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(54) Title: HARD SEGMENT SIZE CONTROL IN POLYURETHANE FORMATION (57) Abstract Improved methods for forming urethane elastomers and corresponding urethane prepolymers are disclosed wherein diiso- cyanate and a low molecular weight diol are simultaneously mixed and reacted to form a hard segment which is subsequently reacted with a long chain diol to form the elastomer. Aliphatic diisocyanates are particularly desirable for the manufacture of contact lenses from the urethane prepolymers of this invention.		

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HARD SEGMENT SIZE CONTROL IN POLYURETHANE FORMATION

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BACKGROUND OF THE INVENTION

The present invention relates to urethane elastomers and methods for their preparation.

10 Polyurethane is a versatile class of polymers with a variety of applications because its properties can be tailored simply by varying the components from which it is constructed (the rigid diols, the flexible polyols, and the polyisocyanate). Ulrich, H., "Urethane
15 Polymer", in Ency. Chem. Tech., Vol. 23, pp. 576-606 (Wiley Intersciences) (1983). Polyurethanes are used as adhesives, coatings, elastomers, foams, and fibers.

Polyurethane elastomers can be either
20 thermoplastic or thermosetting. All linear segmented urethane elastomers are thermoplastic with good tear strength, impact resistance and other excellent mechanical properties. Finelli, A., et al., "Thermoplastic Elastomer", in Ency. Chem. Tech., Vol.
25 8, pp. 626 et seq. (Wiley Intersciences) (1979). These properties are due in part to the strong hydrogen bonding between the hard segments of neighboring chains. Normally the thermoplastic polyurethanes are prepared by first forming the isocyanate-capped
30 prepolymer of a flexible polyetherdiol or polyesterdiol, followed by adding the chain extender, which is the short chain diol, to form the high molecular weight polyurethane. Alternatively, the thermoplastic elastomers can be constructed by mixing
35 the ingredients all at once, but with somewhat less useful physical properties.

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In the two-step process to form the urethane elastomer, the length of the hard segment is relatively uniform in size. But when it becomes necessary to construct the hard segment before forming the soft
5 segment, it is important to control the mode of reaction to preserve the excellent properties of polyurethane such as tear strength and toughness. A more uniform hard segment size enhances the attractive forces, i.e., hydrogen bonding, resulting in improved
10 properties.

One method to control the size of the hard segment is by using an aromatic diisocyanate with differential reactivity between the two isocyanate groups. A
15 prominent example of such a compound is tolylene diisocyanate ("TDI"). This is possible because of electronic and steric effects. However, this approach is not possible when using aliphatic diisocyanates or aromatic diisocyanates wherein the isocyanate groups
20 are attached to different aromatic rings.

SUMMARY OF THE INVENTION

It has now been found that control of the size of
25 hard segments prepared from diisocyanates is dramatically improved by simultaneously mixing the diisocyanate and the short chain diol. This result is desirable when employing aliphatic diisocyanates and aromatic diisocyanates wherein the isocyanate groups
30 are attached to different aromatic rings. It has also been found that lower reaction temperatures enhance the selectivity of the reaction to the desired product.

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DETAILED DESCRIPTION OF THE INVENTION

This invention is concerned with preparing urethane elastomers by first reacting two mole equivalents of a diisocyanate with about one mole equivalent of a low molecular weight diol. If this diol is represented by the symbol $\ast G \ast$, where \ast denotes a hydroxyl radical and G represents the rest of the diol compound, and if the diisocyanate functional compound is represented by $\bullet D \bullet$ where \bullet represents an isocyanate radical, this first reaction can be schematically represented as follows:



where \ast denotes a urethane or a ureido linkage. The first reaction produces a so-called "Hard" segment. As is known to those skilled in polymer chemistry, the product $\bullet D \ast G \ast D \bullet$ is the mathematical average of all reaction product molecules. The reaction product of the actual reaction will contain $\bullet D \bullet$ and $\bullet D (\ast G \ast D)_c \ast G \ast D$ with $c \geq 2$. Again, the formulas are numerical averages.

