

Reactions of polysiloxane intermediates, which contain hydroxyl, amino or thiol groups attached by an intervening alkylene group to the Si-atom, with an equivalent amount of diisocyanate, followed by endcapping with a hydroxy- or amino-alkyl (meth)acrylate, are for instance described in US-PS 4 136 250, US-PS 4 130 708 and 4 486 577. Since urethane and urea formation proceeds at low temperatures and without the development of by-products, this is a practical synthesis, especially where the final objective is a contact lens with uniform properties and maximal reproducibility. Further advantages of polyurethanes and polyureas are their great strength and flexibility and good compatibility and clarity in combination with second polymers, this being a result of hydrogen bonding as e.g. in nylon.

However, a remaining disadvantage of the structure and synthesis described in US Patents 4 136 250 and 4 486 577 is that, due to the statistical nature of step-growth polymerization kinetics, a certain amount of chain-extension reactions always occurs during the reaction of the diisocyanate with the polysiloxanediol, leading at best to an increase in viscosity and increase in polydispersity of the prepolymer that are difficult to control or reproduce, and at worst to premature gelation or at least the risk of premature gelation. Although in applications such as photo-curable coatings, small variations in polymer dispersity and functionality are of little concern, in other applications, for instance in the production of oxygen-permeable hard and soft contact lenses, precise reproducibility from batch to batch is of utmost importance in order to meet narrow specifications of hardness, flexibility and clarity.

It has now been discovered that the above-mentioned problems can be overcome and an unsaturated polydimethyl-

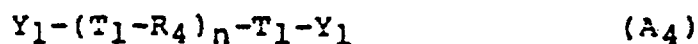
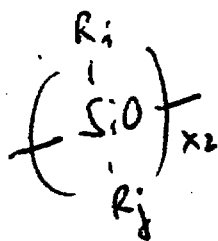
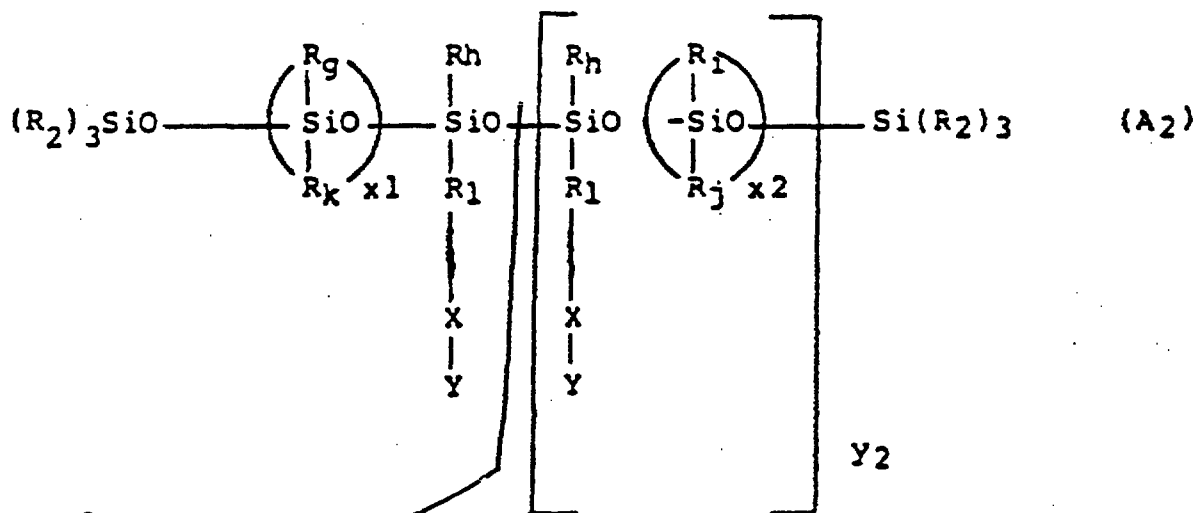
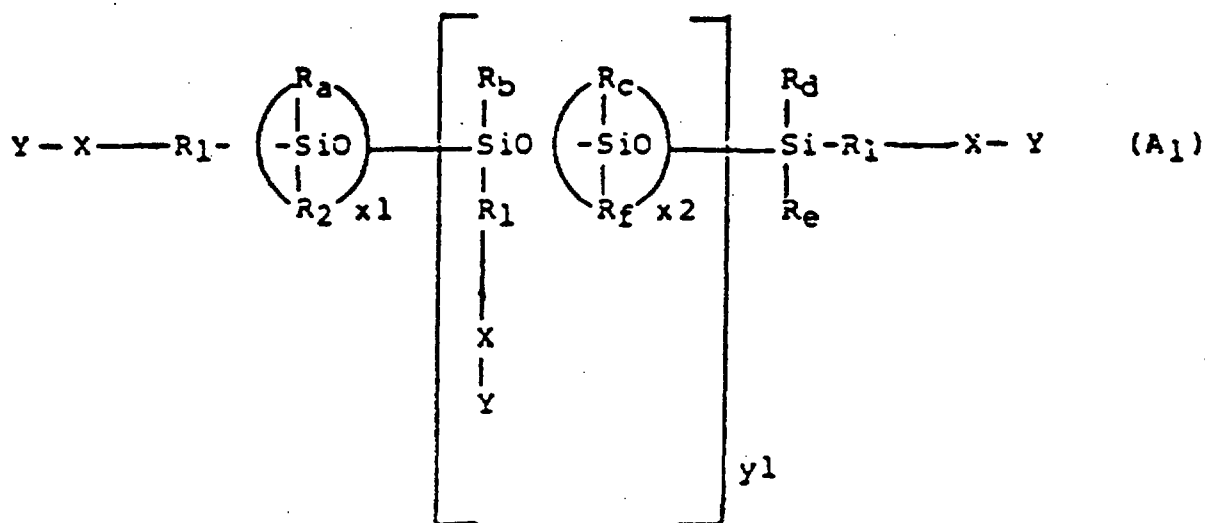
siloxane curable by radiation or heat can be synthesized if a polydimethylsiloxane having a molecular weight of 400-10 000 and containing at least two -OH, -NH or -SH groups is reacted with an unsaturated monoisocyanate, for example with 2-isocyanatoethyl methacrylate (IEM), 2-isocyanoethyl acrylate, 3-isocyanotopropyl methacrylate, 1-methyl- and 1,1-dimethyl-2-isocyanatoethyl acrylate or methacrylate, of which 2-isocyanatoethyl methacrylate is preferred. Within the scope of the invention it is also possible to use vinyl isocyanate and 2-isocyanatoethyl fumarate.

The present invention relates to a polysiloxane containing at least one unsaturated group that is suitable for the subsequent polymerization with one or more vinyl monomers.

The present invention also relates to copolymers containing the polysiloxane as one component, and a vinyl monomer as the second component, and especially to contact lenses formed from the crosslinked copolymerization product of the polysiloxane macromer with one or more water-soluble and/or water-insoluble mono-olefinic and diolefinic monomers.

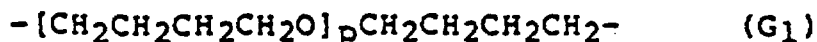
The polysiloxane macromer (A)

The polysiloxane macromer according to the invention is a linear or branched polysiloxane macromer having a molecular weight from about 400 to 100 000, as measured by end group analysis or gel permeation chromatography, the macromer comprising at least one terminal or pendant polymerizable olefinic group, and at least one such polymerizable olefinic group per molecular weight unit of 5000, the said group being attached to the polysiloxane by way of a urethane, thiourethane or urea linkage, and the said macromer having the structure A₁, A₂, A₃ or A₄



wherein:

R_1 is a linear or branched alkylene group having from 2 to 6 carbon atoms or a polyoxyalkylene group of the structure G or G_1



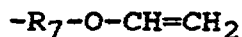
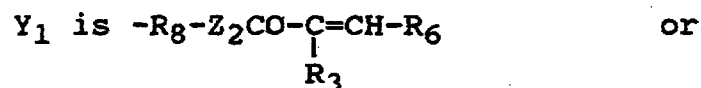
wherein R_3 is hydrogen or methyl and p is an integer from 1-50, R_2 , R_a , R_b , R_c , R_d , R_e , R_f , R_g , R_h , R_i , R_j and R_k are independently methyl or phenyl, x_1 , x_2 are integers from 1 to 500 with the proviso that the sum of $x_1 + x_2$ is 7 to 1300, y_1 is 0 to 14 and y_2 is 1 to 13 with the proviso that the ratio of $\frac{x_1 + x_2}{y_1 + 2}$ or $\frac{x_1 + x_2}{y_2 + 1}$ is not

$$\frac{x_1 + x_2}{y_1 + 2} \quad \frac{x_1 + x_2}{y_2 + 1}$$

greater than 70,

X is $-\text{Z}_1 - \text{CO} - \text{NH} -$,

Z_1 is oxygen, sulfur or $-\text{NR}_5-$, wherein R_5 is hydrogen or C_1 - C_4 alkyl, Z_1 is bonded to R_1 ; with the proviso that, for the Contracting States DE, FR, GB, IT and SE Z_1 in a macromer of the structure A_1 is other than oxygen;



wherein:

R_6 is: hydrogen, methyl, $-\text{COOR}_5$ or $-\text{COOR}_7\text{OH}$,

$\text{Z}_2 = \text{oxygen or } -\text{NR}_5-$,

Y is the same as Y_1 , or Y is H, alkyl having from 1 to 8 carbon atoms, cyclohexyl, phenyl, o-tolyl, m-tolyl or p-tolyl, with the proviso that at least one of the radicals Y must have the same meaning as Y_1 ,

n is 1 to 10.

The compounds of structures (A₁) and (A₂) are thus polysiloxanes connected by a urethane or urea linkage to vinyl groups; the vinyl group may be an acrylic, methacrylic, fumaric or itaconic ester or a vinyl ether.

The compounds of structures (A₃) and (A₄) are extended or oligomeric polysiloxanes wherein the original polysiloxane-polyol, -polyamine or -polythiol is first extended with a diisocyanate molecule to form the group R₄. The resulting extended product is then reacted with a vinyl-containing monoisocyanate to form the compounds of structures A₃ or A₄.

