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(54) Title: NCO-TERMINATED VINYL TELOMERS

(54) Bezeichnung: NCO-TERMINALE VINYLTELOMERE

(57) Abstract

The invention concerns NCO-terminated vinyl telomers which are particularly suitable for use as surface-modifying agents and as coating materials, but also in the production of polymerizable compounds or block copolymers which react to give polymers which can be used to manufacture moulded articles, in particular contact lenses. The NCO-terminated vinyl telomers proposed are compounds of formula (I) $O=C=N-PI^*-(-A-)_p-R_a$ in which PI* is a bivalent photo-initiator group; A is a bivalent substituted 1,2-ethylene group derived from a copolymerizable vinyl monomer by replacing the vinyl double bond by a simple bond, each of the R_a groups, independently of each other, is a monovalent group suitable for use as chair terminator in a polymerization reaction; and p is a whole number from 3 to 500. The vinyl telomers carrying the NCO groups are of use in the production of macromers as well as block, comb, star and graft copolymers, preferably for the manufacture of contact lenses. These telomers are also of use in coating various types of surface, in particular the surfaces of contact lenses.

(57) Zusammenfassung

Die Erfindung betrifft neue NCO-terminale Vinyltelomere, die sich insbesondere für die Modifizierung von Oberflächen und als Beschichtungsmaterial eignen, darüber hinaus aber auch zur Herstellung von polymerisierbaren Verbindungen oder Blockcopolymeren, die sich zu Polymeren umsetzen respektive in Formkörper, insbesondere Kontaktlinsen, überführen lassen. Bei den erfindungsgemässen OCN-terminalen Vinyltelomeren handelt es sich um Verbindungen der Formel (I) $O=C=N-PI^*-(-A-)_p-R_a$, worin PI* für einen zweiwertigen Rest eines Photoinitiators steht, A für einen bivalenten, substituierten 1,2-Ethylenrest steht, der sich von einem copolymerisierbaren Vinylmonomer dadurch ableitet, dass die Vinyl-Doppelbindung durch eine Einfachbindung ersetzt ist, jedes R_a unabhängig voneinander für eine einwertige Gruppe steht, die geeignet ist, als Kettenabbrecher einer Polymerisation zu dienen, und p für eine ganze Zahl von 3 bis 500 steht. Die OCN-funktionellen Vinyltelomere finden Verwendung bei der Herstellung von Makromeren sowie von Block-, Kamm-, Stern- und Pfropfcopolymeren, die bevorzugt zur Herstellung von Kontaktlinsen dienen. Darüberhinaus dienen diese Telomere zur Beschichtung von verschiedenartigen Oberflächen, insbesondere Oberflächen von Kontaktlinsen.

CL/V-20675/P1

NCO-terminated vinyl telomers

The invention relates to novel NCO-terminated vinyl telomers that are suitable especially for the modification of surfaces and as coating materials, and are also suitable for the preparation of polymerisable compounds and segmented copolymers that can be reacted to form polymers and converted into mouldings, respectively, to mouldings comprising such polymers, to the use of the polymers for producing mouldings and to processes for the preparation of the polymers and for the production of the mouldings. Preferred mouldings are opthalmic lenses, especially contact lenses. The vinyl telomers are distinguished from known vinyl telomers *inter alia* by a narrower molecular weight distribution of the chain lengths formed from the vinyl monomer(s) used, and by the fact that they are mono-functionalised with the isocyanate group, which is especially reactive.

The OCN-terminated vinyl telomers according to the invention are compounds of formula I

$$O{=}C{=}N\text{-}PI^{*}\text{-}(A)_{p}\text{-}R_{a} \qquad (I)$$

wherein

PI^* is a bivalent radical of a photoinitiator,

A is a substituted bivalent 1,2-ethylene radical derived from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond.

R_a is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator, and

p is an integer from 5 to 200.

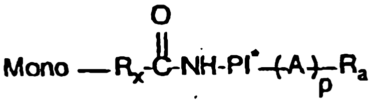
The group $-(A)_p-$ in formula I and the vinyl monomers used for the preparation thereof preferably contain no active-H groups.

The vinyl telomers of formula I according to the invention may be built up by reacting a photoinitiator of formula B

$$OCN\text{-}PI^{*}\text{-}R_{aa} \qquad (B),$$

wherein PI^* is as defined above and R_{aa} is the moiety of a photoinitiator that forms the less reactive free radical on cleavage of the photoinitiator, with a vinyl monomer in a manner known *per se*, which monomer is incorporated as component "A" into the vinyl telomer, A being as defined above. The chain reaction is terminated, for example, by the less reactive free radical of the photoinitiator R_{aa} of formula B or by other suitable chain-reaction terminators that are present in the reaction mixture under the reaction conditions, for example H free radicals or OH free radicals or free radicals formed from solvent. The variable R_a is preferably the component R_{aa} of the photoinitiator of formula B.

The polymerisable compounds according to the invention are compounds of formula C



$$\text{Mono}-R_x-\overset{\overset{\displaystyle O}{\|}}{C}-NH-PI^*-\!\!\left(A\right)_{p}\!-R_a$$

(C)

wherein Mono is a monovalent radical of a vinyl monomer from which the group R_x-H has been removed,

each R_x, independently of the others, is a bond, -O-, $-NR_N-$ or -S- wherein R_N is hydrogen or lower alkyl,

PI^* is a bivalent radical of a photoinitiator,

A is a substituted bivalent 1,2-ethylene radical derivable from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,

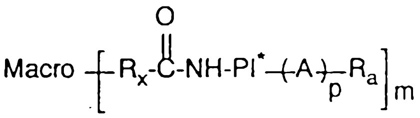
each R_a, independently of the others, is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator, and

p is an integer from 3 to 500.

The definition "bond" for R_x is applicable only in the case where an OH group in the monovalent radical of a vinyl monomer is present as a component of a COOH group. A COOH group reacts with an isocyanate group with the removal of CO_2 and with the formation of a bond "-CO-NH-". Only in that case is R_x a bond in the reaction product, but not in a starting material containing the group "R_x-H".

The polymerisable compounds of formula C according to the invention may be built up by reacting a vinyl telomer of formula I as defined above in a manner known *per se* with a vinyl monomer that contains at least one group R_x-H, R_x being as defined above but being other than a bond.

The segmented copolymers according to the invention are copolymers of formula D that are uncrosslinked but if desired crosslinkable



$$\text{Macro}\left[R_x-\overset{\overset{\displaystyle O}{\|}}{C}-NH-PI^{*}-(A)_p-R_a\right]_m \qquad (D)$$

wherein Macro is an m-valent radical of a macromer from which the number m of groups R_x-H has been removed,
each R_x, independently of the others, is a bond, -O-, -NR_N- or -S- wherein R_N is hydrogen or lower alkyl,
PI^* is a bivalent radical of a photoinitiator,
A is a substituted bivalent 1,2-ethylene radical derivable from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,
each R_a, independently of the others, is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator,
p, independently of m, is an integer from 3 to 500 and
m is an integer from 1 to 100.

The definition "bond" for R_x is applicable only in the case where an OH group in the macromer is present as a component of a COOH group. A COOH group reacts with an isocyanate group with the removal of CO_2 and with the formation of a bond "-CO-NH-". Only in that case is R_x a bond in the reaction product, but not in a starting material containing the group "R_x-H".

Segmented copolymers are to be understood according to the invention as meaning block copolymers, graft copolymers, especially comb copolymers or star copolymers.

The segmented copolymers of formula D according to the invention may be built up by reacting a macromer of formula A:

$$\text{Macro-}(R_xH)_m \qquad (A),$$

wherein Macro, R_x and m are as defined above except that R_x is other than a bond, in a manner known *per se* with a vinyl telomer of formula I

$$O{=}C{=}N\text{-}PI^{*}\text{-}(A)_{p}\text{-}R_{a} \qquad (I)$$

wherein PI*, A, R_a and p are as defined hereinbefore.

The macromer of formula A suitable according to the invention has a number m of groups $-R_xH$, which groups are hydroxy groups (including those that are a component of a carboxy group -COOH), amino groups or lower alkylamino groups (including those that are a component of an amide group $-CONR_N$) or mercapto groups. Those groups are co-reactive with the isocyanate group of the photoinitiator of formula B. The same applies to the vinyl monomers that contribute to the radical "Mono" in a compound of formula C.

The index p is preferably a number from 5 to 200, especially a number from 10 to 100.

The index m is preferably a number from 2 to 15, especially a number from 2 to 5.

The polymers according to the invention are polymerisation products of a polymerisable mixture that comprises the following components:

a) a polymerisable compound of formula C as defined hereinbefore,

b) if desired a copolymerisable vinyl monomer

c) a copolymerisable crosslinker;

or the polymerisation products of a polymerisable mixture that comprises the following components:

aa) a polymerisable compound of formula D as defined hereinbefore, in which a reactive group is present in the component $-(A)_p-$,

bb) if desired a copolymerisable vinyl monomer

cc) a crosslinker that is co-reactive with the reactive group in the component $-(A)_p-$ of the compound of formula D.

In the said polymerisable mixtures, if a copolymerisable vinyl monomer is employed a compound of formula C or D is used preferably in an amount of from 10 to 90 % by weight, especially from 20 to 80 % by weight, and a copolymerisable vinyl monomer is then, that is to say if it is present, used preferably in an amount of from 10 to 90 % by weight, especially from 20 to 80 % by weight, the percentages by weight for the amounts of components a) and b), and aa) and bb), being relative to each other. A crosslinker c) or cc) is used preferably in an amount of up to 25 % by weight, especially in an amount of up to 12.5 % by weight, based on the sum of components a) and b) or aa) and bb).

A copolymerisable crosslinker c), such as is mentioned in the above paragraph, is a typical oligovinylic crosslinker as known from the prior art. A crosslinker cc) such as is mentioned in the above paragraph, is an oligofunctional compound that is co-reactive with reactive groups present in the $-(A)_p-$ moiety.

A reactive group in the $-(A)_p-$ moiety is to be understood as meaning, in principle, any reactive group that is inert towards, or sluggish in reaction with, an isocyanate group, for example the isocyanate group or the epoxy group. A group, co-reactive therewith, of an oligofunctional compound is, for example, the amino group or the hydroxy group. Suitable oligofunctional compounds are accordingly in that case, for example, diamines, diols or amino-alcohols. Further examples are known to the person skilled in the art.

The groups bonded to the macromer of formula A, of which, depending on the meaning of the index m, there may be from 1 to 100, are either terminal or pendant, or terminal and pendant.

In an especially preferred embodiment, the macromer of formula A has two terminal groups R_xH. A segmented copolymer of formula D according to the invention formed therefrom, that is to say a block copolymer of formula D, is also especially preferred and is referred to in this invention as a tri-block copolymer: the central block is formed essentially by the macromer to which two photoinitiator radical-$(A)_p$-R_a- blocks are bonded.

In another preferred embodiment, the macromer of formula A has only pendant groups R_xH. A segmented copolymer of formula D according to the invention formed therefrom, that is to say a graft copolymer of formula D, is also preferred and is referred to in this invention as a comb polymer: the back or ridge of the comb is formed by the macromer, to which several photoinitiators are bonded in pendant manner, and the tines or teeth of the comb are formed essentially by the bivalent radicals A, which are bonded *via* the radical of the photoinitiator.

In another preferred embodiment, a cyclic macromer of formula A has pendant groups R_xH. A segmented copolymer of formula D according to the invention formed therefrom, that is to say a graft copolymer of formula D, is also preferred and is referred to in this invention as a star polymer: the central point of the star is formed by the macromer, to which several photoinitiators are bonded in pendant manner, and the arms of the star are formed essentially by the bivalent radicals A, which are bonded *via* the radical of the photoinitiator.

It is significant that the vinyl telomers according to the invention, the segmented copolymers or polymerisable compounds obtainable therefrom, and the crosslinked polymers obtainable therefrom, differ from conventional components in a surprising manner in respect of their properties. One reason for this is because the chain length of the vinyl monomers (see $-(A)_p-$ in formula I) can be substantially controlled in accordance with the invention, so that, for example, a comparatively narrow molecular weight distribution can be achieved. Also, the vinyl telomers of formula I are surprisingly free, or at least substantially free, of the homopolymers of the respective vinyl monomer used, and of bis-OCN-terminated telomers and polymers, which are otherwise usually formed by secondary reactions. These advantageous properties are transferred to the polymerisable compounds of formula C according to the invention, to the segmented copolymers of formula D and to the mentioned polymers in the course of their preparation.

Also, the vinyl telomers according to the invention and the products obtainable therefrom, as are described, for example, hereinbefore, have the advantages that they are available by a simple and rapid synthesis by means of UV polymerisation, that few secondary reactions occur during their preparation, that the products are generally colourless and that they can also be prepared from thermally labile vinyl monomers. Virtually no isocyanate-group-terminated vinyl telomers or corresponding secondary products are produced in the event of homopolymerisation of the vinyl monomer being initiated by the second free radical fragment of the photoinitiator. Instead, the second, less reactive free radical clearly exhibits a certain cage effect during the photopolymerisation and acts as an efficient chain-reaction terminator instead of itself initiating homopolymerisation of the vinyl monomer. Also, no secondary reactions that lead to α,β-difunctional telomers or polymers have been observed.

The copolymers of formula D according to the invention or the polymerisable compounds of formula C may be reacted or further processed selectively to produce secondary products. Attention is drawn especially to the fact that the uncrosslinked compounds of formula C or D can be incorporated in a simple manner into crosslinked polymers, for example by the reaction of a compound of formula C or D being carried out in the presence of a crosslinker. In addition to such a crosslinking, or as an alternative thereto, compounds of formula C or D according to the invention may be modified if they contain reactive groups in the moiety $-(A)_p-$ according to formula I.

Such reactive groups may be, for example, isocyanate or epoxy groups which originate from a vinyl isocyanate or a vinyl epoxy compound, for example from 2-isocyanatoethyl methacrylate or glycidyl (meth)acrylate, which are subsequently reacted with a hydroxy-lower alkyl (meth)acrylate, for example 2-hydroxyethyl methacrylate or 3-hydroxypropyl methacrylate. The C-C double bonds of a hydroxy-lower alkyl (meth)acrylate incorporated in the manner so described allow crosslinking to form a polymer according to the invention and/or copolymerisation with a further vinyl monomer or divinyl monomer.

Hereinbefore and hereinafter the term "(meth)acrylate" is used as an abbreviation for "methacrylate or acrylate"

As a result of all the properties mentioned hereinbefore, the polymers according to the invention are suitable for a wealth of intended uses as mouldings of varied kinds, such as as biomedical materials, for example implants, opthalmic lenses, especially artificial cornea, intraocular lenses or, more especially, contact lenses, or as medical instruments, devices, membranes and drug-delivery systems, or as coatings on inorganic or organic materials. In addition, the uncrosslinked vinyl telomers of formula I are not only suitable as starting materials for the polymers according to the invention but also excellently suitable for the production of modified surfaces, such as of biomedical materials, opthalmic lenses, especially contact lenses, or implants, as well as for coatings on inorganic or organic materials. All that is required for that purpose is the reaction of the highly reactive isocyanate group of the vinyl telomers of formula I with active-H groups of the surface in question. With hydrophilic components "A", amphiphilic block, comb or star polymers are obtained that have surface-active properties and are suitable, for example, as emulsifiers.

