

INTERPENETRATING POLYMER NETWORKS
FOR CONTACT LENS PRODUCTION

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to interpenetrating polymeric network (IPN) compositions, and the use thereof in contact lenses. More particularly, the present invention relates to an IPN comprised of a polyurea network and polyacrylic network; the former network is prepared from amines and isocyanates while the latter network is prepared from acrylic esters polymerized with a free radical initiator. The polyurea/polyacrylic network may be cross-linked with triamines.

The IPN is used to prepare a lens. The resulting finished contact or intraocular lens produced from the IPNs of the present invention has the clarity, dimensional stability, oxygen permeability, wettability, and durability desired for either daily or extended wear contact lenses or intraocular lenses.

2. DISCUSSION OF THE PRIOR ART

The use of contact lenses as corrective ophthalmic devices as well as for cosmetic purposes is well known. Various materials have been utilized in making contact lenses, but these materials have been found less than ideal.

To be effective as a material for a contact lens, the material must possess certain key properties:

- 1 (a) a high oxygen permeability, (b) good wettability,
(c) durability, (d) good mechanical strength, (e)
optical clarity, (f) flexibility, (g) ability to
transmit light in the visible range, and (h) homogeneity
- 5 and (i) control known changes in the lens parameters in
the ocular environment.

Various materials possess one or more of these properties but lack one or more of the other required properties. For example, contact lenses derived from

10 hydrophobic polymers possess good mechanical strength and durability. Such hydrophobic polymers used in the prior art to make contact lens include urethanes, polyesters, polyamides, siloxanes, epoxides and the like. However, such contact lenses lack wettability and

15 oxygen permeability.

On the other hand, hydrophilic material permits wettability and oxygen permeability. Examples of hydrophilic monomers used in the prior art include hydroxyalkyl methacrylate, vinyl alcohol and vinyl

20 pyrrolidone. But, these materials lack such properties as good mechanical strength and durability.

Thus, the ideal contact lens material is one that is a composite of a hydrophilic and hydrophobic material that maximizes the advantages of both materials

25 and minimizes their weaknesses.

The standard contact lens used almost exclusively for many years was made from poly(methylmethacrylate) (PMMA). PMMA can be readily injection molded, compression molded, or cast molded to

30 give inexpensive, highly transparent, stable, hard, wettable contact lenses. However, as a result of the

- 1 very low oxygen permeability of PMMA, lenses made
therefrom have to be removed from the eye at least once
daily.

In order to overcome the deficiency of the
5 PMMA lenses, numerous other organic polymers have been
proposed for use as contact lenses. Cellulose acetate
butyrate lenses, for example, have a somewhat higher
oxygen permeability than PMMA and are readily fabricated
by injection molding but have a lower dimensional
10 stability than PMMA.

Soft contact lenses based upon crosslinked
polymers from hydrophilic monomers, such as 2-
hydroxyethyl methacrylate or N-vinyl-2-pyrrolidone, are
found to be generally more comfortable to wear than PMMA
15 lenses but are more fragile and have a tendency to
become cloudy because of the ease by which proteinaceous
material and other contaminants are deposited thereon.
Soft lenses prepared from silicone rubber have a very
high oxygen permeability but poor mechanical properties
20 are resistant to wetting and adhere to the cornea.

Improvements in contact lens materials have
been approached by utilizing copolymers. For example,
U.S. Patent No. 3,503,942 to Seiderman describes a
contact lens comprised of a mixture of hydrophilic
25 monomers. The use of various combinations of monomers
to produce copolymers is limited by the ability of these
monomers to copolymerize. If monomers which do not
copolymerize well are chosen (e.g., methyl methacrylate
and vinyl pyrrolidinone), soluble polymer fragments are
30 formed. These soluble fragments must be extracted from
the lens.

1 Lenses prepared from copolymers of a silicone
methacrylate with methyl methacrylate (Gaylord, U.S.
Patent No. 4,120,570) or with methyl itaconate (Ellis,
U.S. Patent No. 4,424,328) have greater but still
5 limited oxygen permeability.

Wichterle in U.S. Patent No. 3,408,429
describes a complex centrifugal casting technique for
converting a mixture of hydroxyethyl methacrylate and
ethylene glycol dimethacrylate into a cross-linked
10 polymer lens which, upon being subjected to normal
saline, is converted into a soft contact lens. This
complex procedure inherently yields products having
optics that are inferior to those of hard contact
lenses.

15 Considerable attention has been given to the
modification of polymer properties through the use of
procedures involving the formation of an
interpenetrating polymer network (IPN). An IPN can be
defined broadly as an intimate network of two or more
20 polymers at least one of which is either synthesized
and/or cross-linked in the presence of the other.

Liu, for example, in U.S. Patent No.
4,618,644, describes the polymerization of methyl
methacrylate in the presence of a silicone polymer to
25 obtain a product of improved toughness. The
polymerization of ethylene glycol dimethacrylate and a
crosslinkable poly- (dimethylsiloxane) to yield a
product stated to be useful for the fabrication of
contact lenses is described by Falcetta (Ger. Offen. DE
30 2,518,904). Contact lenses have also been fabricated
from the interpenetrating network polymer resulting from

1 the polymerization of 2-hydroxyethyl methacrylate in the
presence of poly-N-vinylpyrrolidone (Ewell, U.S. Patent
No. 3,647,736).

Neefe (U.S. Patent No. 4,632,773) shows the
5 polymerization of methyl methacrylate in the presence of
a syrup containing polymerized methacryloxypropyl-
trimethoxysilane and a fluorescent colored pigment to
obtain a solid contact lens blank material which can be
readily identified. Tighe and Gee (U.S. Patent No.
10 4,430,458) disclose the formation of soft contact lens
material by the cross-linking of a polymeric hydrogel of
a copolymer of N-vinyl-2-pyrrolidone during the final
compression or injection molding process. Lim, et al.
(U.S. Patent No. 4,536,554) describes the preparation of
15 soft contact lenses made from the interpenetrating
network polymer obtained by the polymerization of a
mixture containing a hydrophilic and a hydrophobic
monomer and at least two cross-linking agents.

However, until the present invention, no one
20 had recognized that an IPN comprising a network of
polyurea interpenetrated with polyacrylate would be the
material of choice for contact lenses. This IPN
combines a weak hydrophilic polymer with a hydrophobic
polymer.

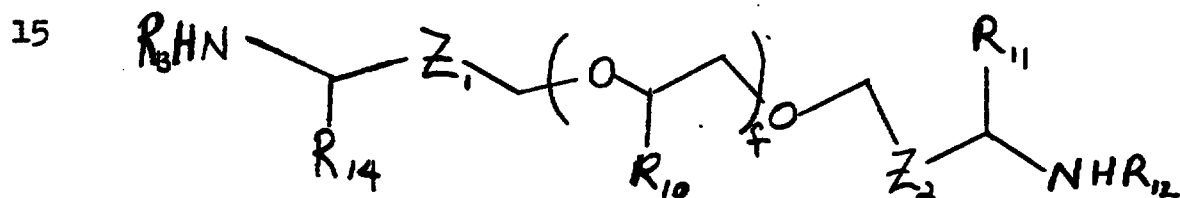
25 Moreover, the present inventors have
discovered that both the ratio of polyurea to acrylate
and the polyamine composition are critical for this
material to be used in a contact lens; however, if the
ratio is within certain specified limits and the
30 polyamine is of certain composition, the resulting IPN
material possesses all of the key properties described

1 hereinabove and is most suitable for making contact lenses.