Preferred embodiments of the invention include the following:

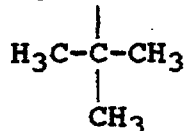
R₁ = alkylene having 3 or 4 carbon atoms,
R₂, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j and R_k = methyl,
x₁ + x₂ = 10 to 100,
y₁ = 0 to 2,
y₂ = 1 to 3,
Z₁ = oxygen or -NH-,
R₄ = a divalent radical of an aliphatic or cycloaliphatic diisocyanate having from 6 to 10 carbon atoms

Y is the same as Y₁,

R₆ = hydrogen,

R₈ = -CH₂CH₂-;

Z₂ = oxygen or -N-



The most preferred embodiments include the polysiloxane of structure (A₂) wherein

Z₁, Z₂ = oxygen, and

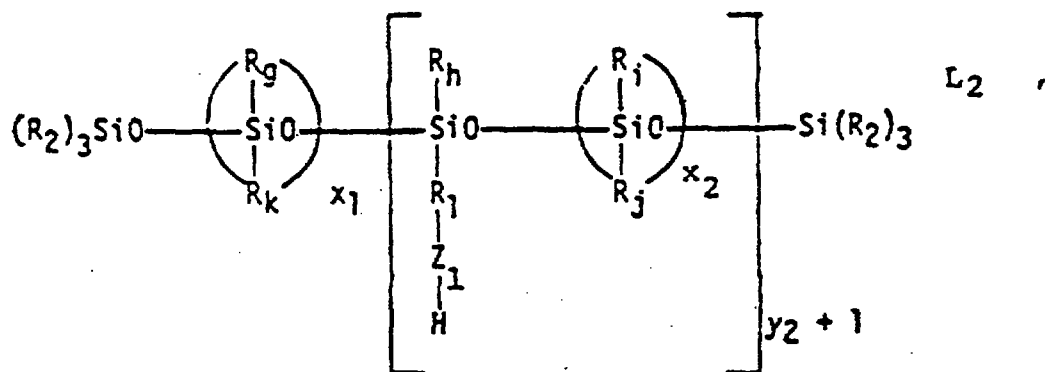
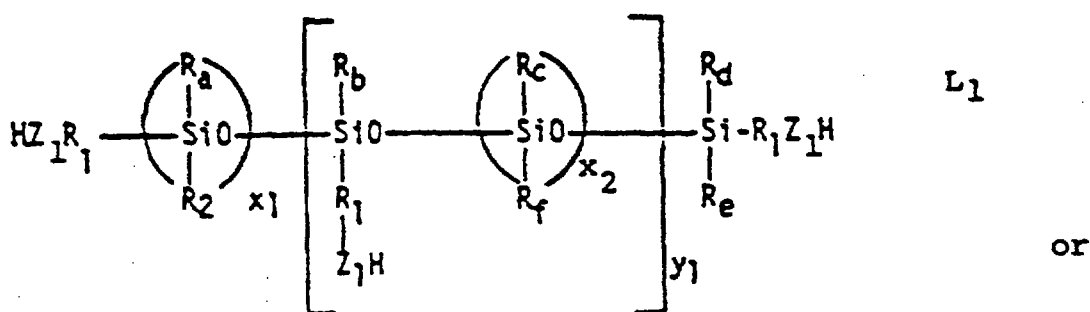
y₂ = 1 or 2;

or polysiloxanes of structures A₃ or A₄ wherein

R₄ = a divalent radical of isophorone diisocyanate.

The unsaturated polysiloxane of the invention is synthesized by reaction of a polysiloxane of the general structure L₁ or L₂ with an isocyanate-substituted vinyl compound. These intermediates are largely commercial products.

Polyfunctional polysiloxanes, suitable for use as starting materials for the macromer (A), are of structures:

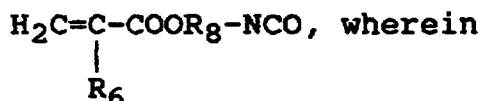


wherein

R₁, R₂, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j, R_k, x₁, x₂, y₁, y₂, and Z₁ are defined as described above.

The isocyanato-functional vinyl compound that may be used

for the reaction with the polysiloxanes of structure L₁ or L₂ is an NCO-substituted alkyl acrylate or methacrylate of the general structure



R₆ is defined as above and

R₈ is an alkylene group having from 2 to 6 carbon atoms.

Examples include:

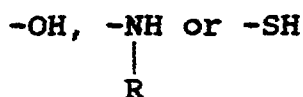
2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate and 1,1-dimethyl-2-isocyanatoethyl acrylate, with 2-isocyanatoethyl methacrylate being preferred. Suitable methods of preparing said isocyanato esters are known, e.g. as shown in US-PS 2 718 516 and GB-PS 1 252 099.

The preferred monomer is 2-isocyanatoethyl methacrylate (IEM). Other monomers include isocyanatoalkyl vinyl ethers, such as 2-isocyanatobutyl vinyl ether, and esters, such as 2-isocyanatoethyl fumarate and vinyl isocyanate. It is also possible to use monoisocyanates obtained by the reaction of 1 mol of a hydroxy- or an amino-functional alkyl vinyl monomer with 1 mol of diisocyanate, for instance the reaction products of 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl methacrylate, 3-hydroxyethyl vinyl ether or t-butylaminoethyl methacrylate with isophorone diisocyanate, (3,3,4)-trimethylhexane-1,6-diisocyanate, toluene diisocyanate or diphenylmethane-4,4'-diisocyanate.

If the polyfunctional polysiloxane of structure L₁ or L₂ contains more than two functional groups, it is also possible to cap one of those groups with acid chlorides,

such as benzoyl chloride, or with anhydrides, such as maleic, phthalic or norbornyl anhydride, or with monoisocyanates, such as butyl or phenyl isocyanate, before carrying out any further polycondensation and chain-extension reaction or capping with the isocyanato-substituted vinyl monomer as described below.

The reaction of the polysiloxane -polyol, -polyamine or -polythiol is carried out under conditions sufficient to cause the isocyanate group to react with the



group of the polysiloxane to form a urethane, urea or thiourethane linkage. Advantageously, polyurethane formation is carried out in the presence of a catalyst, preferably an organometallic catalyst, such as stannous octoate or dibutyltin dilaurate. When carrying out the reaction it is expedient for the reaction mixture of reactive polysiloxane and isocyanatoalkyl ester, preferably neat or, alternatively, dissolved in a non-reactive solvent, such as ether, ethyl acetate, toluene or cellosolve acetate, to be kept in a vessel for a reaction time of from about 1 to about 24 hours at a temperature of from ambient to 140°C. Polyurea formation from a polysiloxane-polyamine with either primary or secondary amino groups proceeds rapidly, without additional catalyst, at room temperature. The amount of the isocyanatoalkyl ester can be stoichiometric or slightly in excess of the pendant functional groups of the polysiloxane. However, the amount of IEM needed is preferably less than the stoichiometric amount, particularly if only partial capping of the polyol is desired.

At least one of the reactive groups on polysiloxanes L₁ or L₂ is reacted with the isocyanato-functional unsaturated monomer, and a mono-, di-, tri- or poly-

unsaturated polysiloxane is obtained that has a molecular weight distribution identical to that of the starting polysiloxane and contains, depending on the degree of vinyl substitution, zero to several remaining hydroxyl, amino or thiol groups.

If all available reactive groups on L_1 or L_2 are replaced with a vinyl group, then the resulting di- or poly-vinyl polysiloxanes can be used directly, with or without additional vinyl monomers for free-radical polymerizations, to form crosslinked polymers. If one or several of the reactive groups remain unsubstituted, the resulting mono- or poly-vinyl polysiloxanes can be used as such either for the free-radical polymerization, or for additional reactions, such as polycondensation reactions with diisocyanates, anhydrides, diacid chlorides, diacids, diesters, epoxides, as well as chain-extension reactions with diisocyanates and diamines or diols.

Chain-extension reactions, especially with polysiloxane dialkanols and diisocyanates, can readily be carried out before the reaction with the isocyanatoalkyl-vinyl monomer, and provide a means of adjusting the crosslink density of the final polymer. It is also possible to introduce additional vinyl groups by reaction of the isocyanato-functional polysiloxane prepolymers with hydroxyalkyl (meth)acrylates or N-tert-butylaminoethyl methacrylate, as described in US-PS 4 136 250.

Suitable building blocks for carrying out such polycondensations include maleic anhydride and 1,4-butanediol or 1,4-butyndiol to introduce unsaturation, or polyethylene oxide diols or diamines to render the polymers hydrophilic. Diisocyanates suitable for carrying out chain-extension reactions include, e.g.:

ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, o-diisocyanatobenzene, m-diisocyanatobenzene, p-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatophenyl)methane, toluene diisocyanate, 3,3-dichloro-4,4'-diisocyanatobiphenyl, tris(4-isocyanatophenyl)methane, 1,5-diisocyanatonaphthalene, hydrogenated toluene diisocyanate, 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (= isophorone diisocyanate), 1,3,5-tris-(6-isocyanatohexyl)biuret, 1,6-diisocyanato-2,2,4-(4,2,2)-trimethylhexane.

It is thus possible to form either linear or branched mono- or poly-unsaturated polysiloxanes with molecular weights ranging from 400 to 100 000, or to form cross-linked unsaturated PDMSi-polyurethane rubbers.

The resulting polysiloxanes having pendant ethylenically unsaturated groups are generally used without further purification. If a solvent has been used in the reaction, it can be removed, or the composition containing the solvent can be employed as such.

The urethane-polysiloxane is generally a resinous (solid or semi-solid) or viscous liquid material which has an average molecular weight (number average M_n) from about 400 to about 100 000, preferably from about 500 to about 10 000, depending on the M_n of the polysiloxane used as a starting material. For the purposes of this invention, M_n is determined by measuring the percentage of active hydrogen of the starting polysiloxane, while the molecular weight distribution is determined by gel permeation chromatography.

Preferably, the unsaturated polysiloxanes of the invention are used in combination with other vinyl monomers to produce crosslinked polysiloxane/polyvinyl block copolymers.

The great variety of monomeric reactants makes it possible to prepare either hard, highly crosslinked copolymers with suitable acrylic, methacrylic or other vinyl monomers, or to prepare soft, rubber-like polymers having a low crosslink density.

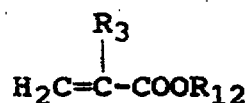
It is also possible to prepare by copolymerization with hydrophilic monomers polysiloxane-hydrogels with water contents of up to 80%; such compositions are especially suitable as highly oxygen-permeable soft contact lenses.

Reactive monomers which can be employed together with the unsaturated polysiloxane include mono- or poly-ethylenically unsaturated monomers which undergo additional polymerization upon exposure to UV-radiation or by means of chemical initiation.

If the polyunsaturated polysiloxanes are to be used in biocompatible materials, especially in either hard or soft contact lenses, a balance between hydrophilic and hydrophobic properties is required; water-soluble as well as water-insoluble comonomers can be used.

Water-insoluble vinyl monomers (B_1) that can be used in the present invention include:

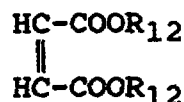
Acrylates and methacrylates of the general structure:



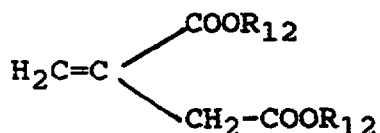
acrylamides and methacrylamides of the structure:



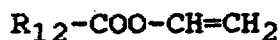
maleates and fumarates of the structure:



itaconates:



vinyl esters:



vinyl ethers:



wherein R_{12} is a linear or branched aliphatic, a cycloaliphatic or an aromatic group with from 1 to 21 carbon atoms and which may contain ether or thioether compounds or a $-\text{CO}-$ group; R_{12} may alternatively be a heterocyclic group containing oxygen, sulfur or nitrogen atoms, or a polypropylene oxide or poly-n-butylene oxide group with from 2 to 50 repeating alkoxy units.

In addition, the R_{12} group may contain halogen atoms, especially fluorine in the form of perfluorinated alkyl groups having from 1-12 carbon atoms, or siloxane groups having from one to six Si atoms, or $-\text{SO}-$ and $-\text{SO}_2-$ groups.