The invention therefore relates *inter alia* to mouldings, especially contact lenses, of the said segmented copolymers, polymerisable compounds or polymers. The invention relates also to the production of mouldings, especially contact lenses, from the said segmented copolymers, polymerisable compounds or polymers, and to the use of the said segmented copolymers, polymerisable compounds or polymers in the production of mouldings, especially contact lenses, and also to the use of the vinyl telomers according to the invention in the production of modified surfaces or coatings, especially the surfaces of contact lenses.

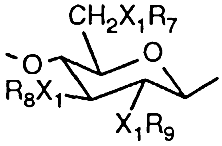
The macromers of formula A are preferably oligomers or polymers having an average molecular weight of from 300 to 10 000 dalton and contain preferably at least 3, more preferably from 3 to 50, and especially from 5 to 20, structural units. As is known, the transition between oligomers and polymers is fluid and cannot be defined exactly. The polymers may contain from 50 to 10 000, more preferably from 50 to 5 000, structural units and may have an average molecular weight of from 10 000 to 2 000 000, preferably from 10 000 to 500 000. The oligomers and polymers may also contain up to 95 mol %, preferably from 5 to 90 mol %, comonomeric structural units having no active-H groups (this term has the same meaning here as "R_xH groups", which are as defined hereinbefore, with the proviso that R_x is in this case other than a bond), based on the polymer.

The oligomers and polymers having active-H groups may be natural or synthetic oligomers or polymers.

Natural oligomers and polymers are, for example, oligo- and poly-saccharides or derivatives thereof, proteins, glycoproteins, enzymes and growth factors. Some examples are peptides, cyclodextrins, starch, hyaluronic acid, deacetylated hyaluronic acid, chitosan, trehalose, cellobiose, maltotriose, maltohexaose, chitohexaose, agarose, chitin 50, amylose, glucanes, heparin, xylan, pectin, galactan, poly-galactosamine, glycosaminoglycanes, dextran, aminated dextran, cellulose, hydroxyalkylcelluloses, carboxyalkylcelluloses, heparin, fucoidan, chondroitin sulfate, sulfated polysaccharides, mucopolysaccharides, gelatin, zein, casein, silk fibroin, collagen, albumin, globulin, bilirubin, ovalbumin, keratin, fibronectin and vitronectin, pepsin, trypsin and lysozyme.

The synthetic oligomers and polymers may be substances containing the groups -COOH, -OH, $-NH_2$ or $-NHR_N$ wherein R_N is lower alkyl, preferably C_1-C_6alkyl. They may be, for example, hydrolysed polymers of vinyl esters or ethers (polyvinyl alcohol); hydroxylated polydiolefins, e.g. polybutadiene, polyisoprene or chloroprene; polyacrylic acid and polymethacrylic acid and also polyacrylates, polymethacrylates, polyacrylamides or polymethacrylamides having hydroxyalkyl or aminoalkyl radicals in the ester group or amide group; polysiloxanes having hydroxyalkyl or aminoalkyl groups; polyethers of epoxides or glycidyl compounds and diols; polyvinylphenols or copolymers of vinylphenol and olefinic comonomers; and copolymers of at least one monomer from the group vinyl alcohol, vinylpyrrolidone, acrylic acid, methacrylic acid, (meth)acrylic acid anhydride, or hydroxyalkyl- or aminoalkyl-containing acrylates, methacrylates, or acrylamide or methacrylamide, or hydroxylated diolefins, with ethylenically unsaturated comonomers, e.g. acrylonitrile, olefins, diolefins, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, styrene, α-methylstyrene, vinyl ethers and vinyl esters; or polyoxaalkylenes having terminal OH or aminoalkyloxy groups.

Preferred oligomers and polymers are, for example, cyclodextrins having a total of from 6 to 8 ring-configured glucose structural units, or hydroxyalkyl or aminoalkyl derivatives or glucose- or maltose-substituted derivatives, of which at least one structural unit corresponds to formula (V)

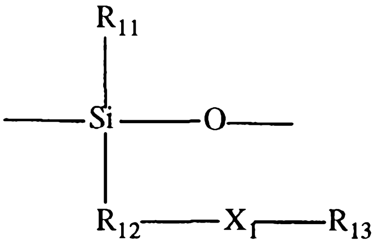


(V),

wherein R_7, R_8 and R_9 are each independently of the others H, C_1-C_4alkyl, especially methyl, C_2-C_6acyl, especially acetyl, C_1-C_4hydroxyalkyl, especially hydroxymethyl or 2-hydroxyeth-1-yl, C_2-C_{10}aminoalkyl or especially C_2-C_4aminoalkyl, for example 2-aminoeth-1-yl or 3-aminoprop-1-yl or 4-aminobut-1-yl, X_1 is -O- or $-NR_{1B}$-, wherein, per cyclodextrin unit, a total of from 1 to 10 and preferably from 1 to 6 radicals X_1 may be $-NR_{1B}$- and the remaining radicals X_1 are -O-, wherein R_{1B} is hydrogen or lower alkyl.

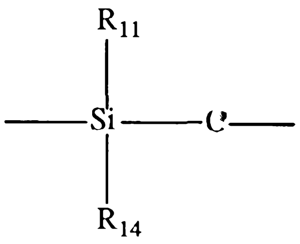
Other preferred oligomers and polymers are, for example, oligo- and poly-siloxanes having OH or NH_2 groups in alkyl, alkoxyalkyl or aminoalkyl terminal groups or side-chains. They may be random or block oligomers or block polymers. Oligomers and

polymers to which greater preference is given are those which contain
a) from 5 to 100 mol % structural units of formula (VII)



$$-\overset{R_{11}}{\underset{R_{12}-X_1-R_{13}}{\mathrm{Si}}}-O- \qquad (VII)$$

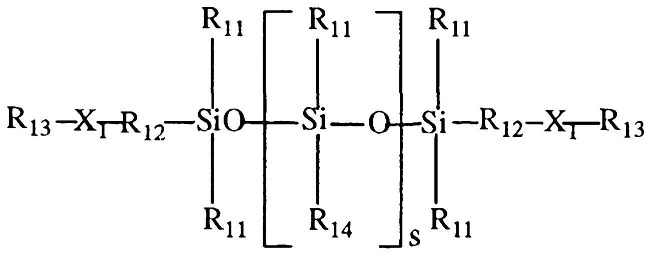
and
b) from 95 to 0 mol % structural units of formula (VIII)



$$-\overset{R_{11}}{\underset{R_{14}}{\mathrm{Si}}}-O- \qquad (VIII),$$

based on the oligomer or polymer, wherein R_{11} is C_1-C_4alkyl, lower alkenyl, cyano-lower alkyl or aryl each unsubstituted or partly or completely substituted by F, and is preferably methyl, ethyl, vinyl, allyl, cyanopropyl or trifluoromethyl, R_{12} is C_2-C_6alkylene, preferably 1,3-propylene, $-(CH_2)_z-(O-CH_2-CHCH_3-)_z-$, $-(CH_2)_z-(O-CH_2-CH_2)_z-$ or $-(CH_2)_z-NH-(CH_2)_z-NH-$, preferably $-(CH_2)_3-(O-CH_2-CHCH_3-)_2-$ or $-(CH_2)_3-NH-(CH_2)_2-NH-$, wherein z is an integer from 2 to 4, R_{14} has the same definitions as R_{11} or is $-R_{12}-X_1-H$ or $-R_{12}-X_1-R_{15}-H$, X_1 is -O- or -NH-, R_{13} is a radical R_xH and R_{15} is a direct bond or a group $-C(O)-(CHOH)_r-CH_2-O-$ wherein r is 0 or an integer from 1 to 4.

Preferred oligomeric and polymeric siloxanes are also those of formula (X)

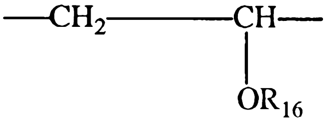


$$R_{13}-X_1-R_{12}-\overset{R_{11}}{\underset{R_{11}}{\mathrm{Si}}}O-\left[\overset{R_{11}}{\underset{R_{14}}{\mathrm{Si}}}-O\right]_s-\overset{R_{11}}{\underset{R_{11}}{\mathrm{Si}}}-R_{12}-X_1-R_{13} \qquad (X)$$

wherein R_{11} is C_1-C_4alkyl, vinyl, allyl or phenyl each unsubstituted or partly or completely substituted by F, and is preferably methyl, R_{12} is C_2-C_6alkylene, preferably 1,3-propylene, R_{14} has the same definitions as R_{11} or is -R_{12}-X_1-H or -R_{12}-X_1-R_{15}-H, X_1 is -O- or -NH-, s is an integer from 1 to 1000 and preferably from 1 to 150, R_{13} is a radical R_xH, and R_{15} is a direct bond or a group -C(O)-(CHOH)$_r$-CH_2-O- wherein r is 0 or an integer from 1 to 4. X_1 is preferably -NH-.

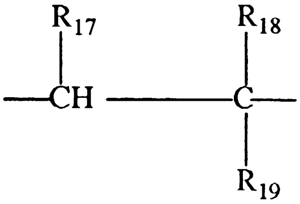
Other preferred oligomers and polymers are those based on oligovinyl and polyvinyl alcohol. They may be homopolymers having -$CH_2CH(OH)$- structural units or copolymers containing other monovalent or bivalent structural units of olefins.

More preferred are those oligomers and polymers which contain
a) from 5 to 100 mol % structural units of formula (XI)



$$-CH_2-\underset{\displaystyle OR_{16}}{\underset{|}{CH}}- \qquad (XI)$$

and
b) from 95 to 0 mol % structural units of formula (XII)



$$-\overset{\displaystyle R_{17}}{\overset{|}{CH}}-\overset{\displaystyle R_{18}}{\overset{|}{\underset{\displaystyle R_{19}}{\underset{|}{C}}}}- \qquad (XII),$$

wherein R_{16} is a radical R_xH, R_{17} is H, C_1-C_6alkyl, -$COOR_{20}$ or -$COO^{\ominus}$, R_{18} is H, F, Cl, CN or C_1-C_6alkyl, and R_{19} is H, OH, R_{10}-H, F, Cl, CN, R_{20}-O-, C_1-C_{12}alkyl, -$COO^{\ominus}$, -$COOR_{20}$, -OCO-R_{20}, methylphenyl or phenyl, wherein R_{10} is a direct bond, -(C_1-C_4alkylene-O)- or -(C_2-C_{10}alkylene-NH)- and R_{20} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, (C_1-C_{12}alkyl)-C_5-C_7cycloalkyl, phenyl, (C_1-C_{12}alkyl)phenyl, benzyl or (C_1-C_{12}alkyl)-benzyl.

R_{17} is preferably H. When R_{17} is alkyl, it is preferably methyl or ethyl. When R_{17} is -$COOR_{20}$, R_{20} is preferably C_1-C_{12}alkyl, especially C_1-C_6alkyl.

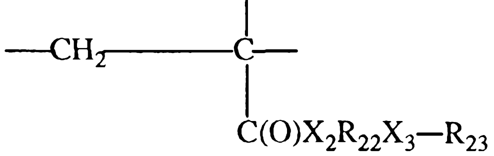
When R_{18} is alkyl, it is preferably C_1-C_4alkyl, e.g. methyl, ethyl, n-propyl or n-butyl. R_{18} is preferably H, Cl or C_1-C_4alkyl.

When R_{19} is the group R_{20}-O-, R_{20} is preferably C_1-C_{12}alkyl, especially C_1-C_6alkyl. When R_{19} is alkyl, it contains preferably from 1 to 6, especially from 1 to 4, carbon atoms. When R_{19} is the group $-COOR_{20}$, R_{20} is preferably C_1-C_{12}alkyl, especially C_1-C_6alkyl, or cyclopentyl or cyclohexyl. When R_{19} is the group $-OCO-R_{20}$, R_{20} is preferably C_1-C_{12}alkyl, especially C_1-C_6alkyl, or phenyl or benzyl.

In a preferred embodiment, R_{17} is H, R_{18} is H, F, Cl, methyl or ethyl, and R_{19} is H, OH, F, Cl, CN, C_1-C_4alkyl, C_1-C_6alkoxy, C_1-C_6hydroxyalkoxy, -COO-C_1-C_6alkyl, -OOC-C_1-C_6alkyl or phenyl.

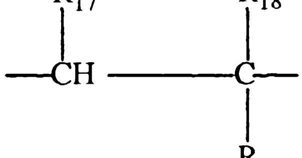
Especially preferred are those oligomers and polymers wherein R_{17} is H, R_{18} is H or methyl, and R_{19} is H, OH, CN, methyl, OCH_3, $O(CH_2)_tOH$ or $-COOCH_3$, and t is an integer from 2 to 6.

Another preferred group of oligomers and polymers comprises partly or completely hydroxyalkylated oligo- or poly-acrylates or -methacrylates, or -acrylamides or -methacrylamides. They may contain, for example, from 5 to 100 mol % structural units of formula (XIII)



$$-CH_2-\overset{R_{21}}{\underset{C(O)X_2R_{22}X_3-R_{23}}{C}}- \qquad \text{(XIII)}$$

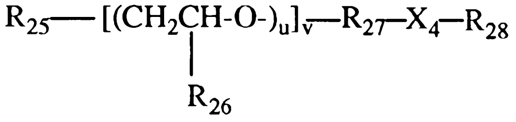
and from 95 to 0 mol % structural units of formula (XIV)



$$-\overset{R_{17}}{CH}-\overset{R_{18}}{\underset{R_{24}}{C}}- \qquad \text{(XIV)},$$

wherein R_{21} is H or methyl, X_2 and X_3 are each independently of the other -O- or -NH-, R_{22} is $-(CH_2)_c-$ and c is an integer from 2 to 12, preferably from 2 to 6, R_{23} is a radical of formula R_xH, R_{17} and R_{18} are as defined hereinbefore, and R_{24} has the same definitions as R_{19} or is $-C(O)X_2R_{22}X_3H$. For R_{17}, R_{18} and R_{19} the preferred definitions mentioned hereinbefore apply. For X_2 and X_3 the preferred definitions mentioned hereinbefore apply.

Other preferred oligomers and polymers are those consisting of polyalkylene oxides. They may, for example, be those of formula (XV) having identical or different repeating structural units $-[CH_2CH(R_{26})-O]-$



$$R_{25}\text{—}[(CH_2\underset{\displaystyle R_{26}}{\underset{|}{C}}H\text{-}O\text{-})_u]_v\text{—}R_{27}\text{—}X_4\text{—}R_{28} \qquad \text{(XV)},$$

wherein

R_{25} is the group R_{28}-X_4- or is the radical of an alcohol or polyol having from 1 to 20 carbon atoms, the valency of that radical being from 1 to v,

R_{26} is H, C_1-C_8alkyl, preferably C_1-C_4alkyl and especially methyl,

R_{27} together with X_4 is a direct bond or

R_{27} is C_2-C_6alkylene, preferably C_3-C_6alkylene and especially 1,3-propylene,

X_4 is -O- or -NH-,

R_{28} is a radical of formula R_xH,

u is a numerical value from 3 to 10 000, preferably from 5 to 5000, especially from 5 to 1000 and more especially from 5 to 100, and

v is an integer from 1 to 6, preferably from 1 to 4.

