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(54) **Title:** PREPARATION OF ORGANIC PIECES OF OPTICAL QUALITY AND ESPECIALLY ORGANIC LENSES

(57) **Abstract**

The main aim of the present invention is a method of preparing photochromic or non–photochromic organic pieces of optical quality and especially organic lenses, by radical polymerisation of a mixture of radically polymerisable monomers, characterised in that it comprises: a) adjusting, by pre–polymerisation, the viscosity of said mixture, to a value between 0.4 and 2 Pa.s; b) pouring said pre–polymerised mixture into a mould; c) photogelifying, in said mould, said pre–polymerised mixture until its gel point; d) completing the polymerisation of said pre–polymerised and gelified mixture in said mould, by heat treatment; adding effective amounts of at least one thermal catalyst and of at least one photoinitiator intervening in said mixture of monomers for the implementation of said pre–polymerisation, photogelification and polymerisation; said photoinitiator(s) intervening in an amount less than or equal to 0.009 parts by weight per 100 parts by weight of said mixture of monomers.

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PREPARATION OF ORGANIC PIECES OF OPTICAL QUALITY AND ESPECIALLY ORGANIC LENSES.

The present invention relates to the preparation of organic pieces of optical quality and especially to the preparation of organic lenses. More specifically, the main aim of the present invention is an original method of preparing such photochromic or non-photochromic organic pieces by radical polymerisation of a mixture of radically polymerisable monomers.

The aim of the present invention is also :

- novel organic pieces of this type, which are preparable by a variant of said method ; this variant makes use of particular monomers ;
- novel radically polymerisable compositions -mixtures of radically polymerisable monomers - which can be used for preparing organic pieces of this type according to the method of the invention.

The present invention is described below with particular reference to the context of the preparation of organic lenses (sight correction glasses, protective glasses). The present invention is in no way limited to said context and the person skilled in the art will easily understand that the claimed method is suitable for obtaining any type of moulded organic pieces, which is without optical defect, such as, therefore, organic lenses, but also windows, optical pieces ...

Purely thermal methods of radical polymerisation of mixtures of monomers (mainly acrylic and/or methacrylic and/or alkenyl monomers, especially vinylic monomers) which contain or do not contain an effective amount of at least one photochromic colorant, have been described and carried out, especially by the Applicant, for preparing photochromic or non-photochromic organic lenses, mainly optical or ophthalmic lenses. Said methods are carried out, in a lens mould, on a mixture containing an effective amount of at least one adequate thermal catalyst or radical polymerisation initiator. Said catalyst, when at least one photochromic colorant intervenes, is generally selected from diazo compounds (catalysts known as "soft" which remain "inert" towards the photochromic colorant(s) present). Such methods do not give entire satisfaction insofar as their implementation is long and insofar as, inescapably, during said implementation, oxygen diffuses into within the mixture

undergoing polymerisation, this oxygen coming from the surrounding air and entering into the mould via its leaktight joint. This generates defects in the appearance and constraints (optical defects) in the lenses thus produced.

An alternative process for preparing such organic lenses was described in the US patent US-A-5 621 017. This alternative method is based on photopolymerisation under ultraviolet irradiation of the mixture of monomers containing an effective amount (0.01 to 1 parts by weight, per 100 parts by weight of monomers) of at least one appropriate photoinitiator. Such a method neither gives entire satisfaction insofar as, especially :

- it may reveal to be delicate, even impossible to find satisfactory operating conditions (nature of the photoinitiator/irradiation band) in the light of the nature of the monomers present, in the light of the presence of at least one photochromic colorant (which reveals to be a competitor of absorption for the photoinitiator), and in the light of the specifications established for the final lens...

- its field of application is limited. It may in fact be suitable for preparing lenses of relatively low thickness (finished lenses of 2 mm thickness (see the Examples of US-A-5 621 017)) but it is not suitable for preparing thicker lenses (for example, semi-finished lenses of greater than 10 mm thickness). In fact, the problem of penetration of the ultraviolet radiation in the material to be polymerised is then come up against. In order to overcome this difficulty, it has been possible to envisage using a photoinitiator which absorbs in the visible. However, in order to guarantee obtaining a suitable result - a complete polymerisation which is homogeneous throughout the whole thickness -, it remains necessary to use a high concentration of photoinitiator and to use a lot of energy. Under such conditions - severe polymerisation conditions - lenses are generally obtained which possess a high degree of yellowing. In any case, in using a low concentration of photoinitiator (which is not susceptible to generate yellowing), it is very difficult to obtain a complete polymerisation throughout the whole of the mass of the material.

In such a context, the Applicant has developed a novel method of preparing organic pieces which enables obtaining said pieces, which are free from optical defects, up to relatively consequent thicknesses and this from various types of mixtures of monomers (even from mixtures which are known to be relatively difficult to

polymerise). Said novel method can be qualified as a mixed method insofar as it includes thermal polymerisation and photochemical polymerisation.

Said original method of preparing organic pieces, and especially organic lenses, is described below. Characteristically, it includes a photogelification and it makes use of a low quantity of photoinitiator(s). Said method of the invention in fact comprises, for preparing photochromic or non-photochromic organic pieces by polymerisation of a mixture of radically polymerisable monomers (said mixture containing, classically in fact, the constituents of the piece or lens under preparation : main and secondary constituents of its matrix, of the monomer type, more generally conventional additives, especially such as the thermal catalyst, the photochromic colorant...), the successive steps below :

a) adjusting, by pre-polymerisation, the viscosity of said mixture, to a value between 0.4 and 2 Pa.s ;

b) pouring said pre-polymerised mixture into a mould (especially a lens mould for preparing a lens) ;

c) photogelifying, in said mould, said pre-polymerised mixture until its gel point ;

d) completing the polymerisation of said pre-polymerised and gelified mixture in said mould, by heat treatment ;

the steps referred to as pre-polymerisation (a), photogelification (c) and polymerisation (d) being implemented out by the intervention, into said mixture of monomers, of effective amounts of at least one thermal catalyst and of at least one photoinitiator ; said photoinitiator(s) intervening in an amount less than or equal to 0.009 parts by weight per 100 parts by weight of said mixture of monomers.

According to the method of the invention, the mixture containing the constituent elements of the piece under preparation is firstly pre-polymerised before it is poured into the mould. The implementation of such a pre-polymerisation out of the mould is very advantageous insofar as :

- it enables neutralising the inhibitors present in said mixture (such polymerisation inhibitors are inescapably present in commercial products) ;

- it enables increasing and adjusting the viscosity of the mixture to be poured afterwards in the mould. In said mould, the polymerisation thus implemented on a pre-

polymerised and therefore viscous mixture is done so under the best circumstances since, within such a viscous mixture, the oxygen diffuses more slowly, the performances of the intervening photoinitiator are improved, the retraction is reduced, and the gel point is attained faster ;

- it can be carried out in a perfectly leaktight recipient, i.e. in the absence of oxygen and, therefore, without a constraint as to its duration.

It is highly recommended to implement said pre-polymerisation in order to bring the viscosity of the mixture to a value between 0.4 and 2 Pa.s. Below 0.4, the beneficial effects of said pre-polymerisation hardly manifest themselves (especially in the light of the problem of the diffusion of oxygen) ; above 2, problems of manipulation of the pre-polymerised mixture are come up against, and the gel point is come too close to.

The pre-polymerisation according to the invention is generally a thermal or photochemical pre-polymerisation which, for its implementation, necessitates the presence, in the mixture to be pre-polymerised, of an effective amount of at least one thermal catalyst and at least one photoinitiator, respectively.

At least one thermal catalyst (generally one thermal catalyst) must therefore intervene, in the mixture of monomers, right from the beginning of the method for the implementation of a thermal pre-polymerisation. It is generally added in an effective amount q, such that it ensures both the implementation of said thermal pre-polymerisation (step a), and then the subsequent step, of the final thermal polymerisation (step d). However, it is in no way excluded from the context of the invention to intervene them in two lots, in a first amount q_1, which is an effective amount for the implementation of the thermal pre-polymerisation, upstream from said pre-polymerisation and then, a second amount q_2 ($q_1 + q_2 = q$), which is an effective amount for the implementation of the final thermal polymerisation, downstream from said thermal pre-polymerisation, advantageously just after the thermal pre-polymerisation, before pouring the pre-polymerised mixture into the mould. In the hypothesis of the implementation of such a thermal pre-polymerisation, the amount of photoinitiator(s) necessary for the further implementation of the photogelification may also, advantageously, be made to intervene into the mixture to be pre-polymerised. Said

amount may however intervene further on, upon completion of the thermal pre-polymerisation, before pouring the pre-polymerised mixture into the mould.

Thus, advantageously, the pre-polymerisation is a thermal pre-polymerisation carried out on the mixture of monomers containing the effective amounts of thermal catalyst(s) and photoinitiator(s) or containing only the effective amount of thermal catalyst(s), the effective amount of photoinitiator(s) being then added to said mixture of monomers upon completion of its thermal pre-polymerisation before it is poured into the mould.

At least one photoinitiator (generally one photoinitiator) must then intervene, into the mixture of monomers, right from the beginning of the method, for the implementation of a photochemical pre-polymerisation. Said photoinitiator may intervene right from the beginning in an effective amount Q such that it ensures both the implementation of said photochemical pre-polymerisation (step a) and then that of the subsequent photogelification step (step c). Advantageously, the photoinitiator may intervene in two lots, in a first amount Q_1, which is an effective amount for the implementation of the photochemical pre-polymerisation, upstream from said pre-polymerisation and then in a second amount Q_2 ($Q_1 + Q_2 = Q$), which is an effective amount for the implementation of the photogelification, downstream from said photochemical pre-polymerisation, advantageously just after the photochemical pre-polymerisation, before pouring the pre-polymerised mixture into mould. In the hypothesis of the implementation of such a photochemical pre-polymerisation, the thermal catalyst(s) subsequently useful in the final thermal polymerisation (step d) may intervene, before said photochemical pre-polymerisation or upon the completion thereof (before pouring the pre-polymerised mixture into the mould).

Thus, according to another variant of the implementation of step a of the method of the invention, the pre-polymerisation is a photochemical pre-polymerisation carried out on the mixture of monomers containing the effective amount of photoinitiator(s) or advantageously containing only 40 % to 60 % of said effective amount expressed by weight, the remainder of photoinitiator(s) being then added to said mixture of monomers, upon the completion of its photochemical pre-polymerisation, before it is poured into the mould ; the effective amount of thermal catalyst(s) being

added to said mixture of monomers before its photochemical pre-polymerisation, or upon the completion thereof.

The following is further specified with reference to said pre-polymerisation step of the method of the invention (step a). It has been seen that in general it is a matter of a thermal or photochemical pre-polymerisation. It is not totally excluded to implement the pre-polymerisation under the joint action of heat and a suitable irradiation, i.e. to carry out a thermal pre-polymerisation and a photochemical pre-polymerisation, the catalyst(s) and photoinitiator(s) thus acting together within the mixture of monomers...

The pre-polymerised mixture according to step a described above is then just poured into a mould.

Its polymerisation is finalised in said mould, and characteristically, this is in two successive steps :

- a photogelification until its gel point, and
- a final or supplementary thermal polymerisation.

The photoinitiator(s) intervening for the implementation of the mixed method of the invention, which thus combines photochemical polymerisation (step c and optionally step a) and thermal polymerisation (step d and optionally step a) in three steps (a, b, c), intervenes, in any case, in a limited amount - equal to or less than 0.009 parts by weight per 100 parts by weight of monomers - and it cannot thus reveal to be detrimental, especially regarding the problem of yellowing.

Furthermore, the intervention of said photoinitiator(s) is optimised by implementing the photogelification and the pre-polymerisation, if it is a case of a photochemical pre-polymerisation, under a radiation which is predominantly in the visible, i.e. almost free from ultraviolet radiation. In fact, conventional UV lamps are not suited or badly suited. It is strongly suggested to use them in making use of UV filters. It is however recommended to implement the photogelification step of the method of the invention and the step of pre-polymerisation, if it is a case of a photochemical pre-polymerisation, with fluorescent tubes as source of radiation which are predominantly in the visible (having their maximum power beyond 400 nm, e.g. at 410 nm or 460 nm). This type of radiation penetrates into the thickness of the irradiated

material and hardly interferes with photochromic colorants which are optionally present.

The person skilled in the art will now have gleaned all the interest of the mixed method of the invention (which includes thermal and photochemical polymerisation), which comprises three main steps (pre-polymerisation /photochromic gelification/thermal polymerisation) and whose implementation enables obtaining thin and thick pieces (especially lenses), which are free from any defect in appearance and constraint, especially insofar as the polymerisation is implemented in the mould (especially the lens mould), rapidly with a diffusion of oxygen which is reduced to a minimum.

The method of the invention is also interesting in that it is suitable for the polymerisation of mixtures of monomers of different types ((meth)acrylic, vinylic monomers...) and especially of mixed type ((meth)acrylic and vinylic monomers). The mixture of monomers to be polymerised according to the invention may in fact contain acrylic and/or methacrylic and/or alkenyl monomers, especially vinylic or allylic monomers.

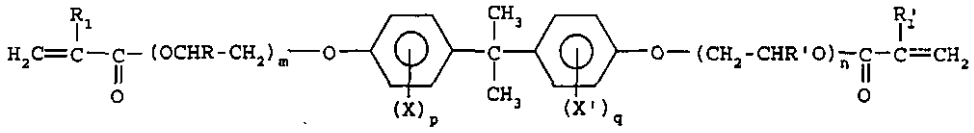
Advantageously, said mixture mainly contains difunctional monomers of type (a) and difunctional monomers of type (b), as defined below. Compositions based on these two types of different monomers were described by the Applicant in the FR 97 05 458 patent application, filed on the 2nd May 1997, published as FR-A-2,762,845. Their use for preparing organic pieces of optical quality, and especially organic lenses by way of the method of the invention has revealed to be particularly advantageous. Said compositions were developed by the Applicant within the context of research for a compromise between the optical properties, even photochromic properties and the mechanical properties of a plastic material which can be used especially in ophthalmology, and obtained by (thermal) radical co-polymerisation of monomers. Characteristically, said compositions include at least one short chain (meth)acrylic difunctional monomer and at least one long chain alkenic difunctional monomer. The resin resulting from their polymerisation thus possesses a nanophasic structure which provides it with the properties sought after. Said short chain (meth)acrylic difunctional monomer(s) (of type (a) and of formula (A), (A') : see further on) do in fact bring about the rigidity, this rigidity being modulated by the presence of

said long chain alkenic difunctional monomer(s) (of type (b) and of formula (B), (B'), (B") : see further on), which, surprisingly, also enable providing said composition with excellent photochromic properties. Thus, the difference in functionality of said monomers of type (a) and (b) advantageously slow down the gelification of the resulting polymerisable composition. This characteristic enables the resin obtained from said composition to give good optical properties and especially in the case wherein photochromic colorants are incorporated within it, to express rapidly and, at best, the photochromic properties.

Thus, the method of the invention is therefore particularly advantageously implemented with a mixture of monomers which contains at least one difunctional monomer of type (a) and at least one difunctional monomer of type (b) :

* the difunctional monomer(s) of type (a) - (meth)acrylic - being of one or the other of the formulae (A) and (A') below :

+ formula (A) :



in which :

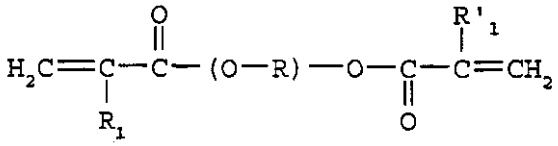
- R_1, R'_1, R and R', identical or different, are independently a hydrogen or a methyl group ;

- m and n are, independently, integers between 0 and 4 (inclusive) ; and are advantageously independently equal to 1 or 2 ;

- X and X', identical or different, are a halogen and preferably represent a chlorine and/or a bromine atom ;

- p and q are, independently, integers between 0 and 4 (inclusive) ;

+ formula (A') :



in which :

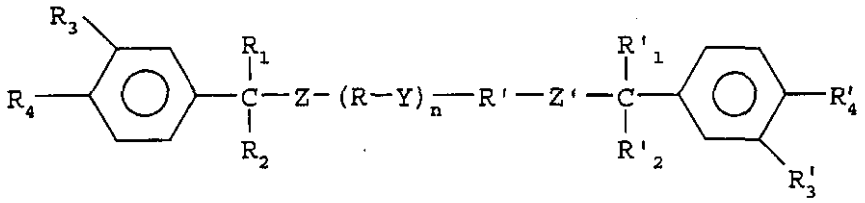
- R_1 and R'_1 , identical or different, are independently a hydrogen or a methyl group ;

- R is a straight or branched alkyl radical having 2 to 8 carbon atoms, a cycloalkyl radical having 3 to 6 carbon atoms, an ether radical of formula (R'-O-R") in which R'

and R", identical or different, are independently a straight or branched alkyl radical having 2 to 4 carbon atoms;

* the difunctional monomer(s) of type (b) - long chain alkenic difunctional oligomer - being of one or the other of the formulae (B), (B') and (B") below:

+ formula (B) :



in which :

- R_1, R'_1, R_2 and R'_2, identical or different, are independently hydrogen or a straight or branched alkyl radical, advantageously straight, having 1 to 4 carbon atoms ; and particularly advantageously correspond to a methyl group ;

- R_3 and R_4, different, are independently one hydrogen and the other an alkenyl radical having 2 to 6 carbon atoms, advantageously 2 to 4 carbon atoms and particularly advantageously an isopropenyl radical ;

- R'_3 and R'_4, different, are independently one hydrogen and the other an alkenyl radical having 2 to 6 carbon atoms, advantageously 2 to 4 carbon atoms and particularly advantageously an isopropenyl radical ;

(advantageously, the two ends of the molecule are identical ; i.e: $R_3 = R'_3$ and $R_4 = R'_4$);

- Z represents a carbamate function (-NH-CO-O-), a thiocarbamate function (-NH-CO-S-) or a urea function (-NH-CO-NH-) ;