Examples of suitable monomers are: 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-, hexafluoroisopropyl-,

1,1,2,2-tetrahydroperfluorododecyl-, or tri-, tetra- or penta-siloxanyl propyl- acrylates and methacrylates, as well as 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 methyl phenyl fumarate and itaconate; methyl vinyl ether and methoxyethyl vinyl ether; vinyl acetate, vinyl propionate, vinyl benzoate, acrylonitrile, styrene, alpha-methylstyrene and tert-butylstyrene.

In order to achieve the high clarity necessary for contact-lens applications, it is especially advantageous to use comonomers or comonomer mixtures whose corresponding polymers closely match, in respect of their solubility parameter (δ) and/or refractive index (RI), the values of polydimethylsiloxane ($\delta = 15$, RI = 1.43). Such monomers are, for example, isobornyl methacrylate, tert-butyl methacrylate and mixtures of hydrocarbon methacrylates (RI 1.46) with fluorine-containing monomers, such as hexafluoroisopropyl methacrylate, trifluoroethyl methacrylate, 1,1,2,2-tetrahydroperfluoroalkyl methacrylate or 4-thia-6-perfluoroalkylhexyl methacrylate, wherein alkyl is a carbon chain of 5-12 C atoms (RI values of 1.38-1.40) ($\delta < 15$). In addition, perfluoroalkyl group-containing monomers greatly enhance the oxygen-permeability of the polymers in a synergistic manner with the polysiloxane; as such they are accordingly especially preferred comonomers.

For making hard lenses, the preferred comonomer content is 50-85% by weight of the total polymer, with the preferred comonomer being methyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate or hexafluoroisopropyl methacrylate, styrene or mixtures

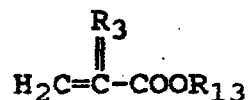
thereof.

Most preferably the comonomer is methyl methacrylate, isobornyl methacrylate, isopropyl methacrylate, isobutyl methacrylate or cyclohexyl methacrylate, or a mixture thereof. Also especially preferred are mixtures of methyl methacrylate and/or isobornyl methacrylate with 1 to 35% by weight, based on the total monomer, of a short-chain crosslinking agent, such as neopentylene glycol diacrylate or ethylene glycol dimethacrylate or the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

Another especially preferred comonomer system for making hard lenses is vinyl acetate/dimethyl maleate (2/1 to 5/1 molar ratios) plus a preferred methacrylate monomer listed above.

Preferred comonomers for the manufacture of soft lenses are 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, n-octyl acrylate, n-octyl methacrylate, n-decyl acrylate, n-decyl methacrylate, perfluoroalkyl-(C₆-C₁₀)-substituted alkyl acrylate or methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-butoxyethyl acrylate, 2-butoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, or mixtures thereof.

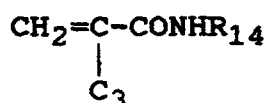
Suitable water-soluble monomers (B₂) which can be used in accordance with the invention are: acrylates and methacrylates of the general structure:



wherein R₁₃ is a hydrocarbon radical having 1 to 10

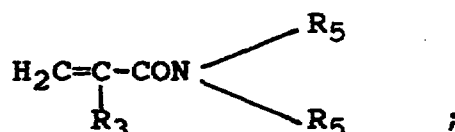
carbon atoms substituted by one of more water-solubilizing groups, such as carboxy, hydroxy or tert-amino, or a polyethylene oxide group having from 2 to 100 repeating units, or a group which comprises sulfate, phosphate, sulfonate or phosphonate groups;

acrylamides and methacrylamides of the structure

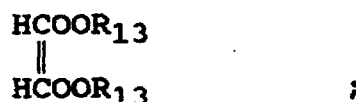


wherein R_{14} is R_{13} or R_5 ;

acrylamides and methacrylamides of the structure



maleates and fumarates of the structure:



vinyl ethers of the structure:



N-vinyl-lactams, such as N-vinyl-2-pyrrolidone.

Examples of suitable water-soluble monomers are:

2-hydroxyethyl-, 2- and 3-hydroxypropyl-, 2,3-dihydroxypropyl-, polyethoxyethyl- and polyethoxypropyl- acrylates and methacrylates, as well as the corresponding acrylamides and methacrylamides. Sucrose, mannose, glucose and sorbitol acrylates and methacrylates.

Acrylamide and methacrylamide; N-methyl acrylamide and methacrylamide, bisacetone acrylamide; 2-hydroxyethyl acrylamide; dimethyl acrylamide and

methacrylamide; methylol acrylamide and methacrylamide.

N,N-dimethyl and N,N-diethyl-aminoethyl acrylate and methacrylate as well as the corresponding acrylamides and methacrylamides; N-tert-butylaminoethyl methacrylate and methacrylamide; 2- and 4-vinylpyridine; 4- and 2-methyl-5-vinyl-pyridine; N-methyl-4-vinylpiperidine; 1-vinyl and 2-methyl-1-vinyl-imidazole; dimethylallylamine and methyldiallylamine. Para- and ortho-aminostyrene; dimethylaminoethyl vinyl ether; N-vinylpyrrolidone; 2-pyrrolidinoethyl methacrylate.

Acrylic and methacrylic acid;

Itaconic acid; cinnamic acid, crotonic acid, fumaric acid, maleic acid and lower hydroxyalkyl mono- and di-esters thereof, such as 2-hydroxyethyl- and di(2-hydroxyethyl) fumarate, maleate and itaconate, 3-hydroxypropylbutyl fumarate, and di-polyalkoxyalkyl fumarates, maleates and itaconates.

Maleic anhydride;

sodium acrylate and methacrylate, 2-methacryloyloxyethylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-phosphatoethyl methacrylate, vinylsulfonic acid, sodium vinylsulfonate, p-styrenesulfonic acid, sodium p-styrenesulfonate, and allylsulfonic acid.

Also suitable are the quaternized derivatives of cationic monomers: obtained by quaternization with selected alkylating agents, such as halogenated hydrocarbons, such as methyl iodide, benzyl chloride or hexadecyl chloride; epoxides such as glycidol, epichlorohydrin, ethylene oxide; acrylic acid, dimethyl sulfate; methyl sulfate;

propanesultone.

A more complete list of water-soluble monomers that can be used within the scope of this invention is contained in:

R. H. Yocum, E. B. Nyquist, Functional Monomers;
Vol. 1, p. 424-440 (M. Dekker, N.Y. 1973).

Preferred monomers are:

(B₁) = methyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate; t-butyl and isobutyl methacrylate, isopropyl methacrylate, hexafluoroisopropyl methacrylate, 2-ethylhexyl acrylate, n-butyl acrylate, n-butyl methacrylate, n-octyl acrylate, 2-ethoxyethyl acrylate, styrene;

(B₂) = 2-hydroxyethyl methacrylate; N,N-dimethylacrylamide; acrylic acid and methacrylic acid; N-vinyl-2-pyrrolidone.

A wide range of divinyl compounds can be used in addition to the monovinyl compounds. Indeed, from 0 to 50% by weight of the total monomer B can be a diolefinic monomer (B_x). Examples of diolefinic monomers are:

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; neopentylene 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.

Bisphenol A diacrylate or dimethacrylate, ethoxylated bisphenol A diacrylate or dimethacrylate; methylene bis-acrylamide or -methacrylamide, dimethylene bis-acrylamide or -methacrylamide; N,N'-dihydroxyethylene bis-acrylamide or -methacrylamide; hexamethylene bis-acrylamide or -methacrylamide; decamethylene bis-acrylamide or -methacrylamide; allyl and diallyl maleate, triallyl melamine, diallyl itaconate, diallyl phthalate, triallyl phosphite, polyallyl sucrose, sucrose diacrylate, glucose dimethacrylate; and also unsaturated polyesters, such as poly-(alkylene glycol maleates) and poly(alkylene glycol fumarates), such as poly(propylene glycol maleate) and poly(polyalkyleneoxide glycol maleate).

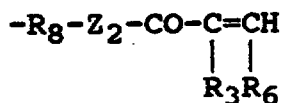
There may also be used as crosslinking agents the reaction products obtained by reacting 1 mol of di- or tri-isocyanate of the structure $\text{OCN-R}_4\text{-(NCO)}_1$ or $\text{OCN-R}_4\text{-(NCO)}_2$ wherein R_4 is as described above with 2 or 3 mol of a hydroxyalkyl acrylate or methacrylate, a hydroxyalkyl vinyl ether, an allyl alcohol, N-tert-butylaminoethyl methacrylate or bis-hydroxyethyl maleate, or of any of the active-hydrogen containing compounds listed above among the water-soluble comonomers. If an excess of the isocyanato-functional (meth-)acrylate is used to cap the polysiloxane-polyalkanol, the unreacted isocyanate can be used for the reaction with a hydroxy- or amino-functional monomer; thus the reaction products of isocyanatoethyl methacrylate with, for example, hydroxyethyl methacrylate or t-butylaminoethyl methacrylate, are also preferred crosslinking agents.

Preferably the diolefinic monomer (B_x) is the acrylate or methacrylate of allyl alcohol, of a straight-chain or branched alkylene glycol having from 2 to 6 carbon atoms, of poly(ethylene oxide) glycols, of poly(n-butylene oxide) glycols, of poly(n-butylene oxide) glycols, of thiodiethylene glycol, of neopentylene glycol, of trimethylolpropane, or of pentaerythritol; also preferred are reaction products obtained by reacting 1 mol of a di- or tri-isocyanate of the structure $OCN-R_4-(NCO)_v$, wherein R_4 is as defined above and v is 1 or 2, with 2 or 3 mol of a hydroxyalkyl acrylate or methacrylate.

An especially preferred difunctional comonomer (B_x) is 0 to 30% by weight, based on total monomer, of neopentylene glycol diacrylate, the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate or ethylene glycol dimethacrylate.

The monomers can be used alone, or in combination with each other with the necessary attention given to their copolymerization parameters to make sure that random copolymerization (statistical copolymerization) takes places. In addition, if the polymers are to be used for contact lenses, a high degree of clarity and the lack of colour are essential for choosing an appropriate monomer combination.

A preferred embodiment of the present invention is a polymer wherein component A is a polysiloxane of the structure A_1, A_2, A_3 or A_4 , R_1 is alkylene having 3 or 4 carbon atoms, $R_2, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j$ and R_k are each methyl, $x_1 + x_2$ is 10 to 100, Y_1 is 0 to 2, Y_2 is 1 to 3, Z_1 is -O-, -S- or -NH- and R_4 is a divalent radical of an aliphatic or cycloaliphatic diisocyanate having from 6 to 10 carbon atoms, Y_1 or Y is



R_8 is ethylene, Z_2 is $-O-$ or $-NC(CH_3)_3-$, R_3 is hydrogen or methyl and R_6 is hydrogen.