R_{25} may be a mono- to tetra-valent radical of an alcohol or polyol. When R_{25} is the radical of an alcohol, R_{25} is preferably linear or branched C_3-C_{20}-alkyl or -alkenyl, C_3-C_8- and especially C_5-C_6-cycloalkyl, $-CH_2-(C_5$-C_6cycloalkyl), C_6-C_{10}aryl and especially phenyl and naphthyl, C_7-C_{16}aralkyl and especially benzyl and 1-phenyleth-2-yl. The cyclic or aromatic radicals may be substituted by C_1-C_{18}alkyl or C_1-C_{18}alkoxy.

When R_{25} is the radical of a diol, R_{25} is preferably branched or especially linear C_3-C_{20}-alkylene or -alkenylene and more preferably C_3-C_{12}alkylene, C_3-C_8- and especially C_5-C_6-cycloalkylene, $-CH_2-(C_5$-C_6cycloalkyl)-, $-CH_2-(C_5$-C_6cycloalkyl)$-CH_2-$, C_7-C_{16}-aralkylene and especially benzylene, $-CH_2-(C_6$-C_{10}aryl)$-CH_2-$ and especially xylylene.

The cyclic or aromatic radicals may be substituted by C_1-C_{12}alkyl or C_1-C_{12}alkoxy.

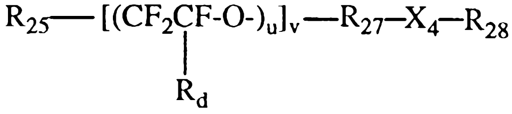
When R_{25} is a trivalent radical, it is derived from aliphatic or aromatic triols. R_{25} is preferably a trivalent aliphatic radical having from 3 to 12 carbon atoms that is derived especially from triols having preferably primary hydroxy groups. Most preferably, R_{25} is $-CH_2(CH-)CH_2-$, $HC(CH_2-)_3$ or $CH_3C(CH_2-)_3$.

When R_{25} is a tetravalent radical, it is derived preferably from aliphatic tetrols. R_{25} is in that case preferably $C(CH_2-)_4$.

Preferably, R_{25} is a radical derived from Jeffamines (Texaco), a Pluriol, a Poloxamer (BASF) or poly(tetramethylene oxide).

Especially preferred are homo- and block oligomers and homo- and block polymers having structural units of the formula $-[CH_2CH_2-O]-$ or $-[CH_2CH(CH_3)-O]-$.

Also suitable are fluorinated polyethers corresponding to formula (XVI)



$$R_{25}—[(CF_2\underset{\displaystyle R_d}{\underset{|}{C}}F\text{-}O\text{-})_u]_v—R_{27}—X_4—R_{28} \qquad \text{(XVI)},$$

wherein

R_{27}, R_{28}, X_4, u and v are as defined hereinbefore,

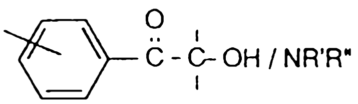
R_{25} is as defined hereinbefore or is the monovalent radical of a partially fluorinated or per-fluorinated alcohol having from 1 to 20, preferably from 1 to 12 and especially from 1 to 6, carbon atoms, or the bivalent radical of a partially fluorinated or per-fluorinated diol having from 2 to 6, preferably from 2 to 4 and especially 2 or 3, carbon atoms, and

R_d is F or perfluoroalkyl having from 1 to 12, preferably from 1 to 6 and especially from 1 to 4, carbon atoms. R_d is especially $-CF_3$.

Other suitable oligomers and polymers are, for example, polyamines, such as polyvinylamine, or polyethyleneimines. Also suitable is poly-ϵ-lysine.

A suitable photoinitiator of formula B is in principle any photoinitiator that contains an isocyanate group. Such photoinitiators have already been described, for example, in

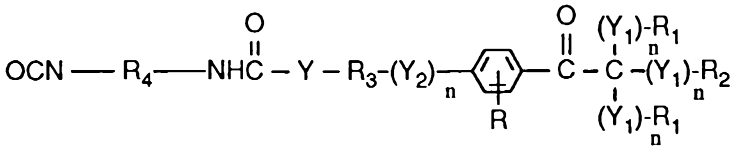
EP-A-632 329. Suitable photoinitiators usually contain the structural unit



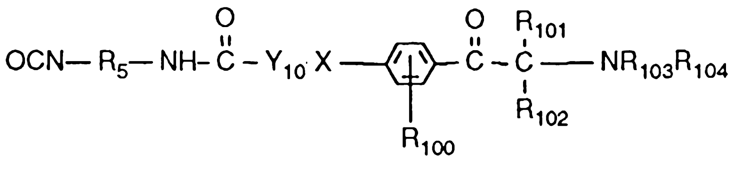
(in which " OH/NR'R" " indicates that the carbon atom in question carries either an OH group or an NR'R" group wherein R' and R" are each independently of the other linear or branched lower alkyl that may be substituted by C_1-C_4alkoxy; or aryl-lower alkyl or lower alkenyl; or R' and R" together are $-(CH_2)_z-Y_{11}-(CH_2)_z-$ wherein Y_{11} is a direct bond, -O-, -S- or $-NR_{1B}-$ and R_{1B} is H or lower alkyl, and z is an integer from 2 to 4), which, on being suitably excited, forms two free radicals as a result of the bond between the benzoyl carbon and the sp^3 carbon being cleaved. Usually, the benzoyl free radical is the more reactive free radical, and that free radical generally initiates polymerisation. The sysmbol PI* from formula B therefore corresponds preferably to such a benzoyl free radical. That benzoyl free radical is substituted, as is known in the prior art, and according to the invention in addition contains an isocyanate group. It can be seen from the foregoing that the sp^3 carbon free radical is the less reactive free radical which, as a rule, does not assist in initiating polymerisation. Instead it reacts preferentially as a chain-reaction terminator. The symbol R_{aa} from formula B therefore corresponds preferably to such an sp^3 carbon free radical.

Photoinitiators especially preferred in accordance with the invention are described below.

The functional photoinitiators of formula B used according to the invention are preferably compounds of formula IIa or IIb



(IIa),



(IIb)

wherein Y is O, NH or NR_{1A};

Y_1 is O;

Y_2 is -O-, -O-(O)C-, -C(O)-O- or -O-C(O)-O-;

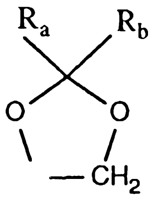
each n independently of the others is 0 or 1;

R is H, C_1-C_{12}alkyl, C_1-C_{12}alkoxy or C_1-C_{12}alkylNH-;

R_1 and R_2 are each independently of the other H, linear or branched C_1-C_8alkyl, C_1-C_8-hydroxyalkyl or C_6-C_{10}aryl, or

two groups R_1-$(Y_1)_n$- together are -$(CH_2)_x$-, or

the groups R_1-$(Y_1)_n$- and R_2-$(Y_1)_n$- together are a radical of the formula



;

R_3 is a direct bond or linear or branched C_1-C_8alkylene that is unsubstituted or substituted by -OH and/or optionally interrupted by one or more groups -O-, -O-C(O)- or -O-C(O)-O-;

R_4 is branched C_3-C_{18}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_6-C_{10}arylene, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_7-C_{18}-aralkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_3-C_8cycloalkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_3-C_8cycloalkylene-C_yH_{2y}- or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted -C_yH_{2y}-(C_3-C_8cycloalkylene)-C_yH_{2y}-;

R_5 independently has the same definitions as R_4 or is linear C_3-C_{18}alkylene;

R_{1A} is lower alkyl;

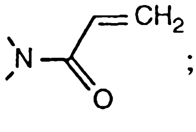
x is an integer from 3 to 5;

y is an integer from 1 to 6;

R_a and R_b are each independently of the other H, C_1-C_8alkyl, C_3-C_8cycloalkyl, benzyl or phenyl;

with the provisos that n in the groups -$(Y_1)_n$-R_1 is 0 when R_2 is H; that not more than two Y_1s of the -$(Y_1)_n$- groups are O and n in the other -$(Y_1)_n$- groups is 0; and that n in the group -$(Y_2)_n$- is 0 when R_3 is a direct bond;

and wherein also

X is bivalent -O-, -NH-, -S-, lower alkylene or  ;

Y_{10} is a direct bond or -O-$(CH_2)_y$- wherein y is an integer from 1 to 6 and the terminal CH_2 group is linked to the adjacent X in formula (IIb);
R_{100} is H, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, C_1-C_{12}alkylNH- or -$NR_{1A}R_{1B}$ wherein R_{1A} is lower alkyl and R_{1B} is H or lower alkyl;
R_{101} is linear or branched lower alkyl, lower alkenyl or aryl-lower alkyl;
R_{102} independently of R_{101} has the same definitions as R_{101} or is aryl, or
R_{101} and R_{102} together are -$(CH_2)_m$- wherein m is an integer from 2 to 6;
R_{103} and R_{104} are each independently of the other linear or branched lower alkyl that may be substituted by C_1-C_4alkoxy; or aryl-lower alkyl or lower alkenyl; or
R_{103} and R_{104} together are -$(CH_2)_z$-Y_{11}-$(CH_2)_z$- wherein Y_{11} is a direct bond, -O-, -S- or -NR_{1B}- and R_{1B} is H or lower alkyl, and z is an integer from 2 to 4.

In a preferred embodiment, Y is O.

R_{1A} as alkyl may be, for example, methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, pentyl or hexyl. R_{1A} is preferably methyl.

The group R contains as alkyl, alkoxy or alkylNH- preferably from 1 to 6 and especially from 1 to 4 carbon atoms. Some examples are methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, pentyl, hexyl, octyl, decyl, dodecyl, methoxy, ethoxy, propoxy, butoxy and methylNH-. Most preferably, R is H.

R_1 as alkyl is preferably linear and contains preferably from 1 to 4 carbon atoms. Some examples are methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, pentyl, hexyl, heptyl and octyl. R_1 is especially methyl or ethyl. R_1 as aryl may be, for example, naphthyl or especially phenyl. When the two groups R_1-$(Y_1)_n$- together are -$(CH_2)_x$-, x is preferably 4 or especially 5. R_1 as hydroxyalkyl is preferably linear and contains preferably from 1 to 4 carbon atoms. Some examples are hydroxymethyl and 2-hydroxyeth-1-yl.

For R_2 the same preferred definitions as for R_1 apply. R_2 is preferably H, methyl or ethyl.

R_a and R_b are preferably each independently of the other H or C_1-C_4alkyl, for example methyl or ethyl.

In a preferred sub-group, R_1 is preferably ethyl and especially methyl, or the two groups R_1-$(Y_1)_n$- together are pentamethylene, n in the group -$(Y_1)_n$-R_2 is preferably 0, R_2 is preferably methyl, hydroxymethyl or H and R is H.

In another preferred embodiment, in the group $-(Y_1)_n-R_2$, Y_1 is O, n is 1 and R_2 is H. In this case, n in the groups $R_1-(Y_1)_n-$ is especially 0.

R_3 as alkylene contains preferably from 1 to 6 and especially from 1 to 4 carbon atoms and the alkylene is preferably linear. Some examples are methylene, ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3- or 1,4-butylene, pentylene, hexylene, heptylene and octylene. Methylene, ethylene, 1,3-propylene and 1,4-butylene are preferred. Most especially, R_3 is ethylene; or a direct bond, in which case n in the group $-(Y_2)_n-$ is 0.

When R_3 is hydroxy-substituted alkylene it may be, for example, especially 2-hydroxy-1,3-propylene or also 2-hydroxy-1,3- or -1,4-butylene. Alkylene interrupted by -O- and unsubstituted or substituted by -OH is, for example, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$, $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$, $[-CH(CH_3)CH_2-O-CH(CH_3)CH_2-]$, $-CH(CH_3)CH_2-O-CH_2CH_2-$, $-CH(C_2H_5)CH_2-O-CH_2CH_2-$, $[-CH(C_2H_5)CH_2-O-CH(C_2H_5)CH_2-]$ or $-CH_2CH_2CH_2CH_2-O-CH_2CH_2CH_2CH_2-$ and $-CH_2CH(OH)CH_2-O-CH_2CH_2-$. Alkylene interrupted by -O-C(O)- or -C(O)-O- is, for example, $-CH_2CH_2-C(O)-O-CH_2-$ or $-CH_2CH_2-O-C(O)-CH_2-$. Alkylene interrupted by -O-C(O)-O- is, for example, $-CH_2CH_2-O-C(O)-O-CH_2CH_2-$ or $-CH_2CH_2-O-C(O)-O-CH_2-$.

The substituents C_1-C_4alkyl and C_1-C_4alkoxy are preferably methyl or ethyl and methoxy or ethoxy.

R_4 as branched alkylene contains preferably from 3 to 14 and especially from 4 to 10 carbon atoms. Examples of alkylene are 1,2-propylene, 2-methyl- or 2,2-dimethyl-1,3-propylene, 1,2-, 1,3- and 2,3-butylene, 2-methyl- or 2,3-dimethyl-1,4-butylene, 1,2-, 1,3- or 1,4-pentylene, 2-methyl- or 3-methyl- or 4-methyl- or 2,3-dimethyl- or 2,4-dimethyl- or 3,4-dimethyl- or 2,3,4-trimethyl- or 2,2,3-trimethyl- or 2,2,4-trimethyl- or 2,2,3,3-tetramethyl- or 2,2,3,4-tetramethyl-1,5-pentylene, 1,2-, 1,3-, 1,4- or 1,5-hexylene, and 2-methyl- or 3-methyl- or 4-methyl- or 2,2-dimethyl- or 3,3-dimethyl- or 2,3-dimethyl- or 2,4-dimethyl- or 3,4-dimethyl- or 2,2,3-trimethyl- or 2,2,4-trimethyl- or 2,2,5-trimethyl- or 2,3,4-trimethyl- or 2,2,4,5-tetramethyl-1,6-hexylene. Further examples are disclosed in EP-A-632 329.

Some preferred branched alkylene radicals are 2,2-dimethyl-1,4-butylene, 2,2-dimethyl-1,5-pentylene, 2,2,3- or 2,2,4-trimethyl-1,5-pentylene, 2,2-dimethyl-1,6-hexylene, 2,2,3- or 2,2,4- or 2,2,5-trimethyl-1,6-hexylene, 2,2-dimethyl-1,7-heptylene, 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6-trimethyl-1,7-heptylene, 2,2-dimethyl-1,8-octylene, and 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6- or 2,2,7-trimethyl-1,8-octylene.

When R_4 is arylene, it is preferably naphthylene and especially phenylene. When the arylene is substituted, one substituent is preferably in the ortho-position with respect to an isocyanate group. Examples of substituted arylene are 1-methyl-2,4-phenylene, 1,5-dimethyl-2,4-phenylene, 1-methoxy-2,4-phenylene and 1-methyl-2,7-naphthylene.

R_4 as aralkylene is preferably naphthylalkylene and especially phenylalkylene. The alkylene group in the aralkylene contains preferably from 1 to 12, more preferably from 1 to 6 and especially from 1 to 4, carbon atoms. Most preferably, the alkylene group in the aralkylene is methylene or ethylene. Some examples are 1,3- or 1,4-benzylene, naphth-2-yl-7-methylene, 6-methyl-1,3- or -1,4-benzylene, 6-methoxy-1,3- or -1,4-benzylene.