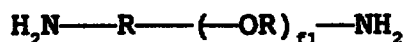
SUMMARY OF THE INVENTION

5 Accordingly, the present invention is directed to a homogeneous interpenetrating polymer network exhibiting a single glass transition temperature prepared from polymerization of a reactive mixture of polymerizable components, said reactive mixture
10 comprising

(a) an amine mixture comprising polyamines A and B, said amines being present in about 20-60% by weight of said reactive mixture, wherein A is



20 and B is



wherein

f_1 is an integer from 1-75;

R is an alkylene containing 3 carbon atoms and

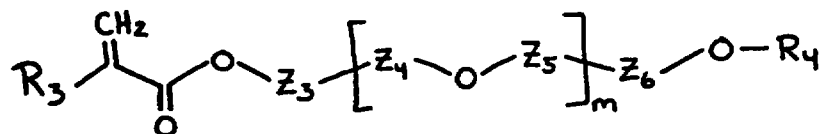
25 each R is the same;

f is an integer between 1 and 150, inclusive;

R_{10} , R_{11} , R_{12} , R_{13} and R_{14} are independently hydrogen or lower alkyl;

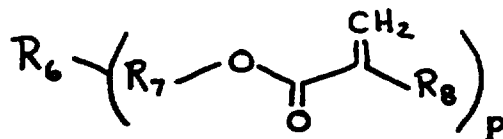
Z_1 and Z_2 are independently a chemical bond or
30 lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A,

- 1 (b) an organic di- or poly-isocyanate present
in sufficient quantity to react with the amine mixture
of (a), forming therefrom a polyurea network;
5 (c) an acrylic ester of the formula



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or

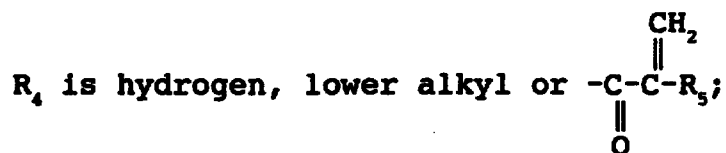


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wherein

- R_3 is hydrogen or lower alkyl;
 m is an integer from 0 to 150;
20 Z_3 and Z_5 are independently lower alkylene;
 Z_4 and Z_6 are independently a chemical bond or
lower alkylene;

25



- R_5 is hydrogen or lower alkyl;
 R_6 and R_8 are independently lower alkyl;
 p is an integer of 1 to 3;
30 and R_7 is lower alkylene or a chemical bond or
 $\text{CH}_2(\text{OCH}_2\text{CH}_2)_q$;

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- 1 q is an integer between 0 and 200, inclusive,
said acrylic ester being present in about 10-50% by
weight in said reactive mixture; and
- (d) a free radical initiator being present in
5 sufficient quantity in said reactive mixture to
polymerize the acrylic ester of (c), forming therefrom a
polyacrylic network, wherein the ratio of polyurea to
polyacrylic ranges from about 90:10 to about 50:50, and
- (e) a triamine present in sufficient
10 quantities to crosslink said amine mixture of (a).

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "lower alkyl", when
used alone or in combination with other groups, refers
15 to an alkyl chain containing 1-6 carbon atoms. The
alkyl groups may be straight chained or branched.
Examples include methyl, ethyl, propyl, isopropyl,
butyl, sec-butyl, t-butyl, isobutyl, pentyl, isopentyl,
neopentyl, hexyl, and the like. It is preferred that
20 the alkyl group contains 1-3 carbon atoms.

As used herein, the term "alkylene" refers to
a hydrocarbyl group derived from an alkyl group by
dropping a hydrogen from the formula. The alkylene is
bonded to two other groups in the main chain. Examples
25 include $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, $-\text{CH}-\text{CH}_2-$, and

|
 CH_3

the like. It is preferred that the alkylene groups
contain 1-3 carbon atoms.

The present invention is directed to
30 interpenetrating network polymers suitable as materials
in the manufacture of contact lens and particularly to

1 such polymers that have been prepared with modifiers and
cross-linking agents and the optical contact lens
prepared from such materials.

More specifically, the present invention is
5 directed to a polyurea network interpenetrated with a
polyacrylic network in such a manner as to form an
interpenetrating network which is completely homo-
geneous and exhibits a single glass transition
temperature.

10 The polyurea network described hereinabove is
a network comprised of amines, i.e., amine terminated
chain extender, with organic di- or polyisocyanates. In
addition, an amine cross-linking agent is required,
which is described hereinbelow.

15 The amines suitable for the present invention
are polymers having two or more terminal amino
functionalities. The most preferred amines are amino
terminated polyethers. Examples of the most preferred
polyamines include poly (oxyethylene) diamine, poly
20 (oxypropylene) diamine, triethylene glycol diamine, and
the like.

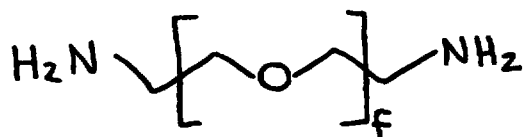
In a preferred embodiment, the amine component
is comprised of a mixture of diamines, i.e., a
polyoxyethylene diamine and a polyoxypropylene diamine.

25 It has been found by the present inventors that the
balance between polyoxyethylene diamine and
polyoxypropylene diamine is very important to the
transparency and water absorption properties of the IPN
elastomers. The presence of poly (oxyethylene) diamines
30 in the formulation is necessary to permit the hydrogel
to absorb water. As the content and molecular weight of

- 1 the polyoxyethylene diamine increases, the resulting hydrogels absorb more water. Unfortunately, the transparency suffers as the poly (oxyethylene) diamines tend to crystallize. The presence of poly
5 (oxypropylene) diamines in the formulation is necessary to obtain transparent hydrogels.

The preferred poly (oxyethylene) diamine used in the present invention has the formula

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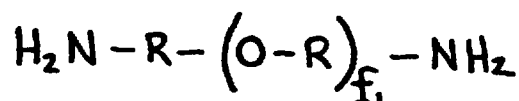


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wherein f is an integer from 30-70.

The poly (oxypropylene) diamine used herein is preferably of the formula

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wherein R is an alkylene chain containing 3 carbon
25 atoms, and

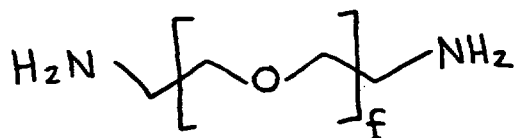
f_1 is an integer of 1-50.

It is preferred that f_1 is 30 and f is 30-70.

In the preferred embodiment of the present invention, a mixture of amines preferably comprises poly
30 (oxyethylene) diamine having the formula

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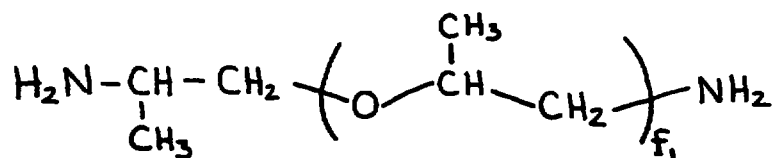
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wherein f is an integer of 1-50 and a poly (oxypropylene) diamine of formula IB

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15 wherein f_1 is an integer of 1-50.

It is preferred that the amine be present in about 20-60% by weight in the starting monomeric mixture. The preferred relative weight of IA and IB ranges from about 60/40 to about 100% A, respectively.

20 It is to be noted that unless indicated to the contrary, the percentages and ratios are by weight.

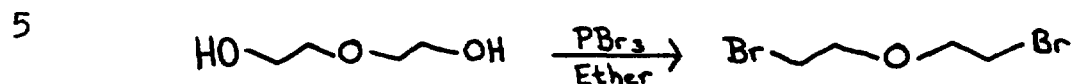
The diamines utilized in the present invention are either commercially available or are prepared by conventional techniques known to one skilled in the art.

25 The following examples are illustrative to show the techniques readily utilized by the skilled artisan to make the diamines used herein.

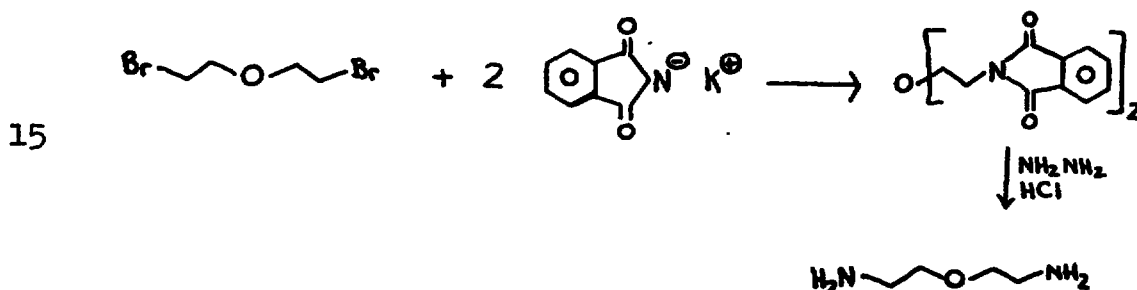
Exemplary procedures are shown below. In the first exemplification, the two terminal hydroxy groups
30 in the glycol are functionalized into facile leaving

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1 groups, e.g., bromide, using phosphorus tribromide in
ether.



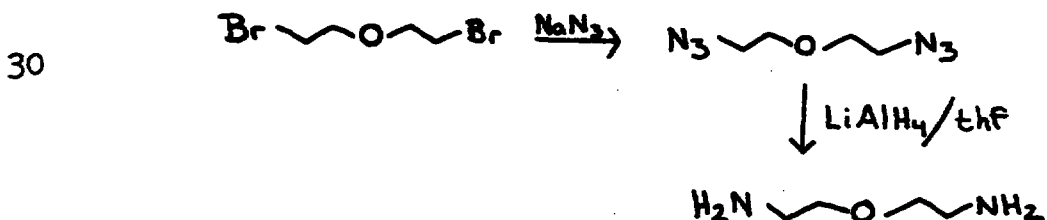
The dibromide can be converted into the
10 diamine using the Gabriel Phthalimide synthesis, wherein
potassium phthalimide is used to displace the bromide.