The transparent, hard and oxygen-permeable polymers of this invention are produced in a final synthesis step by free radical copolymerization, either in bulk or in the presence of a small amount of solvents. The polymerization is suitably carried out with a free-radical-generating initiator at a temperature in the range from about 40°C to about 105°C, the preferred temperature ranging from about 50°C to about 100°C. These initiators are preferably peroxides or azo catalysts having a half-life at the polymerization temperature of at least 20 minutes. Typical peroxy compounds that can be used include: isopropyl percarbonate, tert-butyl peroctoate, benzoyl peroxide, lauroyl peroxide, decanoyl peroxide, acetyl peroxide, succinic acid peroxide, methyl ethyl ketone peroxide, tert-butyl peroxyacetate, propionyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl peroxy-pivalate, pelargonyl peroxide, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, p-chlorobenzoyl peroxide, tert-butyl peroxybutyrate, tert-butyl peroxy-maleic acid, tert-butyl peroxyisopropyl carbonate, bis(1-hydroxycyclohexyl)peroxide. Azo compounds include: 2,2'-azo-bis-isobutyronitrile; 2,2'-azo-bis(2,4-dimethyl-valeronitrile); 1,1'-azo-bis(cyclohexane carbonitrile), 2,2'-azo-bis(2,4-dimethyl-4-methoxyvaleronitrile).

Other free-radical-generating mechanisms can be employed, such as X-rays, electron-beams and UV-radiation. The production of contact-lens blanks by UV radiation in the presence of a photoinitiator, such as diethoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, phenothiazine, diisopropyl-

xanthrogen disulfide, benzoin and benzoin derivatives, is a preferred method.

The amount of initiator can vary from 0.002% to 1% by weight of the monomers and macromers, but is preferably from 0.03 to 0.3% by weight thereof.

A preferred laboratory method of preparing the polymer in the form of a cylinder comprises the filling of flexible polymer tubing with the composition of macromer, monomers and catalyst and reacting the mixture for approximately 2 hours at 80°C. The finished article is removed by slitting the tubing longitudinally and stripping it away from the polymer body.

Another preferred method of preparing the polymer is by irradiation with ultraviolet light in the presence of a photoinitiator and using plastic moulds that are UV-transparent, such as moulds made of polypropylene or other UV-permeable plastics.

The reaction is preferably carried out in an inert atmosphere if done in open moulds. It is known that oxygen inhibits polymerization and gives rise to extended polymerization times. If closed moulds are used to form the article, the moulds are composed of inert materials having low oxygen-permeability and non-stick properties. Examples of suitable mould materials are poly(tetrafluoroethylene), such as Teflon[®], silicone rubber, polyethylene, polypropylene and polyesters, such as Mylar[®]. Glass and metallic moulds may be used if a suitable mould-release agent is employed.

The present invention also relates to a polymerization composition comprising:

(A) from about 5 to about 75% by weight of components (A) and (B) of a linear or branched polysiloxane macromer having a molecular weight from about 400 to about 100 000, as measured by end group analysis or gel permeation chromatography, the macromer comprising at least two terminal or pendant, polymerizable olefinic groups per molecular weight unit of polysiloxane of 5000, said groups being attached to the polysiloxane by way of a urethane, thiourethane or urea linkage, said macromer having the structure A₁, A₂, A₃, A₄, (described in detail above), and

(B) 95 to 25% by weight of one or more mono-, di- or tri-functional vinyl monomer(s) polymerizable by free radical polymerization.

The present invention relates especially to a polymerizable composition comprising:

(A) from 15 to 60% by weight of a linear or branched polysiloxane macromer having a molecular weight of from about 400 to about 100 000, measured by end group analysis or gel permeation chromatography, the macromer comprising at least two terminal or pendant, polymerizable olefinic groups per molecular weight unit of polysiloxane of 5000, the groups being attached to the polysiloxane by way of a urethane, thiourethane or urea linkage and the macromer having the structure A₁, A₂, A₃ or A₄, (described in detail above), and

(B) about 85 to 40 by weight of a mixture of water-soluble and water-insoluble monomers, or of a water-insoluble monomer, the said monomers being monoolefinic, diolefinic or a mixture of monoolefinic and diolefinic monomers, from 0 to 100% by weight of the total monomer content being water-insoluble, from 100 to 0% by weight

of the total monomer content being water-soluble, and from 50 to 0%, especially from 30 to 0% of the total monomer content being replaced by a diolefinic monomer (B_x).

The compositions of this invention and the polymers therefrom can be tailored so that they can be used either as hard contact lens material or as soft contact lens material. Different comonomers and different levels of polysiloxane macromer are required to achieve optimal performance in either contact lens type.

In choosing the polysiloxane component and the vinyl monomer for a hard contact lens composition, it is important to arrive at a mixture which will give clear polymers with sufficient dimensional stability and oxygen-permeability. Sometimes a mixture of comonomers is advantageous in avoiding phase-separation and thereby opacity. Also, it is easier to obtain clear products with polysiloxanes of relatively low molecular weight than with high-molecular-weight polysiloxanes. Polysiloxanes with a short chain length between crosslinks also give harder, dimensionally more stable polymers; however, their oxygen-permeability is reduced compared to polysiloxanes with longer chain length and therefore lower crosslink density. By an appropriate choice of monomer(s) and polysiloxane macromer, it is thus possible to vary to a considerable degree the physical properties and oxygen-permeability of the silicone polymers of the invention from hard and rigid to rubbery and soft. In addition to hard and soft contact lenses, because of their good tissue compatibility and oxygen-permeability and strength and elasticity, the polymers of the invention are also particularly suitable for use as intra-muscular and subcutaneous implants in warm-blooded animals and as contact lens material. For the same

reasons, the materials of the present invention may be fashioned into replacement blood vessels or extra-corporeal shunts.

For producing hard contact lenses, the preferred composition comprises (A) from 15 to 40% by weight of a polysiloxane macromer, and (B) from 85 to 60% by weight of a mixture of water-insoluble monomers (B_1), of water-soluble monomers (B_2) and of a diolefinic monomer (B_x), wherein, based on % by weight of the total weight of monomers, B_1 is from 60 to 95%, B_2 is from 20 to 0%, and B_x is from 20 to 5%. The preferred water-insoluble monomers B_1 are methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate or mixtures thereof. The preferred water-soluble monomers B_2 are 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylic acid, methacrylic acid or N-vinyl-2-pyrrolidone or mixtures thereof. The preferred diolefinic monomer B_x is neopentylene glycol diacrylate, ethylene glycol dimethacrylate or the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

For producing soft contact lenses with low water absorption, the preferred composition comprises (A) from 40 to 60% by weight of a polysiloxane macromer, and (B) from 60 to 40% by weight of a mixture of water-insoluble monomer (B_1), of water-soluble monomer (B_2) and of a diolefinic monomer (B_x), wherein based on % by weight of the total weight of monomers, B_1 is from 70 to 100%, B_2 is from 25 to 0%, and B_x is from 5 to 0%. The preferred water-insoluble monomers (B_1) are ethyl acrylate or methacrylate, n-butyl acrylate or methacrylate, n-hexyl acrylate or methacrylate, 2-ethylhexyl acrylate or methacrylate, n-octyl acrylate or methacrylate, n-decyl acrylate or

methacrylate; or mixtures thereof with methyl or isobornyl methacrylate. The preferred water-soluble monomers (B_2) and diolefinic monomers (B_X) are those listed above for producing hard contact lenses.

For producing hydrogel contact lenses, the preferred composition comprises (A) from 20 to 60% by weight of a polysiloxane macromer, and (B) from 80 to 40% by weight of a mixture of water-insoluble monomer (B_1), of water-soluble monomer (B_2) and of a diolefinic monomer (B_X), wherein based on % by weight of the total weight of monomers, B_1 is from 80 to 0%, B_2 is from 15 to 100%, and B_X is from 5 to 0%. The preferred water-soluble monomers (B_2) are N,N-dimethyl acrylamide, N-vinyl-2-pyrrolidone, 2-hydroxyethyl methacrylate, acrylamide or mixtures thereof. The preferred water-insoluble monomers (B_1) and diolefinic monomers (B_X) are those listed above for producing hard or soft contact lenses.

An example of a preferred composition for making a hard contact lens comprises (A) 30% by weight of the polysiloxane of structure A_2 , Z_1 and Z_2 are each -O-, and y_2 is 2, and 70% by weight of monomer (B) wherein, based on % by weight of total monomers, B_1 is 71.4% of methyl methacrylate, B_2 is 5.7% of 2-hydroxyethyl methacrylate and B_X is 22.9% of neopentylene glycol diacrylate.

An example of a preferred composition for making a soft contact lens comprises (A) 50% by weight of the polysiloxane of structure A_1 wherein x_1 is 25-30, Z_1 and Z_2 are each -O-, and y is 0, and 50% by weight of monomers (B), wherein B_1 is 80% of a 50/50 mixture of methyl methacrylate/2-ethylhexyl acrylate and B_2 is 20% of N,N-dimethylacrylamide.

An example of a preferred composition for making hydro-

gel-type contact lenses comprises (A) 30% by weight of the polysiloxane of structure A₂ wherein Z₁ and Z₂ are each -O-, and Y₂ is 2, and 70% by weight of monomers (B), wherein B₁ is 20% of methyl methacrylate and B₂ is 50% of N,N-dimethylacrylamide.

The invention relates also to a polymer, comprising the copolymerization product of the compositions of components (A) and (B). The preferred embodiments of the compositions apply also to the polymers.

Although this invention is directed primarily toward the manufacture of contact lenses, it is within the scope of this invention to use any of the afore-mentioned monomers to make strong, O₂-permeable polymers with a wide range of physical properties, from hard and rigid to rubbery and soft, which can be used, for instance, as bandages, body implants or catheters.

The polysiloxane copolymers of this invention may also be subjected to conventional treatments for improving the wettability of hydrophobic surfaces, such as plasma-treatment, irradiation-grafting and oxidation.

The contact lenses made from the polymers of this invention are free from fillers, hydrolytically stable, biologically inert, transparent and sufficiently permeable to oxygen for the transport of oxygen to be adequate to meet the requirements of the human cornea.

The following Examples are presented for the purpose of illustration only.

In the following Examples, specific oxygen-permeability (O₂ DK) is determined by measuring dissolved oxygen-permeability at 35°C with a polarographic electrode in

an air-saturated aqueous environment and is expressed in units

$$O_2DK = \frac{cm^3(STP) \times cm}{cm^2 \times sec \times mbar} \times 7.6923076 \times 10^9$$

Wettability is determined by measuring the contact angle of an n-octane droplet which had been formed on the lower surface of a 1 mm thick sample sheet immersed in octane-saturated distilled water at 36°C. In this measurement high numbers signify high wettability.

As reference materials for O₂-DK measurements, water-swollen poly(2-hydroxyethyl methacrylate) (polyhema; 39% water content; the most common soft-lens material) and CAB, cellulose acetate-butyrate (an oxygen-permeable hard-lens material) are used; for wettability and hardness polyhema and poly(methyl methacrylate) are used as reference materials. The O₂.DK, Shore-D and contact angle values for these materials are given below.

Hardness was determined using a Shore-D durometer on polished surfaces of centre-cut buttons of 10 mm diameter and 8 mm height.

<u>Reference Materials</u>	<u>O₂DK</u>	<u>Shore-D</u>	<u>Octane/Water Contact Angle</u>
polyhema (39% H ₂ O)	12	-	151
poly(methyl methacrylate)	<0.1	92	92
cellulose acetate-butyrate	8.2	80	161

Glossary of Abbreviations

P-D-M-S		polydimethylsiloxane
IEM	-	2-isocyanatoethyl methacrylate
DBTL	-	dibutyltin dilaurate
HEMA	-	2-hydroxyethyl methacrylate
IPDI	-	isophorone diisocyanate
NPDA	-	neopentylene glycol diacrylate

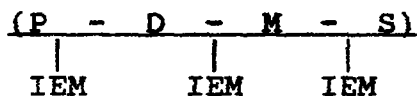
The following two Examples show that a superior polydimethylsiloxane trimethacrylate with the same narrow MW distribution as the starting polysiloxanetriol material is obtained in a 1-step reaction in Example 1 compared to a multi-disperse MW of a prior-art PDMS-methacrylate obtained in a 2-step reaction as seen in Example 2.