20

In the conventional method of urethane polymer preparation, 2 equivalents of diisocyanate is reacted with one equivalent of long chain polyether diol or polyester diol to form a prepolymer with isocyanate end-caps. This prepolymer is then allowed to react with a short chain diol to form high molecular weight polymers. By this synthetic scheme, the hard segment, which is the reaction product of the short chain diol and the isocyanate groups in the prepolymer, is always uniform in size, i.e., it is exactly $\bullet D \ast G \ast D \bullet$, instead of a statistical distribution of sizes as $\bullet D (\ast G \ast D)_c \bullet$ $c=0,1,2,3, \dots$ as described in the preceding paragraph.

30

When it is desirable to prepare a urethane polymer or prepolymer by constructing the hard segment first because of special applications or reaction conditions

35

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required, the hard segment size is not uniform. In this scenario, the control of reaction conditions for hard segment formation is very critical in order to obtain hard segment with a narrow size distribution, which in turn, is very important to maintain the excellent mechanical properties of the urethane polymer. The control of reaction conditions to get the most favorable hard segment product is the subject of this invention.

10

It was found, as shown in the examples, that simultaneous mixing of reagents gave hard segments with the most favorable weight distribution (i.e., it has the highest content of •D•G•D•) while slow addition of short chain diol into a diisocyanate solution produced hard segments with less favorable size distribution. This phenomena is very prominent at high reaction temperature such as 80°C, and less when the reaction temperature is lower. The choice of solvent is irrelevant as long as the reagents are stable in the solvent employed.

20

Any diisocyanate with independent reactivities for the two isocyanate groups may be employed in the method of invention. These diisocyanate include any aliphatic diisocyanate and any aromatic diisocyanate with the isocyanate groups attached to different aromatic rings.

25

Thus, any diisocyanate (i.e., •D•) having independent reactivity may be employed in the method of this invention. "D" may be selected from the group consisting of alkyl, alkyl cycloalkyl, cycloalkyl, alkyl aromatic, and aromatic diradicals having 6 to 30 carbon atoms. Preferred aliphatic diisocyanates (i.e., •D•) are isophorone diisocyanate, hexamethylene-1,6-diisocyanate, biuret of

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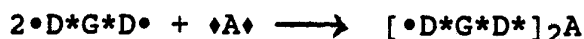
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hexamethylene-1,6-diisocyanate, and
4,4'-dicyclohexylmethane diisocyanate. The preferred
aromatic diisocyanate is
bis(4-isocyanatophenyl)methane.

5

Suitable low molecular weight diols (i.e., ♦G♦) include diols wherein G is selected from the group consisting of alkyl, cycloalkyl, alkyl cycloalkyl, aromatic, and alkylaromatic diradicals having 1 to
10 40 carbon atoms. The diols may have ether, thio, or amine linkages in the main chain. Particularly preferred low molecular weight diols are 2,2-(4,4'-dihydroxydiphenyl)-propane (bisphenol-A), 4,4'-isopropylidene dicyclohexanol (hydrogenated biphenol-A),
15 ethoxylated bisphenol-A, propoxylated bisphenol-A, 2,2-(4,4'-dihydroxydiphenyl)-pentane, α,α'-(4,4'-dihydroxydiphenyl)-p-diisopropyl benzene, 1,3-cyclohexane diol, 1,4-cyclohexane diol-1,4-cyclohexane dimethanol, bicyclic and tricyclic diols such as 4,8-
20 bis-(hydroxymethyl)-tricyclo [5.2.1.0^{2,6}] decane, neopentyl glycol, 1, 4 butanediol, 1,3-propanediol, 1,5-pentanediol, diethylene glycol, triethylene glycol and the like.