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Workup typically involves cleavage using
hydrazine and protonation to liberate the free diamine.

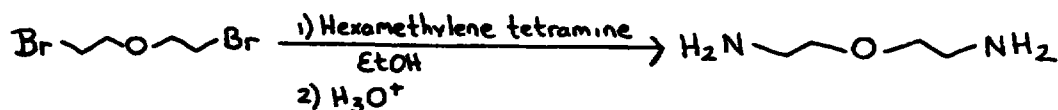
Another exemplary procedure for the synthesis
of the diamine involves the displacement of the bromide
25 using azide anion as the nucleophile. Subsequent
reduction using lithium aluminum hydride yields the
diamine.



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1 Yet another method of synthesizing the diamine
uses hexamethylene tetraamine in ethanol to give a di-
ammonium salt of the dibromide. Subsequent hydrolysis
of the salt yields the diamine.

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Other leaving groups that can be used in place
of the bromide are the other halides such as chloride,
and iodide, tosylate, brosylate, triflates, benzoate and
other anions whose pK_a value is low enough for
15 displacement by nitrogen nucleophiles such as those
described hereinabove.

The organic di- or polyisocyanates used to
form the polyurea network of the present invention is
represented by the formula $\text{Q}(\text{NCO})_t$ wherein t is
20 preferably 1-4 and Q is an hydrocarbyl group, i.e., an
organic radical consisting solely of carbon atoms and
hydrogen atoms. Q may be aliphatic, alicyclic,
aromatic, or combination of any of these groups, such as
aliphatic-aromatic group, aliphatic-alicyclic group, and
25 the like. The Q group may be unsubstituted or
substituted with lower alkyl, hydroxy or lower alkoxy.
It is preferred that the isocyanate is aliphatic. In a
preferred embodiment, it is preferred that Q contains

30

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1 from 3-26 carbon and more preferably from 4-20 carbon
atoms and most preferably from 6-14 carbon atoms. In
the above formula, t is an integer greater than 1 and
preferably 2-4. These isocyanates are readily prepared
5 using art recognized techniques or are commercially
available. Representative examples of the above
isocyanates include tetramethylene diisocyanate;
hexamethylene diisocyanate; trimethylhexamethylene
diisocyanate; dimer acid diisocyanate; isophorone
10 diisocyanate; dimethylbenzene diisocyanate;
diethylbenzene diisocyanate; decamethylene 1, 10-
diisocyanate; cyclohexylene 1, 2-diisocyanate;
cyclohexylene 1, 4-diisocyanate; 2, 4-and 2-6-tolylene
diisocyanates; 4, 4-diphenylmethane diisocyanate; 1, 5-
15 naphthalene diisocyanate; dianisidine diisocyanate;
toluidine diisocyanate; 4,4-methylene bis(cyclohexyl-
isocyanate); neopentyl tetraisocyanate; m-xylylene
diisocyanate; tetrahydronaphthalene -1, 5-diisocyanate
and bis-(4-isocyanatophenyl) methane, and the like.

20 The most preferred isocyanate is 4,4'-
methylene bis (cyclohexylisocyanate). Other preferred
isocyanates are trimethyl hexamethylene diisocyanate and
isophorone diisocyanate.

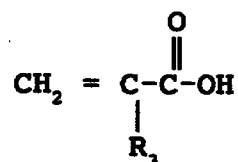
The isocyanates utilized in the present
25 invention react with the amines to form the polyurea
network. The isocyanates are present in such amounts as
to react with the amines present. In essence, the
amount of isocyanate is chosen to substantially equal
the number of equivalents of amine. In the preferred
30 embodiment, the isocyanate is present in 15-50% by

1 weight of the starting monomeric mixture, and preferably
in the amount of 25-40% by weight.

The reaction of the isocyanate with the amines
is spontaneous, and thus no catalyst is needed for the
5 polyurea formation. Moreover, the reaction is
exothermic. The heat generated from the amine-
isocyanate reaction can accelerate the free radical
initiated polymerization of the acrylate, the other
network of the interpenetrating network polymer.

10 The other network is made from acrylic esters.
The acrylic esters suitable for the present invention
are polymerizable polyacrylate derivatives of polyhydric
alcohols.

The acrylic esters are the ester derivatives
15 of acrylic acid of the following formula:



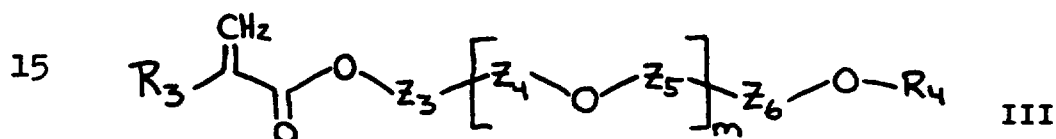
20 wherein R_3 is hydrogen or lower alkyl. It is to be
noted that when R_3 is methyl, the acid is methacrylic
acid.

Monohydric alcohols and polyhydric alcohols
25 having a molecular weight of less than 7,000 daltons are
suitable for esterification to the acrylic acids
described hereinabove for use in the present invention.
Preferred alcohols include monomethoxypolyethylene
glycol and ethoxyethylene glycol, ethylene glycol,
30 diethylene glycol, triethylene glycol, poly
(oxyethylene) glycol, poly (oxypropylene) glycol, poly

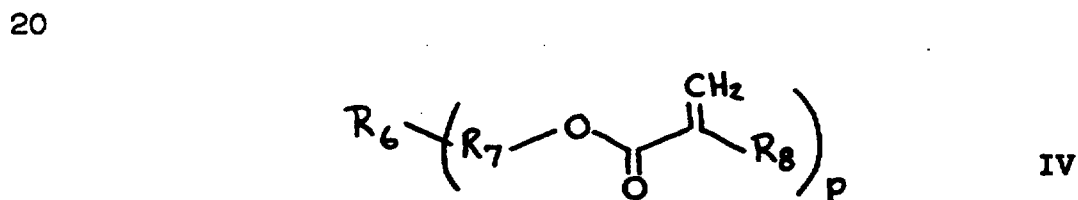
1 (oxypropylene) triol, glycerol, trimethylol ethane,
trimethylol propane, 1, 4-cyclohexane diol,
pentaerythritol, and the like.

Since the polyhydric alcohols contain more
5 than one hydroxy group, when utilized, more than one
acrylate unit can esterify to the polyhydric alcohols.
Thus, acrylic esters of the present invention include
mono-, di-, and poly acrylate derivatives of the
alcohols described hereinabove, especially methacrylate
10 derivatives thereof.

The acrylic esters useful in the present
invention have the formulae:



or



25 wherein R_3 is as defined hereinabove;
m is an integer from 0 to 150; and
 Z_3 and Z_5 are independently lower alkylene;
 Z_4 and Z_6 are independently a chemical bond or
30 lower alkylene;

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R_4 is hydrogen, lower alkyl or $-\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-\text{C}-R_5$;

5

R_5 is hydrogen or lower alkyl;

R_6 and R_8 are lower alkyl;

p is an integer of 1 to 3; and

R_7 is a lower alkylene, a chemical bond or $\text{CH}_2(\text{OCH}_2\text{CH}_2)_q$, and

10

q is an integer of 0 to 200 inclusive.

It is most preferred that R_3 , R_5 and R_8 are alkyl having 1-3 carbon atoms, especially methyl.

15

Preferred values of R_6 and R_8 are lower alkyl having 1-3 carbon atoms. Preferred R_6 is ethyl and preferred R_8 is methyl. It is preferred that R_7 is methylene. Preferred values of R_4 are hydrogen, lower

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alkyl having 1-3 carbon atoms and $-\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-\text{C}-R_5$, especially methacrylate.

It is preferred that m is 0 to 30, and more especially 0 to 20.

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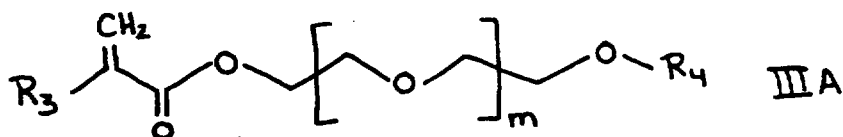
Preferred values of Z_4 and Z_6 are independently chemical bonds or alkylene group having 1-3 carbon atoms, while preferred values of Z_3 and Z_5 are alkylene having 1-3 carbon atoms. It is also preferred that Z_3 is the same as Z_6 and that Z_4 is the same as Z_5 .

