2 is a residue of a cycloaliphatic diisocyanate selected from isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, and mixtures thereof, and j is 2.

6. The polymerizable composition of claim 4 wherein the material of which R_3 is a residue is selected from C_2-C_4 alkylene glycol allyl ether, poly(C_2-C_4 alkylene glycol) allyl ether, trimethylol propane di(allyl ether), trimethylol ethane di(allyl ether), pentaerythritol tri(allyl ether), di-trimethylolpropane tri(allyl ether) and mixtures thereof.

7. The polymerizable composition of claim 6 wherein the material of which R_3 is a residue is selected from poly(ethylene glycol) allyl ether, poly(1,2-propylene glycol) allyl ether and mixtures thereof.

8. The polymerizable composition of claim 1 wherein R is a residue of a poly(C_2-C_4 alkylene glycol), and i is 2.

9. The polymerizable composition of claim 8 wherein R is a residue of diethylene glycol.

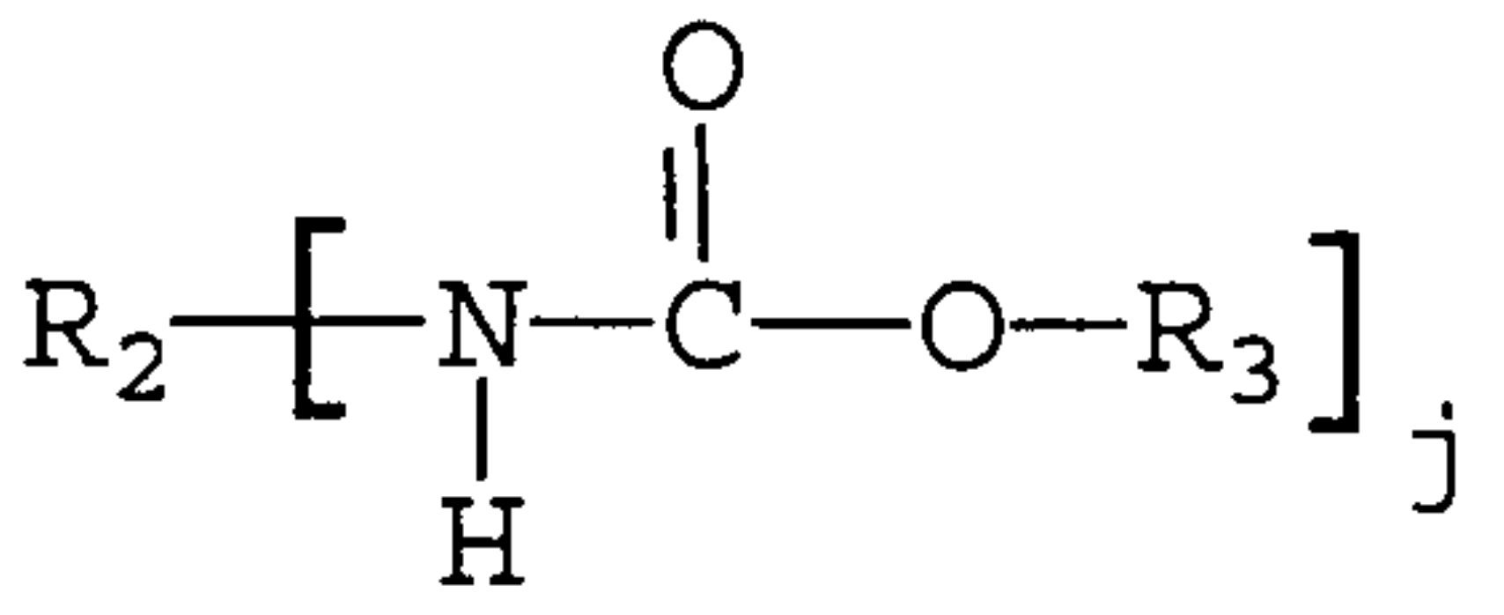
10. A polymerizable composition comprising:

(a) a major amount of a radically polymerizable first monomer represented by the following general formula,

$$R\text{-}[\text{-}O\text{-}C(O)\text{-}O\text{-}R_1]_i$$

wherein R is a divalent residue of a poly(C_2-C_4 alkylene glycol), R_1 is an allyl group, and i is 2; and

(b) a minor amount of a radically polymerizable second monomer represented by the following general formula,



$$R_2\text{—}\left[\underset{\displaystyle H}{\underset{|}{N}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}R_3\right]_j$$

wherein R_2 is a divalent linking group that is free of urethane linkages; R_3 is a residue of a material having a single hydroxy group and at least one allyl group, R_3 being free of urethane linkages; and j is 2.