25 The product of the first reaction (between the diisocyanate and a low molecular weight diol) is reacted in a second stage with a long chain diol to form urethane elastomers. If ♦A♦ represents the long chain diol, the second reaction can be schematically
30 represented as follows:

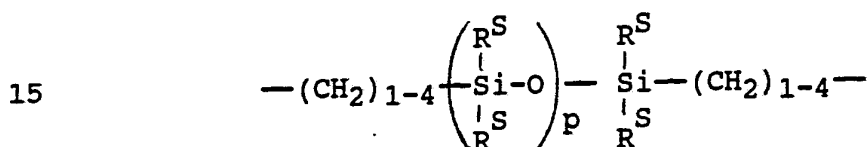
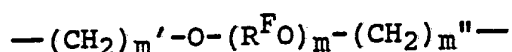
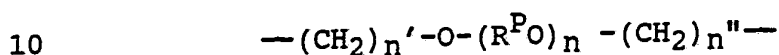


Suitable high molecular weight diols (i.e., ♦A♦)
35 include diols wherein A is selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl,

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aromatic, and alkylaromatic diradicals having molecular weights in excess of 400, preferably 1000-10,000, more preferably 2000-5000. Suitable diols also include fluorinated and silicone-containing analogs of the foregoing.

"A" preferably denotes a divalent polymeric radical chosen from the group of



wherein R^P denotes a straight or branched alkyl group with

1 to 6 carbon atoms and n provides for a moiety

weight of the radical between 2000 and 10,000;

R^F denotes a fluorinated straight or branched alkyl

radical with 1 to 6 carbon atoms and m provides

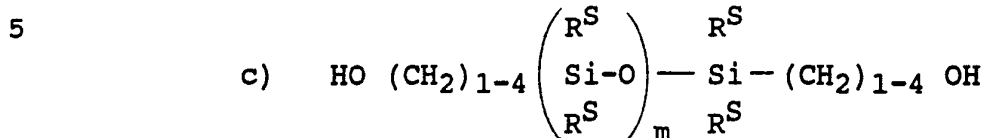
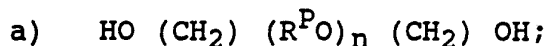
a moiety weight of between 400 and 10,000;

R^S denotes an alkyl radical or a short chain fluorinated alkyl radical with 1 to 3 carbon atoms; and

p provides a moiety weight of 400 to 10,000;

Preferred high molecular weight diols include polymers of the following formulae

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Formulae a) represents polyoxyalkyleneglycols which are
 10 generally commercially available in the molecular
 weight range called for in the present invention.
 These diols include polymers prepared from the
 epoxides: ethylene oxide 1,2-propylene oxide, 1,2-
 butylene oxide, 2,2 epoxydecane, 1,2-epoxyoctane, 2,3-
 15 epoxy norborane, 1,2-epoxy-3-ethoxy propane, 2,2-epoxy-
 3-phenoxypropane, 2,3-epoxypropyl-4-methoxy phenyl
 ether, tetrahydrofluran, 1,2-epoxy-3-cyclohexylóxy
 propane, oxetane, 1,2-epoxy-5-hexene, 1,2-
 epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-methylpropane,
 20 benzyloxy propylene oxide, the like and combinations
 thereof.

The preferred polymers of this class are
 polypropylene glycols of molecular weights, 2000, 3000
 25 and 4000 and more and polyoxyethylene polyoxypropylene
 block copolymers with molecular weight greater than
 2000.

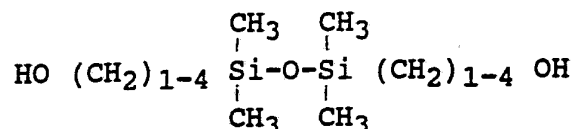
Formulae b) represents polyfluoroethers with α, ω -
 30 active hydrogens. This class of polymers can be
 synthesized as taught in U.S. Patent No. 3,810,874.
 Generally, these polymers should have molecular weights
 between 400 and 10,000.