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A preferred embodiment of Formula III is

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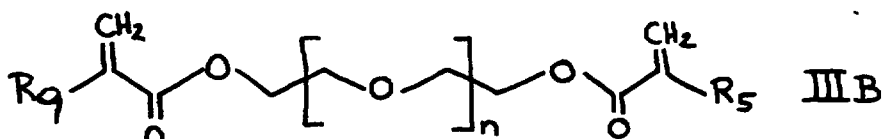
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wherein m , R_3 and R_4 are as defined hereinabove. It is preferred that R_4 is hydrogen or lower alkyl, R_3 is lower alkyl, especially methyl, and m is 0-50, more preferably 0-30 and most preferably 0-20.

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Another preferred acrylic monomer of Formula III is the diacrylate of the formula:

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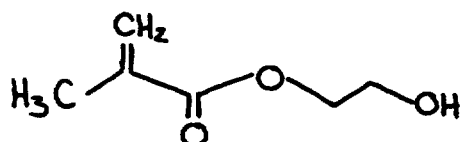
wherein R_5 is as defined hereinabove, preferably methyl, R_9 is hydrogen or lower alkyl and n is 0 to 50, more preferably 0 to 30, and most preferably 0-20.

The acrylic esters are present in about 10-50% by weight in the starting monomer mixture, and more preferably from about 15 to about 35% by weight.

It is preferred that the acrylic ester component consists of a mixture of monomer acrylates. The first acrylic monomer is comprised of the acrylate of Formula IIIA, while the second acrylic monomer comprises the compound of IIIB, IV, or mixture thereof. The first and second acrylic monomers are present in relative weight ratios ranging from about 80/20 to about 95/5, respectively.

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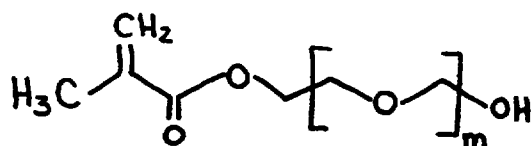
1 The most preferred acrylic esters are mono-,
 di-, and tri-methacrylates of the alcohols described
 hereinabove. Examples of the acrylate monomers of the
 present invention include monomethacrylates, such as
 5 hydroxyethylmethacrylate (HEMA) of the formula



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Another preferred monomethacrylate is poly-
 (ethylene glycol) monomethacrylate having the formula

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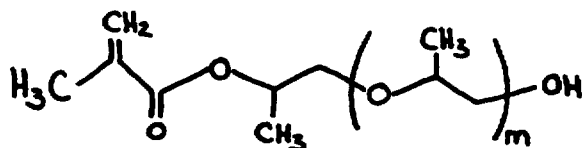


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wherein m is an integer from 0 to 20.

Another preferred monomethacrylate is poly
 (propylene glycol) monomethacrylate having the formula

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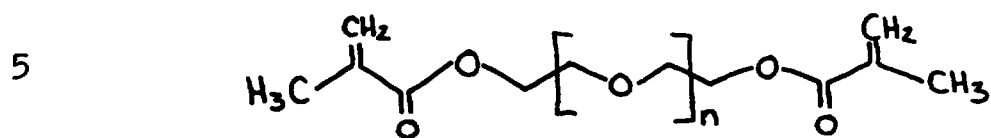


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wherein m is an integer from 0 to 20.

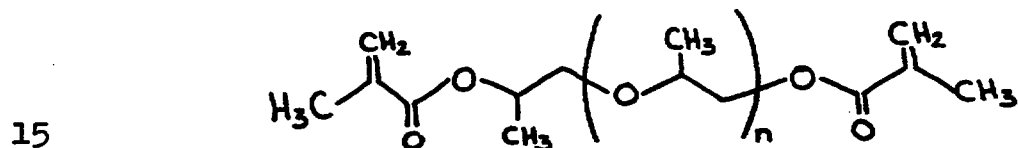
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1 A preferred dimethacrylate is poly (ethylene glycol) dimethacrylate, having the formula



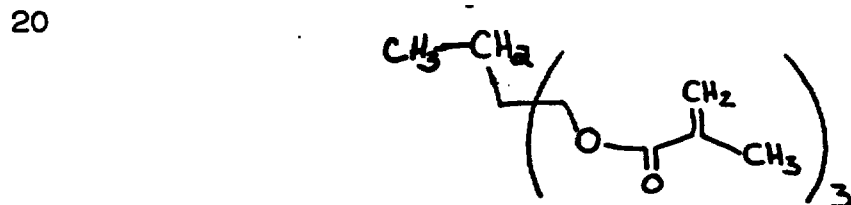
wherein n is an integer from 0 to 20.

10 Another preferred dimethacrylate is poly (propylene glycol) dimethacrylate having the formula



wherein n is integer from 0 to 20.

20 A preferred trimethacrylate is trimethylol propane trimethacrylate having the formula

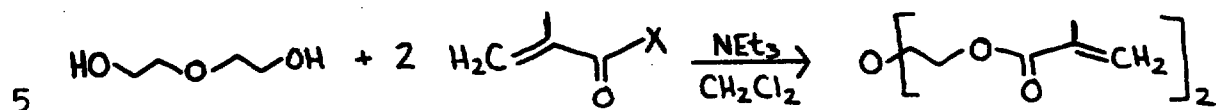


25 The acrylic esters used in the present invention are prepared by art recognized techniques of esterification known to one skilled in the art. The following descriptions are exemplary.

30 The acrylic esters can be synthesized by the condensation of alcohol with an acrylic acid derivative in the presence of a suitable weak base such as

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1 triethylamine. This is illustrated below in the
synthesis of a diacrylate from a diethylene glycol.



In the above synthesis, X is a good leaving group such as Cl, Br, NH₂, OH, lower alkylamino or diloweralkylamino.

10 The corresponding monoacrylate can be synthesized using a stoichiometric amount of the acrylic acid derivative. The reaction can be conducted in polar aprotic solvents like dichloromethane and chloroform.

The use of alkyl substituted acrylic acid
15 derivatives for the above condensation is equally feasible. The most preferred acrylic acid derivatives for the above condensation are methacrylate derivatives having the formula



25 wherein X is a good leaving group, e.g., halide, such as Cl or Br, OH, lower alkylamino or diloweralkylamino.

Another procedure is the reaction of the methacrylic acid and the alcohol in the presence of acid such as hydrochloric acid or p-toluene-sulfonic acid
30 under Fischer esterification conditions.

1 To form the acrylate network, the acrylates
described hereinabove are reacted with a free radical
initiator under polymerization conditions. Free radical
polymerization initiators of the type commonly used in
5 polymerizing ethylenic compounds are suitable for use in
the present invention. They include such representative
initiators as benzoyl peroxide; t-butyl hydroperoxide;
t-butyl peroxide; azo-bis (isobutyronitrile); 2, 5-
dimethyl-2, 5-di (2-ethyl hexanoylperoxy) hexane; 1, 1-
10 di (t-butylperoxy)-3, 3, 5-trimethylcyclohexane; di-t-
butyl-diperoxyphthalate; organic peroxides;
hydroperoxides; mixtures of peroxide and hydroperoxide
(Lupersol DDM-9); 1, 1'-azobis-(1-
cyclohexanecarbonitrile); 2, 2'-azobis [2- (2-
15 imidazolin-2-yl) propane] dihydrochloride; 2, 2'-azobis
(2,4-dimethylvaleronitrile); 2, 2'-azobis (4-methoxy-2,
4-dimethyl valeronitrile); and the like.

The free radical initiators are present in
amounts ranging from amounts greater than 0% to about 2%
20 by weight of the reaction mixture, and preferably from
0.01% to about 1%, and more preferably from 0.02% to
about 0.5%, and most preferably from 0.03% to about 0.1%
of the mixture.

In addition, a triamine is additionally
25 present in the monomeric mix. The triamines are useful
as crosslinker agents in the polyurea-acrylic IPNs.
They also are used as compatibilizers in the polyamine
mixture, especially when the reaction is conducted in
the absence of a mixing device. In order to ensure
30 homogeneity between the polyoxyethylene diamine and the
polyoxypropylene diamine, the amine mixture is

1 preferably constantly stirred. The triamines are
present in amounts ranging from about 30% to about 50%
of the total equivalents of amines. They are preferably
present in amounts ranging from about 1% to about 20% by
5 weight and most preferably 3% - 5% by weight. Examples
of the triamines include diethyltriamine, poly
(oxypropylene) triamine, and the like.