- Z', independent from Z and advantageously respectively with respect to Z, represents a carbamate function (-O-CO-NH-), a thiocarbamate function (-S-CO-NH-) or a urea function (-NH-CO-NH-) ;

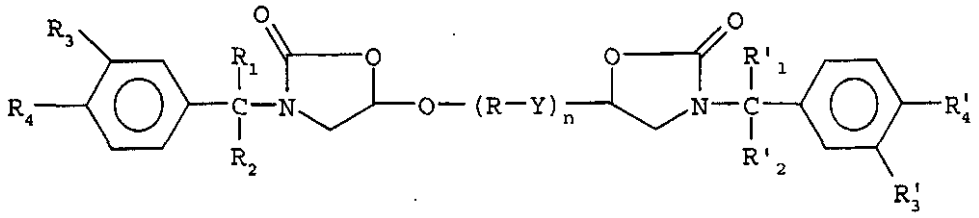
- R' represents a straight or branched alkyl radical having 2 to 4 carbon atoms ;

- R, identical or different when $n \geq 2$, is a straight or branched alkyl radical having 2 to 4 carbon atoms ;

- Y, identical or different when $n \geq 2$, is oxygen or sulphur ;

- n is an integer defined such that the total number of carbon atoms, contained in the long chain situated between the two moieties Z and Z', be at least equal to 18 and advantageously be between 18 and 112 (inclusive) ;

+ formula (B') :

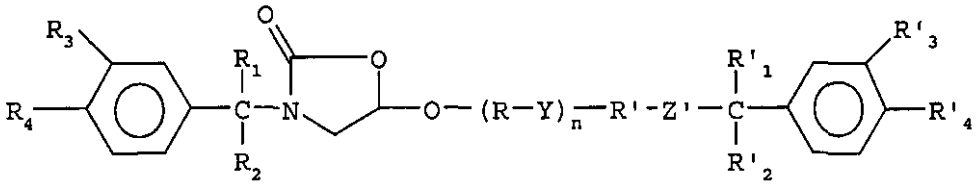


in which :

- R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3, R'_4, R and Y are as defined above with reference to formula (B);

- n is an integer defined such that the total number of carbon atoms, contained in the long chain of moiety $(R\text{-}Y)_n$, be at least equal to 22 and advantageously be between 22 and 104 (inclusive);

+ formula (B") :



in which :

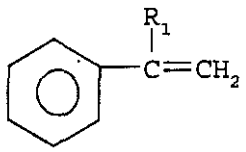
- R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3, R'_4, R, R' and Y are as defined above with reference to formula (B);

- Z' is a carbamate function (-O-CO-NH-) or Z' is a thiocarbamate function (-S-CO-NH-); advantageously, Z' is a carbamate function ;

- n is an integer defined such that the total number of carbon atoms, contained in the long chain of moiety $(R\text{-}Y)_n\text{-}R'$, be at least equal to 22 and advantageously be between 22 and 104 (inclusive).

Furthermore, said mixture of monomers of type (a) and (b) can further contain :

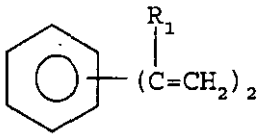
(c) at least one aromatic monovinylic monomer of formula (C) :



in which R_1 = H or CH_3 ; said monovinylic monomer advantageously consisting of styrene ;

and/or

(d) at least one aromatic divinylic monomer of formula (D) :



in which R_1 = H or CH_3 ; said divinylic monomer advantageously consisting of divinylbenzene;

and/or

(e) at least one (meth)acrylic monomer of formula (E) :

$$CH_2 = C(R) \text{-} COOR'$$

in which R = H or CH_3 and R' is a straight or branched alkyl radical having 4 to 16 carbon atoms, an optionally substituted benzyl or phenoxyethyl radical (generally substituted by a C_1-C_6 alkyl group) or a polyethoxy group of formula $-(CH_2\text{-}CH_2\text{-}O)_nR''$ in which n is an integer between 1 and 10 and R" = CH_3 or C_2H_5 ; said (meth)acrylic monomer advantageously consisting of 2-ethylhexyl-methacrylate;

and/or

(f) diallylphthalate.

The compounds listed above ((c) to (f)) advantageously intervene with the difunctional monomers of type (a) and (b). Advantageously, they may intervene within any mixture of monomers to be polymerised according to the method of the invention.

It is now proposed to specify somewhat the nature and the amount of each of the components which intervene or which may intervene in the mixture which is polymerisable according to the method of the invention.

The monomers of type (a) may or may not all be of the same formula (A) or (A') ... Thus the mixtures to be polymerised according to the invention advantageously comprise :

- either monomers of a same formula (A) (at least one);

- or monomers of a same formula (A') (at least one);
- or mixtures (non mixed) of monomers of different formulae (A) ;
- or mixtures (non mixed) of monomers of different formulae (A') ;
- or mixtures (mixed) of monomers of formula(e) (A) and of formula(e) (A').

According to a preferred variant of the invention, one or more symmetrical monomers of type (a) are used. Said monomers of type (a), of formula (A) or (A') in which the R_1 and R'_1 groups are identical, the same as R and R' groups, as well as the X and X' substituents for the compounds of formula (A), are qualified as symmetrical.

Said symmetrical monomers of type (a) of formula (A) are known and are available commercially or are easily accessible to the person skilled in the art. It may be noted that said monomers which do not have a halogen on the aromatic rings do in fact correspond to the first monomers of formula (I) in the sense of the WO-A-92/05209 document. Said monomers of type (a) of formula (A) having halogen(s) on the aromatic ring(s) will be easily obtained by the person skilled in the art by using derivatives which are appropriately substituted on said aromatic ring(s). Within the context of the invention, the monomers of formula (A), in which R and R', identical, are hydrogen or a methyl group, R_1 and R'_1 are a methyl group, m and n are independently equal to 1 or 2, and $p = q = 0$, are preferred. A particularly advantageous variant corresponds to the monomer of formula (A) of the above type with, in addition, $R = R' = H$ and $m = n = 2$. Said monomer is notably marketed by Akzo Nobel (NL) under the commercial designation DIACRYL 121. The synthesis of the dissymmetrical monomers of formula (A) are of no particular problem to the person skilled in the art.

The monomers (a) of formula (A') are also well-known and result from the conventional reaction of an aliphatic diol or a short-chain alkyleneglycol (with a maximum of 8 carbon atoms in said chain) with at least one type of (meth)acrylic derivative depending on whether it is desired to obtain monomers of formula (A') which are symmetrical or dissymmetrical at their ends.

These monomers of type (a) generally intervene in the mixture to be polymerised at a rate of 40 to 99 parts by weight for 100 parts by weight of the mixture of monomers of type (a) and (b). If they intervene in a smaller amount, the polymerisable composition has a tendency to retract during its polymerisation inducing

a premature turn-out which, in turn, is responsible for a deterioration of the optical properties of the final resin.

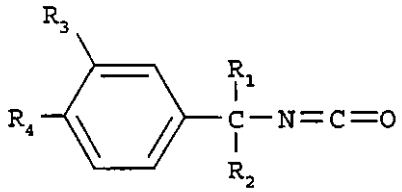
The monomers (b) of formula (B), (B') and (B") are long-chain difunctional alkenic monomers. Said monomers have or have not a more or less pronounced symmetry (R_1/R'_1, R_2/R'_2, R_3/R'_3, R_4/R'_4, Z/Z').

These monomers of type (b) may or may not all have the same formula (B), (B') or (B") ... Thus, the mixtures to be polymerised according to the invention advantageously comprise :

- either monomers of a same formula (B) (at least one);
- or monomers of a same formula (B') (at least one);
- or monomers of a same formula (B") (at least one);
- or mixtures (non mixed) of monomers of different formulae (B) ;
- or mixtures (non mixed) of monomers of different formulae (B') ;
- or mixtures (non mixed) of monomers of different formulae (B") ;
- or mixtures (mixed, binary or ternary) of monomers selected from the monomers of formula(e) (B), of formula(e) (B') and of formula(e) (B").

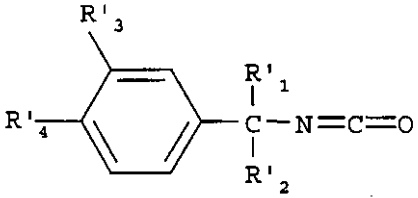
The monomers of type (b) which are long-chain alkenic difunctional oligomers, said chain being a polyoxyalkylene or polymercaptoalkylene chain, even a mixed chain, are obtained according to the conventional conditions of organic synthesis by the reaction:

- between one or several derivatives having a functionality of the alkenylisocyanate type, of formula I and/or II:



formula I

and/or



formula II

in which R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3 and R'_4 are such as defined above. According to a preferred variant of the invention, the monomers of type (b) used are symmetrical at their ends. In order to do this, a single type of alkenylisocyanate derivative (thus formulae I and II are identical) is used. In a particularly advantageous way, a vinylisocyanate derivative is used in which $R_1=R_2=CH_3$ (or $R'_1=R'_2=CH_3$), R_3 (or

R'_3) is an isopropenyl radical and R_4 (or R'_4) is hydrogen, thus corresponding to 3-isopropenyl-α,α-dimethylbenzyl-isocyanate (of general designation m-TMI®). The oligomers (b) obtained from said derivatives are preferred;

- and a compound which intrinsically has a long chain, said compound being:

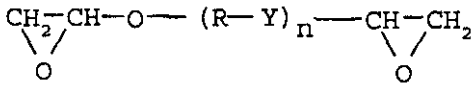
* either a compound which is symmetrical about its terminal functions and which corresponds :

+ to a diol of formula $HO-(R-Y)_n-R'-OH$;

+ or to a dithiol of formula $HS-(R-Y)_n-R'-SH$;

+ or to a diamine of formula $H_2N-(R-Y)_n-R'-NH_2$; which allows obtaining said intrinsically symmetrical oligomers of formula (B) (intrinsically symmetrical means monomers of formula (B) in which the Z and Z' groups are functions of identical nature);

+ or to a biepoxy of formula



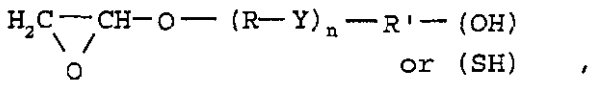
,

the reaction thus leading to the synthesis of said oligomers of formula (B');

* or a compound which is dissymmetrical about its terminal functions :

+ it being possible for said functions to be an alcohol, thiol or amine function; all combinations being possible: these compounds enabling obtaining other intrinsically dissymmetric difunctional oligomers of formula (B) (intrinsically dissymmetrical means monomers of formula (B) in which the Z and Z' groups are functions of different nature);

+ said functions respectively being an epoxy function and an alcohol function or an epoxy function and a thiol function, the compounds then being of formula



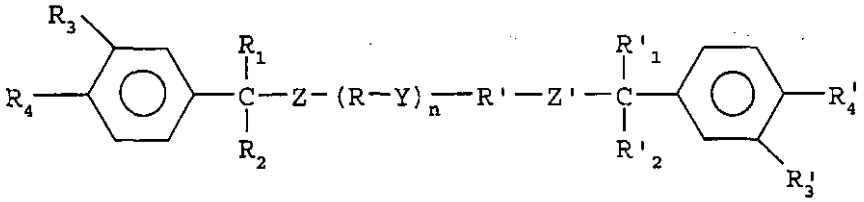
,

the reaction thus leading to the synthesis of said oligomers of formula (B").

In every case, R, R' ,Y and n are such as defined above; preferentially, Y is oxygen (the long chain then being a polyoxyalkylene chain).

The molecular mass of the long polyoxyalkylene and/or polymercaptoalkylene chain which correspond to the $(R\text{-}Y)_n\text{-}R'$ or $(R\text{-}Y)_n$ radical in said formulae (B, B', B") specified above, is generally at least equal to 500 $g.mol^{-1}$ and lower than 2000 $g.mol^{-1}$; and preferentially, said molecular mass is between 600 $g.mol^{-1}$ and 900 $g.mol^{-1}$.

In a particularly advantageous way, one or several intrinsically symmetrical monomers of type (b) of formula (B) (as defined above) are brought to intervene:



in which R, R', R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3, R'_4 are such as defined above (and advantageously so that the two ends of the molecule are identical; i.e. : $R_1=R'_1$, $R_2=R'_2$, $R_3=R'_3$ and $R_4 = R'_4$, with even more advantageously $R_1=R'_1=R_2 = R'_2 = CH_3$ and $R_3 = R'_3$ and $R_4 = R'_4$ with one of R_3 and R_4 being hydrogen and the other being an isopropenyl group) and Y is such as defined above and advantageously consists of an oxygen (X=O) and:

(α) - Z and Z' are carbamate functions of formula (-NH-CO-O-) and (-O-CO-NH-) respectively;

- n is an integer defined in such a way that the total number of carbon atoms contained in the long chain situated between the two motifs Z and Z', is between 18 and 112 ; and advantageously, in the case of a polyoxyalkylene chain, is between 24 and 112 and particularly advantageously between 26 and 50 in the case of a polyoxyalkylene of molecular mass between 600 and 900 $g.mol^{-1}$;

or (β) - Z and Z' are thiocarbamate functions of formula (-NH-CO-S-) and (-S-CO-NH-) respectively

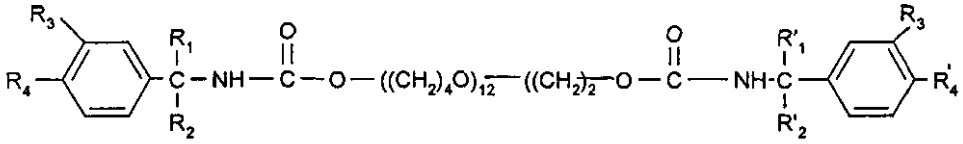
- n is an integer defined in such a way that the total number of carbon atoms contained in the long chain situated between the two motifs Z and Z', is between 18 and 108 ; and advantageously, in the case of a polyoxyalkylene chain, is between 24 and 108 and particularly advantageously between 28 and 46 in the

case of a polyoxyalkylene chain of molecular mass between 600 and 900 g.mol^{-1};

or (γ) - Z and Z' are urea functions (-NH-CO-NH-)

- n is an integer defined in such a way that the total number of carbon atoms contained in the long chain situated between the two motifs Z and Z', is between 18 and 112; and advantageously, in the case of a polyoxyalkylene chain, is between 24 and 112, and particularly advantageously between 28 and 50 in the case of a polyoxyalkylene of molecular mass between 600 and 900 g.mol^{-1}.

The person skilled in the art will have understood that formula (B), in the case (α) above wherein the number of carbon atoms contained in the long chain is equal to 50, may for example be written:



In the same way, the person skilled in the art will have understood that generally the minimal values mentioned above which define the number of carbon atoms in the long chain of motif $(R\text{-}Y)_n\text{-}R'$ or $(R\text{-}Y)_n$, correspond to compounds having a polymercaptoalkylene chain (Y = S).

In a particularly advantageous manner, said monomer(s) of type (b) have a general formula (B) such as defined above in which:

- R_1, R_2, R'_1 and R'_2, identical, are methyl radicals; R_3 and R'_3 are an isopropenyl radical; R_4 and R'_4 are hydrogen and

+ either Z and Z' are urea functions (-NH-CO-NH-) and

- R' represents an ethylene or propylene group;

- n is an integer equal to 13 or 19 which defines a total number of carbon atoms between Z and Z' equal to 28 or 40 when $(R\text{-}Y)_n$ is a polyoxyethylene chain; or n is an integer equal to 10 or 14 which defines a total number of carbon atoms between Z and Z' equal to 33 or 45 when $(R\text{-}Y)_n$ is a polyoxypropylene chain; or n is an integer between the lower limit values (10 to 13) and upper limit values (14 to 19) such as defined above, when $(R\text{-}Y)_n$ is a polyoxyethylene / polyoxypropylene mixed chain;

which thus defines the monomers of type (b) of designation RUDI JEF 600 and RUDI JEF 900 (see the Examples in FR 97 05458), respectively when n has one of the lower limit values (n between 10 and 13 inclusive) and n has one of the upper limit values (n between 14 and 19 inclusive);

+ or Z and Z' are carbamate functions of formulae (-NH-CO-O-) and (-O-CO-NH-) respectively, and

- R' represents an ethylene group ;

- $(R\text{-}Y)_n$ represents a long polyoxyethylene chain;

- n is an integer equal to 13 or 19 which defines the total number of carbon atoms contained in the long chain situated between the two motifs Z and Z' equal to 28 or 40;

which thus define the monomers of type (b) of designation *RUDI 600* and *RUDI 900* (see the Examples of FR 97 05458), when n=13 and n=19 respectively.

It is more particularly preferred to implement the original method of the invention with monomers of type (b) above (of general formula (B) above in which Z and Z' are urea functions) in a mixture with monomers of type (a) as specified above.

The monomers of type (b) generally intervene in the mixture to be polymerised at a rate of 1 to 60 parts by weight for 100 parts by weight of the mixture of monomers of type (a) and (b).

The mixtures to be polymerised according to the invention may further contain, as already indicated, other monomers in combination or not with monomers of type (a) and (b) specified above. For 100 parts by weight of the mixture of monomers of type (a) and (b), said mixtures can contain from 1 to 60 parts by weight (advantageously from 10 to 50 parts by weight) of at least one monomer selected from the alkenic monomers (such as those of formulae (C) and (D) and diallylphthalate (f)), advantageously vinylic and allylic monomers, (meth)acrylic monomers (such as those of formula (E)) and mixtures thereof. In light of the effects sought-after, when these types of monomer are added, the person skilled in the art will know how to determine and optimise the intervening amounts of each type of said monomer (in any case, the total amount of said monomer(s) which intervene in the composition to be polymerised is between 1 to 60 parts by weight of the mixture of monomers of type (a) and (b)).

The vinylic monomers of formula (C) - styrene and/or methylstyrene - intervene in combination with the monomer(s) of type (a) in order to loosen the

network. The intervention at this stage of styrene may be particularly advantageous insofar as this polymerised compound has a rather high refractive index (n = 1.595). Said styrene constitutes the particularly preferred compound of this class of monomer.