35 Formulae c) represents α, ω - dihydroxyl alkyl
 endblocked polysiloxane which for the purpose of the

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present invention should have a molecular weight in the range of 400 to 10,000. These polysiloxanes can be synthesized by reacting a disiloxane of the general formula

5



10 with cyclopolydimethyl siloxane under acidic conditions.

Alternately, the disiloxane can be replaced with dimethoxydimethylsilane or diethoxy dimethyl silane to
15 produce the α,ω - dihydroxy endcapped polysiloxanes.

In general, each of the reaction stages is run until the reactive step is complete. Reaction progress may be monitored by acid base titration. The
20 isocyanate content may be calculated by the difference of acid equivalents between a stock solution dibutylamine and its reaction product with the diisocyanate reaction intermediate. The reaction may also be monitored by ATR-IR for the
25 appearance/disappearance of peaks at 1700 cm^{-1} , which indicated the presence of

$\begin{array}{c} \text{O} \\ || \\ \text{-C-} \end{array}$, and 2250 cm^{-1} which indicated consumption of
30 -N=C=O .

The synthesis of the prepolymer may be run neat or in solution. A wide range of aprotic solvents can be used to synthesize the prepolymers of the present
35 invention. Solvents useful in the synthesis include toluene, methylene, chloride, benzene, cyclohexane,

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hexane, heptane and the like. Preferred solvents are toluene, methylene chloride and mixtures thereof.

Reaction of the precursors may be accomplished in the presence or absence of catalysts for urethane reactions, such catalysts being well known in the art. Among the suitable catalysts are tin salts and organic tin esters, such as dibutyl tin dilaurate, tertiary amines, such as triethyl diamine and other recognized catalysts, such as 1,4-diaza (2.2.2)-bicyclooctane (DABCO).

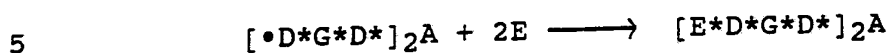
Preferably, the first step of elastomer synthesis in accordance with the present invention is carried out below about 100°C, most suitably within the range of from about 40°C to about 80°C. Thereafter, the second step of the reaction is carried out at comparable temperatures, preferably within the range of from about 40°C to 70°C. As will be apparent to those skilled in the art, optimal reaction conditions, such as temperatures and duration, are selected for each individual reaction system to achieve conditions that produce a favorable rate of reaction without fostering undesirable side reactions.

Optionally, the second stage can be run with molar excess of A to produce multiblock polymers of the general formula $\text{-(D*G*D*A)}_a\text{-D*G*D-}$ where a is at least 1.

The urethane elastomers prepared as described above may be converted to prepolymers by the addition of a polymerizable end-capping agent in a third stage. In this stage, the reaction product from the second stage is reached with a molar excess of an end-capping monomer which has: 1) hydroxyl or amine functionality;

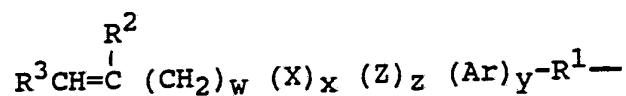
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and 2) some polymerizable unsaturation. If the endcapper is represented by the symbol E \cdot , where \cdot is -OH or -NH₂ or -NH-, the reaction proceeds generally as



Suitable end-capping agents include polymerizable unsaturated organic radicals represented by the general chemical formula

10



wherein R¹ denotes a divalent alkylene radical with 1
15 to 10

carbon atoms;

R² denotes a -H or -CH₃ radical;

R³ denotes a -H radical or an alkyl radical

with

20

1 to 6 carbon atoms or a $\overset{\overset{O}{||}}{C} - Y - R^4$ radical

where

Y is -O-, -S- or -NH- and R⁴ denotes an alkyl radical with 1 to 12 carbon atoms;

25

X denotes $\overset{\overset{O}{||}}{C} -$, or $-O-\overset{\overset{O}{||}}{C}-$

Ar denotes an aromatic radical with 6 to 30

carbon

30

atoms;

a is at least 1;

w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

35

z is 0 or 1.