Thus, the interpenetrating polymers of the
present invention are prepared from the two
10 interpenetrating networks, one network generated from
the reaction of the amine and the isocyanate (to form
polyurea), the other network from the free radical
polymerization of the acrylates (to form the
polyacrylate). In the resulting IPN, the ratio of
15 polyurea to polyacrylate ranges from about 90:10 to
about 50:50, although it is most preferred that the
ratio ranges from 80:20 to 70:30 and most preferably
75/25.

The polymerization reaction, i.e., reaction
20 between the amino, acrylic ester, isocyanate, and free
radical initiator is conducted under conditions to form
simultaneous interpenetrating networks. The networks
are in the same volume and the networks are formed
substantially simultaneously. Techniques for preparing
25 SINS are known to one skilled in the art and are
applicable here. The monomeric precursors, i.e., the
amines and the isocyanate and the acrylic ester and the
initiator are mixed together, and the resultant
polymerization reaction is simultaneous or substantially
30 simultaneous, in accordance therewith. For a general
procedure, see U.S. Patent No. 4,536,554 to Lim, et al.,

U.S. Patent No. 4,983,702 to Mueller, et al., 5,087,392 to Burke, et al., the contents of which are all incorporated by reference. The polymerization is
5 generally carried out at temperatures ranging from about room temperature to about 145°C. It is generally preferred to initiate the polymerization at relatively low temperatures, such as from about 45°C to about 120°C, and then increase the temperature to about 110°C
10 to 130°C as the reaction proceeds. Generally, post-curing is done at about 140°-145°C.

Usually, the polymerization is conducted under an inert nitrogen atmosphere in order to exclude the oxygen of the atmosphere which has deteriorating effects
15 on the formation of polymers of the invention.

Contact lenses can be made by shaping the interpenetrating network polymer using conventional and well known procedures and apparatus such as a mold in the shape of a contact lens and thereafter hydrating the
20 dry lens to the final configuration.

In a preferred embodiment, the interpenetrating polymer network of the present invention is prepared using a Reaction Injection Molding (RIM) Machine. The use of the RIM Machine and the
25 subsequent molding of the IPNs of the present invention are described in copending application assigned to the assignee of the present invention, having Serial No. 08/415,000, entitled, A NOVEL REACTION INJECTION MOLDING PROCESS FOR THE MANUFACTURE OF PRECISION CONTACT LENSES,
30 the contents of which are incorporated herein by reference.

1 Reaction injection molding requires that the
monomer streams mix at high shear rates which produce
turbulent flow. The turbulent mixing assures material
uniformity and complete reaction.

5 The RIM process is well described by L.T.
Manziona in The Encyclopedia of Polymer Science and
Engineering; 2nd Edition Vol 14, pg. 72. It is a
molding process wherein two or more streams of monomers
react in the mold to form a polymer.

10 In a typical polymerization using a two stream
RIM machine, a blend comprising diamines and triamines
are placed in a material reservoir and heated to about
80°C. A second blend comprising the diisocyanate,
acrylic esters and an organic catalyst are placed in the
15 second material reservoir.

The two blends are mixed by impingement at a
pressure between 400-3000 psi and the resulting liquid
which forms an IPN upon curing is injected into a mold
in the shape of a contact lens. The injection time
20 ranges less than one minute, generally from 0.02-0.3
seconds. The polymer may be post-cured for one hour in
an oven at 100°C.

In a typical polymerization using a three
stream RIM machine, a blend (Stream 1) of diamines and
25 triamines is placed in the first reservoir. A second
blend (Stream 2) of acrylic esters is placed in the
second reservoir, while a third blend (Stream 3) of a
diisocyanate and free radical initiators is placed in
the third material reservoir. The three streams are
30 mixed by impingement at a mixhead in the RIM machine and

1 the resulting liquid which forms an IPN upon curing is
injected into a mold in the shape of a contact lens.

The free radical polymerization of the
acrylates is typically very fast, as is the reaction
5 between the polyamines and the isocyanates. Optionally
an inert diluent is added and moderates the reaction,
allowing it to be compatible with the RIM process. The
preferred inert diluent in the present invention is
water. Additionally, water also acts as a mold release
10 agent (see below) for removing the cured polymer from
the mold assembly.

The contact lenses of the present invention
are prepared by casting the IPN generated in the RIM
apparatus in a suitable mold assembly for contact lens.
15 The mold can be made of glass, metal or plastic, but it
is preferred to be made of aluminum or stainless steel.
The mold assembly is preferably comprised of two mold
halves which are positioned to define a cavity in the
shape of a contact lens between the convex surface of
20 one mold half and the concave surface of the other mold
half. The cavity may have variable thickness, as
required to provide the correct dioptric power. The
variable thickness may be calculated using optical
formulas familiar to those skilled in the art. The
25 central thickness of the cavity ranges from about
0.00039 inches to about 0.0118 inches. The two mold
halves are held together by clamping means, such as a
clamp, bolt or hinges and the like. It is preferred
that the molds are two-piece aluminum plates. The mold
30 has a central sprue or gate and is equipped with at
least one vent. The central sprue or gate is the

- 1 opening that connects the RIM machine to the mold and
through which the streams of components are injected
after being mixed at the mixhead. The vent may be
located at each of the four mold edges, at the end of
5 the mold furthest from the sprue, but preferably it is
located within 4-5 inches of the sprue. In a preferred
embodiment, an annular gated mold is utilized. The mold
is usually heated at a temperature of 50°C to 150°C and
preferably from 75-125° and most preferably at 100°C.
- 10 When the mold is at that temperature, the liquid capable
of forming an IPN upon polymerization or curing is
injected into the mold wherein the polymerization is
completed, the resultant product is gelled and hardened.
The material may additionally be post-cured in the mold.
- 15 After this step, the mold is opened manually, and the
elastomeric film is removed from the mold wherein it is
post-cured again in a heated environment such as an
oven. The film is converted to a hydrogel by immersion
in a buffered saline solution.
- 20 The polymeric material obtained by the present
invention can be utilized to make contact lenses, by
altering the shape and dimensions of the injection mold
according to ophthalmic specifications.
- The contact lenses, thus prepared, exhibit
25 excellent optical and mechanical properties.
- Along with a high tensile and shear strength,
the contact lenses additionally show excellent
elongation and wettability. In addition, the lenses
formed from the IPNs of the present invention have high
30 oxygen permeability and are transparent to visible
light. The homogeneous nature of the interpenetrating

1 networks present in the lens is confirmed by the single
glass transition temperature exhibited by the contact
lens of the present invention. The simultaneous nature
of the two polymerization reactions, occurring in the
5 immediate vicinity of each other, is essential in
determining the homogeneity of the resulting polymer
network. In a comparative example, the polyurea and
polyacrylic networks were produced sequentially; i.e.,
the polyamines were condensed with the diisocyanate to
10 give a pure polyurea material. This was mixed with a
mixture of acrylic esters, and polymerized using a free
radical initiator. Such a sequentially produced
polyurea/polyacrylic material exhibited three separate
glass transition temperatures. The pure polyurea
15 material by itself exhibits two glass transition
temperatures. The homogeneity observed in the contact
lenses of the present invention ensures excellent
optical properties in the lens.

The optical clarity of the lens is influenced
20 by the polyurea/polyacrylic ratio present in the lens
material. However at the indicated ratios hereinabove,
the hydrogels are transparent to visible light.

Also, the water uptake decreases as the
polyacrylic content increases. However, the water
25 uptake remains almost constant when the
polyurea/polyacrylic ratio is greater than 70/30.

The following examples will serve to
illustrate the principles and scope of the present
invention.

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1 In the following examples, various
abbreviations are utilized. The table below contains
the abbreviations to which reference is made in the
examples.

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1		CODE	CHEMICAL NAME	MOL.WT.
		Jeffamine ED-900	Poly(oxyethylene) diamine	1179
		Jeffamine ED-2000	Poly(oxyethylene) diamine	2277
5		Jeffamine D-2000	Poly(oxypropylene) diamine	2000
		Jeffamine T-403	Poly(oxypropylene) triamine	440
		Jeffamine EDR148	Triethylene glycol triamine	148
		DETA	Diethylene triamine	103
		Desmodur W	4,4'-Methylene-bis-cyclohexylisocyanate), H ₁₂ MDI	262
10		HEMA	Hydroxyethyl methacrylate	130
		PEGMA	Polyethylene glycol monomethacrylate	306
		TEGDMA	Triethylene glycol dimethacrylate	286
		PEG (600)DMA	Poly(ethylene glycol-600)dimethacrylate	770
15		L-256	Lupersol 256	
		BPO	Benzoyl peroxide	242

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EXAMPLE I

A blend was made of 589.5 parts ED-900, 400 parts D-2000, 155.4 parts EDR-148 and 34.3 parts DETA. This blend was called Stream 1. A second blend was made of 589.5 parts H₁₂MDI, 560.1 parts HEMA, 29.48 parts TEGDMA and 11.9 parts L-256. This blend was called Stream 2. The streams were placed in the material reservoirs of a two stream laboratory scale RIM machine. Stream 1 was heated to about 80°C to maintain fluidity of the materials. Stream 2 was maintained at room temperature to insure stability of the materials. The streams were mixed by impingement at a pressure of 2500 psi. and injected into a two piece aluminum mold. The mixing ratio was 1.010 parts Stream 1 for each part of Stream 2. The injection time is 0.20 seconds. These conditions produced about 20 gm. of polymer in which both networks were separate and simultaneously produced.