Example 1

Synthesis of PDMS-trimethacrylate from a PDMS-triol and IEM.

A 3-neck flask equipped with stirrer, thermometer, condenser and nitrogen inlet tube is charged with 91.5 g (0.015 mol) of a trihydroxyalkyl-functional polydimethylsiloxane (DOW CORNING fluid '1248', MW 6100) which had been stripped free of volatiles by passing it twice through a wiped-film evaporator at 120°C/0.013 mbar. The flask is sparged with nitrogen and 7.68 g (0.0495 mol) of 2-isocyanatoethyl methacrylate (IEM) are added, followed by 0.028 g (0.028% of the total) of dibutyltin dilaurate (DBTL) as catalyst. The mixture is stirred at 25°C and the disappearance of the NCO group is followed by infrared (IR) spectroscopy. After four hours only a minor amount of NCO remained and this excess isocyanate is removed by reaction to completion with 0.62 g (0.0047 mol) of 2-hydroxyethyl methacrylate (HEMA). The resulting product is a clear, colourless viscous resin. Gel permeation chromatography (GPC) shows a narrow, one-peak molecular weight (MW) distribution identical to that of the starting PDMS-triol, and a low MW fraction consisting of the HEMA-IEM adduct.

Schematic structure:



Example 2 (Comparison)

Synthesis of PDMA-trimethylacrylate from a PDMS-triol, isophorone diisocyanate and HEMA.

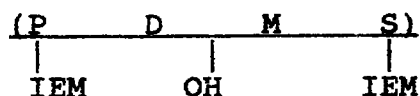
Following the procedure of Example 1, 91.5 g (0.015 mol) of the same PDMS-triol ('1248', DOW CORNING) are stirred under nitrogen with 10.5 g (0.0473 mol) of 1-(isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (isophorone diisocyanate, IPDI) and 0.0125 g of DBTL as catalyst. The mixture is stirred at 25°C for 4 hours, after which time the NCO content has dropped to 1.98% (2% would be the theoretical end point). At that time 11 g of HEMA are added and the mixture is stirred under nitrogen at 25°C until all NCO has reacted, as determined by IR spectroscopy. The resulting product is a clear, colourless viscous resin, whose GPC-scan, in contrast to the resin of Example 1, shows four peaks with four distinct MWs as a result of chain-extension, as well as a low-molecular-weight fraction consisting of the IPDI-HEMA diadduct.

Example 3

Synthesis of PDMS-dimethacrylate from a PDMA-triol and IEM.

Following the procedure of Example 1, a PDMS-dimethacrylate is prepared by using 123 g (0.02 mol) of the '1248'-PDMS-triol and 6.206 g (0.04 mol) of IEM. A clear, viscous resin is obtained with the same MW distribution as the starting material PDMS. The product of Example 3 still contains 1/3 of the original hydroxy groups.

Schematic structure:



Example 4

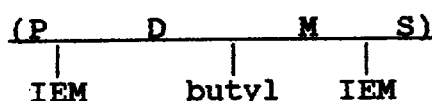
Synthesis of PDMA-dimethacrylate from a partially capped PDMS-triol and IEM.

Following the procedure of Example 1, 100 g (0.0143 mol) of trihydroxyalkyl-functional polydimethylsiloxane (DOW CORNING fluid '1248'; MW 6986) are reacted with 1.42 g (0.0143 mol) of n-butyliisocyanate at 25°C for 4 hours using 0.025% dibutyltin dilaurate as catalyst. The resulting product is a PDMS with, on average, 2 hydroxyl groups per molecule.

3.33 g (0.0048 mol) of this PDMS-diol are reacted with 1.55 g (0.0101 mol) of 2-isocyanatoethyl methacrylate to cap the remaining hydroxy groups. The disappearance of isocyanate functionality is followed by infrared spectroscopy.

A clear, viscous resin is obtained with a molecular weight distribution identical to the resins of Examples 1 and 3 and the starting material PDMS.

Schematic structure:



Example 5

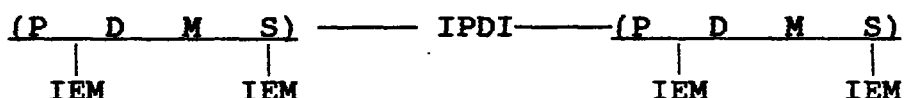
Synthesis of chain-extended polysiloxane-polymethacrylates from partially blocked PDMS-triols.

Following the procedure of Example 1, 123 g (0.02 mol, MW = 6150) of trihydroxyalkyl-polydimethylsiloxane (DOW CORNING Fluid '1248') are reacted with 3.103 g (0.02 mol) of 2-isocyanatoethyl methacrylate.

24.8 g (0.004 mol) of this mono-IEM-substituted PDMS are reacted with 0.467 g (0.002 mol + 5% excess) of iso-

phorone diisocyanate; the disappearance of the NCO functionality is followed by IR spectroscopy. The remaining hydroxy groups are then reacted with 0.62 g (0.004 mol) of IEM. The resulting clear, viscous resin has a much higher MW than the resin of Example 1, as determined by gel permeation chromatography.

Schematic structure:



The following Examples were carried out in order to create a higher-molecular-weight PDMS methacrylate for the synthesis of a less crosslinked and softer contact lens material.

Examples 6-14 (Comparison)

Attempts to control the chain-extension of PDMS-triol by reaction with different amounts of diisocyanate.

Following the procedure of Example 2, PDMS-triol '1248' and isophorone diisocyanate (IPDI) are reacted in the following amounts and ratios.

Example	PDMS-triol '1248/IPDI					Product
	g/g		mol/mol		eqv./eqv.	
6	61	11.1	1	0.5	3/1.0	all materials cross-linked
7	61	16.6	1	0.75	2/1.0	
8	61	19.4	1	0.875	1.7/1.0	
9	30.5	11.1	1	1.00	1.5/1.0	
10	30.5	14.7	1	1.33	1.13/1.0	
11	30.5	16.7	1	1.5	1.0/1.0	
12	30.5	22.2	1	2	1.33/1	
13	30.5	27.8	1	2.5	2/1	
14	30.5	33.3	1	3.0	2.5/1.0	
						clear, very viscous resin

Only Example 14 results in a PDMS-isocyanate intermediate which can be used for the further synthesis of methacrylate-capped PDMS by reaction with 2-hydroxyethyl methacrylate. The methacrylate-capped PDMS-macromer is extremely viscous and, when analyzed by GPC, is seen to consist of at least 4 different MW fractions, compared to the uniform MW distribution of the macromer of Example 1.

Example 15

Synthesis of PDMS-dimethacrylates from PDMS-diols and IEM.

21.94 g (0.005 mol) of a polydimethylsiloxane-dialkanol (Shin-Etsu X-61-504A; MW = 4388) are reacted with 0.555 g (0.0025 mol) of isophorone diisocyanate (IPDI) at 25°C for 6 hours using 0.009 g of dibutyltin dilaurate as catalyst. The residual hydroxy groups are capped in a second step by reaction with 0.776 g (0.005 mol) of 2-isocyanatoethyl methacrylate for 5 hours. The modified polysiloxane macromer with terminal methacrylate groups so-obtained is a clear and viscous resin of approximately 9000 MW.

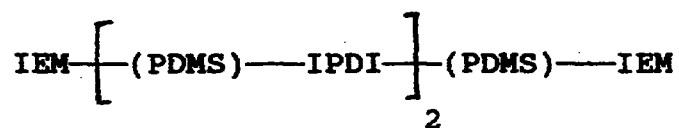
Schematic structure:



Example 16

Using the same procedure as in Example 15, a more chain-extended PDMS-dimethacrylate is prepared from 21.94 g (0.005 mol) of PDMS-diol (Shin Etsu X61-504A), 0.860 g (0.00375 mol) of IPDI and 0.387 g (0.0025 mol) of IEM. The resulting resin is colourless and very viscous with a MW of about 18500.

Schematic structure:



Example 17

Using the same procedure as in Example 15, a polydimethylsiloxane dimethacrylate is prepared by reacting 12.19 g (0.005 mol) of a PDMS-dialkanol (Shin-Etsu X-61-504A 1000, MW = 2438) with 1.552 g (0.01 mol) of 2-isocyanatoethyl methacrylate in the presence of 0.01 g of dibutyltin dilaurate. A clear, slightly viscous resin is obtained with a MW of 2749.

Schematic structure:



Example 18

Using the same procedure as in Example 15, a polydimethylsiloxane dimethacrylate is prepared by reacting 24.59 g (0.005 mol) of a PDMS-dialkanol (Shin-Etsu X-61-504A 2000, MW = 4918) with 1.552 g (0.01 mol) of 2-isocyanatoethyl methacrylate in the presence of 0.01 g of dibutyltin dilaurate. A clear, slightly viscous resin is obtained with a MW of 5228.

Schematic structure:



Example 19

Synthesis of PDMS-dimethacrylate from PDMS-diamine and IEM.

21.9 g (0.01 mol) of a bis-3-aminopropyl-terminated polydimethylsiloxane (MW 2190, Petrarch Systems, Inc. PS-510) are reacted with 3.1 g (0.02 mol + 5% excess) of 2-isocyanatoethyl methacrylate dissolved in 6 g of water-

free diethyl ether. The temperature of the mixture is kept at 25°C and stirring is continued for 3 hours. The disappearance of OCN groups is followed by IR spectroscopy. The solvent is evaporated at 50°C/0.026 mbar using a rotary evaporator. A clear, viscous resin is obtained with a MW of about 2500.

Schematic structure:



Example 20

Following the same procedure as in Example 15, a chain-extended polyurea-PDMS is prepared from 21.9 g (0.01 mol) of bis-3-aminopropyl-terminated PDMS by first reacting it with 1.48 g (0.0067 mol) of IPDI in 10 ml of diethyl ether and then capping the residual NH₂ groups with 1.08 g (0.0067 mol + 5% excess) of IEM. A clear viscous resin is obtained with a MW of about 8000.

Schematic structure:



Example 21

Synthesis of PDMS-dimethacrylate from PDMS-dithiols and IEM.

27.3 g (0.01 mol) of a polydimethylsiloxane-dialkyl-ethanethiol (DOW CORNING Fluid x 2-8024, MW 2730) are reacted with 3.1 g (0.022 mol) of 2-isocyanatoethyl methacrylate at 25°C for 4 hours using 0.066% triethylamine as catalyst. The excess isocyanate is capped with tert-butylaminoethyl methacrylate (0.002 mol). The disappearance of the isocyanate functionality is followed by infrared spectroscopy. A clear, viscous resin is obtained, which consists of a PDMS-dimethacrylate of a MW of about 3100, and a minor amount of the reaction product

of IEM with t-butylaminoethyl methacrylate.