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Specific examples are hydroxyethyl acrylate, hydroxyethyl methacrylate, aminoethyl methacrylate, 3 hydroxypropyl methacrylate, amino propyl methacrylate, hydroxyhexylacrylate, t-butylaminoethyl methacrylate, 5 monoacrylate or monomethacrylate esters of bisphenol-A and/or bisphenol-B.

Prepolymer formation is typically effected at temperatures of from about room temperature to about 10 100°C, preferably from about 20°C to about 40°C.

These prepolymers are especially useful in making biomedical materials due to this combination of physical strength and high oxygen permeability when 15 copolymerized with state of the art ethylenically unsaturated biomedical monomers. The combination of advantageous properties is achieved due to the specific chemistry inherent in the claimed prepolymer.

20 The prepolymers upon polymerization form two domains which can be characterized as hard and soft domains, respectively. The soft domain generally have glass transition temperatures (T_g s) lower than room temperature whereas the hard domains have T_g s higher 25 than room temperature. Upon polymerization, the hard segments of the prepolymer associate with one another and the soft segments form the soft domain which account for the oxygen permeability of the polymeric mass. The combination of hard and soft segments 30 provides the polymer with superior mechanical properties otherwise unavailable.

These hard segments as mentioned before form hard domains in the final polymer or copolymer by 35 association via hydrogen bonding with other rigid segments. The degree of association within the hard

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domain can be modified by controlling the amount of hydrogen bonding between the segments by either 1) decreasing the overall weight content of the hard segment in the prepolymer by increasing the molecular weight of the soft segment or 2) by decreasing the amount of hydrogen bonding density in the hard segment by either using relatively soft, longer chained diols, or by using primary amines or secondary amines capped low molecular weight compounds in conjunction with the diisocyanates rather than the diols.

The prepolymers of the present invention are particularly useful as comonomers with state of the art ethylenically reactive monomers useful in the field of biomedical materials. In general, these monomers are the hydroxyalkyl acrylates and diacrylates such as hydroxyethyl acrylate, hydroxypropyl acrylate, and the corresponding methacrylate compounds, including cyclohexyl methacrylate, methyl methacrylate, isobornyl methacrylate, lauryl methacrylate, triethylene glycol dimethacrylate, isobutyl methacrylate and tetrahydrofurfuryl methacrylate and other unsaturated reactive monomers such as acrylamides, methacrylamides, pyrrolidinones, styrene and acrylonitrile can be used as well and other monomers known in the art including fluorinated analogs of all of the previously mentioned monomers and the organo silicone comonomers known in the art. Specific fluorocomonomers include:

(2,2,2-trifluoroethyl) itaconate
(hexafluoroisopropyl) itaconate
(1H, 1H-perfluorooctyl) itaconate
(1H, 1H, 11H-perfluoroundecyl) itaconate
(perfluoro-t butyl) itaconate
(pentafluorophenyl) itaconate
(2H, 2H-perfluorobenzyl) itaconate

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(pentafluorophenylmethyl) itaconate
(decafluorocyclohexyl) itaconate
(1H-perfluorocyclohexyl) methyl itaconate
(1,1,1-trifluoroisopropyl) itaconate
5 1-methyl-4-(hexafluoroisopropyl) monoitaconate
4-(hexafluoroisopropyl) monoitaconate
1-(1H, 1H-perfluorooctyl)-4-hexafluoroisopropyl)
itaconate

and methacrylate analogs thereof.