The compound of formula (D) consists of divinylbenzene (DVB) or di(methylvinyl)benzene. Divinylbenzene is the particularly preferred compound of formula (D). The intervention of at least one compound of formula (D) may reveal to be advantageous in that notably said compound moderates, in a general manner, the effects of the compound(s) of formula (C). The beneficial action of such a compound of formula (D) has been notably demonstrated on the expression of photochromic properties. With reference to divinylbenzene, insofar as this polymerised compound has a relatively high refractive index (n = 1.61), its intervention is also beneficial in that it leads to an increase in the refractive index of the polymers of the invention.

The mixture to be polymerised according to the method of the invention also contains advantageously at least one compound of formula (E). It is a (meth)acrylic monomer such as defined above. It may also be butyl, pentyl, hexyl, heptyl, octyl or 2-ethylhexyl(meth)acrylate or even ethyltriglycol(meth)acrylate. 2-Ethylhexylmethacrylate (EHMA) is the preferred compound of formula (E). The presence of this type of compound has revealed to be advantageous for the turning-out of the polymerised material and for the implementation of finishing treatments of the latter.

Finally, the polymerisable composition may contain diallylphthalate which notably allows adjusting the index and/or other optical and mechanical properties.

As specified above, the intervention of the compounds of formula (C) and/or (D) and/or (E) and/or diallylphthalate is not obligatory. It does however reveal to be advantageous.

Similarly, it may reveal to be extremely advantageous to intervene at least one acrylic monomer into the mixture of monomers to be polymerised according to the original method of the invention, said acrylic monomer being at least trifunctional (i.e. possessing at least three reactive functions : three double bonds, advantageously possessing three to six reactive functions). Said monomer intervenes as a constituent monomer of the final matrix but above all as an accelerator of the pre-polymerisation (step a) and of the photogelification (step c).

It is advantageously selected from :

- pentaerythritol triacrylate,
- pentaerythritol tetraacrylate,
- propoxylated glycerol triacrylate,
- trimethylolpropane triacrylate,
- polyurethane triacrylate,
- dipentaerythritol hexaacrylate ,

and advantageously consists of pentaerythritol triacrylate.

Its intervention, in substitution, at least partial, of a difunctional acrylic monomer or in addition to a mixture of acrylic and/or methacrylic and/or alkenyl monomers, improves the kinetics of polymerisation, without introducing any defect in the final product.

Generally, the accelerators of polymerisation, said at least trifunctional acrylic monomers, are made to intervene at the rate of 2 to 10%, advantageously 4 to 6%, by weight, of the total weight of the mixture of monomers to be polymerised according to the invention.

After having specified the nature of the monomers which may constitute main constituent elements of the piece prepared by the method of the invention, we now come to the additives to be incorporated in the mixture of monomers in order on the one hand to enable the polymerisation according to the invention of it, and on the other hand, in order to give photochromic properties to the prepared piece, if this is desired.

The mixture of monomers to be polymerised according to the original method of the invention can therefore contain an effective amount of at least one photochromic colorant, in order to give photochromic properties to the pieces prepared.

Said colorant is advantageously selected from the spiroxazines and the chromenes (or a combination thereof) which are endowed with photochromic properties. A large number of photochromic colorants of this type are described in the literature and are commercially available.

Spiroxazine colorants which may be used within the context of the present invention have notably been described in the patents US-A-3,562,172, 4,634,767, 4,637,968, 4,720,547, 4,756,973, 4,785,097, 4,792,224, 4,816,584, 4,831,142, 4,909,963, 4,931,219, 4,936,995, 4,986,934, 5,114,621, 5,139,707, 5,233,038,

4,215,010, 4,342,668, 4,699,473, 4,851,530, 4,913,544, 5,171,636, 5,180,524, 5,166,345, in the patent applications EP-A- 0 508 219, 0 232 295 and 0 171 909 and in the application FR-A-2 738 248 (of the Applicant).

The use of 1,3-dihydro-3,3-dimethyl-1-neopentyl-6'-(4"-N,N-diethyl-amino)-spiro-[2H]-indole-2,3'-3H-naphtho[2,1-b][1,4]oxazine, and the use of the spiroxazines described in the application FR-A-2 738 248, are most particularly recommended within the context of the present invention.

Chromene colorants which are usable within the context of the present invention are notably described in patents US-A-3,567,605, 4,889,413, 4,931,221, 5,200,116, 5,066,818, 5,224,602, 5,238,981, 5,106,998, 4,980,089, 5,130,058, and the application EP-A-0 562 915. Said chromenes may notably consist of naphthopyrans.

The use of 2,2-bis-(4'-methoxyphenyl)-5,6-dimethyl-[2H]-naphtho[1,2-b]pyran, is most particularly recommended within the context of the present invention.

Spiropyran colorants which are also usable within the context of the present invention are notably described in the following texts:

. PHOTOCHROMISM G. Brown, Editor - Techniques of Chemistry - Wiley Interscience - Vol. III - 1971 - Chapter III - Pages 45-294 - R.C. Bertelson.

. PHOTOCHROMISM - Molecules & Systems - Edited by H. Dürr - H. Bouas-Laurent - Elsevier 1990 - Chapter 8 : Spiropyrans - Pages 314-455 - R. Gugliemetti.

The teachings in all these documents are incorporated herein by reference.

The intervention of other photochromic colorants such as fulgides are not excluded within the context of the present invention.

The intervention of spiroxazines and/or chromenes is largely preferred within the context of the present invention.

It has been indicated that the mixtures to be polymerised according to the invention which are intended for generating a photochromic piece, especially a lens, contain an effective amount of at least one photochromic colorant. It is in fact frequent, within the context of the present invention, to make a combination of photochromic colorants intervene, with the aim of obtaining a specific tint in the darkened state. Within the context of particularly preferred embodiments of the invention, the intervening photochromic filler comprises a combination of chromenes. A particularly

preferred combination is that of chromenes below : 2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-5-methyl-7,9-dimethoxy-[2H]-naphtho-[1,2-b]pyran and 3-(p-methoxyphenyl)-3-phenyl-6-morpholino-[3H]-naphtho-[2,1-b]pyran. This combination allows obtaining an interesting grey colour.

By way of reference and in no way limiting, it is herein indicated that said photochromic colorants generally intervene in the mixtures to be polymerised (and those which have been polymerised) of the invention at a rate of 0.01 to 1% by weight, advantageously at a rate of 0.05 to 0.5% by weight with respect to the total weight of monomers.

Said colorants may themselves also very well contain a polymerisable and/or cross-linkable reactive group in their chemical formula as well. They intervene themselves then as co-monomers in the mixture to be polymerised; and they are chemically bound i. e. grafted to the matrix of said polymerised composition. Generally, the pieces of the invention contain their photochromic colorant(s) free or bound to their matrix.

The mixture of monomers to be polymerised according to the invention also contain, before the implementation of step a and/or only before the implementation of step c (see above), the effective amounts of thermal catalyst(s) and photoinitiator(s).

A sole additive of the thermal catalyst type and a sole additive of the photoinitiator type may generally intervene.

The thermal catalyst is generally used at the rate of 0.01 to 1% by weight, preferably from 0.05 to 0.5% by weight, of the weight of the monomers present. The thermal catalyst must obviously be "inert" towards photochromic colorant(s) optionally present. The thermal catalyst is optionally selected from the diazo compounds. These compounds are familiar to the person skilled in the art and are commercially available. Examples of such diazo compounds are azobisisobutyronitrile (AIBN), 2,2'-azobis(2-methylbutyronitrile)(AMBN), and 2,2'-azobis(2,4-dimethylvaleonitrile) (ADVN). It is more particularly recommended to implement the method of the invention in the presence of the latter diazo compound : ADVN.

In the absence of such a thermal catalyst or in the presence of too low an amount of it, it would become necessary to carry out the thermal pre-polymerisation and final thermal polymerisation at higher temperatures and this would render the

reaction difficult to control ... In the presence of too great an amount of catalyst, an excess of free radicals may be generated, this excess of free radicals inducing a destruction of the photochromic colorant(s) optionally present, and an accelerated fatigue of the final material. In this latter hypothesis, the pre-polymerisation and polymerisation may also accelerate and become difficult to control.

The person skilled in the art has even to appreciate in the light of the above indications, and especially of the nature of the monomers present, the effective amounts to intervene in each case. A polymerisation modifier may advantageously intervene, in a manner known *per se*, in combination with said thermal catalyst.

The polymerisation modifier generally intervenes at a maximum content of 5% by weight, advantageously at the rate of 0.01 to 2 % by weight, of the weight of the monomers to be co-polymerised. It is noted here that it is possible to do away with the presence of such a polymerisation modifier in the hypothesis in which the piece is prepared under a reduced thickness (e<2.0 mm). In this hypothesis, the problems of the evacuation of heat are not come up against ... For the preparation of a resin of the invention having a thickness greater than 2.0 mm, the presence of a polymerisation modifier in the amounts indicated above is generally opportune. It is highly advised against going over the maximal content of 5% indicated above since the glass transition temperature of the material prepared becomes too low. It is highly recommended for the preparation of a piece of thickness between 1.5 and 20 mm, a polymerisation modifier content of about 1.2%. It has been noted that the colorability and the darkening kinetics of the photochromic pieces (especially lenses) prepared according to the invention increase with the amount of polymerisation modifier which intervenes. In the same way, when this amount goes up, the mechanical resistance increases and the optical qualities improves ...

It is obviously appropriate that said polymerisation modifier should not destroy the photochromic colorant(s) optionally present during the polymerisation and/or should not induce a discoloration of the material on its own. Said polymerisation modifier is advantageously a chain transfer agent. Said chain transfer agent can be a non-halogenated chain transfer agent such as a linear alkane thiol or bis-mercapto-ethyl ether. Dodecanethiol may be cited as an example of a linear alkane thiol without being limiting. It is not excluded to use other types of chain transfer agents such as alkane

thiols substituted with at least one aryl or alkyl radical or thiophenols. All these compounds are familiar to the person skilled in the art and are commercially available.

It has been seen previously that whatever the implementation variant of the method of the invention, the photoinitiator(s) intervene(s) characteristically in a limited amount : less than or equal to 0.009 parts by weight per 100 parts by weight of the mixture of monomers to be polymerised. It or they advantageously intervene(s) in an amount between 0.002 and 0.009 parts by weight. Below this, the photochromic polymerisation (to be implemented in step c, even in step a) can only be difficult to implement. Above this, and the problems of the photochemical polymerisation techniques of the prior art are come up against.

One sole photoinitiator generally intervenes. It may especially be selected from acyl oxides and diacylphosphine oxides. It advantageously consists of a diacylphosphine oxide.

It is incidentally noted that the irradiation time for the optional implementation of the photochemical pre-polymerisation and that of the photogelification obviously depend upon the wavelength and the intensity of the irradiation, and upon the shape and the thickness of the mixture to be polymerised, upon the amount of photoinitiator present ... and that said irradiation time is generally selected after experimental tests. Said irradiation is implemented for the photogelification through the surface of at least one of the walls of the mould.

It is not excluded from the context of the present invention to also intervene, in adequate amounts, other additives for the implementation of the photochemical polymerisation (step c, and optionally step a).

The method of the invention, as described above under its method and materials aspects on which it is possible to be carried out, is more particularly suited for the preparation of organic pieces of optical quality, and especially lenses, the thickness of which is between 0.2 and 20 mm. As indicted in the introduction of the present text, the field of application of the method of the invention is not limited, with reference to lenses, to the elaboration of thin lenses (the thickness of which is for example limited to 2 mm). In this, the method of the invention is particularly interesting.

It has been seen above that the mixture of monomers to be polymerised according to the method of the invention advantageously comprises at least one acrylic monomer which is at least trifunctional.

The use of this type of monomers for the preparation of organic pieces of optical quality and especially organic lenses is totally innovative. Thus, such organic pieces, obtained by radical polymerisation of a mixture of monomers containing at least one such monomer which is at least trifunctional, are novel and constitute another object of the present invention. Said organic pieces, novel *per se*, are advantageously prepared according to the method described above, which constitutes the first object of the present invention. It is not excluded to obtain them by a method of polymerisation of the prior art which is purely thermal or purely photochemical.

According to its last object, the present invention relates to original polymerisable compositions which are able to constitute the starting product, on which the method of the invention is advantageously implemented, in order to obtain organic pieces of optical quality and especially organic lenses. Said compositions are, as specified already, mixtures of radically polymerisable monomers. Said mixtures optionally contain at least one photochromic colorant. They may be of the type of the compositions according to US-A-5 621 017 but characteristically, they contain at most 0.009 parts by weight (advantageously 0.002 to 0.009 parts by weight), per 100 parts by weight of monomers, of at least one photoinitiator. Characteristically, they may also contain at least one thermal catalyst for the subsequent implementation of the pre-polymerisation step, when it is a case of a thermal pre-polymerisation and of the (thermal) final polymerisation, in the hypothesis in which they are used for the implementation of the method of the invention.

They are advantageously of the type of the compositions according to FR-A-2,762,845 and characteristically they contain at least one acrylic monomer having at least three reactive functions (advantageously three to six reactive functions). Such compositions -mixtures of radically polymerisable monomers, presently claimed per se- comprise :

- at least one difunctional monomer, of type (a), of one or the other of the formulae (A) and (A') as defined above ;

- at least one difunctional monomer, of type (b), of one or the other of the formulae (B), (B') and (B") as defined above ;

and

- at least one acrylic monomer having at least three reactive functions, advantageously selected from the group consisting in:

+ pentaerythritol triacrylate,

+ pentaerythritol tetraacrylate,

+ propoxylated glycerol triacrylate,

+ trimethylolpropane triacrylate,

+ polyurethane triacrylate,

+ dipentaerythritol hexaacrylate.

Such compositions are able to further contain at least one monomer selected from the group consisting in :

- the monomers of type (c), of formula (C) (see above) ;
- the monomers of type (d), of formula (D) (see above) ;
- the monomers of type (e), of formula (E) (see above) ;
- the diallylphthalate (see above).

They advantageously contain :

- at least one difunctional monomer, of type (a), or formula (A), as defined above ;
- at least one difunctional monomer, of type (b), of formula (B), as defined above ;
- at least one acrylic monomer having at least three reactive functions, advantageously selected from the group consisting in:

+ pentaerythritol triacrylate,

+ pentaerythritol tetraacrylate,

+ propoxylated glycerol triacrylate,

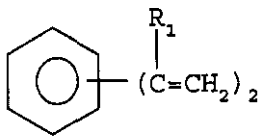
+ trimethylolpropane triacrylate,

+ polyurethane triacrylate,

+ dipentaerythritol hexaacrylate ;

- at least one aromatic divinylic monomer of formula (D) :

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in which R_1 = H or CH_3 ; said divinylic monomer advantageously consisting of divinylbenzene;

and

- at least one (meth)acrylic monomer of formula (E) :

$$CH_2 = C(R) \text{-} COOR'$$

in which R = H or CH_3 and R' is a straight or branched alkyl radical having 4 to 16 carbon atoms, an optionally substituted benzyl or phenoxyethyl radical or a polyethoxy group of formula $-(CH_2\text{-}CH_2\text{-}O)_nR''$ in which n is an integer between 1 and 10 and R" = CH_3 or C_2H_5 ; said (meth)acrylic monomer advantageously consisting of 2-ethylhexylmethacrylate.

The invention, under its different aspects, is illustrated by Examples 1, 1bis, 1ter to 4 below. Its interest reverts to the consideration of said Examples and the Comparative Examples 1 and 2.

Mixtures of monomers (novel *per se*, by virtue of the fact that they contain a low amount of photoinitiator) are polymerised according to the invention (thermal polymerisation + photochemical polymerisation) in order to obtain organic lenses (novel *per se*, when they intervene at least one acrylic monomer which is at least trifunctional, in the starting mixture).

• Preparation of the urea-ended difunctional oligomer of type (b)

In a thermostated glass reactor equipped with a thermometer, a stirrer, a nitrogen purge and a dropping funnel, the following are introduced with stirring :

300 g of JEFFAMINE® ED 2003 (poly(oxyethylene)diamine of average molecular mass 2,000) from Huntsman Corp., and

0.075 g of methoxyphenol.

When the JEFFAMINE has melted (homogeneous mixture) ,

700 g of JEFFAMINE® ED600 (poly(oxyethylene)diamine of average molecular mass 613) de Hunstman Corp. are added.

The temperature of the mixture is brought to 30°C, and 764 g of benzyl methacrylate are then added. The mixture is cooled to 20°C, and 528 g of 3-

isopropenyl-α,α-dimethylbenzylisocyanate (m-TMI® from Cytec) are then added slowly with vigorous stirring. The urea-ended difunctional oligomer of type (b) is thus obtained which is ready to be diluted with the other monomers and other additives which can intervene in a polymerisable composition to be polymerised according to the invention.

The product obtained in solution in benzyl methacrylate is designated by the abbreviation JEFF/BzMA.

• Abbreviations of the compounds :

Diacryl 121 : tetraethoxylated bisphenol A dimethacrylate : difunctional monomer of type (a)

BzMA : benzyl methacrylate

DVB : divinylbenzene

EHMA : ethylhexylmethacrylate

PETA : pentaerythritol triacrylate

NDM : n-dodecyl mercaptan (n-dodecanthiol)

JEFF/BzMA : cf. synthesis described above : difunctional oligomer of type (b)

IRGACURE 819 from CIBA : bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide

ADVN : 2,2'-azobis(2,4-dimethylpentanitrile)

CR49 : 2-(p-dimethylaminophenyl)-2-(p-methoxyphenyl)-5-methyl-7,9-dimethoxy-[2H]naphtho[1,2-b]pyran,

CR59 : 3-(p-methoxyphenyl)-3-phenyl-6-morpholino-3H-naphtho-[2,1-b]pyran,

Ruby Red : 3-phenyl-3-(4'-piperidinophenyl)-6-morpholino-3H-naphtho [2, 1b] pyran.

Example 1

α) Preparation of the mixture to be polymerised.