11. The polymerizable composition of claim 10 wherein said second monomer (b) is present in said composition in an amount at least sufficient such that a polymerizate of said composition is substantially free of tinting defects.

12. The polymerizable composition of claim 10 wherein R_2 is a residue of a cycloaliphatic diisocyanate selected from isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, and mixtures thereof.

13. The polymerizable composition of claim 12 wherein the material of which R_3 is a residue is selected from a poly(C_2-C_4 alkylene glycol) allyl ether, trimethylol propane

di(allyl ether), trimethylol ethane di(allyl ether), and mixtures thereof.

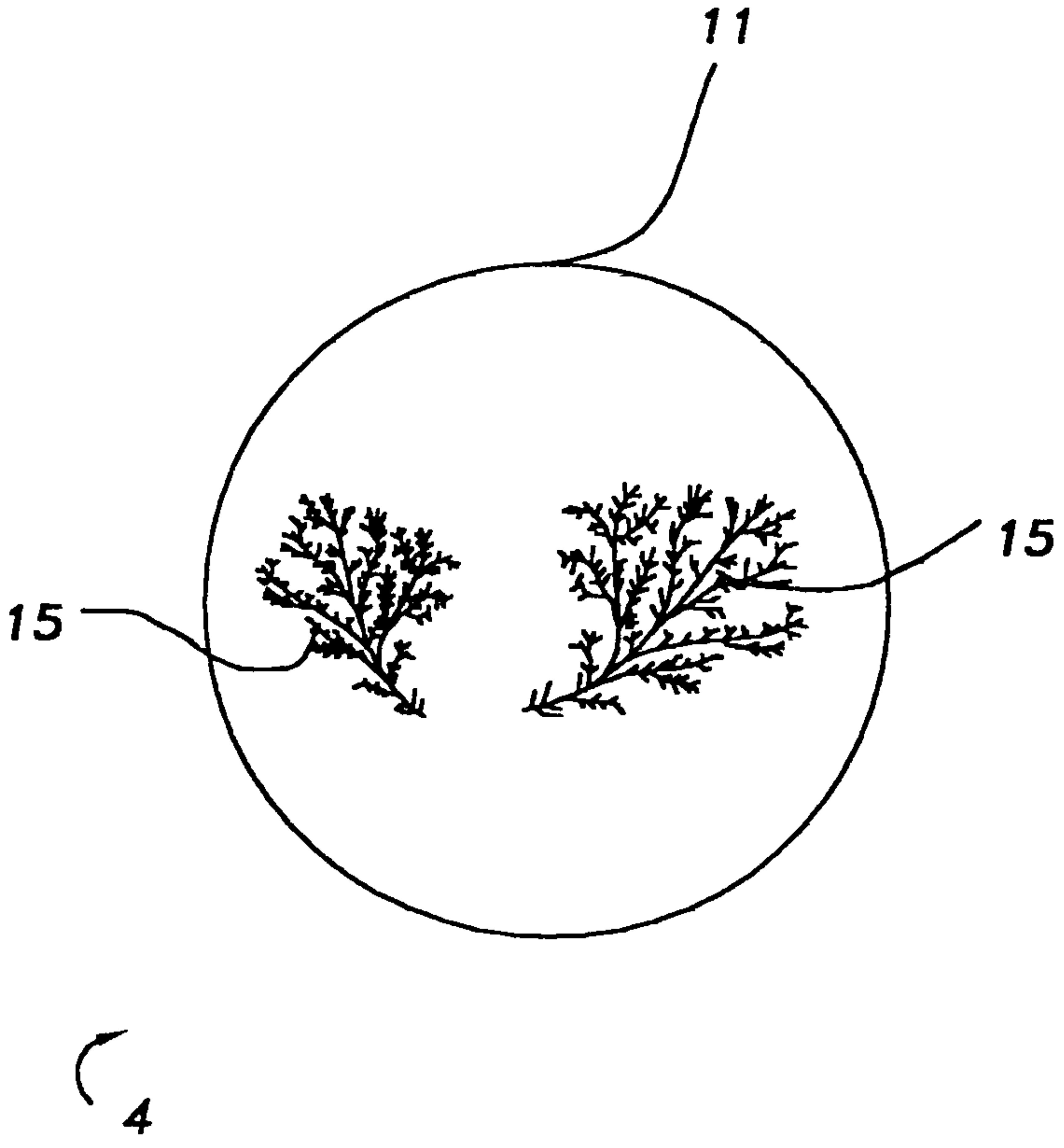
14. The composition of claim 13 wherein R is a residue of diethylene glycol, and the material of which R_3 is a residue is poly(1,2-propylene glycol) allyl ether.