Schematic structure:



Examples 22-27

Synthesis of materials suitable for hard contact lenses.

30 g of the trimethacrylate-PDMS of Example 1 are mixed with 4 g of HEMA, 16 g of neopentylene glycol diacrylate (NPDA) and 50 g of methyl methacrylate. 0.2 g of 1-hydroxycyclohexyl phenyl ketone, photoinitiator A, are added and the mixture is stirred until clear. After degassing three times in vacuo and blanketing with nitrogen, the mixture is polymerized by UV irradiation in the form of contact-lens blanks (round buttons, 13 mm diameter, 9 mm high), in a polypropylene mould for hardness measurements and machinability studies, and in the form of 0.1 mm thick films between Mylar-lined glass plates for measuring oxygen-permeability.

Using the same procedure, monomer mixtures with the compositions listed below are prepared and polymerized; clear and hard polymers are obtained with the following physical properties. All polymers can be cut and polished to form hard to semi-hard contact lenses with excellent oxygen-permeability.

Ex. No.	Comp. From Example	PDMS-IEM Adduct			Comonomer ²⁾ %					Shore D Hardness	O ₂ .DK 34°C
		L ¹⁾	MW	%	MMA	IBMA	NPDA	GMA	HEMA		
22	1	3	6500	30	50	-	16	-	4	76	
23	1	3	6500	30	-	54	16	-	4	78	33
24	1	3	6500	30	-	50	16	4	4	78	30
25	4	2	6500	30	50	-	16	-	4	63	35
26	17	2	3000	30	50	-	16	-	4	78	17
27	17	2	2749	25	55	-	16		4	80	25

1) L = Theoretical functionality

2) MMA: methyl methacrylate

IBMA: isobornyl methacrylate

NPDA: neopentyl glycol diacrylate

GMA: glycidyl methacrylate

HEMA: 2-hydroxyethyl methacrylate

Examples 28-34

Synthesis of materials suitable for soft, hydrophobic (silicone-rubber-type) contact lenses.

Using the same procedure as in Example 22, PDMS-methacrylate macromers are mixed with comonomers and photoinitiator A and polymerized as described. The composition and the physical properties of the materials are shown in the following Table.

Ex. No.	PDMS-IEM			Comonomers ¹⁾	Shore-A Hardness	Tensile Strength N/mm ² x10 ²	Elongation %	Bending ²⁾ Angle °	O ₂ -DK
	of Example	L ³⁾	MW						
28	1	3	6500	EHA 30 GMA 20 " 40 " 20	60	72.5	45.3	36	-
29			"		51	36.12	43.6	40	74.8
30	5	4	13000	BEHA 40 GMA 40 EHA 30 " 20 SiMA 50	48	53.79	55	42	-
31			"		56	91.2	72.7	38	-
32			"		47	126.34	127.8	62	97.5
33	13	2	9000	EEHA 50	39	30.5	-	56	62.8
34	18	2	5228	GMA 30 GMA 20	48	89.23	92.3	33	63.0

- 1)
 EHA: 2-ethylhexyl acrylate
 GMA: glycidyl methacrylate
 BEHA: 2-butoxyethyl acrylate
 EEHA: 2-ethoxyethyl acrylate
 SiMA: 3-methacrylpropyl pentamethyl disiloxane

- 2) The bending angle is a measure of the 'softness' of the polymer. It is obtained by cutting a 2 1/2 x 1/2 inch (6.35 x 1.27 cm) sample of a 1 mm thick sheet, clamping 1/2 inch (1.27 cm) of its length horizontally between two glass plates and measuring the angle formed by the line from end of the support to the end of the overhanging sample.

- 3) L = theoretical functionality

Examples 35-36

Synthesis of polymers suitable for soft contact lenses from PDMS-methacrylates derived from PDMS-diamines.

Following the general procedure of Example 22, 60 g of PDMS-methacrylates from Examples 15 and 16 are each mixed with 40 g of 2-ethylhexyl acrylate and 0.2% photo-initiator A and polymerized by UV-light to give buttons, sheets and films of high optical clarity.

The following Table contains the physical properties of the copolymers prepared. The improved properties show the usefulness of those types of functional siloxanes for the synthesis of water-free, soft contact-lens materials, exhibiting advantageous properties compared with water-swollen polyhydroxyethyl methacrylate.

	Example 35	Example 36	Poly-HEMA ¹⁾ Control Polymer
Shore-A hardness	53	46	31
Tensile Strength N/mm ²	0.391	0.653	0.224
Young's modulus N/mm ²	2.26	0.91	0.53
Elongation to break, %	22.6	151	89
Bending angle	30°	60°	66°
O ₂ DK	38.2	42.2	24.7

- 1) The poly-HEMA used was a copolymer of 99.45% 2-hydroxyethyl methacrylate, 0.25% ethylene glycol dimethacrylate and 0.3% methacrylic acid, tested in the swollen state (38.5% water).

The following Examples show the utility of the novel PDMS-methacrylate for the synthesis of silicone-containing hydrogels.

Examples 37-40

30 g of the PDMS-macromer of Example 1 are mixed with

methyl methacrylate (MMA) and dimethylacrylamide (DMA) in the proportions shown in the Table. To each solution 0.2 g of photoinitiator A is added and the mixture is degassed in vacuo and kept under nitrogen. Each mixture is cast and polymerized by UV radiation in the form of 1 mm thick sheets, 0.1 mm thick sheets, 0.11 mm thick sheets and round buttons of 13 mm diameter and 9 mm height, as described in Example 22. All samples are completely clear. For each material, dry hardness, equilibrium water content, tensile strength (wet state) and O₂ permeability (wet state) are determined, as shown in the Table.

Ex.	Composition %			Hardness Shore-D Dry	% H ₂ O	Tensile Strength (N/mm ²)	Elongation %	O ₂ -DK
	PDMS-IEM	MMA	DMA					
37	30	20	50	82	51.8	1.451	63	64.4
38	30	30	40	79	37	9.347	49	56.5
39	30	40	30	78	22	23.984	49	40.3
40	30	50	20	80	11	29.61	28	39.3

Examples 41-42

Comparison of IEM and IPDI/HEMA-capped macromers

The polysiloxane macromers of the invention contain the group X which is -Z₁-CO-NH-, whereas in the polysiloxane macromers of US-PS Nos. 4 136 250, 4 130 708 and 4 486 577 X is the linking group -Z₁-CO-NH-R₄-NHCO-.

To demonstrate that the absence of the -R₄-NHCO portion of the group X in the macromers of the invention does make a difference, a polysiloxane macromer of the invention is prepared wherein a polysiloxanediol having an equivalent weight of 1219 (molecular weight 2438) is capped with two equivalents of 2-isocyanatoethyl metha-

crylate (IEM) according to the present invention following the general procedure of Examples 1 and 17.

The closest prior art polysiloxane macromer is prepared wherein the same polysiloxanediol is first capped with two equivalents of isophorone diisocyanate (IPDI) and then reacted with two equivalents of 2-hydroxyethyl methacrylate (HEMA) following the general procedure of Example 2.

Each polysiloxane macromer is copolymerized according to the general procedure of Examples 22-27 to prepare polymers for use in hard contact lenses.

The polymers are prepared from the following monomers (all percents are in % by weight of the final polymer):

polysiloxane macromer	25
methyl methacrylate	55
neopentylene glycol acrylate	16
2-hydroxyethyl methacrylate	4

The physical properties of the polymers produced are given in the Table below.

Table
Comparison of IEM and IPDI/HEMA-capped macromers

<u>Macromer and Polymer According to Example *</u>	<u>Capping Method</u>	<u>Appear.</u>	<u>Swelling % H₂O / Eth.</u>	<u>% Si Macromer</u>	<u>in Polymer</u>	<u>Shore-D Hardness</u>	<u>O₂.DK</u>
41	IEM	clear	2.42/28.07	33.5	8.38	79	8.1
42	IPDI/ HEMA	"	2.60/21.45	29.3	7.33	81	5.7

* The polysiloxane macromer in Example 41 is prepared according to the invention.

The polysiloxane macromer in Example 42 is prepared according to the prior art.

The polysiloxane macromer according to the invention with the same polymer composition provides a higher silicon content in the final polymer along with a perceptibly higher oxygen-permeability which is so important in the field of contact lenses.

Example 43

Macromer Properties

The dispersity, average molecular weight, number of peaks observed by gel permeation chromatography (GPC) and viscosity of polysiloxane macromers prepared according to Examples 1 and 2 are compared to show that there are major differences in these properties depending on whether the polysiloxane macromer has been produced according to the invention (as in Example 1) or according to the prior art (as in Example 2).

<u>Polysiloxane Macromer according Example</u>	<u>Dispersity*</u>	<u>Average Molecular Weight</u>	<u>GPC peaks</u>	<u>Viscosity</u>
1	6	1.4×10^4	1	low
2	29	8.9×10^4	4	high
starting siloxanetriol (¹²⁴⁸)	2.2	1.4×10^4	1	low

The dispersity is the ratio of weight-average molecular weight to number-average molecular weight. A broader molecular weight distribution correlates with a higher dispersity value.

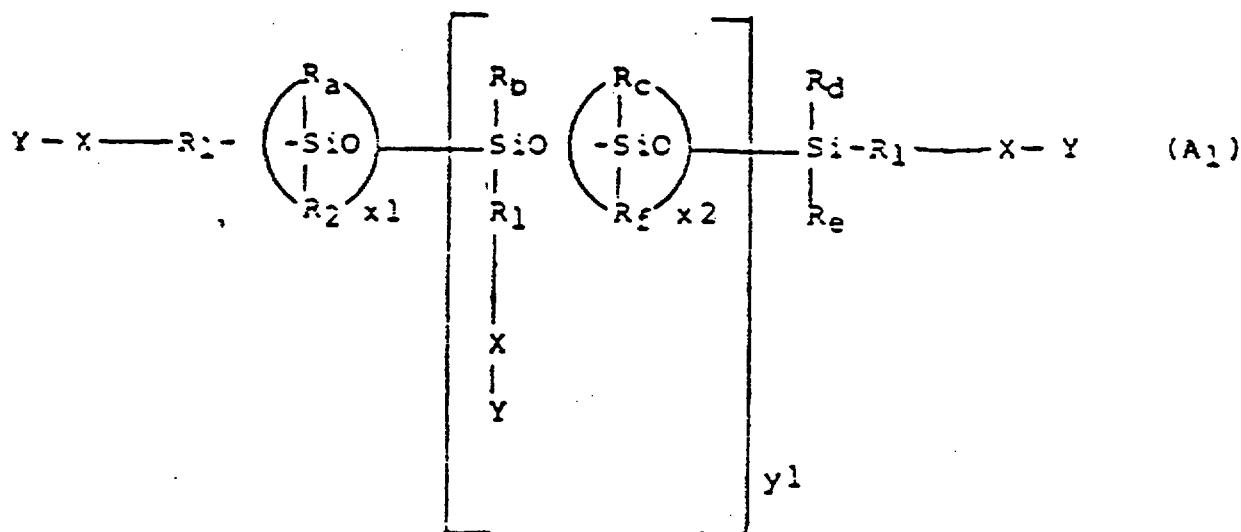
The polysiloxane macromer according to the invention has a narrow molecular weight distribution, gives only one peak in the GPC and is of low viscosity. The prior art polysiloxane macromer has a much broader molecular weight distribution, a number of peaks in the GPC and is of high