When R_4 is cycloalkylene, it is preferably C_5- or C_6-cycloalkylene that is unsubstituted or substituted by methyl. Some examples are 1,3-cyclobutylene, 1,3-cyclopentylene, 1,3- or 1,4-cyclohexylene, 1,3- or 1,4-cycloheptylene, 1,3- or 1,4- or 1,5-cyclooctylene, 4-methyl-1,3-cyclopentylene, 4-methyl-1,3-cyclohexylene, 4,4-dimethyl-1,3-cyclohexylene, 3-methyl- or 3,3-dimethyl-1,4-cyclohexylene, 3,5-dimethyl-1,3-cyclohexylene, 2,4-dimethyl-1,4-cyclohexylene.

When R_4 is cycloalkylene-C_yH_{2y}-, it is preferably cyclopentylene-C_yH_{2y}- or especially cyclohexylene-C_yH_{2y}- that is unsubstituted or substituted by preferably from 1 to 3 C_1-C_4alkyl groups, especially methyl groups. In the group -C_yH_{2y}-, y is preferably an integer from 1 to 4. More preferably, the group -C_yH_{2y}- is ethylene and especially methylene. Some examples are cyclopent-1-yl-3-methylene, 3-methyl-cyclopent-1-yl-3-methylene, 3,4-dimethyl-cyclopent-1-yl-3-methylene, 3,4,4-trimethyl-cyclopent-1-yl-3-methylene, cyclohex-1-yl-3- or -4-methylene, 3- or 4- or 5-methyl-cyclohex-1-yl-3- or -4-methylene, 3,4- or 3,5-dimethyl-cyclohex-1-yl-3- or -4-methylene, 3,4,5- or 3,4,4- or 3,5,5-trimethyl-cyclohex-1-yl-3- or -4-methylene.

When R_4 is -C_yH_{2y}-cycloalkylene-C_yH_{2y}- , it is preferably -C_yH_{2y}-cyclopentylene-C_yH_{2y}- and especially -C_yH_{2y}-cyclohexylene-C_yH_{2y}- that is unsubstituted or substituted by preferably from 1 to 3 C_1-C_4alkyl groups, especially methyl groups. In the group $-C_yH_{2y}-$, y is preferably an integer from 1 to 4. More preferably, the groups $-C_yH_{2y}-$ are ethylene and especially methylene. Some examples are cyclopentane-1,3-dimethylene, 3-methyl-cyclopentane-1,3-dimethylene, 3,4-dimethyl-cyclopentane-1,3-dimethylene, 3,4,4-trimethyl-cyclopentane-1,3-dimethylene, cyclohexane-1,3- or -1,4-dimethylene, 3- or 4- or 5-methyl-cyclohexane-1,3- or -1,4-dimethylene, 3,4- or 3,5-dimethyl-cyclohexane-1,3- or -1,4-dimethylene, or 3,4,5- or 3,4,4- or 3,5,5-trimethyl-cyclohexane-1,3- or -1,4-dimethylene.

When R_5 has the same definitions as R_4, the preferred definitions given hereinbefore for R_4 also apply. R_5 as linear alkylene contains preferably from 3 to 12 and especially from 3 to 8 carbon atoms. Some examples of linear alkylene are 1,3-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexylene, 1,7-heptylene, 1,8-octylene, 1,9-nonylene, 1,10-decylene, 1,11-undecylene, 1,12-dodecylene, 1,14-tetradecylene and 1,18-octadecylene.

A preferred definition of X is -O-, -NH-, -S- or lower alkylene. More preferably, X is -O- or -S- and especially -O-.

In a preferred definition of Y_{10}, the index y is from 1 to 5, more preferably from 2 to 4, and most preferably 2 or 3, so that Y_{10} is, for example, ethyleneoxy or propyleneoxy. In another preferred definition, Y_{10} is a direct bond, X then preferably being or containing at least one hetero atom.

The group R_{100} as alkyl, alkoxy, alkylNH- or $-NR_{1A}R_{1B}$ contains preferably from 1 to 6 and especially from 1 to 4 carbon atoms. Some examples are methyl, ethyl, n- or iso-propyl, n-, iso- or tert-butyl, pentyl, hexyl, octyl, decyl, dodecyl, methoxy, ethoxy, propoxy, butoxy, N,N-dimethylamino and N-methylamino. Most preferably, R is H. A preferred definition of $-NR_{1A}R_{1B}$ is N,N-dimethylamino, N-methylamino, N-methyl-N-ethylamino, N-ethylamino, N,N-diethylamino, N-isopropylamino or N,N-diisopropylamino.

R_{101} is preferably allyl, benzyl or linear C_1-C_4alkyl, for example methyl or ethyl.

R_{102} has preferably the same definitions as R_{101} and is more preferably linear lower alkyl having from 1 to 4 carbon atoms and especially 1 or 2 carbon atoms. R_{102} as aryl may be, for example, naphthyl or especially phenyl that is unsubstituted or substituted by lower alkyl or lower alkoxy. When R_{101} and R_{102} together are -$(CH_2)_m$-, m is preferably 4 or 5 and especially 5.

R_{103} is preferably linear lower alkyl having from 1 to 4 carbon atoms, benzyl or allyl, and more preferably methyl or ethyl.

R_{104} is preferably linear lower alkyl having from 1 to 4 carbon atoms and more preferably methyl or ethyl.

When R_{103} and R_{104} together are -$(CH_2)_z$-Y_{11}-$(CH_2)_z$-, Y_{11} is preferably a direct bond, -O- or -N(CH_3)- and most preferably -O-; z is preferably 2 or 3 and especially 2.

A preferred sub-group of compounds of formula IIa comprises those wherein
in the groups R_1-$(Y_1)_n$-, n is 0,
Y, Y_2 and Y_1 in the group R_2-$(Y_1)_n$- are each O,
n in the group R_2-$(Y_1)_n$- is 0 or 1,
R_1 is C_1-C_4alkyl or phenyl or
the groups R_1-$(Y_1)_n$- together are tetramethylene or pentamethylene,
R_2 is C_1-C_4alkyl or H,
R is hydrogen,
n in the group -(Y_2)-$_n$ is 0 or 1 and
R_3 is linear or branched C_2-C_4alkylene, or is a direct bond, in which case n in the group -(Y_2)-$_n$ is 0,
R_4 is branched C_5-C_{10}alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}-, or cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}- substituted by from 1 to 3 methyl groups,
R_5 has the same definitions as R_4 or is linear C_3-C_{10}alkylene, and
y is 1 or 2.

An especially preferred sub-group of compounds of formula IIa comprises those wherein
in the groups R_1-$(Y_1)_n$- and -(Y_2)-$_n$, n is 0,
Y, Y_2 and Y_1 in the group R_2-$(Y_1)_n$- are each O,
n in the group R_2-$(Y_1)_n$- is 0 or 1,
R_1 is methyl or phenyl or

the groups R_1-$(Y_1)_n$- together are pentamethylene,
R_2 is methyl or H,
R is hydrogen,
n in the group -(Y_2)-$_n$ is 1 and
R_3 is ethylene or
n in the group -(Y_2)-$_n$ is 0 and
R_3 is a direct bond,
R_4 is branched C_6-C_{10}alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, or cyclohexyl-CH_2- or cyclohexyl-CH_2- substituted by from 1 to 3 methyl groups, and
R_5 has the same definitions as R_4 or is linear C_5-C_{10}alkylene.

A preferred sub-group of compounds of formula IIb comprises those wherein
R_{101} is linear lower alkyl, lower alkenyl or aryl-lower alkyl;
R_{102} independently of R_{101} has the same definitions as R_{101} or is aryl;
R_{103} and R_{104} are each independently of the other linear or branched lower alkyl that may be substituted by C_1-C_4alkoxy; or aryl-lower alkyl or lower alkenyl; or
R_{103} and R_{104} together are -$(CH_2)_z$-Y_{11}-$(CH_2)_z$- wherein Y_{11} is a direct bond, -O-, -S- or -NR_{1B}- and R_{1B} is H or lower alkyl, and z is an integer from 2 to 4; and
R_5 is linear or branched C_3-C_{18}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_6-C_{10}arylene, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_7-C_{18}aralkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_{13}-C_{24}-arylenealkylenearylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_3-C_8-cycloalkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_3-C_8cycloalkylene-C_yH_{2y}- or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted -C_yH_{2y}-(C_3-C_8cycloalkylene)-C_yH_{2y}- wherein y is an integer from 1 to 6.

A preferred sub-group of compounds of formula IIb comprises those wherein
X is bivalent -O-, -NH-, -S- or -$(CH_2)_y$-;
Y_{10} is a direct bond or -O-$(CH_2)_y$- wherein y is an integer from 1 to 6 and the terminal CH_2 group is linked to the adjacent X in formula (IIb);
R_{100} is H, C_1-C_{12}alkyl or C_1-C_{12}alkoxy;
R_{101} is linear lower alkyl, lower alkenyl or aryl-lower alkyl;
R_{102} independently of R_{101} has the same definitions as R_{101} or is aryl, or
R_{101} and R_{102} together are -$(CH_2)_m$- wherein m is an integer from 2 to 6;

R_{103} and R_{104} are each independently of the other linear or branched lower alkyl that may be substituted by C_1-C_4alkoxy; or aryl-lower alkyl or lower alkenyl; or
R_{103} and R_{104} together are $-(CH_2)_z-Y_{11}-(CH_2)_z-$ wherein Y_{11} is a direct bond, -O-, -S- or $-NR_{1B}-$ and R_{1B} is H or lower alkyl, and z is an integer from 2 to 4; and
R_5 is branched C_6-C_{10}alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, or cyclohexylene-CH_2- or cyclohexylene-CH_2- substituted by from 1 to 3 methyl groups.

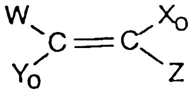
An especially preferred sub-group of compounds of formula IIb comprises those wherein
R_{101} is methyl, allyl, toluylmethyl or benzyl,
R_{102} is methyl, ethyl, benzyl or phenyl, or
R_{101} and R_{102} together are pentamethylene,
R_{103} and R_{104} are each independently of the other lower alkyl having up to 4 carbon atoms or
R_{103} and R_{104} together are $-CH_2CH_2OCH_2CH_2-$, and
R_5 is branched C_6-C_{10}alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, or cyclohexylene-CH_2- or cyclohexylene-CH_2- substituted by from 1 to 3 methyl groups.

The groups R_4 and R_5 are especially groups that reduce the reactivity of the OCN group, this being achieved essentially by steric hindrance or electronic influences at at least one adjacent carbon atom. Preferably, R_4 and R_5 are therefore, *inter alia*, asymmetric radicals, for example alkylene that is branched in the α-position or especially the β-position with respect to the OCN group, or cyclic hydrocarbon radicals that are substituted as defined in at least one of the α-positions.

In the context of this invention, a copolymerisable vinyl monomer is to be understood as meaning especially a monomer that contains a vinyl group and has already been mentioned in connection with copolymers used for contact lenses. A vinyl group is to be understood in this context not as meaning exclusively the vinyl grouping "$-CH=CH_2$" but as meaning generally any grouping that has a carbon-carbon double bond. Especially preferred definitions of the word "vinyl" in vinyl monomers will become clear from the following explanations in connection with compounds of formula III. Copolymerisable vinyl monomers in the sense of this invention have already been disclosed, for example, in

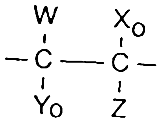
EP-A-374 752, EP-A-417 235 and EP-A-455 587.

The monomers used as starting materials to prepare component A of formula I for the vinyl telomers, block copolymers, polymerisable compounds, polymers or contact lenses of the invention, are especially compounds of formula III



(III)

which, symbolised by the letters A, are incorporated into the vinyl telomer of formula I in the form of the partial formula IV



$$-\overset{W}{\underset{Y_0}{C}}-\overset{X_0}{\underset{Z}{C}}-$$

(IV)

wherein the substituents W, X_0, Y_0 and Z are defined as follows: three of those substituents are hydrogen and the fourth substituent is selected from acyl, halogen, a heterocyclic radical and aryl, or two of those substituents are hydrogen, a third is lower alkyl and the fourth substituent is selected from acyl, halogen, a heterocyclic radical and aryl, or two of those substituents are hydrogen and the other two substituents together form a hydrocarbon bridge that is uninterrupted or is interrupted by one or two hetero atoms, or the other two substituents are each independently acyl. The monomers of formula III are either hydrophilic vinyl monomers or hydrophobic vinyl monomers.

Preferably, the copolymerisable vinyl monomers used to prepare vinyl telomers of formula I contain no active-H groups, or at any rate no unprotected active-H groups. Those monomers are referred to in the following as "group I vinyl monomers". By contrast, the vinyl monomers used to prepare polymerisable compounds of formula C expressly have at least one active-H group. Those monomers are referred to in the following as "group C vinyl monomers"

Aryl is especially an aromatic hydrocarbon radical having from 6 to 15 carbon atoms, such as phenyl or phenyl substituted by one or more, especially up to three, radicals of the kind lower alkyl, lower alkoxy, halogen, amino or hydroxy. Examples are phenyl and tolyl.

Halogen is especially chlorine, bromine or fluorine, but may also be iodine.

A heterocyclic radical is especially a 5- or 6-membered aromatic or saturated ring having one or two hetero atoms, such as oxygen or nitrogen atoms, especially having one or two nitrogen atoms. Lactams are also included.

A hydrocarbon bridge that is uninterrupted or interrupted by one or two hetero atoms is especially lower alkylene or lower alkylene interrupted by oxygen or by nitrogen. Lower alkylene interrupted by nitrogen may also be substituted, for example by lower alkyl. Examples are 1,3-propylene, 2-aza-1,3-propylene and N-methyl-2-aza-1,3-propylene.

Acyl is carboxy, aroyl, cycloalkanoyl or alkanoyl and is especially carboxy, unsubstituted or substituted aryloxycarbonyl, unsubstituted or substituted cycloalkyloxycarbonyl or unsubstituted or substituted alkoxycarbonyl.

Aroyl is, for example, benzoyl or benzoyl substituted by one or more, especially up to three, radicals of the kind lower alkyl, lower alkoxy, halogen or hydroxy, but may also be phenylsulfonyl or phenyloxysulfonyl, or phenylsulfonyl or phenyloxysulfonyl substituted by lower alkyl, lower alkoxy, halogen or by hydroxy.

Alkanoyl is preferably lower alkanoyl and is, for example, acetyl, propanoyl or butanoyl.

Cycloalkanoyl is preferably cycloalkyloxycarbonyl having up to 8 carbon atoms and is, for example, cyclohexyloxycarbonyl.

Unsubstituted alkoxycarbonyl is preferably lower alkoxycarbonyl and is, for example, methoxycarbonyl, ethoxycarbonyl, propyloxycarbonyl, butoxycarbonyl, tert-butoxycarbonyl, tert-butylmethyloxycarbonyl or 2-ethylhexyloxycarbonyl.

Unsubstituted aryloxycarbonyl is preferably phenyloxycarbonyl.