The mold consisted of two aluminum plates. One of the plates was machined such that it had two compartments. One compartment was designed to produce a film 100 microns thick. The other compartment was designed to produce a film 800 microns thick. The mold was held together by bolts. The mold was heated to 100°C. It is attached to the RIM machine. The material was post-cured in the mold for 10 minutes following the injection molding operation.

The mold was opened manually and the elastomeric film was removed from the mold. The demolded film was post cured for one hour in an oven at

1 100°C. The film was converted to a hydrogel by immersion in a buffered saline solution.

The material produced was a clear IPN hydrogel of 75% (weight) urea component and 25% (weight)

5 methacrylic portion. Following hydration the material had the following properties:

Water content	34%
Modulus	262 psi
Tensile strength	300 psi
10 Elongation at break	238%

This material was suitable for use as a contact lens.

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EXAMPLES II TO V

A series of IPN elastomers were prepared using the methods of Example 1. The formulations and properties are shown in Table II.

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EXAMPLE	II	III	IV	V
Stream 1				
ED-900	589.5	589.5	589.5	471.6
ED-2000	-	-	-	-
D-2000	200	-	400	400
EDR-148	155.4	155.4	229.4	-
DETA	34.3	34.3	-	34.3
Stream 2				
H ₁₂ MDI	563.3	537.1	589.5	1133.8
HEMA	483.6	412.68	566.9	-
PEGMA	-	-	-	454.0
TEGDMA	25.4	21.7	29.8	23.9
L-256	10.2	8.7	11.9	9.6
UREA/ACRYLIC RATIO	75/25	75/25	75/25	75/25
STREAM 1/STREAM 2	0.90	0.76	1.02	1.37
Water content (%)	37.5	47.1	33.1	60.8
Modulus (psi)	218	87	-	133
Tensile strength (psi)	263	101	110	81
Elongation at break (%)	206	103	169	101
Appearance	clear	opaque	hazy	clear

The materials of Example II and Example V were suitable for contact lens use.

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EXAMPLE VI

A blend was made of 471.6 parts ED-900, 228 parts ED-2000, 400 parts D-2000 and 34.3 parts DETA.

5 This blend was called Stream 1. A second blend was made of 314.4 parts H₁₂MDI, 454.0 parts HEMA, 23.91 parts TEGDMA and 9.6 parts L-256. This blend was called Stream 2. The streams were placed in the material reservoirs of a two stream laboratory scale RIM machine.

10 Stream 1 was heated to about 80°C to maintain fluidity of the materials. The streams were mixed by impingement at a pressure of 900 psi. and injected into a two piece aluminum mold. The mixing ratio was 1.37 parts Stream 1 for each part of Stream 2. The injection time was 0.25
15 seconds. These conditions produced about 25 gm. of polymer in which both networks are separate and simultaneously produced.

The mold used for this example was described in Example I.

20 The mold was opened manually within one minute of injection and the elastomeric film is removed from the mold. The demolded film was post-cured for about 40 minutes in an oven at 100°C. The film was converted to a hydrogel by immersion in a buffered saline solution.

25 The material produced was a clear IPN hydrogel of 75% (weight) urea component and 25%(weight) methacrylic portion. Following hydration the material has the following properties:

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1	Water content	50%
	Modulus	93 psi
	Tensile strength	91 psi
	Elongation at break	239%

5 This material is suitable for use as a contact lens.

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EXAMPLES VII TO IX

A series of IPN elastomers were prepared using the methods of Example VI. The formulations and properties are shown in Table III.

TABLE III

EXAMPLE	VII	VIII	IX
Stream 1			
ED-900	353.7	471.6	471.6
ED-2000	227.9	455.8	455.8
D-2000	400	200	200
DETA	34.3	34.3	34.3
Stream 2			
H ₁₂ MDI	288.2	314.4	314.5
HEMA	408	463	463
TEGDMA	21.5	24.3	24.3
I-256	8.6	19.4	9.8
UREA/ACRYLIC RATIO	75/25	75/25	75/25
STREAM 1/STREAM 2	1.35	1.37	1.39
Water content	40.1	43.1	42.2
Modulus	-	254	245
Tensile Strength	141	292	221
Elongation at break	260	165	221
Appearance	clear	clear	clear

The materials of Examples VII, VIII and IX were suitable for contact lens use.

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EXAMPLE X

A Hi-Tech three stream RIM machine was used for this example. The machine was fitted with an Edge-Sweets four component mixhead. The mixing was by impingement.

The chemical system consisted of eight separate chemicals. The materials were blended as follows:

10 Stream 1

870.9 gm	Jeffamine ED-900	Poly(oxyethylene) diamine MW 1179
420.9 gm	Jeffamine ED-2000	Poly(oxyethylene) diamine MW 2277
738.7 gm	Jeffamine D-2000	Poly(oxypropylene) diamine MW 2000
63.5 gm	DETA	Diethylene Triamine

(Jeffamine is a trademark of the Texaco Chemical

15 Company)

Stream 2

3502 gm	HEMA	Hydroxyethyl Methacrylate
72.4 gm	TMPTMA	Trimethylolpropanetrimethacrylate

Stream 3

20 3140 gm H₁₂MDI 4,4'-methylene bis (cyclohexyl isocyanate)

96.6 gm Benzoyl peroxide

The process conditions were:

	<u>Stream</u>	<u>Pressure</u>	<u>Orifice</u>	<u>Flow Rate</u>	<u>Viscosity</u>
25	1	2700psi	0.75mm	99.3gm/sec	52cps
	2	1900psi	1.25mm	42.30gm/sec	6cps
	3	1900psi	0.50mm	28.4gm/sec	24cps

Stream 1 was split and injected into two separate ports. The ports were chosen to be 90° apart. This gave direct impingement of one-half the amine and the isocyanate streams.

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1 The injection time was set at 0.03 sec. and a
shot weight of 13.6gm obtained.

 The injection head of the RIM machine was
affixed to a hardened steel mold. The mold had a
5 channel 2mm wide and 4mm deep leading to a contact lens
shaped cavity. The injection of the formulation into
the mold produced a contact lens.

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EXAMPLES XI, XII, XIII

Examples XI, XII, XIII were duplicates of Example X except that the flow rate of Stream 2 was changed to change the ratio of urea to acrylic fractions of the IPN's. The flow rates of Stream 1 and Stream 3 were adjusted to obtain a constant shot size. The orifice size was controlled to maintain at the pressures of Example X.

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Example		XI	XII	XIII
Stream 1	Flow rate (gm/sec)	104.0	78.3	92.8
Stream 2	Flow rate (gm/sec)	33.2	66.7	50.8
Stream 3	Flow rate (gm/sec)	29.7	22.4	26.5
UREA/ACRYLIC RATIO		80/20	60/40	70/30

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When these formulations were injected into a heated mold with a contact lens shaped cavity with an annular gate, a contact lens was formed.

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EXAMPLES XIV, XV, XVI

Examples XIV, XV, XVI were duplicates of
Example XI, XII and XIII except that the flat plate mold
5 of Example 1 was used.

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Example		XIV	XV	XVI
Stream 1	Flow rate (gm/sec)	120.2	78.3	92.8
Stream 2	Flow rate (gm/sec)	38.4	66.7	50.8
Stream 3	Flow rate (gm/sec)	34.4	22.4	26.5
UREA/ACRYLIC RATIO		80/20	60/40	70/30

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These materials were used for thermal property testing.

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1 Comparative Example I

Polyurea films were prepared using the method of Example X except that Stream 2 was blocked to prepare a clear polyurea film.

5 Comparative Example II

A solution of 47.5g HEMA, 2.5g polyethylene glycol (600) dimethacrylate and 1 g benzoyl peroxide was prepared. This is the acrylic portion of Example X.