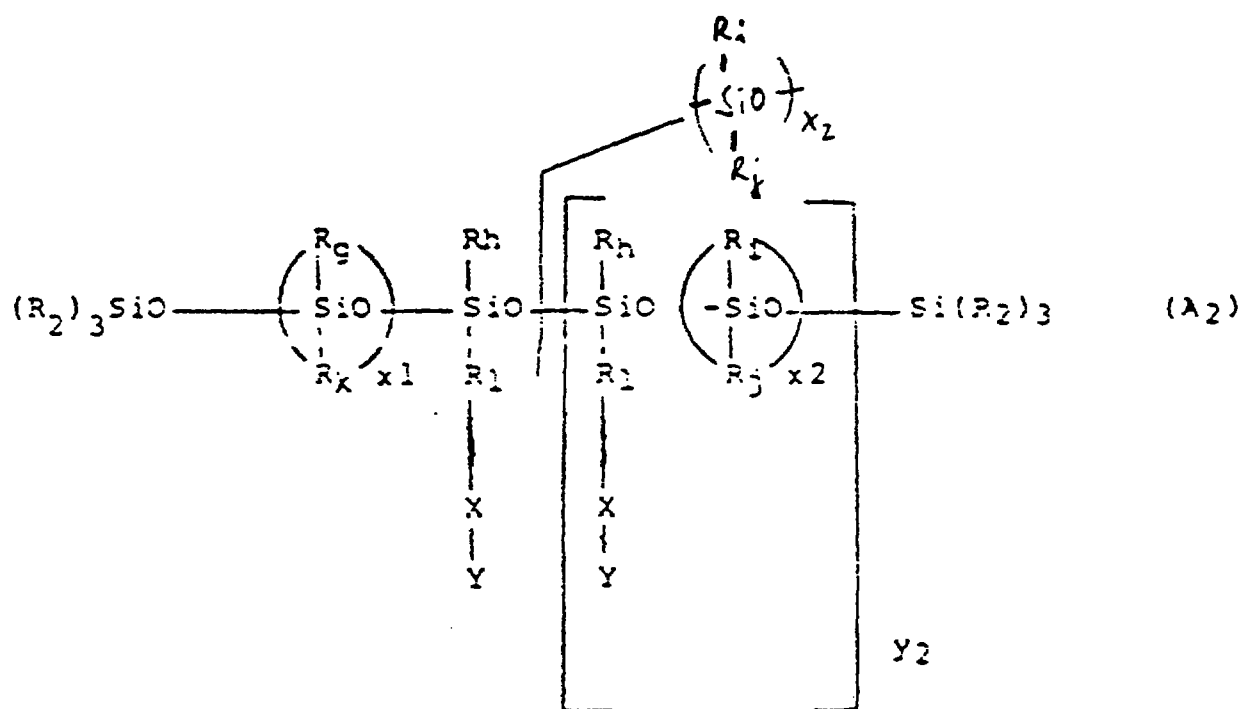
viscosity.

The polysiloxane macromer of the invention represents a more reproducible product of more closely defined structure with all the benefits arising therefrom.

PATENT CLAIMS for the Contracting States DE, FR, GB, IT, SE

1. A linear or branched polysiloxane macromer having a molecular weight from about 400 to 100 000, as measured by end group analysis or gel permeation chromatography, the macromer comprising at least one terminal or pendant polymerizable olefinic group, and at least one such polymerizable olefinic group per 5000 molecular weight unit of polysiloxane, the said group being attached to the polysiloxane by way of a urethane, thiourethane or urea linkage, and the said macromer having the structure A₁, A₂, A₃ or A₄



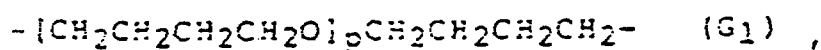
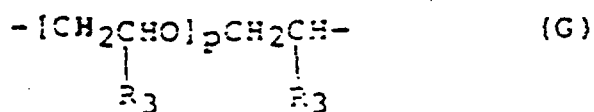


or



wherein:

R₁ is a linear or branched alkylene group having from 2 to 6 carbon atoms or a polyoxyalkylene group of the structure G or G₁



wherein R_3 is hydrogen or methyl and p is an integer from 1-50, $R_2, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j$ and R_k are independently methyl or phenyl, x_1, x_2 are integers from 1 to 500 with the proviso that the sum of $x_1 + x_2$ is 7 to 1300, y_1 is 0 to 14 and y_2 is 1 to 13 with the proviso that the ratio of $\frac{x_1 + x_2}{y_1 + 2}$ or $\frac{x_1 + x_2}{y_2 + 1}$ is not

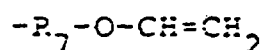
$$\frac{x_1 + x_2}{y_1 + 2} \quad \frac{x_1 + x_2}{y_2 + 1}$$

greater than 70,

X is $-Z_1-CO-NH-$,

Z_1 is oxygen, sulfur or $-NR_5-$, wherein R_5 is hydrogen or C_1-C_4 alkyl, Z_1 is bonded to R_1 ; with the proviso that Z_1 in a macromer of the structure A_1 is other than oxygen;

Y_1 is $-R_8-Z_2-CO-\underset{\substack{| \\ R_3}}{C}=CH-R^6$ or



wherein:

R_6 is: hydrogen, methyl, $-COOR_5$ or $-COOR_7OH$,

Z_2 = oxygen or $-NR_5-$,

Y is the same as Y_1 , or Y is H, alkyl having from 1 to 8 carbon atoms, cyclohexyl, phenyl, o-tolyl, m-tolyl or p-tolyl, with the proviso that at least one of the radicals Y must have the same meaning as Y_1 ,

R_7 is a linear or branched alkylene having from 2 to 10 carbon atoms, phenylene or phenylalkylene having from 2 to 10 carbon atoms in the alkylene, or polyoxyalkylene of the structure G or G_1 ;

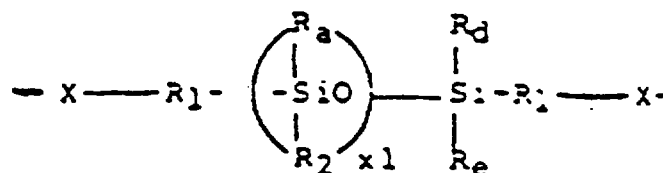
R_8 is an alkylene group having from 2 to 6 carbon atoms,

R_4 is a divalent radical obtained by removing the

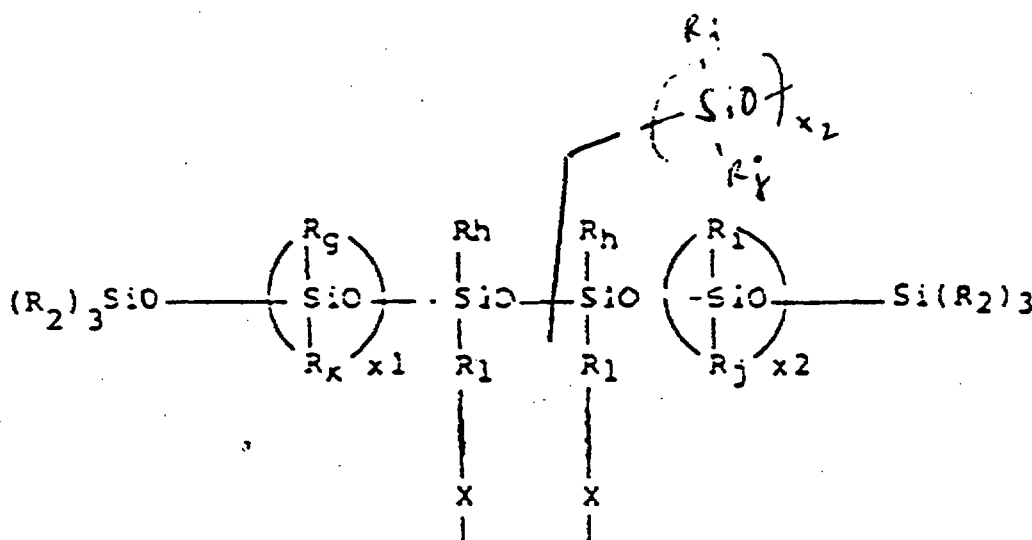


NCO groups from an aliphatic, cycloaliphatic, arali-
phatic or aromatic diisocyanate;

T is the group



T₁ is the group



and

n is 1 to 10.

2. A polysiloxane macromer according to claim 1, wherein R₁ is alkylene having 3 or 4 carbon atoms, R₂, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j and R_k are each methyl, x₁ + x₂ is 10 to 100, y₁ is 0 to 2, y₂ is 1 to 3, Z₁ is -O- or -NH- and R₄ is a divalent radical of an aliphatic or cycloaliphatic diisocyanate having from 6 to 10 carbon atoms, and Y is the same as Y₁, R₆ is hydrogen, R₈ is ethylene, and Z₂ is -O- or -NC(CH₃)₃-.



3. A polysiloxane macromer according to claim 2, wherein the polysiloxane has the structure A_2 , Z_1 and Z_2 are each -O-, and y_2 is 1 or 2.

4. A polysiloxane macromer according to claim 1, wherein the polysiloxane has the structure A_3 or A_4 wherein R_4 is the divalent radical derived from isophorone diisocyanate.

5. A polymerizable composition, comprising

(A) from 5 to 75 % by weight, based on components (A) and (B), of a polysiloxane macromer according to claim 1, and

(B) from 95 to 25 % by weight of one or more mono-, di- or tri-functional vinyl monomer(s) polymerizable by free radical polymerization.

6. A composition according to claim 5, comprising

(A) from 15 to 60 % by weight of the linear or branched polysiloxane macromer, and

(B) from 85 to 40 % by weight of a mixture of water-soluble and water-insoluble monomers, or of a water-insoluble monomer, the said monomers being monoolefinic, diolefinic or a mixture of monoolefinic and diolefinic monomers, from 0 to 100 % by weight of the total monomer content being water-insoluble (B_1), from 100 to 0 % by weight of the total monomer content being water-soluble (B_2), and from 50 to 0 % by weight of the total monomer content being replaced by a diolefinic monomer (B_X).

7. A composition according to claim 5, wherein R_1 is alkylene having 3 or 4 carbon atoms, R_2 , R_a , R_b , R_c , R_d ,



R_e , R_f , R_g , R_h , R_i , R_j and R_k are each methyl, $x_1 + x_2$ is 10 to 100, y_1 is 0 to 2, y_2 is 1 to 3, Z_1 is -O- or -NH- and R_4 is the divalent radical of an aliphatic or cycloaliphatic diisocyanate having from 6 to 10 carbon atoms, and Y is the same as Y_1 , R_6 is hydrogen, R_8 is ethylene, and Z_2 is -O- or -NC(CH₃)₃-.

8. A composition according to claim 7, wherein the polysiloxane has the structure A_2 , Z_1 and Z_2 are each -O-, and Y_2 is 1 or 2.

9. A composition according to claim 5, wherein the polysiloxane has the structure A_3 or A_4 wherein R_4 is the divalent radical derived from isophorone diisocyanate.