Substituted aryloxycarbonyl is preferably phenyloxycarbonyl substituted by one or more, especially up to three, radicals of the kind lower alkyl, lower alkoxy, halogen or hydroxy.

Substituted alkoxycarbonyl is substituted preferably by hydrophobic groups, such as halogen, for example fluorine, siloxane groups or hydrophilic groups, such as hydroxy, amino, mono- or di-lower alkylamino, isocyanato or by a lower alkylene glycol. Other definitions of substituted alkoxycarbonyl, and also of substituted aryloxycarbonyl and substituted cycloalkyloxycarbonyl, are indicated implicitly by the following description of especially suitable vinyl monomers of formula III.

The hydrophilic vinyl monomers that can be used in accordance with the invention are preferably
acrylates and methacrylates of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is a group $-Z^1-Z^2$ wherein Z^1 is -COO- bonded *via* oxygen to Z^2 and Z^2 is a hydrocarbon radical having from 1 to 10 carbon atoms that is mono- or poly-substituted by a water-solubilising group, such as carboxy, hydroxy or tert-amino, for example tert-lower alkylamino having from 1 to 7 carbon atoms per lower alkyl group, a polyethylene oxide group having from 2 to 100 repeating units, preferably from 2 to 40 repeating units, or a sulfate, phosphate, sulfonate or phosphonate group, for example a correspondingly substituted alkyl, cycloalkyl or phenyl radical or a combination of such radicals, such as phenylalkyl or alkylcycloalkyl;
also acrylamides and methacrylamides of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is aminocarbonyl or di-lower alkylaminocarbonyl;
acrylamides and methacrylamides of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is monosubstituted aminocarbonyl substituted by one of the groups Z^2 defined above or by lower alkyl;
maleates and fumarates of formula III wherein W and X_0 (or W and Z) are hydrogen, and Y_0 and Z (or X_0 and Y_0) are each independently of the other a group $-Z^1-Z^2$ wherein Z^1 and Z^2 are as defined above;
crotonates of formula III wherein W and X_0 are hydrogen, Y_0 is methyl and Z is a group $-Z^1-Z^2$ wherein Z^1 and Z^2 are as defined above;
vinyl ethers of formula III wherein W, X_0 and Y_0 are hydrogen, and Z is a group $-Z^1-Z^2$ wherein Z^1 is oxygen and Z^2 is as defined above;
vinyl-substituted five- or six-membered heterocycles having one or two nitrogen atoms and also N-vinyl-lactams, such as N-vinyl-2-pyrrolidone, of formula III wherein W, X_0 and Y_0 are hydrogen and Z is a five- or six-membered heterocyclic radical having one or two nitrogen atoms, as well as the radical, bonded *via* nitrogen, of a lactam, for example the nitrogen-bonded radical of 2-pyrrolidone;
and vinylically unsaturated carboxylic acids of formula III having a total of from 3 to 10 carbon atoms, such as methacrylic acid, crotonic acid, fumaric acid or cinnamic acid.

Preference is given, for example, to hydroxy- or amino-substituted C_2-C_4alkyl (meth)-

acrylates, five- to seven-membered N-vinyl-lactams, N,N-di-C_1-C_4alkyl(meth)acrylamides and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms. Of those, five- to seven-membered N-vinyl-lactams and N,N-di-C_1-C_4alkyl(meth)-acrylamides are group I vinyl monomers, while hydroxy- or amino-substituted C_2-C_4alkyl (meth)acrylates and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms are group C vinyl monomers. The former and latter vinyl monomers, representing the group I type and the group C type, have not been categorised in each individual case here, since the differentiation between the two can readily be made on the basis of the criterion of whether or not an active-H group is present. The two groups of vinyl monomers are, on the basis of that differentiation criterion, to be regarded as being disclosed independently of each other.

Water-soluble monomers that can be used include: 2-hydroxyethyl, 2- and 3-hydroxypropyl, 2,3-dihydroxypropyl, polyethoxyethyl and polyethoxypropyl acrylates and methacrylates and the corresponding acrylamides and methacrylamides, acrylamide and methacrylamide, N-methyl-acrylamide and -methacrylamide, bisacetone-acrylamide, 2-hydroxyethylacrylamide, dimethyl-acrylamide and -methacrylamide and also methylol-acrylamide and -methacrylamide, N,N-dimethyl- and N,N-diethyl-aminoethyl acrylate and methacrylate and the corresponding acrylamides and methacrylamides, N-tert-butylaminoethyl methacrylate and methacrylamide, 2- and 4-vinylpyridine, 4- and 2-methyl-5-vinylpyridine, N-methyl-4-vinylpyridine, 1-vinyl- and 2-methyl-1-vinyl-imidazole, dimethylallylamine and methyldiallylamine and also para-, meta- and ortho-aminostyrene, dimethylaminoethylvinyl ether, N-vinylpyrrolidone and 2-pyrrolidinoethyl methacrylate, acrylic and methacrylic acid, itaconic acid, cinnamic acid, crotonic acid, fumaric acid, maleic acid and the hydroxy-lower alkyl mono- and di-esters thereof, such as 2-hydroxyethyl and di(2-hydroxy)ethyl fumarate, maleate and itaconate, and also 3-hydroxypropylbutyl fumarate and di-polyalkoxyalkyl fumarates, maleates and itaconates, maleic acid anhydride, N-methylmaleic acid imide, sodium acrylate and methacrylate, 2-methacryloyloxyethylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-phosphatoethyl methacrylate, vinylsulfonic acid, phenyl vinylsulfonate, sodium vinylsulfonate, p-styrenesulfonic acid, sodium p-styrenesulfonate and allylsulfonic acid, N-vinylpyrrolidone, N-vinylpyridone, N-vinylcaprolactam, and also the quaternised derivatives of cationic monomers, obtained by quaternisation with selected alkylating agents, for example halogenated hydrocarbons, such as methyl iodide, benzyl chloride or hexadecyl chloride, epoxides, such as glycidol, epichlorohydrin or ethylene oxide, acrylic acid, dimethyl sulfate, methyl sulfate and propanesultone.

A more complete list of water-soluble monomers that can be used in connection with this invention can be found in: R.H. Yocum and E.B. Nyquist, Functional Monomers, volume 1, pages 424-440 (M. Dekker, N.Y. 1973).

Preferred hydrophilic vinyl monomers are 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, N-vinyl-2-pyrrolidone, polyethylene glycol methacrylate, especially having an ethylene glycol content of a molecular weight of approximately 400, N,N-dimethylacrylamide, N,N-diethylaminoethyl (meth)acrylate and also acrylic and methacrylic acid.

Suitable as hydrophobic vinyl monomers that may be used in accordance with the invention are, for example:

acrylates and methacrylates of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is a group $-Z^1-Z^3$ wherein Z^1 is -COO- bonded *via* oxygen to Z^3 and Z^3 is a linear or branched aliphatic, a cycloaliphatic or an aromatic group having from 1 to 21 carbon atoms, for example a correspondingly substituted alkyl, cycloalkyl or phenyl radical or a combination of such radicals, such as phenylalkyl or alkylcycloalkyl, which may contain ether or thioether bonds, sulfoxide or sulfone groups or a carbonyl group; or Z^3 is a heterocyclic group that contains oxygen, sulfur or nitrogen atoms and 5 or 6 or, if it is bicyclic, up to 10, ring atoms, or a polypropylene oxide or poly-n-butylene oxide group having from 2 to 50 recurring alkoxy units, or Z^3 is an alkyl group having from 1 to 12 carbon atoms that contains halogen atoms, especially fluorine atoms, or Z^3 is a siloxane group having from 1 to 6 Si atoms;
acrylamides and methacrylamides of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is monosubstituted aminocarbonyl substituted by a group Z^3 as defined above;
maleates and fumarates of formula III wherein W and X_0 (or W and Z) are hydrogen and Y_0 and Z (or X_0 and Y_0) are each independently of the other a group $-Z^1-Z^3$ wherein Z^1 and Z^3 are as defined above;
itaconates of formula III wherein W and Y_0 are hydrogen, X_0 is a group $-Z^1-Z^3$ wherein Z^1 and Z^3 are as defined above, and Z is a group $-CH_2-Z^1-Z^3$ wherein Z^1 and Z^3 are as defined above;
crotonates of formula III wherein W and X_0 are hydrogen and Y_0 is methyl and Z is a group $-Z^1-Z^3$ wherein Z^1 and Z^3 are as defined above;
vinyl esters of formula III wherein W, Y_0 and X_0 are hydrogen and Z is a group $-Z^1-Z^3$

wherein Z^1 is -COO- bonded *via* carbon to Z^3 and Z^3 is as defined above;
vinyl ethers of formula III wherein W, X_o and Y_o are hydrogen and Z is a group $-Z^1-Z^3$ wherein Z^1 is oxygen and Z^3 is as defined above.

Special preference is given to C_1-C_4alkyl esters or C_5-C_7cycloalkyl esters of vinylically unsaturated carboxylic acids having from 3 to 5 carbon atoms.

The following are examples of suitable hydrophobic monomers: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, ethoxyethyl, methoxyethyl, benzyl, phenyl, cyclohexyl, trimethylcyclohexyl, isobornyl, dicyclopentadienyl, norbornylmethyl, cyclododecyl, 1,1,3,3-tetramethylbutyl, n-butyl, n-octyl, 2-ethylhexyl, decyl, dodecyl, tridecyl, octadecyl, glycidyl, ethylthioethyl, furfuryl and tri-, tetra- and penta-siloxanylpropyl acrylates and methacrylates, and the corresponding amides; N-(1,1-dimethyl-3-oxobutyl)-acrylamide; mono- and di-methyl fumarate, maleate and itaconate; diethyl fumarate; isopropyl and diisopropyl fumarate and itaconate; mono- and di-phenyl and methylphenyl fumarate and itaconate; methyl and ethyl crotonate; methyl vinyl ether and methoxyethyl vinyl ether; vinyl acetate, vinyl propionate, vinyl benzoate, acrylonitrile, vinylidene chloride, styrene, α-methylstyrene and tert-butylstyrene.

Preferred hydrophobic vinyl monomers are methyl methacrylate, n-butyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate and mixtures thereof.

Of the afore-mentioned vinyl monomers, two special types of hydrophobic vinyl monomers are worthy of special mention in connection with the invention, those being siloxane monovinyl components and fluorine-containing vinyl compounds.

Especially preferred siloxane monovinyl components are compounds of formula III wherein W and Y_o are hydrogen, X_o is hydrogen or methyl and Z is a group $-Z^1-Z^4$ wherein Z^1 is -COO- bonded *via* oxygen to Z^4 and Z^4 is silyl-lower alkyl mono- or poly-substituted, for example tri- to nona-substituted, by tri-lower alkylsilyloxy. Silyl-lower alkyl in this context is to be understood as meaning a lower alkyl radical substituted by one or more silicon atoms, the free valencies of which radical are saturated at the silicon atoms especially by tri-lower alkylsilyloxy. Individual compounds to which special attention is drawn are, for example, tris(trimethylsiloxy)silylpropyl methacrylate and tris(tris(trimethylsiloxy)siloxy)silylpropyl methacrylate.

Especially preferred fluorine-containing vinyl compounds are compounds of formula III wherein W and Y_0 are hydrogen, X_0 is hydrogen or methyl and Z is a group $-Z^1-Z^5$ wherein Z^1 is -COO- bonded *via* oxygen to Z^5 and Z^5 is fluorine-substituted alkyl, especially lower alkyl. Specific examples are 2,2,2-trifluoroethyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate and hexafluoroisopropyl methacrylate.

As already mentioned, the polymers according to the invention are preferably prepared using as starting materials a compound of formula C or D, and if desired a vinyl monomer, in the presence of a crosslinker.

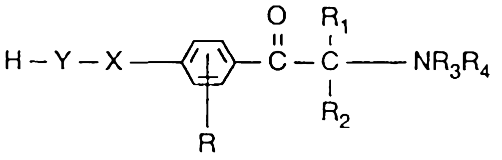
Suitable vinylic crosslinkers are especially oligo-olefinic, especially diolefinic, monomers, e.g. allyl acrylate and methacrylate, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and, generally, polyethylene oxide glycol diacrylates and dimethacrylates, 1,4-butanediol and poly-n-butylene oxide glycol diacrylates and dimethacrylates, propylene glycol and polypropylene oxide glycol diacrylates and dimethacrylates, thiodiethylene glycol diacrylate and dimethacrylate, di(2-hydroxyethyl)sulfone diacrylate and dimethacrylate, neopentyl glycol diacrylate and dimethacrylate, trimethylolpropane tri- and tetra-acrylate, pentaerythritol tri- and tetra-acrylate, divinylbenzene, divinyl ether, divinylsulfone, disiloxanyl-bis-3-hydroxypropyl diacrylate or methacrylate and related compounds. Ethylene glycol dimethacrylate is preferred.

Suitable crosslinkers also include oligovinyl macromers, for example divinyl macromers, as described, for example, in US-A-4 136 250. Also suitable as crosslinkers in the context of the invention are oligovinylsiloxane compounds, for example bis(meth)acryloxy-lower alkylsiloxanes having up to 10 silicon atoms. Examples are 3,5-bis(3-methacryloxypropyl)-3,5-bis(trimethylsiloxy)-1,1,1,7,7,7-hexamethyltetrasiloxane and 1,3-dimethacryloxypropyl-tetramethyldisiloxane.

The starting materials used in the preparation of the vinyl telomers, segmented copolymers, polymerisable compounds and polymers according to the invention, for example starting materials of formulae A, B and III and the crosslinkers, are known *per se* and/or are described herein.

The compounds of formula II can be prepared in a manner known *per se* by the reaction of diisocyanates with the appropriate acid-H photoinitiators. The compounds are obtained in high yields and a high degree of purity, even when two differently reactive acid-H groups are present simultaneously in the photoinitiator, for example two OH groups. It is especially advantageous to use diisocyanates having isocyanate groups of different reactivity, because by that means the formation of isomers and diadducts can be substantially suppressed. The different reactivity can be achieved, for example, as described hereinbefore by means of steric hindrance. The different reactivity can also be achieved by masking one isocyanate group in the diisocyanate, for example with carboxylic acids or hydroxylamine. The compounds of formula IIa are known from EP-A-632 329.

Compounds of formula (IIb) can be prepared by reacting a compound of formula IIc



(IIc)

wherein X, Y, R, R_1, R_2, R_3 and R_4 are as defined hereinbefore, preferably in an inert organic solvent, with a diisocyanate of formula IId or with such a diisocyanate mono-masked where necessary,

$$OCN\text{-}R_5\text{-}NCO \qquad \text{(IId)}$$

wherein R_5 is as defined hereinbefore.

Masking agents are known from urethane chemistry. They may be, for example, phenols (cresol, xylenol), lactams (ε-caprolactam), oximes (acetoxime, benzophenone oxime), active-H methylene compounds (diethyl malonate, ethyl acetoacetate), pyrazoles or benzotriazoles. Masking agents are described, for example, by Z. W. Wicks, Jr. in Progress in Organic Coatings, 9 (1981), pages 3-28.

The starting materials of the formula IIc type are known and are described, for example, in EP-A-284 561, EP-A-117 233 and EP-A-088 050.