A 1 l thermostated glass reactor equipped with a stirrer, a thermometer and a nitrogen purge, is loaded with :

92 g of DVB, to which 0.456 g of CR49, 0.0536 g of CR59 as photochromic compounds, 2.08 g of ADVN as thermal initiator of radical polymerisation, 0.072 g of IRGACURE 819 as photoinitiator of radical polymerisation, are added.

The mixture thus obtained is maintained with stirring up to the total dissolution of the compounds at 25°C.

345.6 g of monomer of reference JEFF/BzMA, 338.4 g of Diacryl 121, 23.2 g of EHMA, 40 g of PETA and 4 g of NDM, are then added.

The mixture is maintained with stirring and under nitrogen purge for about 30 minutes at ambient temperature.

β) Thermal pre-polymerisation.

The temperature is then maintained at 46°C until a partially polymerised syrupy mixture is obtained which has a viscosity of 0.4 Pa.s. (about 35 min).

At this stage, the reaction is stopped by cooling the reaction mixture to 20°C and bubbling dry air in for 15 minutes.

The mixture (the resin) thus obtained is then pumped out *in vacuo* and maintained with stirring for about 2 hours.

γ) Photogelification.

This resin is then poured into a lens mould constituted of a mould and a glass counter-mould having a curved edge of about 87 mm and a PVC joint of thickness 11 mm.

The assemblies thus prepared are then exposed to the light of fluorescent tubes (Brillant 840 from Mazda, E=0.30 mW/cm^2 to 460 nm) until the resin gelifies, i.e. about 15 to 30 min.

δ) Thermal polymerisation.

The assemblies are then placed in an oven and are subjected to the following cycle :

- rise from 25 to 50°C in 5 h and then from 50 to 95°C in 3 h and finally a plateau at 95°C of 2 h.

After sufficient cooling, the samples are turned out of their moulds and inspected visually.

The samples prepared following this method of the invention possess no visible optical defect, such as striations, cords, fissuring ...

Examples 1bis and 1ter

α) Preparation of the mixtures to be polymerised.

A 1 l thermostated glass reactor equipped with a stirrer, a thermometer and a nitrogen purge is loaded with :

for Example 1bis		for Example 1ter	
338.4	g of JEFF/BzMA	338.4	g of JEFF/BzMA
331.2	g of Diacryl 121	331.2	g of Diacryl 121
90.4	g of DVB	90.4	g of DVB
39.2	g of PETA	39.2	g of PETA
0.456	g of CR49	0.352	g of CR49
0.0536	g of CR59	0.12	g of CR59
		0.0832	g of Ruby Red
4	g of NDM	4	g of NDM
0.072	g of Irgacure 819	0.072	g of Irgacure 819
2.08	g of ADVN	2.08	g of ADVN

The mixture thus obtained is maintained with stirring up to the total dissolution of the compounds at 25°C.

The said mixture is then maintained with stirring and under nitrogen purge for about 30 minutes at ambient temperature.

β) Thermal pre-polymerisation.

γ) Photogelification.

δ) Thermal polymerisation.

These successive operations are identical to those described previously in Example 1. The samples prepared following this method of the invention (grey samples for example 1bis, brown samples for example 1ter) possess no visible optical defect.

Example 2

The operations are identical to those described previously in Example 1, except for step (β) of partial thermal polymerisation at 46°C (pre-polymerisation) which in this case is replaced by a partial photopolymerisation step (β')

In order to do this, the glass reactor is subjected to a luminous flux originating from fluorescent tubes which are identical to those described in the preceding Example [E = 0.30 mW/cm^2].

The partially polymerised syrupy mixture having a viscosity of 0.4 Pa.s. is obtained after an exposure time of about 50 minutes at ambient temperature.

The operations that follow are identical as that described in Example 1.

The lenses obtained after turn-out are free from defects.

Example 3

Carried out in the same way as that described in Example 2 except that the photoinitiator IRGACURE 819 is introduced in two lots as follows :

0.032 g of IRGACURE 819 only are loaded into the reactor in order to enable the partial photopolymerisation of the mixture as indicated in Example 2.

The remainder, i.e. 0.040 g of IRGACURE 819 is added to the partially polymerised syrupy mixture (upon completion of step β')

The lenses obtained by following this method are free from optical defects.

Example 4

The operations are identical to those described in Example 3, except that the thermal polymerisation initiator, ADVN, is introduced after the partial photopolymerisation of the mixture, at the same time as the remainder of IRGACURE 819.

As previously, the lenses possess a very good optical quality.

Comparative Example 1

Carried out as in Example 1, but in omitting the gelification step (step γ) under fluorescent tube (logically, in step α, no IRGACURE 819 intervenes). The thermally partially polymerised mixture having a viscosity of 0.4 Pa.s. is therefore

poured directly into the moulds and then subjected to the curing cycle in an oven described in Example 1.

The lenses possess numerous striations and cords, which renders them unsuitable for a use such as for ophthalmic lenses.

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Comparative Example 2

Carried out as in Example 1, but by omitting the partial polymerisation step (thermal pre-polymerisation step β) of the mixture.

Thus, the composition is poured directly into the moulds and is exposed to
10 the luminous flux originating from the same fluorescent tubes as those used for the preceding Examples in order to ensure the gelification of the mixture.

The gelification time is then about 1 hour 30 minutes , and the lenses obtained have numerous defects (striations, cords).

CLAIMS

1. A method of preparing photochromic or non-photochromic organic pieces of optical quality and especially organic lenses, by radical polymerisation of a mixture of radically polymerisable monomers, characterised in that said method comprises :

a) adjusting, by pre-polymerisation, the viscosity of said mixture, to a value between 0.4 and 2 Pa.s ;

b) pouring said pre-polymerised mixture into a mould ;

c) photogelifying, in said mould, said pre-polymerised mixture until its gel point;

d) completing the polymerisation of said pre-polymerised and gelified mixture in said mould, by heat treatment ;

adding effective amounts of at least one thermal catalyst and of at least one photoinitiator in said mixture of monomers for the implementation of said pre-polymerisation, photogelification and polymerisation ; said photoinitiator(s) intervening in an amount less than or equal to 0.009 parts by weight per 100 parts by weight of said mixture of monomers.

2. The method according to claim 1, characterised in that said pre-polymerisation is a thermal or photochemical pre-polymerisation.

3. The method according to one of claims 1 or 2, characterised in that said pre-polymerisation is a thermal pre-polymerisation carried out on the mixture of monomers containing the effective amounts of thermal catalyst(s) and photoinitiator(s) or containing only the effective amount of thermal catalyst(s), the effective amount of photoinitiator(s) being then added to said mixture of monomers, upon completion of its thermal pre-polymerisation, before it is poured into the mould.

4. The method according to one of claims 1 or 2, characterised in that said pre-polymerisation is a photochemical pre-polymerisation carried out on the mixture of monomers containing the effective amount of photoinitiator(s) or advantageously only containing 40 % to 60 % of said effective amount expressed by weight, the remainder of photoinitiator(s) being then added to said mixture of monomers, upon completion of its photochemical pre-polymerisation, before it is poured into the mould; the effective amount of thermal catalyst(s) being added to said mixture of monomers before its photochemical pre-polymerisation, or upon completion thereof.

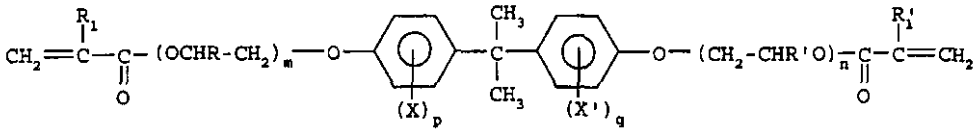
5. The method according to any one of claims 1 to 4, characterised in that said photogelification and said pre-polymerisation, in the case of a photochemical pre-polymerisation, are carried out under an irradiation which is predominantly in the visible and which is almost free from ultraviolet radiation.

6. The method according to any one of claims 1 to 5, characterised in that said mixture of monomers contains acrylic and/or methacrylic and/or alkenyl monomers, especially vinylic or allylic monomers.

7. The method according to any one of claims 1 to 6, characterised in that said mixture of monomers contains one or more difunctional monomers of type (a) and one or more difunctional monomers of type (b):

* *the difunctional monomer(s) of type (a) being of one or the other of the* formulae (A) and (A') below :

+ formula (A) :



in which :

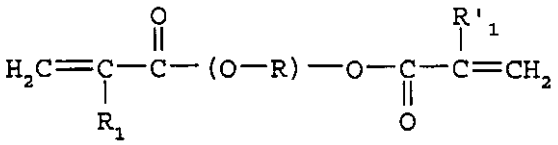
- R_1, R'_1, R and R', identical or different, are independently a hydrogen or a methyl group ;

- m and n are, independently, integers between 0 and 4 (inclusive) ; and are advantageously independently equal to 1 or 2 ;

- X and X', identical or different, are a halogen and preferably represent a chlorine and/or a bromine atom ;

- p and q are, independently, integers between 0 and 4 (inclusive) ;

+ formula (A') :



in which :

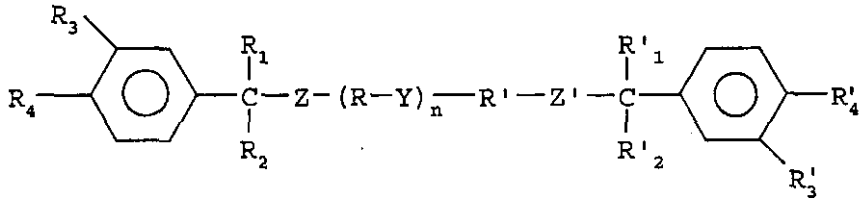
- R_1 and R'_1 , identical or different, are independently a hydrogen or a methyl group ;

- R is a straight or branched alkyl radical having 2 to 8 carbon atoms, a cycloalkyl radical having 3 to 6 carbon atoms, an ether radical of formula (R'-O-R") in which R'

and R", identical or different, are independently a straight or branched alkyl radical having 2 to 4 carbon atoms;

* the difunctional monomer(s) of type (b) - long chain alkenic difunctional oligomer - being of one or the other of the formulae (B), (B') and (B") below:

+ formula (B) :



in which :

- R_1, R'_1, R_2 and R'_2, identical or different, are independently hydrogen or a straight or branched alkyl radical, advantageously a straight alkyl radical, having 1 to 4 carbon atoms ; and correspond particularly advantageously to a methyl group ;

- R_3 and R_4, different, are independently one hydrogen and the other an alkenyl radical having 2 to 6 carbon atoms, advantageously 2 to 4 carbon atoms and particularly advantageously an isopropenyl radical ;

- R'_3 and R'_4, different, are independently one hydrogen and the other an alkenyl radical having 2 to 6 carbon atoms, advantageously 2 to 4 carbon atoms and particularly advantageously an isopropenyl radical ;

- Z represents a carbamate function (-NH-CO-O-), a thiocarbamate function (-NH-CO-S-) or a urea function (-NH-CO-NH-) ;

- Z', independent from Z and advantageously respectively with respect to Z, represents a carbamate function (-O-CO-NH-), a thiocarbamate function (-S-CO-NH-) or a urea function (-NH-CO-NH-) ;

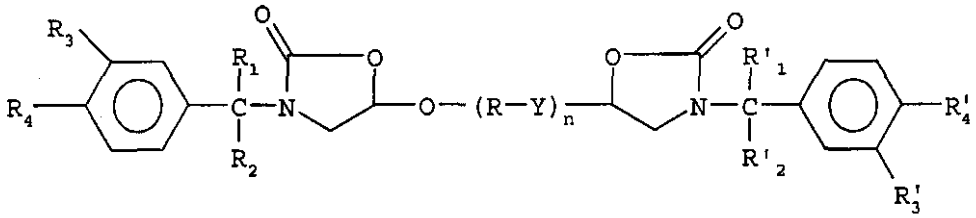
- R' represents a straight or branched alkyl radical having 2 to 4 carbon atoms ;

- R, identical or different when $n \geq 2$, is a straight or branched alkyl radical having 2 to 4 carbon atoms ;

- Y, identical or different when $n \geq 2$, is oxygen or sulphur ;

- n is an integer defined such that the total number of carbon atoms, contained in the long chain situated between the two moieties Z and Z', be at least equal to 18 and advantageously be between 18 and 112 (inclusive) ;

+ formula (B') :

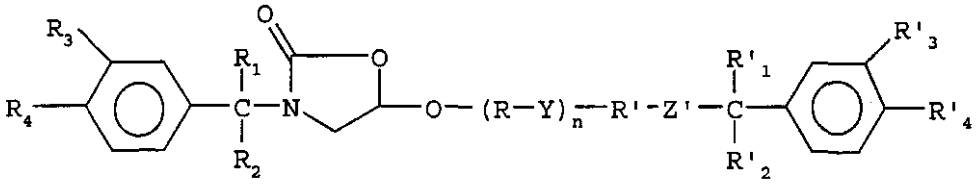


in which :

- R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3, R'_4, R and Y are as defined above with reference to formula (B);

- n is an integer defined such that the total number of carbon atoms, contained in the long chain of moiety $(R\text{-}Y)_n$, be at least equal to 22 and advantageously be between 22 and 104 (inclusive);

+ formula (B") :



in which :

- R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3, R'_4, R, R' and Y are as defined above with reference to formula (B);

- Z' is a carbamate function (-O-CO-NH-) or Z' is a thiocarbamate function (-S-CO-NH-); advantageously Z' is a carbamate function ;

- n is an integer defined such that the total number of carbon atoms, contained in the long chain of moiety $(R\text{-}Y)_n\text{-}R'$, be at least equal to 22 and advantageously be between 22 and 104 (inclusive).

8. The method according to claim 7, characterised in that said mixture of monomers contains at least one monomer of type (b) - vinylic difunctional monomer - of formula (B) in which :

- Z and Z' are urea functions (-NH-CO-NH-) ;

- R_1, R'_1, R_2 and R'_2 are identical and represent a methyl group ;

- R_3 and R'_3, identical, represent an isopropenyl group ;

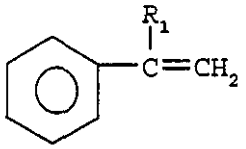
- R_4 and R'_4, identical, are hydrogen ;

- R' represents an ethylene or propylene group;

- n is an integer equal to 13 or 19 which defines a total number of carbon atoms, between Z and Z', equal to 28 or 40 when $(R\text{-}Y)_n$ is a polyoxyethylene chain; or n is an integer equal to 10 or 14 which defines a total number of carbon atoms, between Z and Z', equal to 33 or 45 when $(R\text{-}Y)_n$ is a polyoxypropylene chain; or n is an integer between the lower limit values (n is between 10 and 13 (inclusive)) and upper limit values (n is between 14 and 19 (inclusive)), when $(R\text{-}Y)_n$ is a polyoxyethylene/polyoxypropylene mixed chain.

9. The method according to any one of claims 1 or 8, characterised in that said mixture of monomers further contains :

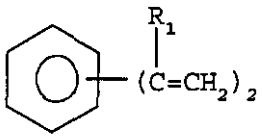
(c) at least one aromatic monovinylic monomer of formula (C) :



in which R_1 = H or CH_3 ; said monovinylic monomer advantageously consisting of styrene ;

and/or

(d) at least one aromatic divinylic monomer of formula (D) :



in which R_1 = H or CH_3 ; said divinylic monomer advantageously consisting of divinylbenzene;

and/or

(e) at least one (meth)acrylic monomer of formula (E) :

$$CH_2 = C(R) \text{-} COOR'$$

in which R = H or CH_3 and R' is a straight or branched alkyl radical having 4 to 16 carbon atoms, an optionally substituted benzyl or phenoxyethyl radical or a polyethoxy group of formula $-(CH_2\text{-}CH_2\text{-}O)_nR''$ in which n is an integer between 1 and 10 and R" = CH_3 or C_2H_5 ; said (meth)acrylic monomer advantageously consisting of 2-ethylhexylmethacrylate ;

and/or

(f) diallylphthalate.

10. The method according to any one of claims 1 to 9, characterised in that said mixture of monomers contains at least one acrylic monomer having at least three reactive functions, advantageously selected from :

- pentaerythritol triacrylate,
- pentaerythritol tetraacrylate,
- propoxylated glycerol triacrylate,
- trimethylolpropane triacrylate,
- polyurethane triacrylate,
- dipentaerythritol hexaacrylate,

and preferably consisting of pentaerythritol triacrylate.

11. The method according to any one of claims 1 to 10, characterised in that said mixture of monomers contains an effective amount of at least one photochromic colorant intended to give photochromic properties to the prepared pieces ; said colorant(s) being advantageously selected from the group of spiroxazines, chromenes, and mixtures thereof.

12. The method according to any one of claims 1 to 11, characterised in that said thermal catalyst is selected from diazo compounds and advantageously consists of 2, 2'-azobis (2,4-dimethylvaleronitrile)(ADVN).

13. The method according to any one of claims 1 to 12, characterised in that said photoinitiator is selected from acyl oxides and diacylphosphine oxides and advantageously consists of a diacylphosphine oxide.

14. The method according to any one of claims 1 to 13, characterised in that it is used for preparing pieces the thickness of which is between 0.2 and 20 mm.

15. Organic pieces of optical quality and especially organic lenses preparable by the method according to any one of claims 10 to 14.

16. Mixtures of radically polymerisable monomers, containing or not containing an effective amount of at least one photochromic colorant, characterised in that they contain up to 0.009 parts by weight, and advantageously 0.002 to 0.009 parts by weight, per 100 parts by weight of said mixtures of monomers, of at least one photoinitiator.

17. Mixtures of radically polymerisable monomers, containing or not containing an effective amount of at least one photochromic colorant, characterized in that they comprise:

- at least one difunctional monomer, of type (a), of one or the other of the formulae (A) and (A') as defined in claim 7;

- at least one difunctional monomer, of type (b), of one or the other of the formulae (B), (B') and (B") as defined in claim 7 ;

and

- at least one acrylic monomer having at least three reactive functions, advantageously selected from the group consisting in:

+ pentaerythritol triacrylate,

+ pentaerythritol tetraacrylate,

+ propoxylated glycerol triacrylate,

+ trimethylolpropane triacrylate,

+ polyurethane triacrylate,

+ dipentaerythritol hexaacrylate.