10. A composition according to claim 6, wherein monomer B is a water-insoluble monomer B_1 which is an acrylate or methacrylate of formula $CH_2=CR_3COOR_{12}$, an acrylamide or methacrylamide of formula $CH_2=CR_3CONHR_{12}$, a maleate or fumarate of formula $R_{12}OCOCH=CHCOOR_{12}$, an itaconate of formula $R_{12}OCOC(=CH_2)CH_2COOR_{12}$, a vinyl ester of formula $R_{12}COOCH=CH_2$, a vinyl ether of formula $CH_2=CHOR_{12}$, or a mixture of those monomers, wherein R_3 is hydrogen or methyl and R_{12} is a linear or branched aliphatic, cycloaliphatic or aromatic group having from 1 to 21 carbon atoms and may comprise ether or thioether linkages or a -CO-, -SO- or -SO₂- group; or R_{12} is a heterocyclic group comprising oxygen, sulfur or nitrogen atoms, or a polypropylene oxide or poly-n-butylene oxide group having from 2 to 50 repeating alkoxy units; or is a perfluorinated alkyl group having from 1 to 12 carbon atoms; or is an alkyl-containing siloxane group having from 1 to 6 silicon atoms.

11. A composition according to claim 10, wherein the



water-insoluble monomer B_1 is selected from the group consisting of methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, isobornyl methacrylate, cyclohexyl methacrylate, hexafluoroisopropyl methacrylate and mixtures thereof.

12. A composition according to claim 11, wherein the water-insoluble monomer B_1 is selected from the group consisting of methyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate and mixtures thereof.

13. A composition according to claim 6, wherein component (B) comprises from 1 to 30 %, based on the total weight of monomer, of a diolefinic monomer (B_x).

14. A composition according to claim 6, wherein the diolefinic monomer (B_x) of component B is the acrylate or methacrylate of allyl alcohol, of a straight or branched-chain alkylene glycol having from 2 to 6 carbon atoms, of poly(ethylene oxide)glycols, of poly(propylene oxide)glycols, of poly(n-butylene oxide)glycols, of thiodiethylene glycol, of neopentylene glycol, of trimethylolpropane, or of pentaerythritol; or the reaction product obtained by reacting 1 mol of a di- or tri-isocyanate of the structure $OCN-R_4(NCO)_v$, wherein R_4 is the radical derived from the said isocyanate by removing the NCO group(s) and v is 1 or 2, with 2 or 3 mol of a hydroxyalkyl acrylate or methacrylate.

15. A composition according to claim 6, wherein component B is a mixture of methyl methacrylate and 1 to 25 % by weight, based on the total monomer content, of neopentylene glycol diacrylate, ethylene glycol dimethacrylate or the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.



16. A composition according to claim 10, wherein the water-insoluble monomer B_1 is a mixture of vinyl acetate and dimethyl maleate in a 2/1 to 5/1 molar ratio plus methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate or hexafluoroisopropyl methacrylate or mixtures thereof.

17. A composition according to claim 10, wherein the water-insoluble monomer B_1 is selected from the group consisting of 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, n-butyl acrylate, n-butyl methacrylate, n-octyl acrylate, n-octyl methacrylate, n-decyl acrylate, n-decyl methacrylate, perfluoroalkyl-(C_6 - C_{10})-substituted alkyl acrylate or methacrylate, and mixtures thereof.

18. A composition according to claim 6, wherein in monomer B the water-soluble monomer B_2 is an acrylate or methacrylate of formula $CH_2=CR_3COOR_{13}$, an acrylamide or methacrylamide of formula $CH_2=CR_3CONHR_{14}$ or $CH_2=CR_3CON(R_5)_2$, a maleate or fumarate of formula $R_{13}OCOCH=CHCOOR_{13}$, a vinyl ether of formula $CH_2=CHOR_{13}$, an N-vinyl lactam, or a mixture of those monomers,

wherein R_3 is hydrogen or methyl, R_5 is hydrogen or C_1 - C_4 alkyl, R_{13} is a hydrocarbon radical having from 1 to 10 carbon atoms that is substituted by one or more water-solubilizing groups, such as carboxy, hydroxy or tert-amino, or a polyethylene oxide group having from 2 to 100 repeating units, or a group which comprises sulfate, phosphate, sulfonate or phosphonate groups, and R_{14} has the meaning given for R_{13} or R_5 .

19. A composition according to claim 18, wherein the water-soluble monomer B_2 is selected from the group consisting of 2-hydroxyethyl methacrylate, N,N-dimethyl-



acrylamide, acrylic acid, methacrylic acid and N-vinyl-2-pyrrolidone.

20. A composition according to claim 6, wherein component A is a polysiloxane structure wherein R_1 is alkylene having 3 or 4 carbon atoms, $R_2, R_a, R_b, R_c, R_d, R_e, R_f, R_g, R_h, R_i, R_j$ and R_k are each methyl, $x_1 + x_2$ is 10 to 100, y_1 is 0 to 2, y_2 is 1 to 3, z_1 is -O- or -NH- and R_4 is the divalent radical of an aliphatic or cycloaliphatic diisocyanate having from 6 to 10 carbon atoms, and Y is the same as Y_1 , R_6 is hydrogen, R_8 is ethylene, and z_2 is -O- or $-NC(CH_3)_3-$, and component B comprises from 0 to 30 %, based on the total monomer content, of a diolefinic monomer (B_x), which is the acrylate or methacrylate of allyl alcohol, of a straight or branched-chain alkylene glycol having from 2 to 6 carbon atoms, of poly(ethylene oxide)glycols, of poly(propylene oxide)glycols, of poly(n-butylene oxide)glycols, of thiodiethylene glycol, of neopentylene glycol, of trimethylolpropane, or of pentaerythritol; or the reaction product obtained by reacting 1 mol of a di- or tri-isocyanate of the structure $OCN-R_4-(NCO)_v$, wherein R_4 is the radical derived from the said isocyanate by removing the NCO group(s) and v is 1 or 2, with 2 or 3 mol of a hydroxyalkyl acrylate or methacrylate.

21. A composition according to claim 20, wherein B_x is neopentylene glycol diacrylate, ethylene glycol dimethacrylate or the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

22. A composition according to claim 20, wherein component B comprises a water-insoluble monomer B_1 selected from the group consisting of methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, isobornyl methacrylate, cyclohexyl meth-



acrylate and hexafluoroisopropyl methacrylate and mixtures thereof.

23. A composition according to claim 22, wherein component B comprises a water-insoluble monomer B₁ selected from the group consisting of methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate and mixtures thereof.

24. A composition according to claim 21, wherein component B comprises as the water-insoluble monomer B₁ methyl methacrylate, isobornyl methacrylate or a mixture thereof.

25. A composition according to claim 20, wherein component B comprises a water-insoluble monomer B₁ which is a mixture of vinyl acetate and dimethyl maleate in a 2/1 to 5/1 molar ratio plus methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate or hexafluoroisopropyl methacrylate or a mixture thereof.

26. A composition according to claim 20, wherein component B comprises a water-insoluble monomer B₁ selected from the group consisting of 2-ethylhexyl acrylate, n-butyl acrylate, n-butyl methacrylate, n-octyl acrylate, n-octyl methacrylate, n-decyl acrylate, n-decyl methacrylate, perfluoroalkyl-(C₆-C₁₀)-substituted alkyl acrylate or methacrylate, and mixtures thereof.

27. A composition according to claim 20, wherein component B comprises a water-soluble monomer B₂ selected from the group consisting of 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylic acid, methacrylic acid and N-vinyl-2-pyrrolidone.



28. A composition according to claim 20, which comprises

(A) from 15 to 40 % by weight of a polysiloxane of the structure A_2 , wherein Z_1 and Z_2 are each -O- and y_2 is 1 or 2, and

(B) from 85 to 60 % by weight of a mixture of a water-insoluble monomer (B_1), of a water-soluble monomer (B_2), and of a diolefinic monomer (B_x), wherein, based on the percentage by weight of the total weight of monomers,

B_1 is from 60 to 95 % of a water-insoluble monomer selected from the group consisting of methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate and mixtures thereof,

B_2 is from 20 to 0 % of a water-soluble monomer selected from the group consisting of 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone and mixtures thereof, and

B_x is from 20 to 5 % of a diolefinic monomer selected from the group consisting of neopentylene glycol diacrylate, ethylene glycol dimethacrylate and the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

29. A composition according to claim 20, which comprises

(A) from 40 to 60 % by weight of a polysiloxane of the structure A_2 , wherein Z_1 and Z_2 are each -O- and y_2 is 1 or 2, and

(B) from 60 to 40 % by weight of a mixture of a water-



insoluble monomer (B_1), of a water-soluble monomer (B_2), and of a diolefinic monomer (B_x), wherein, based on the percentage by weight of the total weight of monomers,

B_1 is from 70 to 100 % of a water-insoluble monomer selected from the group consisting of ethyl acrylate or methacrylate, n-butyl acrylate or methacrylate, n-hexyl acrylate or methacrylate, 2-ethylhexyl acrylate or methacrylate, n-octyl acrylate or methacrylate, n-decyl acrylate or methacrylate and mixtures thereof and with mixtures thereof with methyl or isobornyl methacrylate,

B_2 is from 25 to 0 % of a water-soluble monomer selected from the group consisting of 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone and mixtures thereof, and

B_x is from 5 to 0 % of a diolefinic monomer selected from the group consisting of neopentylene glycol diacrylate, ethylene glycol dimethacrylate and the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

30. A composition according to claim 20, which comprises

(A) from 20 to 60 % by weight of a polysiloxane of the structure A_2 wherein Z_1 and Z_2 are each -O-, and y_2 is 1 or 2, and

(B) from 80 to 40 % by weight of a mixture of a water-insoluble monomer (B_1), of a water-soluble monomer (B_2), and of a diolefinic monomer (B_x), wherein, based on the percentage by weight of the total weight of monomers,

B_1 is from 0 to 80 % of a water-insoluble monomer selected from the group consisting of methyl meth-



acrylate, 2-ethylhexyl acrylate, hexafluoroisopropyl methacrylate, perfluoroalkyl-(C₆-C₁₀) acrylate or methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate and mixtures thereof,

B₂ is from 100 to 15 % of water-soluble monomer selected from the group consisting of 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, N-vinyl-2-pyrrolidone acrylamide and mixtures thereof, and

B_x is from 0 to 5 % of a diolefinic monomer selected from the group consisting of neopentylene glycol diacrylate, ethylene glycol dimethacrylate and the reaction product of 1 mol of isophorone diisocyanate and 2 mol of 2-hydroxyethyl methacrylate.

31. A hard contact lens prepared from the polymer of the composition according to claim 5.

32. A hard contact lens prepared from the polymer of the composition according to claim 28.

33. A soft contact lens prepared from the polymer of the composition according to claim 5.

34. A soft contact lens prepared from the polymer of the composition according to claim 29.

35. A soft hydrogel contact lens prepared from the polymer of the composition according to claim 5.

36. A soft hydrogel contact lens prepared from the polymer of the composition according to claim 30.

37. A polymer comprising the copolymerization product of



the composition according to claim 5.

38. A process for the production of a polymer from the composition according to claim 5, comprising the reaction of components (A) and (B) under the action of heat or irradiation.



* C L M S *