Suitable inert solvents are aprotic, non-polar or polar solvents, such as, for example, hydrocarbons (petroleum ether, methylcyclohexane, benzene, toluene, xylene), halogenated hydrocarbons (chloroform, methylene chloride, trichloroethane, tetrachloroethane, chlorobenzene), ethers (diethyl ether, dibutyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran (THF), dioxane), ketones (acetone, dibutyl ketone, methyl isobutyl ketone), carboxylic acid esters and lactones (ethyl acetate, butyrolactone, valerolactone), alkylated carboxylic acid amides (N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP)), nitriles (acetonitrile), sulfones and sulfoxides (dimethyl sulfoxide (DMSO), tetramethylene-sulfone). Polar solvents are preferably used.

The reactants are advantageously used in equimolar quantities. The reaction temperature may, for example, be from 0 to 200°C. When using catalysts, the temperatures may advantageously be in the range from -20° to 60°C and preferably in the range from -10° to 50°C. Suitable catalysts are, for example, metal salts, such as alkali metal salts, of carboxylic acids, tertiary amines, for example $(C_1\text{-}C_6\text{alkyl})_3N$ (triethylamine, tri-n-butylamine), N-methylpyrrolidine, N-methylmorpholine, N,N-dimethylpiperidine, pyridine and 1,4-diaza-bicyclooctane. Tin compounds have been found to be especially effective, especially alkyltin salts of carboxylic acids, such as, for example, dibutyltin dilaurate, or, for example, tin dioctoate.

If free NH groups are present in the compounds of formula IIc, those groups can initially be protected by suitable protecting groups during the reaction with a diisocyanate and subsequently freed again by removing the protecting groups. Suitable protecting groups are known to the person skilled in the art. Representative examples can be found, for example, in T.W. Greene, "Protective Groups in Organic Synthesis", Wiley Interscience, 1981.

The isolation and purification of the compounds prepared are carried out in accordance with known methods, for example extraction, crystallisation, re-crystallisation or chromatographic purification methods. The compounds are obtained in high yields and purity. The yields in the case of non-optimised processes may be more than 85 % of the theoretical yields.

The reaction between a photoinitiator of formula B and a copolymerisable vinyl monomer being incorporated as component "A" into the vinyl telomer can be effected in a manner known *per se*. For example, a vinyl monomer being incorporated as component "A" into the vinyl telomer may be polymerised in the absence or presence of a suitable solvent, at room temperature or at a temperature up to, at most, the boiling temperature of any solvent used. In this context, a suitable solvent is distinguished by the fact that it contains no active hydrogen atoms that are able to react with the isocyanate group, and by the fact that it does not absorb UV light. Examples include a hydrocarbon, especially a cycloaliphatic hydrocarbon, such as hexane, methylcyclohexane, benzene or toluene, a ketone, such as acetone, methyl isopropyl ketone or cyclohexanone, an ester, such as ethyl acetate, a fluorinated solvent, such as hexafluoroacetone, an ether, preferably a cyclic ether, such as diethyl ether, dimethoxyethane, dioxane or tetrahydrofuran, or an amide, such as N-methylpyrrolidone or DMA, or dimethyl sulfoxide or acetonitrile, or a mixture of several of those solvents. The purification is carried out in a manner known *per se.* In principle, the same conditions may be employed for the crosslinking reaction to form polymers according to the invention.

It is advantageous so to control the reaction that the vinyl telomers formed precipitate and can be removed from the reaction mixture continuously by centrifugal filtration. It is furthermore advantageous to use solvents that exert a sensitizing or accelerating effect on the phototelomerisation.

An advantageous reaction procedure may comprise carrying out the reaction until only approximately 40 % of the vinyl monomer has been consumed, so as to avoid secondary products. This applies especially when all the components are in the reaction mixture from the outset, since in that case relatively rapid depletion of photoinitiator may occur, making the possible formation of non-NCO-terminated homopolymer more likely.

Alternatively, it may be advantageous to meter in a solution of the monomer and a solution of the photoinitiator simultaneously during the UV irradiation.

The reaction of a vinyl telomer of formula I with a vinyl monomer in order to prepare a compound of formula C may be carried out easily and in a manner known *per se* in urethane chemistry. This applies also to the reaction of a vinyl telomer of formula I with a macromer of formula A.

The preparation of the polymers according to the invention may be carried out in a manner known *per se*, for example under the conditions already indicated hereinbefore, but it is not necessary in that process step for the solvent to be free of active-H groups.

Suitable olefins for the mentioned graft polymerisation are, for example, acrylamide, N,N-dimethylacrylamide, methacrylamide, hydroxyethyl methacrylate, glyceryl methacrylate, oligoethylene oxide mono- and bis-acrylates, ethylene glycol dimethacrylate, methylene bisacrylamide, vinylcaprolactam, acrylic acid, methacrylic acid, fumaric acid monovinyl esters, vinyl trifluoroacetate and vinylene carbonate, it being possible for reactive esters to be hydrolysed subsequently where necessary.

The photopolymerisation may furthermore be accelerated by the addition of photosensitizers, which shift or broaden the spectral sensitivity. These are especially aromatic carbonyl compounds, for example derivatives of thioxanthone, anthraquinone and 3-acylcoumarin, and 3-(aroylmethylene)-thiazolines.

The effectiveness of a photoinitiator can be increased by the addition of titanocene derivatives having fluoro-organic radicals, as are described in EP-A-122 223 and EP-A-186 626, for example in an amount of from 1 to 20 %. Examples of such titanocenes are bis(methylcyclopentadienyl)-bis(2,3,6-trifluorophenyl)titanium, bis(cyclopentadienyl)-bis(4-dibutylamino-2,3,5,6-tetrafluorophenyl)titanium, bis(methylcyclopentadienyl)-2-(trifluoromethyl)phenyl-titanium isocyanate, bis(cyclopentadienyl)-2-(trifluoromethyl)phenyl-titanium trifluoroacetate and bis(methylcyclopentadienyl)-bis(4-decyloxy-2,3,5,6-tetrafluorophenyl)titanium. Liquid α-aminoketones are especially suitable for those mixtures.

Mouldings, especially contact lenses, may be produced in a manner known *per se* especially from the polymers according to the invention. For that purpose, for example, the polymers according to the invention are polymerised in a cylindrical mould and, after removal from the mould, the obtainable rods are divided into disks or buttons which can be further processed mechanically, especially by turning processes. In addition, the mouldings or lenses according to the invention may also be produced according to other methods that are known *per se*, such as casting in static moulds, spin casting, compression, deep-drawing, heat-moulding, turning or laser machining. Those process steps are known *per se* and accordingly do not require any detailed explanation for the person skilled in the art.

The production of the mouldings is carried out preferably under an inert atmosphere when open moulds are used. Oxygen is known to inhibit polymerisation and result in prolonged polymerisation times. If closed moulds are used to form the polymerisation product, then the moulds advantageously consist of inert materials of low oxygen permeability having non-adhesive properties. Examples of suitable mould materials are polytetrafluoroethylene, such as Teflon®, silicone rubber, polyethylene, polypropylene and polyester, such as Mylar®. If a suitable mould-release agent is used, it is also possible to employ moulds made of glass and metal.

Casting in static moulds may, for example if moulds having an inner curve and an outer curve are used, result in contact lenses directly. For example, by polymerisation in suitable moulds it is possible to produce contact lenses requiring no further processing ("full-mold" process) or having only one finished face ("semi-mold" process).

Spin-casting may also be employed according to the invention by introducing a solution of the starting materials of the invention into a spin-casting mould, which is then set in rotation. During rotation, the solvent evaporates. The finished contact lens, the dimensions of which can be controlled by the dimensions of the mould, the spinning speed and the viscosity of the solution introduced, remains in the mould.

Compression is effected in accordance with the invention, for example, by compression-moulding a sheet of the polymer according to the invention. A sheet of the polymer can be produced in a manner known *per se*, for example by casting a solution.

From a sheet produced, for example, as mentioned above, it is possible to produce a contact lens in a manner known *per se* by deep-drawing or heat-moulding.

Turning is also a possible last process step in the production of contact lenses of the invention. That step is used whenever a blank obtainable, for example, in accordance with one of the above-mentioned procedures requires further processing. Turning is to be understood as meaning the machining, known *per se*, of contact lens blanks. Appropriate blanks may be produced, for example, by extruding round rods and dividing them into sections, or by casting from a solution. The term "contact lens blank" includes in this context buttons or semi-mold products, for example inner curve blanks. Typical blanks have thicknesses of from 4 to 6 mm and diameters of from 10 to 17 mm, for example 12 or 14 mm. It may be necessary for soft materials to be frozen, especially below the softening point, before undergoing the relevant machining and, if necessary, for the temperatures required for that purpose to be maintained during the machining.

Laser machining may also be used in accordance with the invention, such machining being carried out on blanks, or on contact lenses produced according to one of the other procedures where they still require an additional fine machining of their surface.

The coating of a surface with a vinyl telomer of formula I is carried out in a manner known *per se*, the isocyanate group of the vinyl telomer reacting with active-H groups of the surface. The surface already contains appropriate active-H groups, or such groups are produced on the surface beforehand in a manner known *per se*, for example by plasma treatment (see in this connection, for example, WO 94/06485).

The coating process according to the invention is distinguished by the following steps:

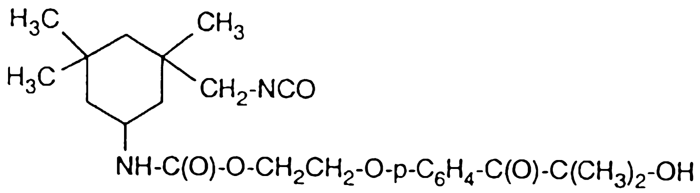
a) if the surface to be coated does not already contain active-H groups, it is provided by a chemical or physical treatment, for example a plasma treatment, with active-H groups that are co-reactive with isocyanate groups, those active-H groups being especially groups R_x-H wherein each R_x, independently of the others, is -O-, -NR_N- or -S- wherein R_N is hydrogen or lower alkyl,
b) the surface containing active-H groups that are co-reactive with isocyanate groups is brought into contact with a vinyl telomer of formula I in the manner described hereinbefore, the isocyanate groups of the vinyl telomer forming covalent bonds with the active-H groups of the surface.

The surfaces are preferably the surfaces of contact lenses. The structure of the surface layers obtained corresponds to a so-called brush structure, which is extremely advantageous.

The following Examples illustrate the subject of the invention without, for example, limiting it to the scope of the Examples. Percentages are by weight, unless expressly indicated to the contrary. In the following Examples, unless indicated to the contrary temperatures are in degrees Celsius and molecular weights, as elsewhere in the description, are average molecular weights (symbol "Mw") unless expressly defined otherwise. The vinyl telomers according to the invention are referred to in this description of the invention also as phototelomers.

A-Examples: Preparation of OCN-functional photoinitiators

Example A1: Preparation of

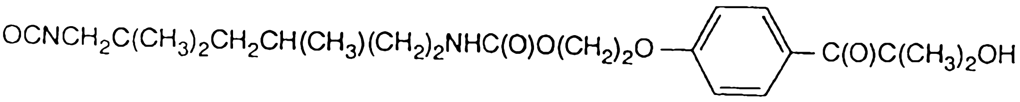


In a 500 ml flask fitted with a reflux condenser, a thermometer, a stirrer and a nitrogen inlet pipe, a solution of 11.125 g (0.05 mol) of freshly distilled isophorone diisocyanate (IPDI) in 50 ml of dry methylene chloride is mixed, under nitrogen, with a solution of 11.2 g (0.05 mol) of 4'-(β-hydroxyethoxy)-2-hydroxyprop-2-ylphenone (Darocure® 2959) in 300 ml of dry methylene chloride and, after the addition of 20 mg of dibutyltin dilaurate as catalyst, the mixture is stirred at room temperature for 48 hours. The course of the reaction is monitored by thin-layer chromatography (eluant: toluene/acetonitrile 7:3) on silica gel plates (60 F_{254}, Art. 5719 Merck). The product obtained is freed of small amounts of unreacted Darocure® 2959 and of disubstituted IPDI by column chromatography on silica gel 60 (eluant toluene/acetonitrile 7:3). After concentration by evaporation of the pure fractions using a rotary evaporator, a colourless oil is obtained which, on cooling to -16°C, slowly crystallises and is then recrystallised from dry diethyl ether. 15.6 g of a white crystalline product are obtained (70 % of the theoretical yield), which has a melting point of 76°C.

The isocyanate content of the product is ascertained by titration with dibutylamine in toluene: calculated 2.242 m.equiv./g, found 2.25 m.equiv./g.

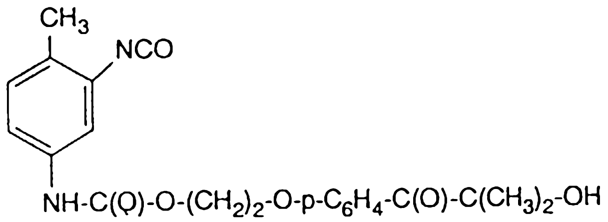
The method is described in "Analytical Chemistry of Polyurethanes" (High Polymer Series XVI, Part III, D.S. David + H.B. Staley editors, Interscience Publishers, New York 1969 p. 86).

Example A2: Preparation of



Analogously to Example A1, 10.5 g (0.05 mol) of 1,6-diisocyanato-2,2,4-trimethylhexane (TMDI) are reacted for 40 hours at room temperature, under nitrogen, with 11.1 g (0.05 mol) of Darocure® 2959 in 400 ml of dry methylene chloride. 14.5 g (67 % of the theoretical yield) of a white crystalline product having a melting point of 41-43°C are obtained. NCO titration: calculated 2.30 m.equiv./g, found 2.36 m.equiv./g.

Example A3: Preparation of

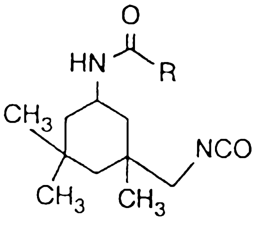


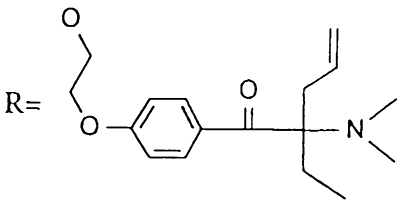
In the apparatus described in Example A1, 1.74 g (0.01 mol) of toluylene-2,4-diisocyanate (TDI) in 20 ml of dichloromethane are reacted with 2.24 g (0.01 mol) of Darocure® 2959 dissolved in 60 ml of dry dichloromethane. The reaction mixture is stirred for 48 hours at room temperature and for 1 hour at 40°C, without the addition of a catalyst, until unreacted Darocure® 2959 can no longer be detected in a thin-layer chromatogram. The product is isolated by precipitation of the reaction solution with 180 ml of dry petroleum ether (b.p. 40-60°C) and is then recrystallised twice from dichloromethane/petroleum ether 1:3.

A white crystalline product having a melting point of 124-125°C is obtained. Yield 17.2 g corresponding to 87 % of the theoretical yield. OCN titration: calculated 2.50 m.equiv./g, found 2.39 m.equiv./g.