18. Mixtures of radically polymerisable monomers according to claim 17, characterized in that they comprise:

- at least one difunctional monomer, of type (a), or formula (A), as defined in claim 7 ;

- at least one difunctional monomer, of type (b), of formula (B), as defined in claim 7 ;

- at least one acrylic monomer having at least three reactive functions, advantageously selected from the group consisting in:

+ pentaerythritol triacrylate,

+ pentaerythritol tetraacrylate,

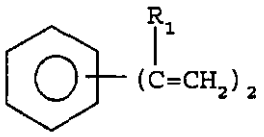
+ propoxylated glycerol triacrylate,

+ trimethylolpropane triacrylate,

+ polyurethane triacrylate,

+ dipentaerythritol hexaacrylate ;

- at least one aromatic divinylic monomer of formula (D) :



in which R_1 = H or CH_3 ; said divinylic monomer advantageously consisting of divinylbenzene;

and

- at least one (meth)acrylic monomer of formula (E) :

$$CH_2 = C(R) \text{-} COOR'$$

in which R = H or CH_3 and R' is a straight or branched alkyl radical having 4 to 16 carbon atoms, an optionally substituted benzyl or phenoxyethyl radical or a polyethoxy group of formula $-(CH_2\text{-}CH_2\text{-}O)_nR''$ in which n is an integer between 1 and 10 and R" = CH_3 or C_2H_5 ; said (meth)acrylic monomer advantageously consisting of 2-ethylhexylmethacrylate.

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权利要求书6页 说明书21页 附图页数0页

[54]发明名称 具有光学质量的有机片材尤其是有机透镜的制备

[57]摘要

本发明的主要目的是一种制备具有光学质量的光致变色或非光致变色有机片材、尤其是有机透镜的方法，该方法是使可自由基聚合的单体混合物发生自由基聚合，其特征在于该方法包括：a)通过预聚合调节所述混合物粘度至0.4－2Pa·s之间；b)将所述预聚合的混合物倒入模具内；c)使所述预聚合的混合物在所述模具内光胶凝化至其胶凝点；d)通过热处理使所述预聚合的且胶凝化的混合物在所述模具中完成聚合；为实现所述预聚合、光胶凝化和聚合，在所述单体混合物中掺入有效量的至少一种热催化剂和至少一种光敏引发剂；每100重量份所述单体混合物中掺入所述光敏引发剂的量少于或等于0.009重量份。

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权 利 要 求 书

1．一种制备具有光学质量的光致变色或非光致变色有机片材、尤其是有机透镜的方法，该方法是使可自由基聚合的单体混合物发生自由基聚合，其特征在于所述方法包括：

a)通过预聚合调节所述混合物的粘度至 0.4-2Pa·s 之间；

b)将所述预聚合的混合物倒入模具内；

c)使所述预聚合的混合物在所述模具内光胶凝化，直至其胶凝点；

d)通过热处理使所述预聚合的且胶凝化的混合物在所述模具中完成聚合；

在实现所述预聚合、光胶凝化和聚合的所述单体混合物中加入有效量的至少一种热催化剂和至少一种光敏引发剂；每 100 重量份所述单体混合物中掺入所述光敏引发剂的量少于或等于 0.009 重量份。

2．根据权利要求 1 所述的方法，其特征在于，所述预聚合是热预聚合或光化学预聚合。

3．根据权利要求 1 或 2 之一所述的方法，其特征在于，所述预聚合是在单体混合物上进行的热预聚合，所述单体混合物含有有效量的热催化剂和光敏引发剂，或只含有效量的热催化剂，而有效量的光敏引发剂是在单体混合物热预聚合完成后、倒入模具之前加入所述单体混合物内的。

4．根据权利要求 1 或 2 之一所述的方法，其特征在于，所述预聚合是在单体混合物上进行的光化学预聚合，所述单体混合物含有有效量的光敏引发剂，或宜只含所述有效量的 40-60%重量，而其余的光敏引发剂是在所述单体混合物光化学预聚合完成后、倒入模具之前加入所述单体混合物中的；有效量的热催化剂是在所述单体混合物光化学预聚合之前或预聚合完成后加入单体混合物中的。

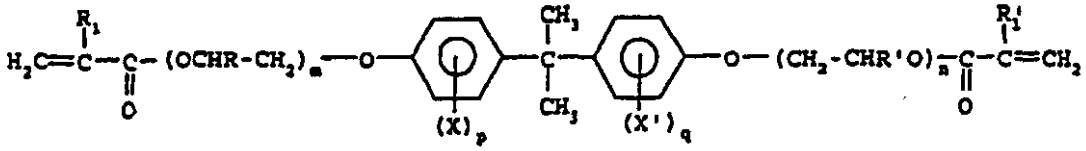
5．根据权利要求 1-4 任一项所述的方法，其特征在于，在光化学预聚合的情况下，所述光胶凝化和所述预聚合在辐照下进行，所述辐照主要在可见光内且几乎没有紫外辐射。

6．根据权利要求 1-5 任一项所述的方法，其特征在于，所述单体混合物含有丙烯酸和/或甲基丙烯酸和/或链烯基单体，尤其是乙烯基单体或烯丙基单体。

7．根据权利要求 1-6 任一项所述的方法，其特征在于，所述单体混合物含有一种或多种(a)型双官能单体以及一种或多种(b)型双官能单体：

*(a)型双官能单体是具有下式(A)或(A')的一种或其它单体：

+式(A)：



其中：

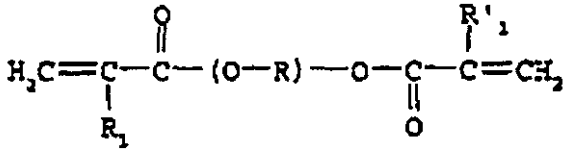
-R_1、R'_1、R 和 R'是相同或不同的，独立为氢或甲基；

-m 和 n 独立为 0-4 的整数，包括 0 和 4；较佳的独立等于 1 或 2；

-X 或 X'是相同或不同的，是卤素，较佳的代表氯和/或溴原子；

-p 和 q 独立为 0-4 的整数，包括 0 和 4；

+式(A')：



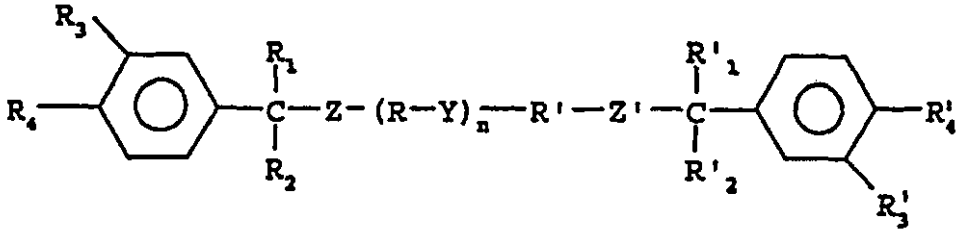
其中：

-R_1 和 R'_1 是相同或不同的，独立为氢或甲基；

-R 是有 2-8 个碳原子的直链或支链烷基、有 3-6 个碳原子的环烷基、式为(R'-O-R")的醚基，其中 R'和 R"是相同或不同的，独立为有 2-4 个碳原子的直链或支链烷基；

*(b)型双官能单体—长链烯双官能低聚物，它是具有下式(B)、(B')和(B")的一种或其它单体：

+式(B)：



其中：

-R_1、R'_1、R_2 和 R'_2 是相同或不同的，独立为氢或直链或支链烷基，较佳的为有 1-4 个碳原子的直链烷基；特别佳的对应于甲基；

-R_3 和 R_4 是不同的，一个独立为氢，另一个是有 2-6 个碳原子的链烯基，较佳的有 2-4 个碳原子，特别佳的是异丙烯基；

-R'_3 和 R'_4 是不同的，一个独立为氢，另一个是有 2-6 个碳原子的链烯基，较佳的有 2-4 个碳原子，特别佳的是异丙烯基；

-Z 代表氨基甲酸官能团-NH-CO-O-、硫代氨基甲酸官能团-NH-CO-S-或脲官能团-NH-CO-NH-；

-Z'独立于 Z，较佳的分别对应于 Z，代表氨基甲酸官能团-O-CO-NH-、硫代氨基甲酸官能团-S-CO-NH-或脲官能团-NH-CO-NH-；

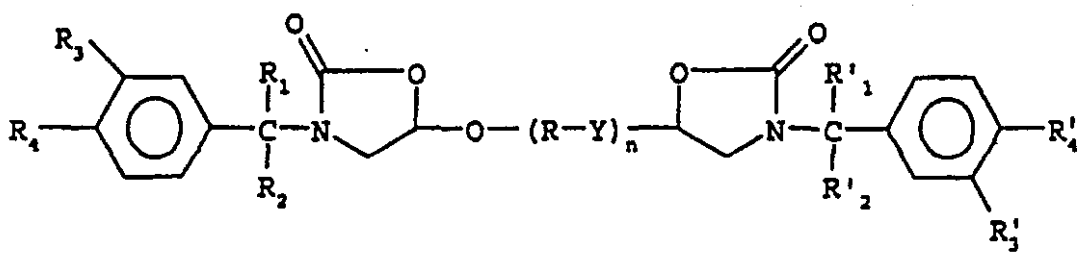
-R'代表有 2-4 个碳原子的直链或支链烷基；

-R 是相同或不同的，当 n≥2 时，是有 2-4 个碳原子的直链或支链烷基；

-Y 是相同或不同的，当 n≥2 时，是氧或硫；

-n 是定义为 Z 和 Z'两个部分之间长链所含碳原子总数的整数，它至少等于 18，较佳的在 18-112 之间，包括 18 和 112；

+式(B')：

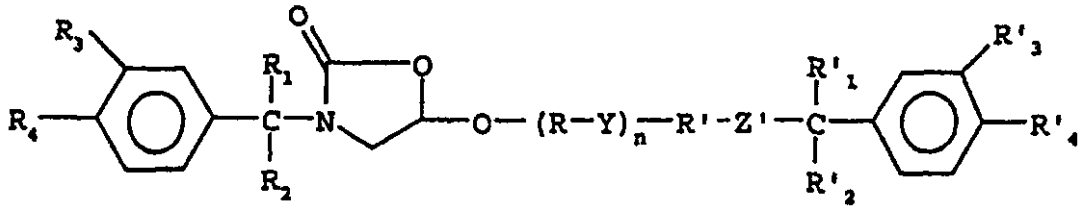


其中：

$-R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3,R'_4$,R 和 Y 如式(B)所定义；

-n 是定义为 (R-Y)n 部分长链中含有的碳原子总数的整数，它至少等于 22，较佳的在 22-104 之间，包括 22 和 104；

+式(B")：



其中

$-R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3,R'_4$,R,R'和 Y 如式(B)所定义；

-Z'是氨基甲酸酯官能团-O-CO-NH-，或 Z'是硫代氨基甲酸酯-S-CO-NH-官能团；较佳的，Z'是氨基甲酸酯官能团；

-n 是定义为 (R-Y)n-R'部分长链中含有的碳原子总数的整数，它至少等于 22，较佳的在 22-104 之间，包括 22 和 104。

8．根据权利要求 7 所述的方法，其特征在于，所述单体混合物含有至少一种式（B）的（b）型单体，乙烯基双官能单体：

-Z 和 Z'是脲官能团-NH-CO-NH-；

$-R_1,R'_1,R_2$ 和 R'_2 是相同的，代表甲基；

$-R_3$ 和 R'_3 是相同的，代表异丙烯基；

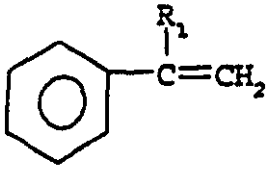
-R_4和 R'_4是相同的，代表氢；

-R'代表亚乙基或亚丙基；

-n 是 13 或 19，当(R-Y)n 是多氧乙烯链时，它确定了 Z 和 Z'之间的碳原子总数为 28 或 40；或 n 是 10 或 14，当(R-Y)n 是聚氧丙烯链时，它确定了 Z 和 Z'之间的碳原子总数为 33 或 45；或当(R-Y)n 是聚氧乙烯/聚氧丙烯混合链时，n 是下限值和上限值之间的整数，下限值在 10-13 之间并包括 10 和 13，上限值在 14-19 之间并包括 14 和 19。

9．根据权利要求 1-8 任一项所述的方法，其特征在于，所述单体混合物进一步包含：

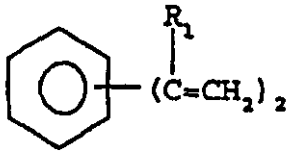
(c)至少一种式(C)的芳族单乙烯基单体：



其中 R_1=H 或 CH_3；所述单乙烯基单体宜由苯乙烯组成；

和/或

(d)至少一种式(D)的芳族二乙烯基单体：



其中 R_1=H 或 CH_3；所述二乙烯基单体宜由二乙烯基苯组成；

和/或

(e)至少一种式(E)的(甲基)丙烯酸单体：

$$CH_2=C(R)\text{-}COOR'$$

其中 R=H 或 CH_3，R'是有 4-16 个碳原子的直链或支链烷基，被任选取代的苄基或苯氧基乙基，或是式-$(CH_2\text{-}CH_2\text{-}O)_nR''$的聚乙氧基，其中 n 是 1-10 的整数，R''=CH_3 或 C_2H_5；所述(甲基)丙烯酸单体宜由甲基丙烯酸 2-乙基己酯组成；

和/或

(f)邻苯二甲酸二烯丙酯。

10．根据权利要求 1-9 任一项所述的方法，其特征在于，所述单体混合物含有至少一种具有至少三个反应官能团的丙烯酸单体，较佳的单体选自：

-三丙烯酸季戊四醇酯，

-四丙烯酸季戊四醇酯，

-丙氧基化的甘油三丙烯酸酯，

-三羟甲基丙烷三丙烯酸酯，

-聚氨酯三丙烯酸酯，

-六丙烯酸二季戊四醇酯，

较佳的由三丙烯酸季戊四醇酯组成。

11．根据权利要求 1-10 任一项所述的方法，其特征在于，所述单体混合物含有有效量的至少一种待赋予制得的片材光致变色性能的光致变色着色剂；所述着色剂宜选自螺噁嗪、色烯及其混合物。

12．根据权利要求 1-11 任一项所述的方法，其特征在于，所述热催化剂选自重氮化合物，较佳的由 2,2'-偶氮二(2,4-二甲基戊腈)ADVN 组成。

13．根据权利要求 1-12 任一项所述的方法，其特征在于所述光敏引发剂选自氧化酰和二酰基氧化膦，较佳的由二酰基氧化膦组成。

14．根据权利要求 1-13 任一项所述的方法，其特征在于它用来制备厚度在 0.2-20 毫米之间的片材。

15．具有光学质量的有机片材尤其是有机透镜，它可用权利要求 10-14 任一项所述的方法制得。

16．可自由基聚合的单体的混合物，它含有或不含有效量的至少一种光致变色着色剂，其特征在于，每 100 份重量所述单体混合物中含有高达 0.009 份重量，较佳的为 0.002-0.009 份重量的至少一种光敏引发剂。

17．可自由基聚合的单体的混合物，它含有或不含有效量的至少一种光致变色着色剂，其特征在于，它们包含：

-至少一种如权利要求 7 定义的式(A)或（A'）的(a)型双官能单体；

-至少一种如权利要求 7 定义的式(B)、（B'）或（B"）的(b)型双官能单体；

和

-至少一种具有至少三个反应官能团的丙烯酸单体，较佳的单体选自：

+三丙烯酸季戊四醇酯，

+四丙烯酸季戊四醇酯，

+丙氧基化的甘油三丙烯酸酯，

+三羟甲基丙烷三丙烯酸酯，

+聚氨酯三丙烯酸酯，

+六丙烯酸二季戊四醇酯。

18．根据权利要求 17 所述的可自由基聚合的单体的混合物，其特征在于，它们

包含：

-至少一种如权利要求 7 定义的式(A)的(a)型双官能单体；

-至少一种如权利要求 7 定义的式(B)的(b)型双官能单体；

-至少一种具有至少三个反应官能团的丙烯酸单体，较佳的单体选自：

+三丙烯酸季戊四醇酯，

+四丙烯酸季戊四醇酯，

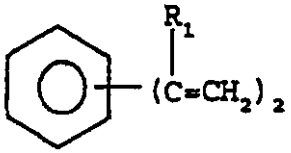
+丙氧基化的甘油三丙烯酸酯，

+三羟甲基丙烷三丙烯酸酯，

+聚氨酯三丙烯酸酯，

+六丙烯酸二季戊四醇酯。

-至少一种式(D)的芳族二乙烯基单体：



其中 R_1=H 或 CH_3；所述二乙烯基单体宜由二乙烯基苯组成；

和

-至少一种式(E)的(甲基)丙烯酸单体：

$$CH_2=C(R)-COOR'$$

其中 R=H 或 CH_3，R'是有 4-16 个碳原子的直链或支链烷基，被任选取代的苄基或苯氧基乙基，或是下式-$(CH_2-CH_2-O)_nR''$的聚乙氧基，其中 n 是 1-10 的整数，R"=CH_3 或 C_2H_5；所述(甲基)丙烯酸单体宜由甲基丙烯酸 2-乙基己酯组成。

说　明　书

具有光学质量的有机片材尤其是有机透镜的制备

本发明涉及具有光学质量的有机片材的制备，尤其涉及有机透镜的制备。更具体地说，本发明的主要目的是通过可自由基聚合的单体混合物自由基聚合制备这种光致变色或非光致变色有机片材的初始方法。

本发明的目的还有：

•可用所述方法的变化方案制得的此类新的有机片材；该变化方案利用了特定的单体；

•新的可自由基聚合的组合物，它是可自由基聚合单体的混合物，可用来根据本发明的方法制备此类有机片材。

下面具体参照有机透镜(视力矫正眼镜、防护眼镜)的制备内容描述了本发明。本发明绝对没有局限于所述的这些内容，本领域技术人员很容易理解，本发明所要求的方法适合获得任何类型的模制的没有光学缺陷的有机片材，例如是有机透镜、以及窗口、光学片材等。