10

Specific organosilicon comonomers include:
tris(2-acetoxyethyl dimethylsiloxy)silylpropyl
acrylate and methacrylate
tris(2-carboxyethyl dimethylsiloxy)silylpropyl
15 acrylate and methacrylate
tris(3-hydroxypropyl dimethylsiloxy)silylpropyl
acrylate and methacrylate
acrylate and methacrylate functional,
fluorosubstituted alkyl/aryl siloxanes such
20 as:
tris(3,3,3 trifluoropropyl dimethylsiloxy) silyl
propyl acrylate and methacrylate
tris[3-heptafluoroisopropoxy propyl)] dimethylsiloxy
silylpropyl acrylate and methacrylate
25 tris(pentafluorophenyl dimethylsiloxy)silyl propyl
acrylate and methacrylate.

Other potentially useful organosilicon comonomers
include:

30 p-(pentamethyldisiloxanyl) styrene
bis(trimethylsiloxy)
pyrrolidinonyldimethyl
siloxy-silylpropyl acrylate and methacrylate.

35 When used as comonomers these materials can be used
from 5 to 85 weight percent of the final copolymer

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weight with the balance comprising the prepolymer portion.

Other di-ethylenically reactive monomers can also
5 be used to effect the mechanical and surface properties. Such crosslinks are generally employed in the 0.1 to 5 wt % range.

The polymers and copolymers are formed by a free
10 radical mechanism using a wide variety of known free radical catalysts such as the diacyl peroxides such as benzoyl peroxide; dialkyl peroxides such as di-tert, -butyl peroxide; ketone peroxides such as methylethyl ketone peroxide; and peresters which readily hydrolyze,
15 e.g. tert-butyl peracetate, tert-butyl perbenzoate, di-tert-butyl diperphthalate, etc. A particularly useful class of peroxy initiators are the organic hydroperoxides such as cumene hydroperoxide, methylethyl ketone hydroperoxide, tert-butyl
20 hydroperoxide, etc. The initiators should be used at a concentration of about 0.01 percent to about 10 percent by weight of the total formulation, preferably about 0.1 percent to about 5 percent by weight. Another useful class of initiators comprises carbonyl-
25 containing ultraviolet-activated free radical generators, such as acetophenone, benzophenone, and the benzoin ethers. Other suitable UV initiators are known in the art. Initiator mixtures may also be used.

30 Solvents can be used in the final copolymerization and/or polymerization process. Solvent choice will depend upon the solubility parameters of the prepolymer and of the comonomers used, if any, and should be chosen to allow full solubilization of all polymerizate
35 components.

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In certain instances, the copolymerization process should be carried out without solvent. For instance, when 2-hydroxyethyl methacrylate (HEMA) is copolymerized with one of the prepolymers formed with polyethylene glycol, use of toluene causes the HEMA to form heterogenous domains which are not stable under aggressive hydrolytic conditions.

As mentioned, the prepolymers of the present invention are particularly useful in forming shaped articles used in biomedical applications. These polymers and copolymers can be used to make biomedical devices i.e. shaped articles, such as dialyzer diaphragms, to prepare artificial kidneys and other biomedical implants, such as disclosed in Wichterle, U.S. Pat. No. 2,976,576 and Wichterle, U.S. Pat. No. 3,220,960. The instant polymers and copolymers can be used in preparing therapeutic bandages as disclosed in Shephard, U.S. Pat. No. 3,428,043. The instant polymers and copolymers can also be used in preparing medical surgical devices e.g. heart valves, vessel substitutes, intra-uterine devices, membranes and other films, dialyzer diaphragms, catheters, mouth guards, denture liners and other such devices as disclosed in Shephard U.S. Pat. No. 3,520,949 and Shephard U.S. Pat. 3,618,231. The instant polymers and copolymers can be used to modify collagen to make blood vessels, urinary bladders and other such devices as disclosed in Kliment U.S. Pat No. 3,563,925. The instant polymers and copolymers can be used to make catheters as disclosed in Shephard U.S. Pat. No. 3,566,874. The instant polymers and copolymers can be used as semipermeable sheets for dialysis, artificial dentures and all of such disclosures as set forth in Stoy U.S. Pat. No. 3,607,848. The instant polymers and copolymers can be used in ophthalmic prostheses and all other uses

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disclosed in Wichterle U.S. Pt. No. 3,679,504. They may also be used as a polymeric matrix for controlled release of active pharmaceutical agents.