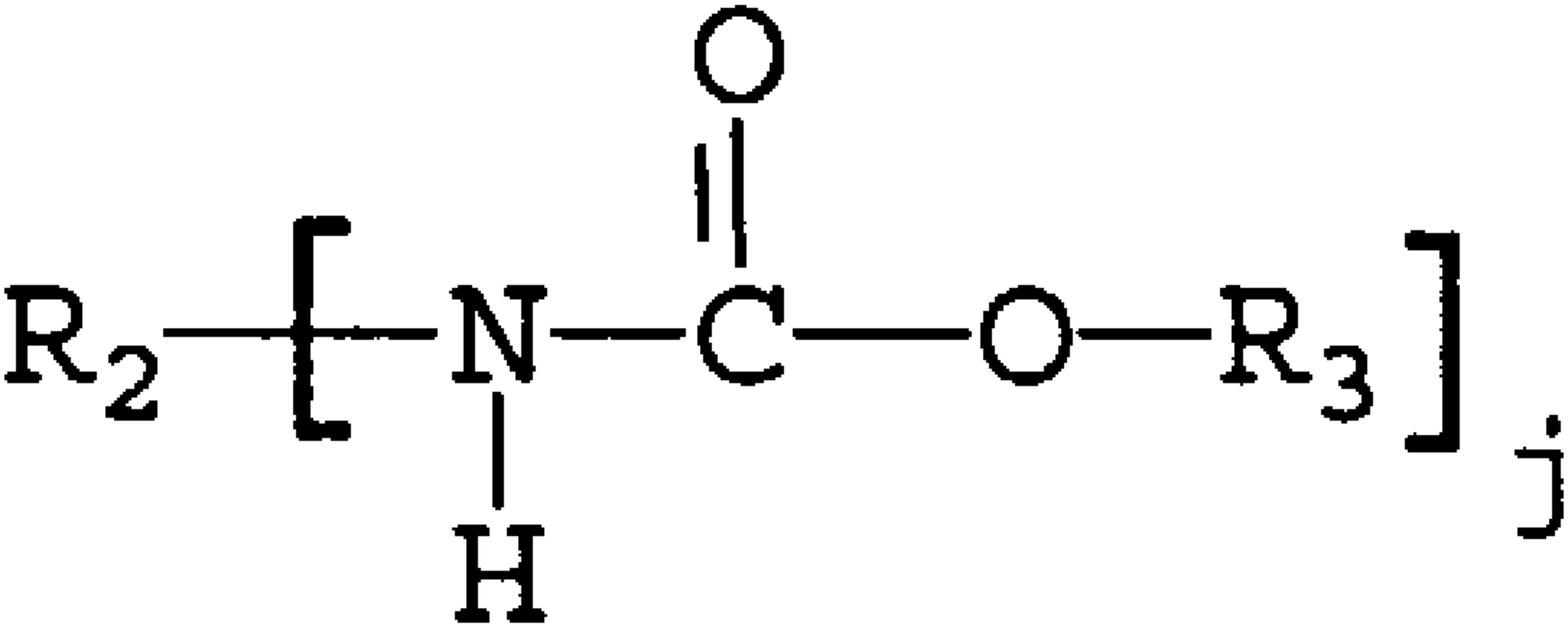
15. The polymerizate of any one of claims 1 to 9.

16. The polymerizate of any one of claims 10 to 13.

17. The polymerizate of claim 16 wherein said polymerizate is a lens having a positive diopter.

FIGURE 1





$$R_2-\left[-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_3\right]_j$$

(II)