申请人已经描述了含有或不含有效量的至少一种光致变色着色剂的单体混合物(主要是丙烯酸和/或(甲基)丙烯酸和/或链烯基单体，尤其是乙烯基单体)自由基聚合的单纯的热方法，并且已实施该方法来制备光致变色或非光致变色的有机透镜(主要是光学或眼用镜头)。所述方法在镜头模具中在一混合物上进行，该混合物含有有效量的至少一种合适的热催化剂或自由基聚合引发剂。当掺入至少一种光致变色着色剂时，所述催化剂通常选自重氮化合物(称为“软”催化剂，它对存在的光致变色着色剂呈“惰性”)。这些方法并不完全令人满意，因为它们的进行过程很长，而且在所述进行过程中氧气会不可避免地扩散入正在聚合的混合物中，该氧气来自周围的空气，其通过模具密封接头进入模具。这使制得的镜头在外观和约束方面产生缺陷(光学缺陷)。

美国专利 US-A-5 621 017 中描述了制备这些有机透镜的其它方法。该方法根据的是含有有效量(每 100 重量份单体 0.01-1 重量份)的至少一种合适的光敏引发剂的单体混合物在紫外辐照下光聚合。该方法也不令人完全满意，尤其是因为：

-根据所存在单体的特征、至少一种光致变色着色剂(显示它是光敏引发剂的吸收竞争者)的存在以及针对镜头成品建立的规格，可能显示很难或甚至不可能寻找到令

人满意的操作条件(光敏引发剂/辐照频带的特征)。

-其应用领域有限。实际上，它可能适合制备厚度较小的镜头(镜头成品的厚度为2毫米(见US-A-5 621 017的实施例))，但是它不适合制备较厚的镜头(例如厚度大于10毫米的镜头半成品)。实际上，然后会遇到紫外辐射穿透待聚合材料的问题。为了克服这一困难，预计可以使用在吸收可见光的光敏引发剂。然而，为了确保获得合适的结果，即在整个厚度内均匀地完全聚合，仍然需要采用高浓度的光敏引发剂并用大量能量。在这些条件(严格的聚合条件)下，通常获得了高度发黄的镜头。无论如何，在使用低浓度光敏引发剂(它不易产生发黄)时，很难在整个材料中获得完全聚合。

在这种情况下，申请人已经开发出一种制备有机片材的新方法，该方法能获得没有光学缺陷、有相对合理的厚度的所述片材，且该片材可从各种单体混合物获得(甚至是从已知较难聚合的混合物获得)。所述新方法可看作是混合的方法，因为它包括热聚合和光化学聚合。

下面将说明制备有机片材尤其是有机透镜的所述初始方法。其特征在于，该方法包括光胶凝化作用，并采用了少量光敏引发剂。本发明的方法实际上包括通过可自由基聚合的单体混合物的聚合来制备光致变色或非光致变色的有机片材，所述混合物含有实际上通常用于制备片材或镜头的组分：单体类型的基质的主要和次要组成，更常用的常规添加剂，尤其例如是热催化剂、光致变色的着色剂等)，该方法的步骤依次如下：

a)通过预聚合调节所述混合物的粘度至0.4-2Pa·s之间；

b)将所述预聚合的混合物倒入模具(尤其是用于制备镜头的镜头模具)内；

c)使所述预聚合的混合物在所述模具内光胶凝化，直至其胶凝点；

d)通过热处理使所述预聚合的且胶凝化的混合物在所述模具中完成聚合；

称为预聚合(a)、光胶凝化(c)和聚合(d)的步骤是由本发明实现的，在所述单体混合物中加入有效量的至少一种热催化剂和至少一种光敏引发剂；每100重量份所述单体混合物中掺入所述光敏引发剂的量少于或等于0.009重量份。

根据本发明的方法，使含有待制备片材组成成分的混合物首先预聚合，然后将其倒入模具中。在模具外进行这样的预聚合是非常有利的，因为：

-它能中和所述混合物中的抑制剂(这种聚合抑制剂不可避免地存在于市售产品中)；

-它能提高和调节随后待倒入模具中的混合物的粘度。在所述模具中，在预聚合的因此有粘性的混合物上实现的聚合是在最佳环境下进行的，因为在这种粘稠的混合物内，氧气的扩散更慢，因此掺入的光敏引发剂的性能得到改善，收缩减少，并更快

地获得胶凝点；

-它能在完全密封的容器中(即没有氧气存在)进行，因此其时间没有限制。

为了使混合物的粘度值达到 0.4-2Pa·s 之间，强烈建议进行所述的预聚合。低于 0.4，所述预聚合的有益效果很难体现出来(尤其是在氧气扩散方面)；高于 2，预聚合混合物的操作会遇到问题，且胶凝点太靠近。

本发明的预聚合通常是热或光化学预聚合，其进行分别需要待预聚合的混合物中存在有效量的至少一种热催化剂和至少一种光敏引发剂。

因此，为了进行热预聚合，在方法一开始就必须在单体混合物中掺入至少一种热催化剂(通常是一种热催化剂)。通常是加入有效量 q，以使所述热预聚合(步骤 a)以及随后最终热聚合的步骤(步骤 d)得以进行。然而，本发明的内容并不排除分两批加入(第一批用量为 q_1，该用量是进行热预聚合的有效量，在所述预聚合前加入；第二批用量为 q_2($q_1+q_2=q$)，该用量是进行最终热聚合的有效量，在所述热预聚合之后加入，较佳的是在紧接热预聚合后、在预聚合混合物倒入模具内之前加入)。假设在进行该热预聚合时，待预聚合的混合物中也可有利地掺入进一步进行光胶凝化所需量的光敏引发剂。然而，所述用量也可在热预聚合完成后、预聚合的混合物倒入模具中之前加入。

因此，较佳的是，预聚合是在单体混合物上进行的热预聚合，该混合物含有有效量的热催化剂和光敏引发剂，或只含有有效量的热催化剂，而有效量的光敏引发剂是在所述单体混合物热预聚合完成后、倒入模具内之前加入单体混合物中的。

为了进行光化学预聚合，在方法一开始就必须在单体混合物中掺入至少一种光敏引发剂(通常是一种光敏引发剂)。所述光敏引发剂可在一开始就加入有效的量 Q，以确保所述光化学预聚合(步骤 a)和随后的光胶凝化步骤(步骤 c)能够进行。较佳的，光敏引发剂可分两批加入，第一批用量(Q_1)是在所述预聚合前加入的进行光化学预聚合的有效量，第二批用量(Q_2，$Q_1+Q_2=Q$)是进行光胶凝化的有效量，它可在所述光化学预聚合后加入，较佳的是在紧接光化学预聚合之后、在预聚合混合物倒入模具内之前加入。假设在进行该光化学预聚合时，以后用于最终热聚合(步骤 d)的热催化剂可在所述光化学预聚合之前或其完成后(在预聚合的混合物倒入模具内之前)加入。

因此，根据实现本发明方法步骤 a 的另一方案，预聚合是在单体混合物上进行的光化学预聚合，所述单体混合物含有有效量的光敏引发剂，或较佳的只含所述有效量的 40-60%(用重量表示)，而其余的光敏引发剂是在所述单体混合物光化学预聚合完成后、倒入模具之前加入所述单体混合物中的；有效量的热催化剂是在所述单体混合物光化学预聚合之前或预聚合完成后加入单体混合物中的。

下面参照本发明方法的预聚合步骤(步骤 a)作进一步的详细说明。可以看出该步

骤大体上是热或光化学预聚合。并不完全排除在热和合适辐射的组合作用下进行预聚合，即进行热预聚合以及光化学预聚合，这样，催化剂和光敏引发剂一同在单体混合物内起作用。

然后将步骤 a 的预聚合的混合物倒入模具内。

混合物的聚合在所述模具中结束，其特征在于这是一个两个连续的步骤：

-光胶凝化直至其胶凝点，和

-最终的或补充的热聚合。

加入用来实现本发明混合方法的光敏引发剂将三个步骤中的光化学聚合(步骤 c 和任选的步骤 a)和热聚合(步骤 d 和任选的步骤 a)结合起来，在任一情况下，其加入量是有限的—等于或小于 0.009 重量份/100 重量份单体，因此它不可能是有害的，尤其是在发黄的问题上。

另外，如果是光化学预聚合的情况，通过在主要在可见光中的辐射(即几乎没有紫外辐射)下进行光胶凝化和预聚合，可优化所述光敏引发剂的掺入。实际上，常规的 UV 灯是不适合的。强烈建议用这些 UV 灯时使用 UV 滤光器。然而，如果是光化学预聚合的场合，建议用荧光管作为主要为可见光的辐射源(其最大功率在 400 纳米以外，例如为 410 纳米或 460 纳米)进行本发明方法的光胶凝化步骤和预聚合步骤。此类辐射穿透受辐照材料的厚度，并且很难干扰任选存在的光致变色着色剂。

现在本领域技术人员已经了解了本发明混合方法的所有方面(包括热和光化学聚合)，该混合方法包括三个主要步骤(预聚合/光致变色胶凝化/热聚合)，该方法能获得外观和约束上没有缺陷的薄的和厚的片材(尤其是镜头)，这是因为聚合是在模具(尤其是镜头模具)中迅速进行的，而氧气的扩散被减少到最低程度。

本发明的感兴趣之处还在于它适合不同类型单体((甲基)丙烯酸单体、乙烯基单体等)混合物、尤其是混合的类型((甲基)丙烯酸单体和乙烯基单体)的聚合。根据本发明聚合的单体混合物实际上可含有丙烯酸和/或(甲基)丙烯酸和/或链烯基单体，尤其是乙烯或烯丙基单体。

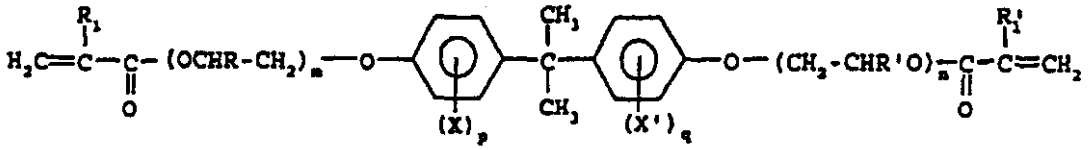
较佳的，所述混合物主要含有下述的(a)型双官能单体和(b)型双官能单体。申请人在 1997 年 5 月 2 日提交的、FR 97 05 458 专利申请(公布号为 FR-A-2,,762,,845)中描述了基于这两类不同单体的组合物。已经表明，它们通过本发明方法来制备具有光学用途的有机片材、尤其是有机透镜的用途是特别有利的。申请人在研究塑料材料(尤其可用于眼用，可通过(热的)单体自由基共聚获得)的光学性能(甚至是光致变色性能)与机械性能之间的折衷方案时，开发出该组合物。所述组合物的特征在于，它包括至少一种短链(甲基)丙烯酸双官能单体和至少一种长链烯双官能单体。因此，它们聚合

产生的树脂具有纳米相结构，该结构提供了所需的性能。所述短链(甲基)丙烯酸双官能单体((a)型，式(A),(A')：见下文)实际上产生刚性，该刚性通过所述长链烯双官能单体((b)型，式(B),(B'),(B")：见下文)的存在来调节，令人惊奇的是，该烯双官能单体也能为所述组合物提供优良的光致变色性能。因此，所述(a)型和(b)型单体的官能度差别有利地减慢了所得可聚合组合物的胶凝化。这一特征使得从所述组合物获得的树脂具有优良的光学性能(尤其是在其中掺入了光致变色着色剂的场合)，且能迅速地最好地表现出光致变色性能。

因此，特别佳的是，本发明方法是用含有至少一种(a)型双官能单体和至少一种(b)型双官能单体的单体混合物来实现的：

*(a)型双官能单体—(甲基)丙烯酸，它是具有下式(A)或(A')的一种或其它单体：

+式(A)：



其中：

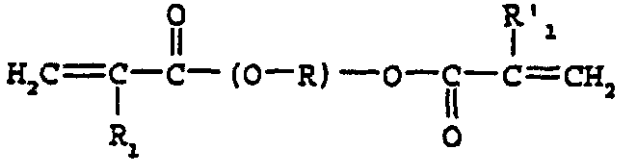
-R_1、R'_1、R 和 R'是相同或不同的，独立为氢或甲基；

-m 和 n 独立为 0-4 的整数(包括 0 和 4)；较佳的独立等于 1 或 2；

-X 或 X'是相同或不同的，是卤素，较佳的代表氯和/或溴原子；

-p 和 q 独立为 0-4 的整数(包括 0 和 4)；

+式(A')：



其中：

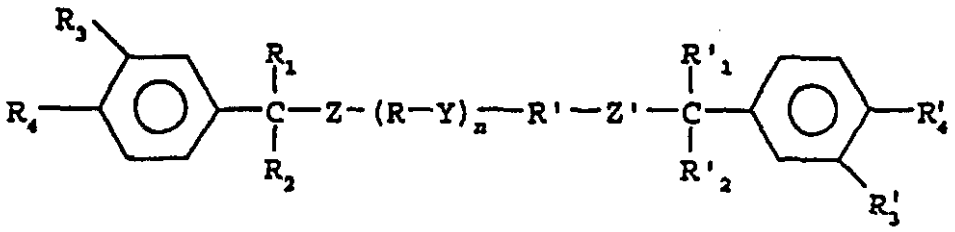
-R_1 和 R'_1 是相同或不同的，独立为氢或甲基；

-R 是有 2-8 个碳原子的直链或支链烷基、有 3-6 个碳原子的环烷基、式为(R'-O-R")的醚基，其中 R'和 R"是相同或不同的，独立为有 2-4 个碳原子的直链或支链烷基；

*(b)型双官能单体—长链烯双官能低聚物，它是具有下式(B)、(B')和(B")的一种或其它单体：

+式(B)：

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其中：

-R_1、R'_1、R_2 和 R'_2 是相同或不同的，独立为氢或直链或支链烷基，较佳的为有 1-4 个碳原子的直链；特别佳的为甲基；

-R_3 和 R_4 是不同的，一个独立为氢，另一个是有 2-6 个碳原子的链烯基，较佳的有 2-4 个碳原子，特别佳的是异丙烯基；

-R'_3 和 R'_4 是不同的，一个独立为氢，另一个是有 2-6 个碳原子的链烯基，较佳的有 2-4 个碳原子，特别佳的是异丙烯基；

(较佳的，分子的两个末端是相同的；即 R_3=R'_3，R_4=R'_4)；

-Z 代表氨基甲酸官能团(-NH-CO-O-)、硫代氨基甲酸官能团(-NH-CO-S-)或脲官能团(-NH-CO-NH-)；

-Z'独立于 Z，较佳的分别对应于 Z，代表氨基甲酸官能团(-O-CO-NH-)、硫代氨基甲酸官能团(-S-CO-NH-)或脲官能团(-NH-CO-NH-)；

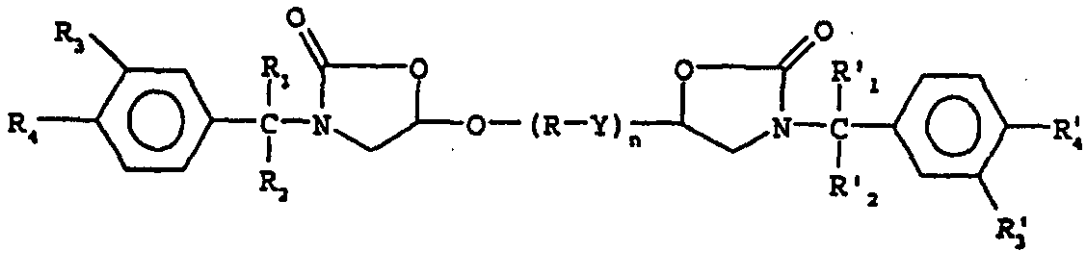
-R'代表有 2-4 个碳原子的直链或支链烷基；

-R 是相同或不同的，当 n≥2 时，是有 2-4 个碳原子的直链或支链烷基；

-Y 是相同或不同的，当 n≥2 时，是氧或硫；

-n 是定义为两个部分 Z 和 Z'之间长链所含碳原子总数的整数，它至少等于 18，较佳的在 18-112 之间(包括 18 和 112)；

+式(B')：



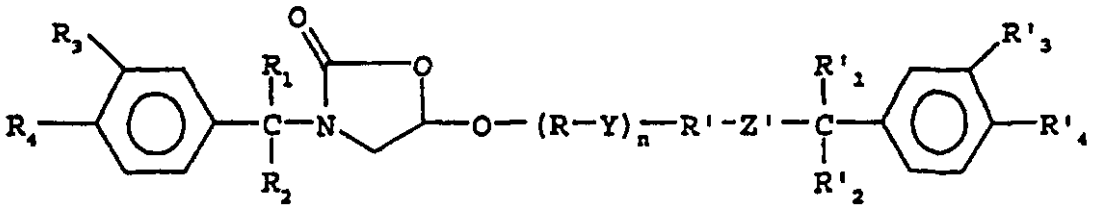
其中：

-R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3,R'_4,R 和 Y 如式(B)所定义；

-n 是定义为部分(R-Y)n 长链中含有的碳原子总数的整数，它至少等于 22，较佳的在 22-104 之间(包括 22 和 104)；

+式(B")：

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其中：

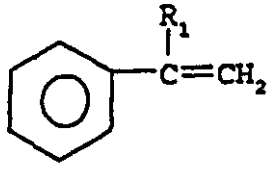
-R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3,R'_4,R,R'和 Y 如式(B)所定义；