5 A preferred application for the urethane prepolymers of this invention is the manufacture of contact lenses. Because aromatic diisocyanates have been found to discolor contact lenses, aliphatic diisocyanates are preferred for this application.

10 Separation of the urethane elastomers and prepolymers of this invention from byproducts is difficult, if not impossible, because of the high reactivity of the materials. Accordingly, increased
15 selectivity in the reactions leading to the desired elastomer/prepolymer product is essential. This is particularly so when prepolymers are incorporated in contact lens materials as is contemplated in particularly preferred embodiments of this invention.

20 The isophorone diisocyanate ("IPDI") used in the following examples was distilled under reduced pressure. Gas chromatographic analysis indicated that it was 72% cis and 28% trans. When diethylene glycol
25 ("DEG") was used in the following examples with toluene as a reaction solvent, DEG (99%+ with less than 0.04 % water as determined by the Karl-Fisher method) was azeotropically distilled with toluene prior to use. Otherwise, it was dried over 3A molecular sieves.
30 Toluene was dried with sodium. Methylene chloride was dried by 3A molecular sieve, with resulting water content less than 0.01%.

Table 1

Example	A	B	C	1	D	2	3	4
Temperature (#C)	100	80	80	80	50	50	50	25
Solvent	-----toluene----- CH ₂ Cl ₂							
Mixing Time (hours)	3	3	1.5	0	3	0	0	0
Distribution of Products (weight %)								
A	31	37	25	21	25	22	21	30
B	42	35	41	55	52	59	57	56
C	27	28	33	24	23	19	20	14
Ratio of B/A	1.35	0.95	1.64	2.62	2.08	2.68	2.71	1.87

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EXAMPLES 1-4 and COMPARATIVE EXAMPLES A-D

IPDI solution (1 equivalent) in toluene or in methylene chloride, with dibutyltin dilaurate (1.1% of the weight of the reactants--IPDI and DEG) was added to
5 a dry, three-necked flask under nitrogen blanket. The solution was heated at the specified temperature. Then the dry DEG solution (0.5 equivalent) was added over the period of time indicated. The contents were then heated and stirred under a nitrogen blanket until the
10 isocyanate content was reduced one-half as determined by acid-base titration.

An aliquot was removed, reacted with excess butylamine and then vacuum stripped. The butylamine
15 was added to form a stable urea for characterization purposes. When the isocyanate-capped adduct was not properly deactivated, it would pick up moisture, resulting in erroneously large molecular weight values.

20 The urethane-urea adduct was then analyzed by gel permeation chromatography for size distribution. Results are shown below in Table 1. In the Table, A represents urea-capped IPDI-(DEG-IPDI)_n wherein n is no less than 2; B represents urea-capped IPDI-DEG-IPDI
25 which is the desired product; and C represents urea-capped IPDI.

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The data shows the effects of modes of addition and reaction temperature on the size distribution of hard segments. With toluene at 80°C, it was found that

5 simultaneous mixing of DEG with IPDI gave the highest concentration (55%) of the end-capped DEG (IPDI-DEG-IPDI), while slow addition (3 hours) of DEG gave the lowest concentration (35%). Note that reaction at a

10 temperature of 80°C) gave a higher concentration of the desired hard segment regardless of mode of addition. Simultaneous mixing of reagents gave superior results at all temperatures studied. Alternate solvents did not change the distribution of reaction products.

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WHAT IS CLAIMED IS:

1. An improved method for forming a urethane elastomer wherein a diisocyanate selected from the group consisting of aliphatic diisocyanates and aromatic diisocyanates wherein the isocyanate groups are attached to different aromatic rings is reacted with a low molecular weight diol to form a hard segment which is subsequently reacted with a long chain diol, the improvement which comprises simultaneously mixing the diisocyanate and low molecular weight diol used to form the hard segment.