A sequential IPN was prepared from 6.06g piece
10 of film from Example X and 2.54g of the above described HEMA solution. The HEMA solution was mixed with 30ml of methyl alcohol. This step was performed to assure a uniform distribution of the HEMA mixture through the film. The urea film was immersed in the methanol HEMA
15 mixture. The jar containing the components was placed on a roller mill (US Stoneware) and mixed 24 hours. The methanol was removed using a vacuum of 20 mmHg. The methanol free sample was placed in an 80°C oven for 4 hours. The recovered film has a mass of 6.61g. This
20 indicates that the HEMA evaporated more quickly than it polymerized under these conditions.

Comparative Examples III and IV

The procedure of Comparative Example II was repeated using different urea/HEMA ratios. 30 ml of
25 methanol was used in all cases.

<u>Comparative Example</u>	<u>urea (g)</u>	<u>HEMA (g)</u>	<u>post polymerization weight (g)</u>
III	7.24	2.41	7.92
IV	5.36	1.34	5.31

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1 In both of these examples the final weight
indicated that the HEMA was lost before polymerization
could occur.

Comparative Example V

5 A 1.45g piece of polyurea film was immersed in
0.48g of HEMA and 5 ml of methanol. The methanol was
removed with a vacuum of 20mmHg. The HEMA containing
polyurea film was tightly wrapped in aluminum foil. The
foil packet was placed in an 80°C oven for 4 hours. The
10 resulting film had a mass of 1.92g and a dry feel. The
sequential IPN was evaluated by thermal analysis.

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1 Comparative Example VI

 The HEMA mix of Comparative Example I was
polymerized by placing 1g in an aluminum weighing dish.
The material was placed into an oven at 80°C for four
5 hours. A clear glassy solid was formed.

Determination of the Glass Transition Temperature

 The glass transition is a second order
transition where the motions of a polymer chain are
abruptly increased or decreased. The temperature at
10 which the transition occurs is the glass transition
temperature. The change in chain motion results in a
change of polymer properties. One property that changes
is known as Tan δ .

 The glass transition temperatures of the
15 materials of Examples XIII, XIV and XV were determined
using a Perkin Elmer dynamic mechanical analyzer (DMA
7). Samples were rectangular samples in an extension
geometry. The samples were heated at a rate of 2°C per
minute. The samples were heated from -50°C to 150°C.

20	<u>EXAMPLE</u>	<u>urea/acrylic</u>	<u>Glass Transitions</u>		
			<u>1</u>	<u>2</u>	<u>3</u>
	XIII	75/25	2.3°C		
	XIV	80/20	-28.3°C	2.4°C	
	XVI	70/30	7.0°C		
25	Comparative I	100/1	-41.7°C	-8.0°C	
	Comparative VI	75/25	-29.2°C	5.0°C	48.6°C

 These data show that the base urethane
30 material has two glass transitions. The simultaneous
IPN materials disclosed herein have a single glass

1 transition. This is characteristic of a homogeneous
material. The sequential material exhibits three glass
transitions. This is characteristic of a non-
homogeneous material. Clearly, the simultaneous process
5 produces a different material than the sequential
material.

The above preferred embodiments and examples
are given to illustrate the scope and spirit of the
present invention. These embodiments and examples will
10 make apparent to those skilled in the art other
embodiments and examples. These other embodiments and
examples are within the contemplation of the present
invention. Therefore, the present invention should be
limited only by the appended claims.

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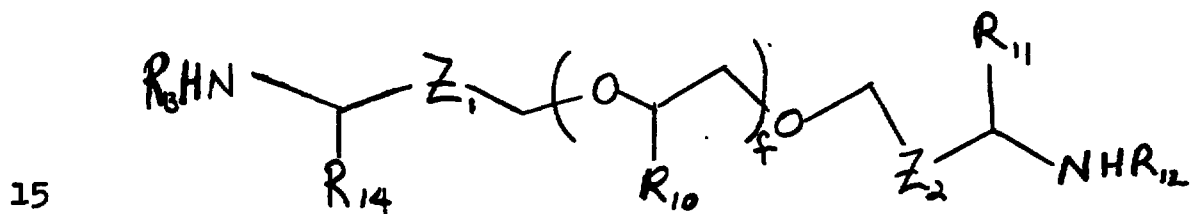
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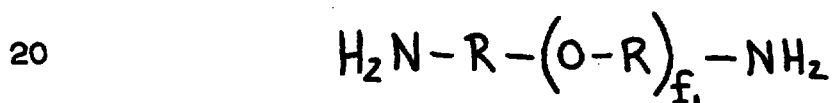
1 WHAT IS CLAIMED IS:

1. A homogenous interpenetrating polymer network exhibiting a single glass transition temperature
 5 formed by polymerization of a reactive mixture of polymerizable components, said reactive mixture comprising

(a) an amine mixture consisting of diamines A and B, said amine mixture being present in about 20-60%
 10 by weight in said reactive mixture wherein A is



and B is



f_1 is an integer from 1-75;
 25 R is an alkylene containing 3 carbon atoms and each R is the same;
 f is an integer between 1 and 150 inclusive;
 R_{10} , R_{11} , R_{12} , R_{13} and R_{14} are independently
 hydrogen or lower alkyl;

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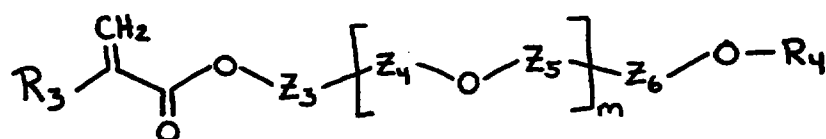
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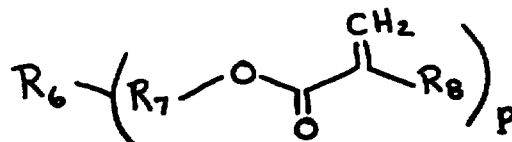
1 Z_1 and Z_2 are independently a chemical bond or lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A;

5 (b) an organic di- or poly-isocyanate present in sufficient quantity in said reactive mixture to react with the amine mixture of (a), forming therefrom a polyurea network;

 (c) an acrylic ester of the formula:



or



wherein

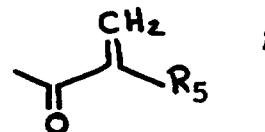
R_3 is hydrogen or lower alkyl;

m is an integer from 0 to 150;

25 Z_3 and Z_5 are independently lower alkylene.

Z_4 and Z_6 are independently a chemical bond or lower alkylene;

R_4 is hydrogen, lower alkyl or



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1 R_5 is hydrogen or lower alkyl;
 R_6 and R_8 are independently lower alkyl;
 p is an integer of 1 to 3; and
 R_7 is lower alkylene or chemical bond or -

5 $CH_2(OCH_2CH_2)_q$;

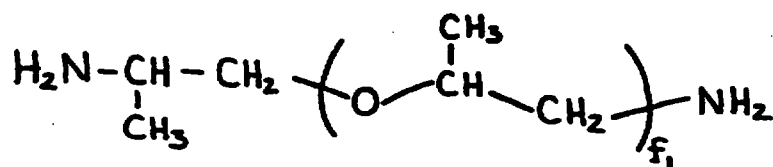
q is an integer from 0 to 200 inclusive;
said acrylic ester being present in about 10-50% by
weight in the reactive mixture; and

(d) a free radical initiator being present in
10 sufficient quantity in the reactive mixture to
polymerize the acrylic esters of (c), forming a
polyacrylic network;

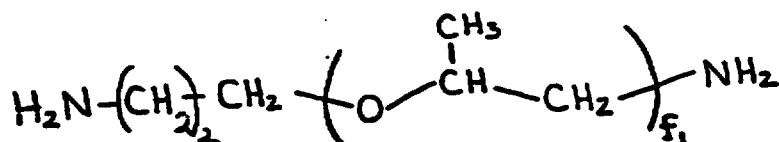
(e) a triamine being present in sufficient
amount to crosslink the amine mixture of (a);

15 wherein the ratio of polyurea to polyacrylic
ranges from about 50:50 to about 90:10, and wherein the
weights of the components in the reactive mixture sum up
to 100%.

2. The interpenetrating polymer network
20 according to Claim 1 wherein B is a polyoxypropylene
diamine of the formula:



or





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3. The interpenetrating polymer network according to Claim 1 wherein the triamine is present in the reactive mixture in an amount ranging from 30 to 50% total amine equivalents.

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4. The interpenetrating polymer network according to Claim 1 wherein the triamine is diethylene triamine or polyoxypropylene triamine.