-Z'是氨基甲酸酯官能团(-O-CO-NH-)，或 Z'是硫代氨基甲酸酯(-S-CO-NH-)官能团；较佳的，Z'是氨基甲酸酯官能团；

-n 是定义为部分(R-Y)n-R'长链中含有的碳原子总数的整数，它至少等于 22，较佳的在 22-104 之间(包括 22 和 104)。

另外，所述(a)和(b)型单体的混合物可进一步含有：

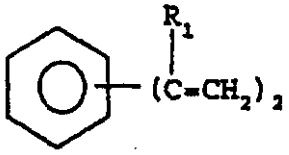
(c)至少一种式(C)的芳族单乙烯基单体：



其中 R_1=H 或 CH_3；所述单乙烯基单体宜由苯乙烯组成；

和/或

(d)至少一种式(D)的芳族二乙烯基单体：



其中 R_1=H 或 CH_3；所述二乙烯基单体宜由二乙烯基苯组成；

和/或

(e)至少一种式(E)的(甲基)丙烯酸单体：

$$CH_2=C(R)-COOR'$$

其中 R=H 或 CH_3，R'是有 4-16 个碳原子的直链或支链烷基，被任选取代的苄基或苯氧基乙基(通常被 C_1-C_6 烷基取代)，或是式-$(CH_2-CH_2-O)_nR$"的聚乙氧基，其中 n 是 1-10 的整数，R"=CH_3 或 C_2H_5；所述(甲基)丙烯酸单体宜由甲基丙烯酸 2-乙基己酯组成；

和/或

(f)邻苯二甲酸二烯丙酯。

上述(c)至(f)的混合物宜掺入(a)型和(b)型双官能单体。较佳的，它们可掺入任何根据本发明方法聚合的单体混合物中。

下面将说明掺入或可能掺入可根据本发明方法聚合的混合物中的每种组分的特征和用量。

(a)型单体可能具有或不具有全部相同的式(A)或(A')。因此，根据本发明聚合的混合物宜包含：

-具有相同式(A)的单体(至少一种)；

-或具有相同式(A')的单体(至少一种)；

-或不同式(A)单体的混合物(不混合)；

-或不同式(A')单体的混合物(不混合)；

-或式(A)和式(A')单体的混合物(混合)。

本发明的一个较佳方案采用一种或多种对称的(a)型单体。所述具有式(A)或(A')的(a)型单体(其中 R_1 和 R'_1 相同，R 和 R'相同，式(A)化合物的 X 和 X'取代基相同)被认为是对称的。

所述式(A)的(a)型对称单体是已知的，本领域技术人员可市售购得或容易获得。可能注意到，芳族环上没有卤素的所述单体实际上对应于 WO-A-92/05209 文献中式(I)的第一个单体。本领域技术人员利用在所述芳族环上合适取代的衍生物很容易获得芳族环上有卤素的式(A)的(a)型单体。在本发明中，较佳的式(A)单体是，其中相同的 R 和 R'是氢或甲基，R_1 和 R'_1 是甲基，m 和 n 独立为 1 或 2，p=q=0。特别佳的变化方案对应于上述类型的式(A)单体，其中 R=R'=H，m=n=2。所述单体特别由 Akzo Nobel (NL) 以 DIACRYL 121 的商品名出售。式(A)的不对称单体的合成对于本领域技术人员来说不成问题。

式(A')的单体(a)也是众所周知的，它可通过脂族二醇或短链烷撑二醇(所述链中最多有 8 个碳原子)与至少一种(甲基)丙烯酸衍生物的常规反应获得，这取决于是希望获得末端对称还是不对称的式(A')单体。

这些(a)型单体掺入待聚合混合物中的比例通常为每 100 重量份(a)型和(b)型单体混合物中 40-99 重量份。如果其掺入量较少，则可聚合的组合物在其聚合期间有收缩的趋势，诱导过早切断(premature turn-out)，进而导致树脂成品的光学性能变差。

式(B),(B')和(B")的单体(b)是长链双官能烯单体。所述单体具有或不具有或多或少的显著的对称性(R_1/R'_1，R_2/R'_2，R_3/R'_3，R_4/R'_4，Z/Z')。

这些单体(b)型可能具有或不具有全部相同的式(B)、(B')或(B")。因此，根据本发明聚合的混合物宜包含：

-相同式(B)的单体(至少一种)；

-或相同式(B')的单体(至少一种)；

-或相同式(B")的单体(至少一种)；

-或不同式(B)的单体的混合物(不混合)；

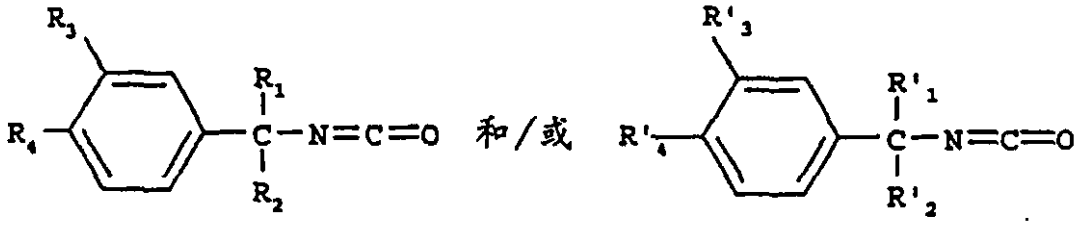
-或不同式(B')的单体的混合物(不混合)；

-或不同式(B")的单体的混合物(不混合)；

-或选自式(B)单体、式(B')单体和式(B")单体的单体混合物(混合的，二元或三元)。

(b)型单体是长链烯双官能低聚物，所述链是聚氧化烯或聚巯基亚烷基链甚至是混合链，它通过下列物质之间的反应根据常规有机合成条件来获得：

-一种或几种式 I 和/或 II 的具有链烯基异氰酸酯型官能团的衍生物：



式 I　　式 II

其中 R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3 和 R'_4 如上定义。根据本发明的一个较佳方案，所用的(b)型单体其末端是对称的。为了实现这个目的，采用一种类型的链烯基异氰酸酯衍生物(因此式 I 和式 II 是相同的)。在一个特别佳的方案中，使用了乙烯基异氰酸酯衍生物，其中 R_1=R_2=CH_3(或 R'_1=R'_2=CH_3)，R_3(或 R'_3)是异丙烯基，R_4(或 R'_4)是氢，因此它对应于 3-异丙烯基-α,α-二甲基苄基-异氰酸酯(通用名为 m-TMI®)。由所述衍生物获得的低聚物(b)是较佳的；

-以及内在具有长链的化合物，所述化合物是：

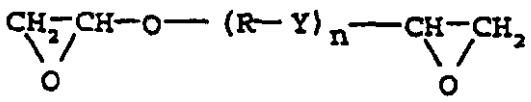
*末端官能团对称的化合物，它对应于：

+式 HO-(R-Y)n-R'-OH 的二硫醇；

+或式 HS-(R-Y)n-R'-SH 的二醇；

+或式 H_2N-(R-Y)n-R'-NH_2 的二胺；它能获得所述内部对称的式(B)低聚物(内部对称指式(B)的单体中 Z 和 Z'基团是具有相同特征的官能团)；

+或下式的二环氧化合物，



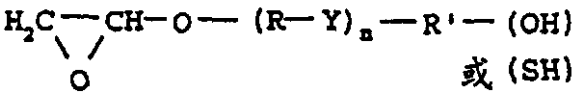
该反应导致合适所述式(B')低聚物；

*或末端官能团不对称的化合物：

+所述官能团可以是醇、硫醇或胺官能团；其所有的组合均是可能的：这些化合物能获得其它内在不对称的双官能的式(B)低聚物(内在不对称指式(B)单体中 Z 和 Z'

基团是具有不同特征的官能团)；

+所述官能团分别是环氧官能团和醇官能团，或环氧官能团和硫醇官能团，然后该化合物具有下式

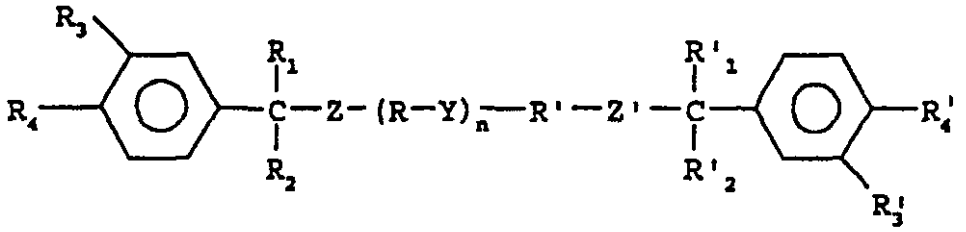


该反应导致合成所述式(B")低聚物。

在各种情况下，R,R',Y 和 n 如上定义；较佳的，Y 是氧(则长链是聚氧化烯链)。

对应于上述所述式(B,B',B")的(R-Y)n-R'或(R-Y)n 基团的聚氧化烯和/或聚巯基亚烷基长链的分子量通常至少等于 500 克/摩尔且低于 2000 克/摩尔，较佳的，所述分子量在 600-900 克/摩尔之间。

在一个特别佳的方案中，掺入一种或几种内部对称的式(B)的(b)型单体(如上定义)：



其中 R,R',R_1,R_2,R_3,R_4,R'_1,R'_2,R'_3 和 R'_4 如上定义(较佳的是分子的两个端基是相同的；即 $R_1=R'_1$，$R_2=R'_2$，$R_3=R'_3$，$R_4=R'_4$，更佳的是 $R_1=R'_1=R_2=R'_2=CH_3$，且 $R_3=R'_3$，$R_4=R'_4$，R_3 和 R_4 中的一个是氢，其它是异丙烯基)，Y 如上定义，较佳的由氧(X=O)组成，且；

(α)-Z 和 Z'分别是式(-NH-CO-O-)和(-O-CO-NH-)的氨基甲酸酯官能团；

-n 是定义两个基元 Z 和 Z'之间的长链中碳原子总数的整数，它在 18 和 112 之间；较佳的，就聚氧化烯链而言，它在 24 和 112 之间；特别佳的是，当聚氧化烯分子量在 600-900 克/摩尔内时，它在 26-50 之间；

或(β)-Z 和 Z'分别是式(-NH-CO-S-)和(-S-CO-NH-)的硫代氨基甲酸酯官能团；

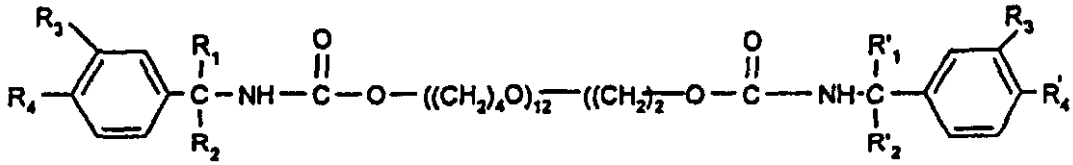
-n 是定义两个基元 Z 和 Z'之间的长链中碳原子总数的整数，它在 18 和 108 之间；较佳的，就聚氧化烯链而言，它在 24 和 108 之间；特别佳的是，当聚氧化烯分子量在 600-900 克/摩尔内时，它在 28-46 之间；

或(γ)-Z 和 Z'是脲官能团(-NH-CO-NH-)；

-n 是定义两个基元 Z 和 Z'之间的长链中碳原子总数的整数，它在 18 和 112 之间；较佳的，就聚氧化烯链而言，它在 24 和 112 之间；特别佳的是，当聚氧化烯分子量在 600-900 克/摩尔内时，它在 28-50 之间。

本领域技术人员将会理解，其长链中所含碳原子数等于 50 的上述情况(α)下，式

(B)例如可写成如下：



同样，本领域技术人员将会理解，定义基元(R-Y)n-R'或(R-Y)n 长链中碳原子数的最小值对应于具有聚巯基亚烷基链(Y=S)的化合物。

在一个特别佳的方案中，所述(b)型单体具有上述定义的通式(B)，其中：

-R_1,R_2,R'_1 和 R'_2 是相同的，是甲基；R_3 和 R'_3 是异丙烯基；R_4 和 R'_4 是氢，且

+Z 和 Z'是脲官能团(-NH-CO-NH-)和

-R'代表亚乙基或亚丙基；

-n 是 13 或 19 的整数，当(R-Y)n 是聚氧乙烯链时，它确定了 Z 和 Z'之间的碳原子总数为 28 或 40；或 n 是 10 或 14 的整数，当(R-Y)n 是聚氧丙烯链时，它确定了 Z 和 Z'之间的碳原子总数为 33 或 45；或当(R-Y)n 是聚氧乙烯/聚氧丙烯混合链时，n 是如上定义的下限值(10-13)和上限值(14-19)之间的整数；因此，当 n 具有下限值之一(n 在 10 和 13 之间，包括 10 和 13)时以及 n 具有上限值之一(n 在 14-19 之间，包括 14 和 19)时，它确定了通用名为 RUDI JEF 600 和 RUDI JEF 900(见 FR 97 05458 中的实施例)的(b)型单体；

+或 Z 和 Z'分别是式(-NH-CO-O-)和(-O-CO-NH)的氨基甲酸酯，且

-R'代表亚乙基；

(R-Y)n 代表聚氧乙烯长链；

-n 是 13 或 19，它确定了两个基元 Z 和 Z'之间的长链所含碳原子总数等于 28 或 40；因此当 n 分别为 13 和 19 时，它确定了通用名为 RUDI 600 和 RUDI 900(见 FR 97 05458 的实施例)的(b)型单体。

特别佳的是，用上述(b)型单体(上述通式(B)，其中 Z 和 Z'是脲官能团)与上述(a)型单体在混合物中进行本发明的初始方法。

(b)型单体掺入待聚合混合物中的比例通常为每 100 重量份(a)型和(b)型单体混合物中 1-60 重量份。

如上所述，本发明待聚合的混合物还可含有其它单体与上述(a)型和(b)单体组合或不组合。对于 100 重量份(a)型和(b)型单体的混合物，所述混合物可含有 1-60 重量份(较佳的为 10-50 重量份)至少一种单体，该单体选自烯单体(如式(C)和(D)的那些单体以及邻苯二甲酸二烯丙酯(f))，较佳的是乙烯基单体和烯丙基单体、(甲基)丙烯酸单体(如式(E)的那些单体)及其混合物。根据所需寻找的效果，当加入这些类型的单体后，

本领域技术人员会知道怎样确定和优化所述每种单体的掺入量(其任何情况下，所述单体掺入待聚合组合物的总量在(a)型和(b)型单体混合物的 1-60 重量份之间)。

式(C)的乙烯基单体(苯乙烯和/或甲基苯乙烯)与(a)型单体组合插入，以便松开网状结构。在此阶段掺入苯乙烯可能是特别有利的，因为该聚合的化合物具有相当高的折射率(n=1.595)。所述苯乙烯提供了此类单体的特别佳的化合物。

式(D)化合物由二乙烯基苯(DVB)或二(甲基乙烯基)苯组成。二乙烯基苯是特别佳的式(D)化合物。至少一种式(D)化合物的掺入可能表现出是有利的，因为所述化合物明显以通常的方式缓和了式(C)化合物的效果。式(D)化合物的有益作用明显表现在光致变色性能上。关于二乙烯基苯，由于此聚合的化合物具有相当高的折射率(n=1.61)，因此它的掺入也是有利的，因为它使本发明聚合物的折射率增加。

较佳的，根据本发明方法聚合的混合物还含有至少一种式(E)化合物。它是如上所述的(甲基)丙烯酸单体。它也可以是(甲基)丙烯酸丁酯、戊酯、己酯、庚酯、辛酯或 2-乙基己酯，或甚至是乙基三乙二醇(甲基)丙烯酸酯。甲基丙烯酸 2-乙基己酯(EHMA)是较佳的式(E)化合物。此类化合物的存在对于聚合材料的生产以及随后最终处理的进行是有利的。

最后，可聚合的组合物可含有邻苯二甲酸二烯丙酯，它能显著调节折射率和/或其它光学和机械性能。

如上所述，式(C)和/或式(D)和/或式(E)和/或邻苯二甲酸二烯丙酯的掺入不是必要的。然而，它的确显示出优点。

类似的，在根据本发明初始方法聚合的单体混合物中掺入至少一种丙烯酸单体是非常有利的，所述丙烯酸单体至少是三官能的(即具有至少三种反应官能团：三个双键，较佳的是具有 3-6 个反应官能团)。所述单体作为最终基质的组成单体掺入，但是最重要的是作为预聚合(步骤 a)和光胶凝化(步骤 c)的加速剂。

它宜选自：

-三丙烯酸季戊四醇酯，

-四丙烯酸季戊四醇酯，

-丙氧基化的甘油三丙烯酸酯，

-三羟甲基丙烷三丙烯酸酯，

-聚氨酯三丙烯酸酯，

-六丙烯酸二季戊四醇酯，

较佳的由三丙烯酸季戊四醇酯组成。

它的掺入(替换至少部分双官能丙烯酸单体或是除丙烯酸和/或甲基丙烯酸和/或

链烯基单体混合物外另行加入)改善了聚合动力学，且没有在最终产品中引入任何缺陷。

通常，聚合加速剂(所述至少三官能的丙烯酸单体)掺入的比例为待根据本发明聚合的单体混合物总重量的 2-10%重量(较佳的为 4-6%重量)。

在说明了构成本发明方法制得片材的组成元件的单体特征后，我们下面说明待掺入单体混合物的添加剂，掺入添加剂一方面是使单体混合物能根据本发明聚合，另一方面是为了为制得的片材提供光致变色性能(如果这需要的话)。

因此，待根据本发明初始方法聚合的单体混合物可含有有效量的至少一种光致变色着色剂，以便为制得的片材提供光致变色性能。

所述着色剂宜选自赋予光致变色性能的螺噁嗪(spiroxazine)和色烯(或其组合)。大量此类光致变色着色剂在文献中有所描述并且是市售的。

可用于本发明的螺噁嗪着色剂在下列文献中有所描述：专利 US-A-3,563,172, 4,634,767, 4,637,968, 4,720,547, 4,756,973, 4,785,097, 4,792,224, 4,816,584, 4,831,142, 4,909,963, 4,931,219, 4,936,995, 4,986,934, 5,114,621, 5,139,707, 5,233,038, 4,215,010, 4,342,668, 4,699,473, 4,851,530, 4,913,544, 5,171,636, 5,180,524, 5,166,345、专利申请 EP-A- 0 508 219, 0 232 295 和 0 171 909 以及申请 FR-A-2 738 248(本申请人的申请)。