Example A4:

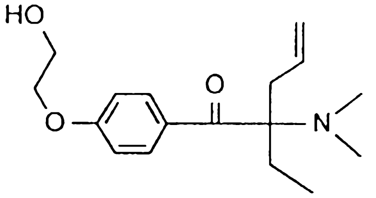
Preparation of the following compound:





In a 100 ml flask fitted with a reflux condenser, a thermometer, a stirrer and a nitrogen inlet pipe, 2.92 g (10 mmol) of 2-ethyl-2-dimethylamino-1-(4-(2-hydroxyethoxy)-phenyl)-pent-4-en-1-one are dissolved in 30 ml of dry methylene chloride, and mixed with 2.22 g (10 mmol) of IPDI dissolved in 30 ml of dry methylene chloride. 2.0 mg of the catalyst DBTDL are added thereto and the mixture is stirred at RT for 72 hours. The course of the reaction is monitored by TLC (eluant: toluene/acetone 6:1). The reaction solution is subsequently stirred into water. The organic phase is removed and washed twice more with water. The organic phase is dried over $MgSO_4$ and concentrated using a rotary evaporator. The residue remaining is purified by column chromatography (toluene/acetone 6:1). 3.4 g (66 %) of a yellow oil remain. The structure is verified by proton NMR, IR and elemental analysis.

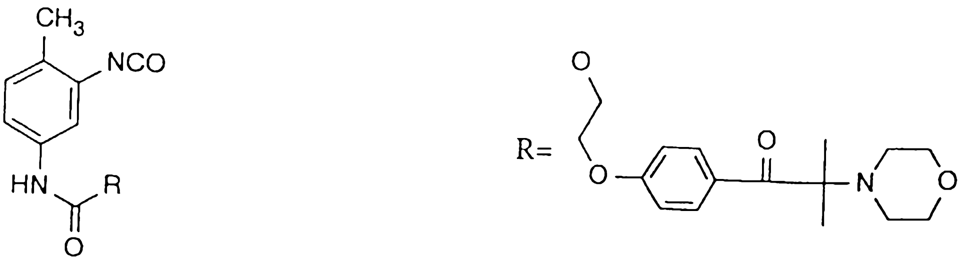
The preparation of 2-ethyl-2-dimethylamino-1-(4-(2-hydroxyethoxy)phenyl)-pent-4-en-1-one



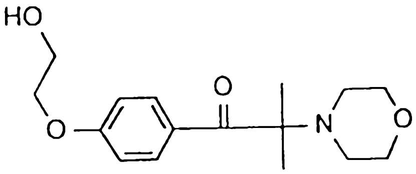
is carried out in accordance with the synthesis described in EP-A-284 561, giving a quantitative yield. Yellowish crystals having a melting point of 80-82°C remain.

Example A5:

In analogy to Example A4, the isocyanate shown below is prepared from 1.17 g (4 mmol) of 1-(4-(2-hydroxyethoxy)phenyl)-2-methyl-2-morpholino-propan-1-one, 0.7 g (4 mmol) of 2,4-TDI, and DBTDL as catalyst in methylene chloride. After the addition of 50 ml of ether and 200 ml of petroleum ether to the reaction mixture, the target compound precipitates in crystalline form. It is filtered off, washed with petroleum ether and then dried *in vacuo*. The compound reproduced below, having a melting point of 97-102°C, is obtained.



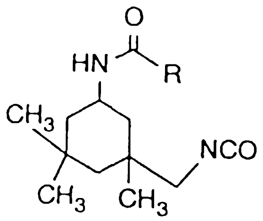
The preparation of 1-(4-(2-hydroxyethoxy)phenyl)-2-methyl-2-morpholino-propan-1-one



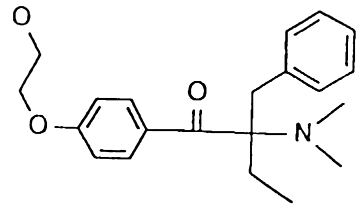
is carried out in accordance with the synthesis described in EP-A-088 050.

Example A6:

In analogy to Example A4 the following compound



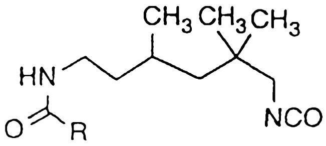
, wherein R is the radical



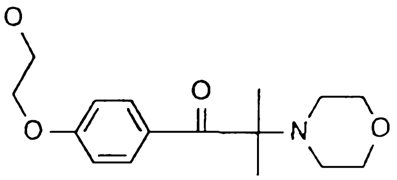
is prepared.

Example A7:

In analogy to Example A4, the following compound is prepared:



R=



B-Examples:

Example B1:

3 g (6.72×10^{-3} mol) of the photoinitiator prepared in Example A1 and 7.5 g (6.72×10^{-2} mol) of freshly distilled N-vinylpyrrolidone are dissolved in 60 ml of dry acetone and introduced into a DEMA-3H photoreactor that has a water-cooled mercury high pressure immersion lamp. The solution in the reactor is then freed of oxygen by three times applying a vacuum and introducing dry nitrogen. The solution prepared in that manner is irradiated with UV light for 100 minutes, with vigorous stirring, under dry nitrogen. During that time, a slightly yellowish solid product is deposited on the wall of the vessel. Once the acetone reaction solution has been removed, it is possible for the deposit to be dissolved away using dry DMSO. By means of precipitation of the two solutions thus obtained using 10 times the volume of non-solvent (dry!), two solids, product A and product B, are obtained.

Product A:

Solution in 50 ml of DMSO precipitated with 500 ml of dry diethyl ether,

amount: 1.4 g of white powder, after drying under a high vacuum over P_2O_5 for 14 hours,

OCN content: 0.041 m.equiv./g, ascertained by titration,

IR spectrum: clear OCN absorption bands at 2145 cm^{-1},

molecular weight: calculated from the OCN content: Mn approximately 25 000 D, measured (vapour pressure osmometry) in DMF: Mn approximately 27 600 ± 3100 D, average degree of polymerisation: calculated from the molecular weight: DPn approximately 220.

Product B: Reaction solution in 50 ml of acetone precipitated with 500 ml of dry diethyl ether,
amount: 1.6 g of white powder,
OCN content: 0.191 m.equiv./g,
IR spectrum: strong OCN absorption bands at 2145 cm^{-1},
molecular weight: calculated from the OCN content: Mn approximately 5260 D, measured (vapour pressure osmometry) in DMF: Mn approximately 5370 +/- 400 D,
average degree of polymerisation: DPn approximately 44.

Example B2:

In the manner described in Example B1, 3 g of the functional photoinitiator and 7.5 g of N-vinylpyrrolidone are reacted with one another under analogous reaction conditions, except that initially only 30 ml of acetone are placed in the photoreactor. Subsequently, with continuous UV irradiation, a solution of 3 g of photoinitiator in 20 ml of acetone and a solution of 7.5 g of NVP in 20 ml of acetone are simultaneously slowly added dropwise over a period of 5 hours. After a further half an hour's irradiation time, the reaction product, which in this case has remained fully in solution, is isolated by precipitation from 700 ml of dry diethyl ether and dried. Yield 5.63 g (53.6 % of the theoretical yield), OCN content: 0.266 m.equiv./g, molecular weight: Mn approximately 3760.

Examples B3 to B10:

Analogously to Example B2, a number of other hydrophilic and hydrophobic vinyl monomers are reacted to form OCN-functional phototelomers:

Example B3: 3 g of photoinitiator from Example A1,
vinyl monomer: 10 g of DMA
OCN content (m.equiv./g): 0.236 Mn: 4240

Example B4: 3 g of photoinitiator from Example A2,
vinyl monomer: 12 g of diethylene glycol monomethyl ether methacrylate
OCN content (m.equiv./g): 0.122 Mn: 8200

Example B5: 3 g of photoinitiator from Example A3,
vinyl monomer: 12 g of 2-(N,N-dimethylaminoethyl) methacrylate
OCN content (m.equiv./g): 0.568 Mn: 1760

Example B6: 3 g of photoinitiator from Example A4,
vinyl monomer: 17 g of TRIS
OCN content (m.equiv./g): 0.444 Mn: 2250

Example B7: 3 g of photoinitiator from Example A1,
vinyl monomer: 10 g of MMA
OCN content (m.equiv./g): 0.068 Mn: 14 700

Example B8: 3 g of photoinitiator from Example A1,
vinyl monomer: 22 g of 2,2,3,4,4,4-hexafluorobutyl methacrylate
OCN content (m.equiv./g): 0.30 Mn: 3340

Example B9: 3 g of photoinitiator from Example A1,
vinyl monomer: 20 g of 3-(pentamethyldisiloxy)propyl methacrylate
OCN content (m.equiv./g): 0.140 Mn: 7160

Example B10: 3 g of photoinitiator from Example A1,
vinyl monomer: 15 g of glycidyl methacrylate
OCN content (m.equiv./g): 0.089 Mn: 11 200

C-Examples: Surface modification, by means of OCN phototelomers, of films and planar substrates

Examples C1-C4:

Films of various polymer materials that contain reactive groups are wetted on the surface with a solution of the phototelomer prepared according to Example B1 in a suitable solvent (conc. ~20 % by weight), the technique used being immersion, spraying or spreading. The films treated in that manner are heated at 60°C for 24 hours under dry nitrogen, and then freed of unreacted phototelomer by washing with acetone. After drying in the absence of light, the films are analysed by means of FTIR microscopy.

Example	Polymer film	$\overline{M}n$	Solvent	IR bands (cm^{-1})
C1	polyvinyl alcohol	~70 000	DMSO	PVP: 1660 (C=O) 1440-1470 (C-H) 1280 (C-N)
C2	chitosan	~145 000	DMSO	PVP: 1660 (C=O) 1440-1470 (C-H) 1280 (C-N)
C3	collagen	~80 000	DMSO	PVP: 1660 (C=O) 1440-1470 (C-H) 1280 (C-N)
C4	polyvinyl alcohol crosslinked with 1 % TMDI	-	MEK +1% DMSO	PVP: 1660 (C=O) 1440-1470 (C-H) 1280 (C-N)

TMDI = trimethylhexane diisocyanate, MEK = methyl ethyl ketone

Example C5:

Flat plates (5 x 5 x 0.5 cm) of a) polyurethane, b) glass and c) aluminium coated with Kapton-polyimide are subjected to conventional treatment with an argon plasma in the presence of n-heptylamine. By means of that process a film a few nanometres thick that contains reactive amino groups is produced on the substrates. In the manner described in Examples C1 to C4, the plates so pretreated are treated with a solution of product A from Example B1 in DMSO. In that manner a hydrophilic coating of polyvinylpyrrolidone is produced on the plates, the coating having a brush structure. The following contact angles are measured on the plates using a Krüss G40 instrument:

	Substrate a)	Substrate b)	Substrate c)
contact angle untreated [°]:	78	46	96
contact angle treated [°]:	38	36	42

Example C6: (plasma-treated silicone film)
A silicone rubber film produced by UV-curing PS-2067 (Petrarch Hüls America Inc., Bristol USA), which has been applied to a Folanorm sheet (Folex, Zürich, Switzerland) to produce a coating, is heated thoroughly at 80°C and 10^{-3} torr. The film is then placed in a commercially available 13.6 megahertz radiofrequency plasma reactor and the system is evacuated to 0.1 mbar. At that pressure, and with an oxygen stream of 10 standard cubic centimetres and 40 watt power, the film is exposed for 30 seconds to an oxygen plasma. After disconnecting the plasma and aerating the reactor, the film is stored in air.

Example C7: (Polybutadiene film, plasma-treated)
A 0.5 millimetre-thick film is cast from a THF solution of poly-1,2-butadiene (syndiotactic polybutadiene, Polysciences Inc., Product 16317) on a Folanorm support sheet in a nitrogen atmosphere. The film is subjected to treatment with oxygen plasma as described in Example C6.

Example C8:
A film is cast from a mixture of 92 % 2-hydroxyethyl methacrylate (HEMA), 7.7 % ethylene glycol dimethacrylate and 0.3 % Irgacure® 184 (0.3 %) on a Folanorm support sheet and fully cured in customary manner by UV irradiation.

Example C9:
A 10 % DMSO solution of 99 % polyvinyl alcohol (PVA), Mn 72 000, (Fluka AG, Switzerland), and 1 % isophorone diisocyanate (Aldrich) is spread on Folanorm to form a film and fully cured by heating for two hours at 70°C, latterly at 0.01 torr. The film is freed of DMSO and excess IPDI by washing with THF and then residual solvent is removed over a period of 6 hours at 80°C and 0.001 torr.

Examples C10 to C13:

The following Table shows the contact angles (Krüss G40) of polymer films such as are described in Examples C6 to C9, which have been treated according to the method indicated in Example C1 with the OCN-functional NVP phototelomer prepared in Example B2.

Example	Material (film)	Contact angle [°] untreated	treated
C10	silicone (C6)	100.4	54.5
C11	polybutadiene (C7)	79.5	46.2
C12	poly-HEMA (C8)	78.4	38.5
C13	PVA (C9)	47.1	32.5

Example C14:

Soft hydrogel lenses (STD-Cibasoft^{TM}, Tefilcon, CIBA Vision, Atlanta, USA) based on crosslinked poly-HEMA, washed free of salts and freeze-dried, are treated for 12 hours with a solution of a phototelomer (1 g in 10 ml of dry DMSO) that contains 10 mg of dibutyltin dilaurate as catalyst. The phototelomers described in Examples B1 (A), B1 (B), B3, B4 and B5 are used. Subsequently, the lenses are washed carefully with acetone and water and dried *in vacuo* at 0.1 mbar. The Table which follows gives the contact angles of the lenses which have been so treated and then autoclaved (120°C, 30 minutes) in phosphate-buffered (pH 7.4) physiological saline. The data show that a hydrophilic surface has been produced on the lenses by the treatment.