2. An improved method for forming a urethane prepolymer wherein:

- (a) a diisocyanate selected from the group consisting of aliphatic diisocyanates and aromatic diisocyanates wherein the isocyanate groups are attached to different aromatic rings is reacted with a low molecular weight diol to form a hard segment,
- (b) the hard segment is reacted with a long chain diol to form a urethane elastomer,
- (c) and the elastomer is reacted with an end-capping agent having a polymerizable functionality;

the improvement which comprises simultaneously mixing the diisocyanate and the low molecular weight diol used to form the hard segment.

3. The methods of claims 1 or 2 wherein the diisocyanate is an aliphatic diisocyanate.

4. The methods of claim 3 wherein the aliphatic diisocyanate is selected from the group consisting of isophorone diisocyanate,

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hexamethylene-1,6-diisocyanate, biuret of
hexamethylene-1,6-diisocyanate, and
4,4'-dicyclohexylmethane diisocyanate.

5 5. The methods of claim 3 wherein the aliphatic
diisocyanate is isophorone diisocyanate.

6. The methods of claim 1 or 2 wherein the
diisocyanate is bis(4-isocyanatophenyl)methane.
10

7. The methods of claim 1 or 2 wherein the
diisocyanate and the low molecular weight diol are
reacted at a temperature within the range of about 40°
to about 80°C.
15

8. An improved urethane prepolymer prepared by a
method wherein:

- 20 (a) a diisocyanate selected from the group
consisting of aliphatic diisocyanates
and aromatic diisocyanates wherein the
isocyanate groups are attached to
different aromatic rings is reacted with
a low molecular weight diol to form a
hard segment,
25 (b) the hard segment is reacted with a long
chain diol to form a urethane elastomer,
 (c) and the elastomer is reacted with an
end-capping agent having a polymerizable
functionality;
30 the improvement which comprises simultaneously mixing
the diisocyanate and the low molecular weight diol used
to form the hard segment.

9. A contact lens prepared from a monomer
35 mixture comprising the urethane prepolymer of claim 8.

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10. The contact lens of claim 9 wherein the prepolymer is prepared from an aliphatic diisocyanate.

5 11. The contact lens of claim 10 wherein the prepolymer is prepared by reacting the aliphatic diisocyanate and the low molecular weight diol are reacted at a temperature within the range of about 40° to about 80°C.

10 12. The contact lens of claim 11 wherein the aliphatic diisocyanate is isophorone diisocyanate.

INTERNATIONAL SEARCH REPORT

PCT/US 91/08736

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G18/80; C08G18/67; C08F283/00; G02B1/04

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08G ; G02B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR,A,2 353 581 (BAYER) 30 December 1977 see claims 1-4 see page 5, line 4 - page 6, line 3 ---	1,6,7
X	GB,A,886 818 (BAYER) 10 January 1962 see claims 1,6-8,11 see page 3, line 51 - line 56 see page 3, line 72 - line 129 ---	1,3,4
X	DE,A,2 523 987 (VEB CHEMIEANLAGENBAU) 2 January 1976 see claims 1-4 see page 3, paragraph 2 see examples 1,4 --- -/--	1,6

⁹ Special categories of cited documents : ¹⁰^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

08 APRIL 1992

Date of Mailing of this International Search Report

06.05.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

VAN PUymbroeck M. A.

Van Puymbroeck

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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X	FR,A,2 303 835 (LOCTITE CORP.) 8 October 1976 see claims 1-6,16 see page 3, line 16 - line 34 see page 4, line 7 - line 26 see page 5, line 3 - line 19 see page 6, line 13 - line 30 see examples 4-7 ---	1-4,6-8
A	FR,A,1 466 598 (U.C.C.) 20 January 1967 *abstract points A,A1-A4* see page 3, left column, paragraph 3 - right column, paragraph 3 ---	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9108736
SA 55468**

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 08/04/92

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