特别建议在本发明中使用 1,3-二氢-3,3-二甲基-1-新戊基-6'-(4"-N,N-二乙基-氨基)-螺-[2H]-吲哚-2,3'-3H-萘并[2,1-b][1,4]噁嗪以及申请 FR-A-2 738 248 中描述的螺噁嗪。

可用于本发明的色烯着色剂在下列文献中有所描述：美国专利 US-A-3,567,605, 4,889,413, 4,913,221, 5,200,116, 5,066,818, 5,224,602, 5,238,981, 5,106,998, 4,980,089, 5,130,058，以及申请 EP-A-0 562 915。所述色烯可由萘并吡喃组成。

特别建议在本发明中使用 2,2-双-(4'-甲氧基苯基)-5,6-二甲基-[2H]-萘并[1,2-b]吡喃。

螺吡喃也可用于本发明，其在下列文献中有所描述：

· PHOTOCHROMISM G. Brown 编，Techniques of Chemistry, Wiley Interscience, III 卷，1971，第 III 章，45-294 页，R.C. Bertelson。

· PHOTOCHROMISM-Molecules & Systems，H.Durr 编，H. Bouas-Laurent-Elsevier 1990，第 8 章：螺吡喃，314-455 页，R. Gugliemetti。

所有这些文献的内容均纳入本文作为参考。

本发明也不排除掺入其它光致变色着色剂(如俘精酸酐)。

在本发明中掺入螺噁嗪和/或色烯在大都是较佳的。

已经表明，根据本发明聚合的打算制备光致变色片材(尤其是镜头)的混合物含有有效量的至少一种光致变色着色剂。在本发明中，实际上通常掺入了光致变色着色剂的组合物，其目的是在增黑状态下获得特定的颜色。在本发明的特别佳的实施方案中，掺入的光致变色填充剂含有色烯的组合。特别佳的组合是以下的色烯：2-(对-二甲氨基苯基)-2-(对甲氧基苯基)-5-甲基-7,9-二甲氧基-[2H]-萘并-[1,2-b]吡喃和 3-(对甲氧基苯基)-3-苯基-6-吗啉代-[3H]-萘并[2,1-b]吡喃。该组合能获得有趣的灰色。

通过参考而没有限制，本文已经表明所述光致变色着色剂掺入本发明待聚合混合物(以及已经聚合的那些混合物)的比例为单体总重量的 0.01-1%(重量)，较佳的比例为 0.05-0.5%(重量)。

所述着色剂本身化学式中也可含有可聚合的和/或可交联的反应基团。然后它们作为共聚单体掺入待聚合的混合物中；并且它们被化学结合，即接枝到所述结合组合物的基体上。通常，本发明的片材所含的光致变色着色剂与其基体结合或游离在基体外。

根据本发明聚合的单体混合物在进行步骤 a 和/或仅仅步骤 c 之前(见上文)，还含有有效量的热催化剂和光敏引发剂。

通常可掺入热催化剂型的单独添加剂或光敏引发剂型的单独添加剂。

热催化剂通常所用的比例为单体重量的 0.01-1%(重量)，较佳的为 0.05-0.5%(重量)。热催化剂必须对任选存在的光致变色着色剂是明显“惰性的”。热催化剂任选地选自重氮化合物。这些化合物对于本领域技术人员来说是熟知的，可市售购得。这些重氮化合物的例子是偶氮二异丁腈(AIBN)、2,2'-偶氮二(2-甲基丁腈)(AMBN)和 2,2'-偶氮二(2,4-二甲基戊腈(valeonitrile))(ADVN)。更特别建议在后一重氮化合物 ADVN 存在下进行本发明的方法。

在没有此热催化剂存在或其存在量太少时，必须在较高温度下进行热预聚合和最终热聚合，这使得反应难以控制。存在过多催化剂时，可能会产生过量的自由基，该过量的自由基诱导破坏任选存在的光致变色着色剂，加速最终材料的老化。在后一假设中，预聚合和聚合也有可能加速并难以控制。

本领域技术人员根据上述说明，尤其是是存在单体的特征，能够理解在每种情况下掺入的有效量。聚合改性剂宜以本身已知的方式与所述热催化剂组合掺入。

聚合改性剂掺入的最大比例通常为待共聚单体重量的 5%重量，较佳的为 0.1-2%重量。本文注意到，如果制得的片材的厚度较小(e<2.0 毫米)，则该聚合改性剂可以不存在。在该假设的情况下，不会遇到热量排出的问题。为了制备厚度大于 2.0 毫米的本发明的树脂，存在上述量的聚合改性剂通常是适宜的。强烈建议不超过 5%的最大

含量，因为制得的材料的玻璃转化温度太低。对于厚度在 1.5-20 毫米之间的片材的制备，强烈建议聚合改性剂的含量约为 1.2%。已经注意到根据本发明制得的光致变色片材(尤其是镜头)的着色性和变黑动力学随掺入的聚合改性剂的量而增加。同样，当该用量增加时，机械抗性和光学质量也增加。

显然所述聚合改性剂不应破坏在聚合期间任选存在的光致变色着色剂，和/或不应诱导材料本身变色。所述聚合改性剂宜为链转移剂。所述链转移剂可以是非卤代的链转移剂，如直链链烷硫醇或双-巯基乙醚。十二烷硫醇可作为直链烷硫醇的一个例子，它没有限制性。也不排除使用其它类型的链转移剂，如被至少一个芳基或烷基取代的链烷硫醇或硫代苯酚。所有这些化合物均是本领域技术人员熟知的，且可市售购得。

从上面已经看出，无论本发明方法变化方案如何进行，光敏引发剂均特征性地掺入有限量：每 100 份重量待聚合单体混合物小于或等于 0.009 重量份。它或它们掺入的量宜为 0.002-0.009 重量份。在该用量之下，光致变色聚合(在步骤 c 甚至步骤 a 中进行)会难以进行。高于该用量，会遇到现有技术中光化学聚合技术的问题。

通常掺入单独一种光敏引发剂。它尤其可以选自氧化酰和二酰基氧化膦。它宜由二酰基氧化膦组成。

顺便注意到，任选地进行光化学预聚合的辐照时间以及光胶凝化的辐照时间明显取决于辐照波长和强度，并取决于待聚合混合物的形状和厚度以及光敏引发剂的含量，所述辐照时间通常在实验测试后来选择。进行所述辐照，使光胶凝化通过模具至少一个侧壁的表面进行。

本发明也不排除掺入用于进行光化学聚合(步骤 c 以及任选的步骤 a)的足量的其它添加剂。

上面根据可以实施的方法和材料方面描述的本发明方法更特别适用于制备具有光学质量的有机片材，尤其是厚度在 0.2-20 毫米之间的镜头。如上文引言部分所述，本发明方法的应用领域在镜头方面不局限于薄的镜头(厚度例如局限在 2 毫米)。因此，本发明方法是特别令人感兴趣的。

从上文看出，根据本发明方法待聚合的单体混合物宜包含至少一种至少是三官能的丙烯酸单体。

用此类单体来制备具有光学质量的有机片材(尤其是有机透镜)是完全创新的。因此，通过含有至少一种至少三官能的此单体的单体混合物自由基聚合获得的有机片材是新的，它构成了本发明的另一个目的。所述有机片材本身是新的，它宜通过构成本发明第一目的的上述方法来制得。不排除用现有技术中单纯热的或单纯光化学的聚合

方法来获得这些片材。

本发明的最后一个目的涉及原创的可聚合的组合物，该组合物能构成起始产品，较佳的是采用本发明的方法，以获得具有光学质量的有机片材尤其是有机透镜。如上所述，所述组合物是可自由基聚合的单体的混合物。所述混合物任选地含有至少一种光致变色着色剂。它们可以是 US-A-5 621 017 的组合物类型，但是它们的特征在于每 100 重量份单体含有至多 0.009 重量份(较佳的为 0.002-0.009 重量份)的至少一种光敏引发剂。它们的特征还在于，在热预聚合和最终热聚合的场合下(假设用这些方法实现本发明的方法)，它们还含有至少一种用于随后进行预聚合步骤的热催化剂。

它们宜为 FR-A-2,762,845 中的组合物类型，特征是它们含有至少一种具有至少三个反应官能团(较佳的是 3-6 个反应官能团)的丙烯酸单体。本文本身要求的该组合物(可自由基聚合的单体的混合物)包含：

-至少一种具有上述式(A)和(A')任一的双官能(a)型单体；

-至少一种具有上述式(B),(B')和(B")任一的双官能(b)型单体；

和

-至少一种具有至少三个反应官能团的丙烯酸单体，较佳的单体选自：

+三丙烯酸季戊四醇酯，

+四丙烯酸季戊四醇酯，

+丙氧基化的甘油三丙烯酸酯，

+三羟甲基丙烷三丙烯酸酯，

+聚氨酯三丙烯酸酯，

+六丙烯酸二季戊四醇酯。

这些组合物能进一步含有至少一种选自下列的单体：

-具有式(C)(见上文)的(c)型单体；

-具有式(D)(见上文)的(d)型单体；

-具有式(E)(见上文)的(e)型单体；

-邻苯二甲酸二烯丙酯(见上文)。

它们宜含有：

-至少一种上述定义的式(A)的(a)型双官能单体；

-至少一种上述定义的式(B)的(b)型双官能单体；

-至少一种具有至少三个反应官能团的丙烯酸单体，较佳的单体选自：

+三丙烯酸季戊四醇酯，

+四丙烯酸季戊四醇酯，

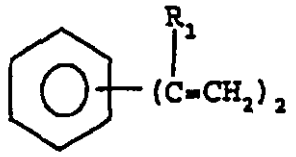
+丙氧基化的甘油三丙烯酸酯，

+三羟甲基丙烷三丙烯酸酯，

+聚氨酯三丙烯酸酯，

+六丙烯酸二季戊四醇酯。

-至少一种式(D)的芳族二乙烯基单体：



其中 R_1=H 或 CH_3；所述二乙烯基单体宜由二乙烯基苯组成；

和

-至少一种式(E)的(甲基)丙烯酸单体：

$$CH_2=C(R)-COOR'$$

其中 R=H 或 CH_3，R'是有 4-16 个碳原子的直链或支链烷基，被任选取代的苄基或苯氧基乙基，或是下式-$(CH_2-CH_2-O)_nR$"的聚乙氧基，其中 n 是 1-10 的整数，R"=CH_3 或 C_2H_5；所述(甲基)丙烯酸单体宜由甲基丙烯酸 2-乙基己酯组成。

下面参照实施例 1、1-2、1-3 或 4 描述本发明的不同方面。其特征回复到考虑所述实施例以及对比例 1 和 2。

根据本发明(热聚合+光化学聚合)聚合单体混合物(本身是新的，因为它们含有少量光敏引发剂)，以获得有机透镜(当起始混合物中掺入至少一种至少三官能的丙烯酸单体时，该有机透镜本身是新的)。

•脲端基(b)型双官能低聚物的制备

在装有温度计、搅拌器、氮气喷口和滴液漏斗的恒温玻璃反应器中，搅拌加入下列物质：

300 克 Huntsman Corp.的 JEFFAMINE®ED 2003(聚氧乙烯二胺，平均分子量 2000)

和

0.075 克甲氧基苯酚。

当 JEFFAMINE 熔化(形成均匀混合物)后，加入 700 克的 de Hunstamn Corp.的 JEFFAMINE® ED600(聚氧乙烯二胺，平均分子量为 613)。

使混合物温度变为 30℃，然后加入 764 克甲基丙烯酸苄酯。冷却混合物至 20℃，然后缓慢加入 528 克 3-异丙烯基-α,α-二甲基苄基异氰酸酯(m-TMI®，购自 Cytec)，并剧烈搅拌。然后获得脲端基(b)型双官能低聚物，它可用其它单体或添加剂稀释，这些单体或添加剂能掺入本发明待聚合的可聚合组合物中。

在甲基丙烯酸苄酯溶液中获得的产品用缩写 JEFF/BzMA 表示。

•化合物的缩写

Diacryl 121：四乙氧基化的双酚 A 二甲基丙烯酸酯：(a)型双官能单体

BzMA：甲基丙烯酸苄酯

DVB：二乙烯基苯

EHMA：甲基丙烯酸乙基己酯

PETA：三丙烯酸季戊四醇酯

NDM：正-十二烷基硫醇(正-十二烷基硫醇)

JEFF/BzMA：如上所述合成：(b)型双官能低聚物

CIBA 的 IRGACURE 819：双(2,4,6-三甲基苯甲酰)-苯基氧化膦

ADVN：2,2'-偶氮二(2,4-二甲基戊腈)

CR49：2-(对-二甲氨基苯基)-2-(对甲氧基苯基)-5-甲基-7,9-二甲氧基-[2H]萘并[1,2-b]吡喃

CR59：3-(对甲氧基苯基)-3-苯基-6-吗啉代-3H-萘并[2,1-b]吡喃

Ruby Red：3-苯基-3-(4'-哌啶子基苯基)-6-吗啉代-3H-萘并[2,1b]吡喃

实施例 1

α)待聚合混合物的制备

在装有搅拌器、温度计和氮气喷口的 1 升恒温玻璃反应器中加入 92 克 DVB，其中加入 0.456 克 CR49、0.0536 克 CR59 作为光致变色化合物，2.08 克 ADVN 作为自由基聚合的热引发剂，0.072 克 IRGACURE 819 作为自由基聚合的光敏引发剂。

对获得的混合物维持搅拌，直至各化合物在 25℃下全部溶解。

然后加入 345.6 克参照 JEFF/BzMA 的单体、338.4 克 Diacryl 121、23.2 克 EHMA、40 克 PETA 和 4 克 NDM。

维持对混合物搅拌，并在室温下充氮下维持大约 30 分钟。

β)热预聚合

然后保温于 46℃，直至获得粘度为 0.4Pa·s 的部分聚合的浆状混合物(大约 35 分钟)。

在此阶段，将反应混合物冷却至 20℃，吹入干燥空气 15 分钟，停止反应。

然后将如此获得的混合物(树脂)在真空中泵出，并维持搅拌大约 2 小时。

γ)光胶凝化

然后将该树脂倒入镜头模具中，该模具由模具和玻璃副模具组成，弯曲边缘约为

87 毫米，PVC 接头的厚度为 11 毫米。

然后将如此制得的装配件暴露于荧光管(Mazda 的 Brillant 840，E=0.30mW/cm^2，至 460 纳米)灯光下，直至树脂胶凝化(即大约 15-30 分钟)。

δ)热聚合

然后将装配件置于烘箱内，使其经历如下循环：

-在 5 小时内从 25℃升高至 50℃，然后在 3 小时内从 50℃升高至 95℃，最后在 95℃稳定 2 小时。

充分冷却后，从模具中取出样品，用肉眼观察。

根据本发明该方法制得的样品没有可见的光学缺陷(如擦痕、条纹、裂缝等)。

实施例 1-2 和 1-3

α)待聚合混合物的制备

在装有搅拌器、温度计和氮气喷口的 1 升恒温玻璃反应器中加入下列物质

实施例 1-2	实施例 1-3
338.4 克 JEFF/BzMA	338.4 克 JEFF/BzMA
331.2 克 Diacryl 121	331.2 克 Diacryl 121
90.4 克 DVB	90.4 克 DVB
39.2 克 PETA	39.2 克 PETA
0.456 克 CR49	0.352 克 CR49
0.0536 克 CR59	0.12 克 CR59
	0.0832 克 Ruby Red
4 克 NDM	4 克 NDM
0.072 克 Irgacure 819	0.072 克 Irgacure 819
2.08 克 ADVN	2.08 克 ADVN

对获得的混合维持搅拌，直至各化合物在 25℃下全部溶解。

维持对所述混合物的搅拌，并在室温下充氮下维持大约 30 分钟。

β)热预聚合

γ)光胶凝化

δ)热聚合

这些连续的操作与上文实施例 1 所述相同。

根据本发明该方法制得的样品(实施例 1-2 为灰色样品，实施例 1-3 为棕色样品)

没有可见的光学缺陷。

实施例 2

操作与上文实施例 1 所述相同，只是在本实施例中用部分光聚合步骤(β')代替在46℃下部分热聚合(预聚合)的步骤β。

为了进行该步骤，使玻璃反应器接受来自前一实施例所述的相同荧光管的光通量[$E=0.30mW/cm^2$]。

在室温下曝光约 50 分钟后，获得粘度为 0.4Pa·s 的部分聚合的浆状混合物。

然后的操作与实施例 1 相同。

取出后获得的镜头没有缺陷。

实施例 3

用与实施例 2 所述相同的方式进行，只是如下分两批加入光敏引发剂 IRGACURE 819：在反应器中只加入 0.032 克 IRGACURE 819，以使混合物如实施例 2 所述那样部分光聚合。

将其余的即 0.040 克 IRGACURE 819 加入部分聚合的浆状混合物中(在步骤β'完成后)。

根据该方法获得的镜头没有光学缺陷。

实施例 4

操作与实施例 3 描述的相同，只是在混合物部分光聚合后在与加入其余 IRGACURE 819 的同时加入热聚合引发剂 ADVN。

和前面一样，镜头具有非常好的光学质量。

对比例 1

对比例 1 如实施例 1 那样进行，只是省略了在荧光管下胶凝化的步骤(步骤γ)(逻辑上说是在步骤α中不掺入 IRGACURE 819)。然后将部分热聚合的粘度为 0.4Pa·s 的混合物直接倒入模具中，然后如实施例 1 所述在烘箱内经受固化循环。

镜头有许多擦痕和条纹，使得它们不适合用作(例如)眼用镜头。

对比例 2

对比例 2 如实施例 1 那样进行，只是省略了混合物的部分聚合步骤(热预聚合步

骤β)。

因此，将组合物直接倒入模具中，并曝光于来自荧光管(该荧光管与前面实施例所用的相同)的光通量下，以确保混合物胶凝化。

凝胶时间约为 1 小时 30 分钟，获得的镜头具有许多缺陷(擦痕，条纹)。