Example	Phototelomer of Example	Contact angle untreated	treated
a)	B1 (A)	78	52
b)	B1 (B)	78	46
c)	B3	78	42
d)	B4	78	36
e)	B5	78	50

Example C15:

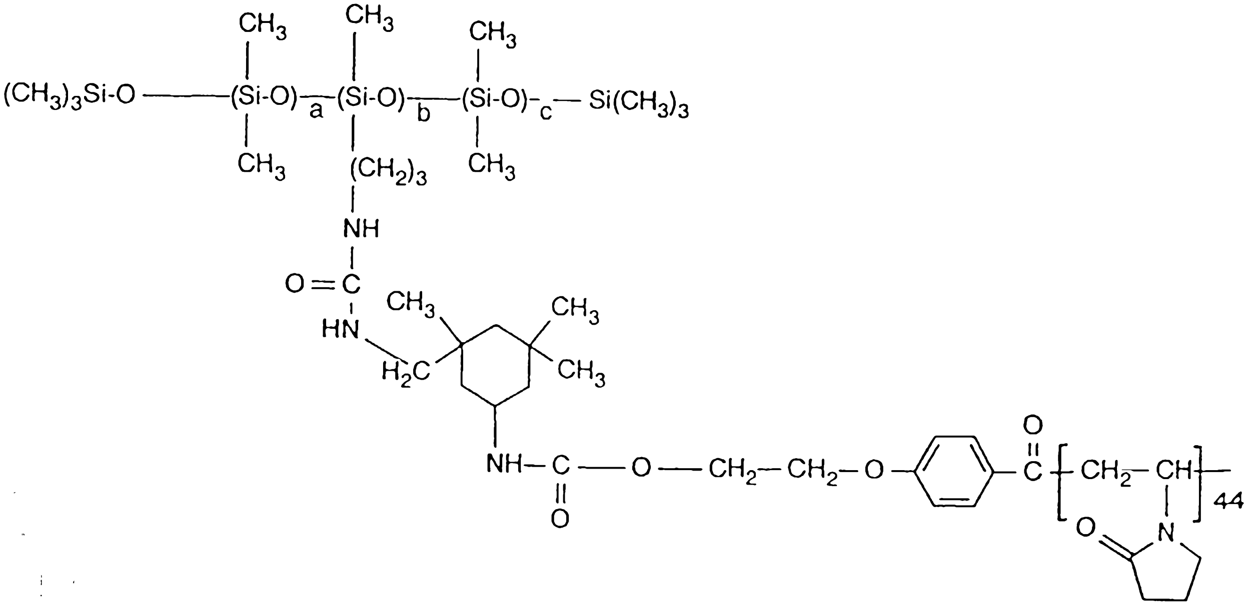
Various contact lenses are subjected to a plasma treatment in customary manner in the presence of ammonia gas or of n-heptylamine, in order to produce reactive amino groups on the surface. The so pretreated lenses are then treated in the manner described in Example C1 with a solution of the PVP phototelomer prepared in Example B2. The contact angles (Krüss G40 instrument) indicated in the Table which follows show that the treated and then autoclaved contact lenses have a hydrophilic surface.

Example	Contact lens material	Plasma gas	Contact angle	
			untreated	treated
a)	Tefilcon	ammonia	-	32
b)	silicone*	ammonia	104	52
c)	silicone*	heptylamine	104	48
d)	Atlafilcon A	heptylamine	-	37

*The silicone material used is a copolymer that consists of 15 % by weight of methyl methacrylate, 15 % by weight of TRIS and 70 % by weight of a polydimethylsiloxane macromer having an average molecular weight Mn of approximately 4000 that contains two terminal hydroxybutyl groups each of which has been terminated by isocyanatoethyl methacrylate.

D-Examples:

Example D1: Preparation of a comb polymer using an OCN-functional phototelomer



In a 250 ml flask fitted with a reflux condenser, a thermometer, a stirrer and a nitrogen inlet pipe, a solution of 11.78 g (0.00224 mol) of the OCN-terminated poly(N-vinylpyrrolidone) telomer B described in Example B1 in 100 ml of dry DMSO is reacted, under dry nitrogen, with 4.37 g of aminoalkylpolydimethylsiloxane (0.515 m.equiv. NH_2/g, Petrarch PS 813®: Mn ~3000, b = 3, a+c = 37) dissolved in 50 ml of dry dichloromethane. The reaction mixture is stirred for 2 hours at room temperature and is then heated at 40°C for one hour. After evaporation of the dichloromethane using a rotary evaporator, the viscous DMSO solution of the amphiphilic PDMS-poly-NVP comb polymer is isolated by precipitation from 1000 ml of dry diethyl ether. After removal of solvent residues latterly under a high vacuum at 40°C and 10^{-4} torr, 15.9 g (98 % of the theoretical yield) of a viscous colourless product having surface-active properties are obtained. The IR spectrum no longer indicates OCN absorption.

Examples D2-D6:

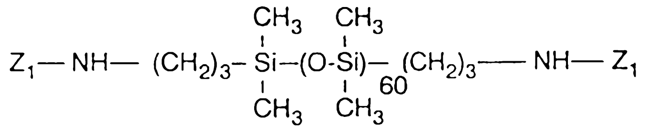
Analogously to Example D1, further block and comb polymers are obtained from the described OCN-functional phototelomers by reaction with aminofunctional macromers. The results are listed in the Table which follows, "Z_x" in the structural formulae denoting in each case the radical of the phototelomer bonded by way of a urea bridge. The index "x" denotes the number of the phototelomer Example from the series of B-Examples.

Table

Example	Aminofunctional macromer	Compound according to Ex. B1-B10	Structure (product)	Yield
D2	X-22-161c (Shin Etsu, JP) 7.8 g (0.43 m.equiv. NH_2/g) $\overline{M} \sim 4600$	12.63 g of B1A (3.36 mmol)	a	19.6 g (96 %)
D3	Jeffamine® T 403 (Texaco, USA) 2.8 g (6.38 m.equiv. NH_2/g)	14.3 g of B6 (6.36 mmol)	b	17.0 g (99.4 %)

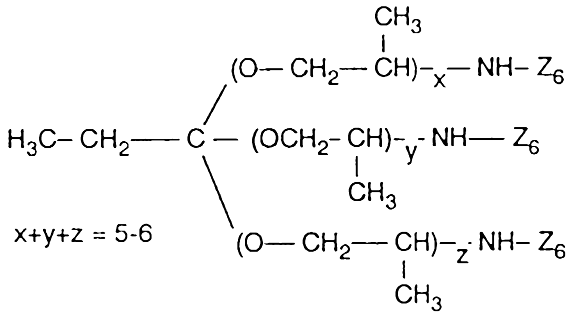
D4	Jeffamine® D2000 (Texaco, USA) 4.0 g (1 m.equiv. NH_2/g)	6.6 g of B8 (2.0 mmol)	c	10.2 g (96 %)
D5	KF-8003 (Shin Etsu, JP) 4.6 g (0.49 m.equiv. NH_2/g)	9.55 g of B3 (2.25 mmol)	d	13.9 g (98 %)
D6	X-22-161B (Shin Etsu, JP) 3.23 g (0.699 m.equiv. NH_2/g) $\overline{M}$ ~ 2900	4.0 g of B5 (2.29 mmol)	e	6.85 g (95.4 %)

a =



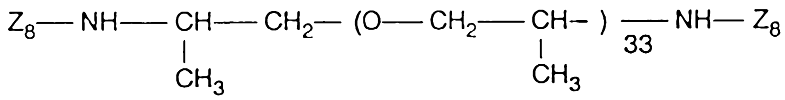
$$Z_1{-}NH{-}(CH_2)_3{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}(O{-}\underset{CH_3}{\overset{CH_3}{Si}})_{60}{-}(CH_2)_3{-}NH{-}Z_1$$

b =



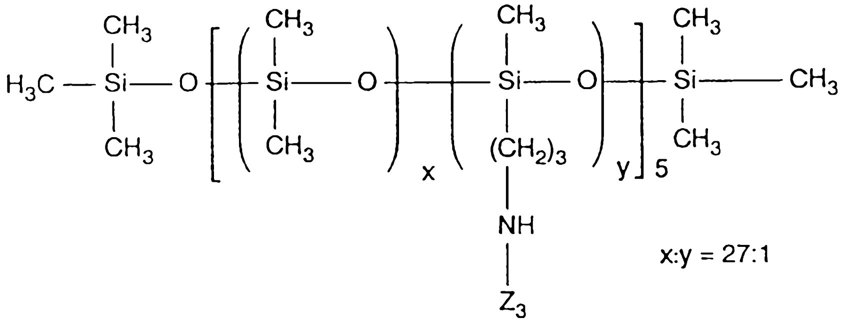
x+y+z = 5-6

c =



$$Z_8{-}NH{-}\underset{CH_3}{CH}{-}CH_2{-}(O{-}CH_2{-}\underset{CH_3}{CH}{-})_{33}{-}NH{-}Z_8$$

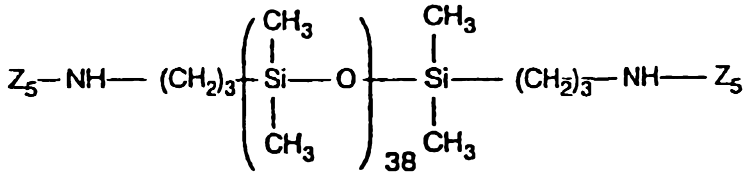
d =



$$H_3C{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\left[\left(\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right)_x\left(\underset{\underset{\underset{Z_3}{|}}{\underset{NH}{|}}}{\underset{(CH_2)_3}{|}}{\overset{CH_3}{\overset{|}{Si}}}{-}O\right)_y\right]_5{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_3$$

x:y = 27:1

e =



$$Z_5-NH-(CH_2)_3-\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_{38}-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-NH-Z_5$$

wherein Z_1, Z_3, Z_5, Z_6 and Z_8 are the corresponding radicals from Examples B1, B3, B5, B6 and B8.

<u>Example E1:</u> (Preparation of a polymerisable macromonomer)

Under the reaction conditions listed in Example D1, 37.6 g (0.01 mol) of the OCN-functional PVP phototelomer described in Example B2 are reacted with 1.31 g of 2-hydroxyethyl methacrylate (HEMA) in 250 ml of dry DMSO, with 10 mg of dibutyltin dilaurate being added as catalyst. After precipitation with dry diethyl ether and drying at 10^{-4} torr, 38.8 g of a white pulverulent product are obtained.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The claims defining the invention are as follows:

1. A vinyl telomer of formula I

$$O{=}C{=}N\text{-}PI^{*}\text{-}(A)_{p}\text{-}R_{a} \qquad (I)$$

wherein
PI^{*} is a bivalent radical of a photoinitiator,
A is a substituted bivalent 1,2-ethylene radical derived from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,
R_a is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator, and
p is an integer from 5 to 200.

2. A process for the preparation of a compound of formula I according to claim 1, which comprises reacting a photoinitiator of formula B

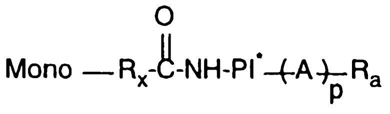
$$OCN\text{-}PI^{*}\text{-}R_{aa} \qquad (B),$$

wherein PI^{*} is as defined in claim 1 and R_{aa} is the moiety of a photoinitiator that forms the less reactive free radical on cleavage of the photoinitiator, with a vinyl monomer in a manner known *per se*, wherein the monomer is incorporated as component "A" into the vinyl telomer, and the chain reaction is terminated by a radical R_a which may be the moiety R_{aa} or another chain reaction terminator being present in the reaction mixture.

3. A process according to claim 2, which comprises carrying out the reaction under the action of UV irradiation.

4. A process according to claim 3, wherein a solution comprising a photoinitiator of formula B, and a second solution comprising a vinyl monomer, are simultaneously metered in during UV irradiation.

5. A polymerisable compound of formula C

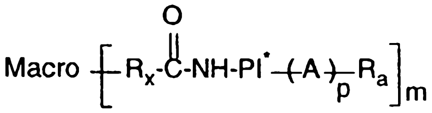


$$\text{Mono} - R_x - \overset{\overset{\displaystyle O}{\|}}{C} - NH - PI^{*} - (A)_p - R_a \qquad (C)$$

wherein Mono is a monovalent radical of a vinyl monomer from which the group R_x-H has been removed,
each R_x, independently of the others, is a bond, -O-, -NR_N- or -S- wherein R_N is hydrogen or lower alkyl,
PI^* is a bivalent radical of a photoinitiator,
A is a substituted bivalent 1,2-ethylene radical derived from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,
R_a is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator, and
p is an integer from 5 to 200.

6. A process for the preparation of a compound of formula C according to claim 5, wherein a vinyl telomer of formula I as defined in claim 1 is reacted in a manner known *per se* with a vinyl monomer that contains at least one R_x-H group wherein R_x is -O-, -NR_N- or -S-, R_N being hydrogen or lower alkyl.

7. A block copolymer of formula D that is uncrosslinked but if desired crosslinkable



$$\text{Macro} \left[R_x - \overset{\overset{\displaystyle O}{\|}}{C} - NH - PI^{*} - (A)_p - R_a \right]_m \qquad (D)$$

wherein Macro is an m-valent radical of a macromer from which the number m of groups R_x-H has been removed,
each R_x, independently of the others, is a bond, -O-, -NR_N- or -S- wherein R_N is hydrogen or lower alkyl,
PI^* is a bivalent radical of a photoinitiator,
A is a substituted bivalent 1,2-ethylene radical derived from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,
each R_a, independently of the others, is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator,
p, independently of m, is an integer from 5 to 200 and
m is an integer from 1 to 100.

8. A process for the preparation of a compound of formula D according to claim 7, which comprises reacting a macromer of formula A:

$$\text{Macro-}(R_xH)_m \qquad (A),$$

wherein Macro, R_x and m are as defined in claim 7 except that R_x is other than a bond, in a manner known *per se* with a vinyl telomer of formula I

$$O{=}C{=}N\text{-}PI^{*}\text{-}(A)_p\text{-}R_a \qquad (I)$$

wherein PI^*, A, R_a and p are as defined in claim 7.

9. A polymer, which is a polymerisation product of a polymerisable mixture that comprises the following components:

a) a polymerisable compound of formula C as defined in claim 5,

b) if desired a copolymerisable vinyl monomer

c) a copolymerisable crosslinker.

10. A polymer, which is a polymerisation product of a polymerisable mixture that comprises the following components:

aa) a polymerisable compound of formula D as defined in claim 7, in which a reactive group is present in the component $-(A)_p-$,

bb) if desired a copolymerisable vinyl monomer

cc) a crosslinker that is co-reactive with the reactive group in the component $-(A)_p-$ of the compound of formula D.

11. A process for the preparation of a polymer according to either claim 9 or claim 10, which comprises polymerising components a), b) and c) as defined in claim 9, or components aa), bb) and cc) as defined in claim 10, in a manner known *per se*.

12. A moulding comprising essentially a polymer according to either claim 9 or claim 10.

13. A moulding according to claim 12, which is a contact lense.

14. The use of a vinyl telomer of formula I as defined in claim 1 for the coating of surfaces.

15. Use according to claim 14, wherein the surfaces are the surfaces of contact lenses.

16. Vinyl telomers of formula I, processes for their preparation; polymerisable compounds of formula C, processes for their preparation; block copolymers of formula D, processes for their preparation; and polymers of claim 9 or 10, processes for their preparation and mouldings thereof substantially as hereinbefore described with reference to the Examples.

DATED this 10th day of December 1998

NOVARTIS AG

By its Patent Attorneys
DAVIES COLLISON CAVE

Abstract

The invention relates to novel NCO-terminated vinyl telomers that are suitable especially for the modification of surfaces and as coating materials, and are also suitable for the preparation of polymerisable compounds and block copolymers that can be reacted to form polymers and converted into mouldings, especially contact lenses, respectively. The OCN-terminated vinyl telomers according to the invention are compounds of formula I

$$O=C=N-PI^{*}-(A)_{p}-R_{a} \qquad (I)$$

wherein
PI^{*} is a bivalent radical of a photoinitiator,
A is a substituted bivalent 1,2-ethylene radical derivable from a copolymerisable vinyl monomer by replacing the vinyl double bond by a single bond,
each R_a, independently of the others, is a monovalent group that is suitable to act as a polymerisation chain-reaction terminator, and
p is an integer from 3 to 500.

The OCN-functional vinyl telomers are used in the preparation of macromers and block, comb, star and graft copolymers, which are preferably used in the production of contact lenses. In addition, the telomers are used for the coating of a wide variety of surfaces, especially contact lens surfaces.