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5. The interpenetrating polymer network according to Claim 1 wherein the isocyanate is methylene-bis (4,4'-cyclohexylisocyanate) or isophorone diisocyanate.

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6. The interpenetrating polymer network according to Claim 1 wherein the free radical initiator is 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy) hexane, benzoyl peroxide, t-butyl hydroperoxide, t-butyl peroxide or lauryl peroxide.

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7. The interpenetrating polymer network according to Claim 1 wherein the polyurea/polyacrylic weight ratio ranges from about 80:20 to about 70:30.

8. The interpenetrating polymer network according to Claim 1 wherein the polyurea/polyacrylic weight ratio is about 75:25.

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9. The interpenetrating polymer network according to Claim 1 wherein the isocyanate is present in the reactive mixture in an amount ranging from about 15% to about 50% by weight.

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10. The interpenetrating polymer network according to Claim 9 wherein the isocyanate is present in an amount ranging from about 25% to about 40% by weight.

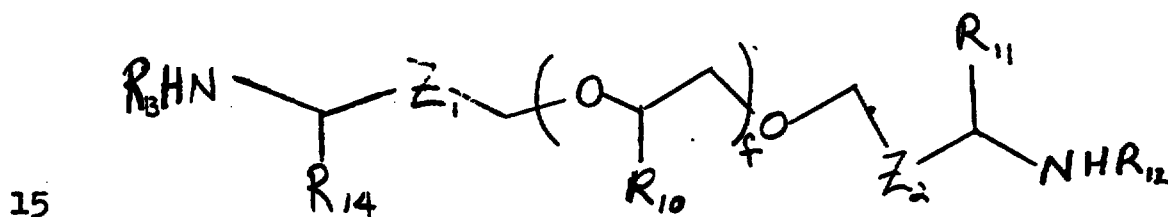
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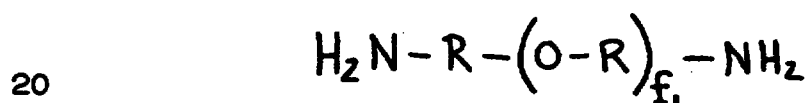
11. The interpenetrating polymer network according to Claim 1 wherein the free radical initiator is present in the reactive mixture an amount ranging from about 0.01% to about 1% by weight.

12. The interpenetrating polymer network according to Claim 1 formed by polymerization of a reactive mixture comprising

(a) an amine mixture consisting of polyamines A and B, said polyamines being present in said reactive mixture in about 20-60% by weight, wherein A is



and B is



f_1 is an integer from 1-75;

R is an alkylene containing 3 carbon atoms and each R is the same;

f is an integer between 1 and 150, inclusive, R_{10} , R_{11} , R_{12} , R_{13} and R_{14} are independently hydrogen or lower alkyl;

Z_1 and Z_2 are independently a chemical bond or lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A;



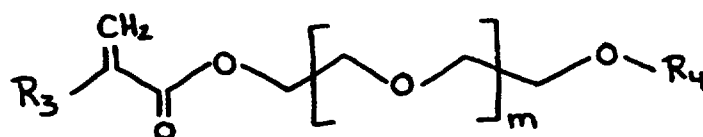
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(b) an organic di- or poly-isocyanate present in sufficient quantity in said reactive mixture to react with the amine mixture of (a), forming therefrom a polyurea network;

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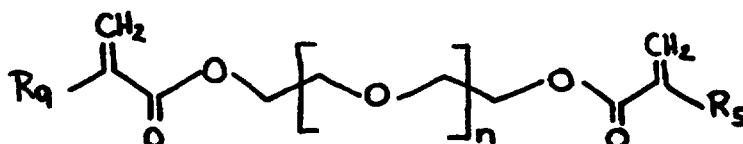
(c) 10-50% by weight in the reactive mixture of an acrylic ester component consisting of a mixture of a first acrylate of the formula

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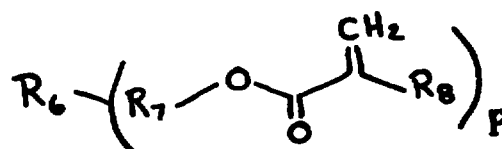
and a second acrylate being a diacrylate of the formula



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or a triacrylate of the formula

25



or a mixture thereof, wherein

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R_3 , R_4 , R_3 , R_5 and R_6 are independently hydrogen or lower alkyl;

R_6 is lower alkyl;

R_7 is a chemical bond or lower alkylene;

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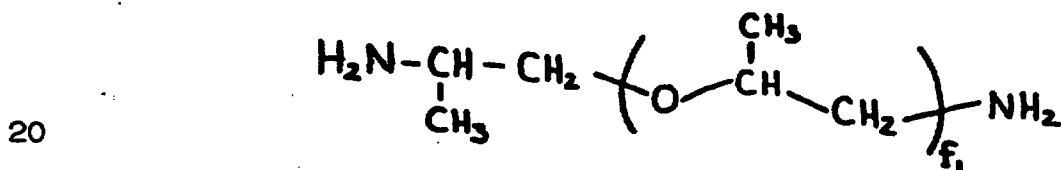
m and n are independently integers of 0-30 and
p is an integer of 1-3;

5 said ratio of the first acrylate to second acrylate
ranges from about 80:20 to about 95:5,

(d) a free radical initiator being present in
sufficient quantity in said reactive mixture to
polymerize the acrylic ester of (c), forming therefrom a
polyacrylic network, and

10 (e) a triamine present in sufficient quantity
to crosslink the amine mixture of (a), wherein the ratio
of polyurea to polyacrylic ranges from about 90:10 to
about 50:50.

15 13. The interpenetrating polymer network
according to Claim 12 wherein B is a polyoxypropylene
diamine of the formula:



25 14. The interpenetrating polymer network
according to Claim 12 wherein the triamine is present in
the reactive mixture in an amount ranging from about 30
to 50% of the total amine equivalents.

15. The interpenetrating polymer network
according to Claim 14 wherein the triamine is diethylene
triamine or polyoxypropylene triamine.

30 16. The interpenetrating polymer network
according to Claim 12 wherein the isocyanate is

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1 methylene-bis (4,4'-cyclohexylisocyanate) or isophorone diisocyanate.

17. The interpenetrating polymer network according to Claim 12 wherein the free radical initiator
5 is 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy) hexane, benzoyl peroxide, t-butyl hydroperoxide, t-butyl peroxide or lauryl peroxide.

18. The interpenetrating polymer network according to Claim 12 wherein the polyurea/polyacrylic
10 weight ratio ranges from about 70:30 to 80:20.

19. The interpenetrating polymer network according to Claim 12 wherein the polyurea/polyacrylic weight ratio is about 75:25.

20. The interpenetrating polymer network
15 according to Claim 12 wherein the isocyanate is present in the reactive mixture in an amount ranging from about 15% to about 50% by weight.

21. The interpenetrating polymer network according to Claim 20 wherein the isocyanate is present
20 in an amount ranging from about 25% to about 40% by weight.

22. The interpenetrating polymer network according to Claim 12 wherein the free radical initiator is present in the reactive mixture an amount ranging
25 from about 0.01% to about 1% by weight.

23. The interpenetrating polymer network according to Claim 12 wherein R_3 , R_4 , R_5 and R_6 are CH_3 .

24. The interpenetrating polymer network according to Claim 12 wherein R_3 , R_5 , and R_6 are CH_3 , m
30 is 0, R_4 is hydrogen and n is 2.



1 25. The interpenetrating polymer network
according to Claim 12 wherein R_3 , R_5 and R_9 are CH_3 , m is
4, R_4 is hydrogen and n is 2.

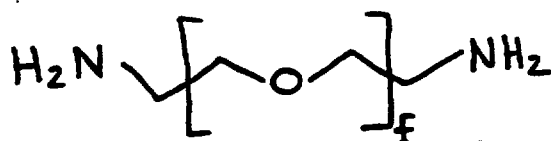
26. The interpenetrating polymer network of
5 Claim 12 wherein m is 4, R_4 is hydrogen, p is 3, R_6 is
ethyl, R_7 is ethylene, and R_3 and R_8 are CH_3 .

27. An article of manufacture comprised of
the interpenetrating polymer network of any one of
Claims 1-26.

10 28. The article of manufacture according to
Claim 27 which is a contact lens.

29. The interpenetrating polymer network of
Claim 1 in which A is

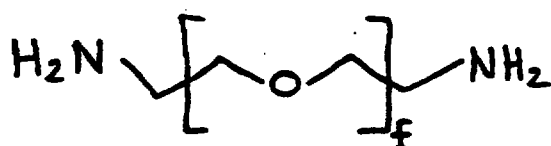
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30. The interpenetrating polymer network of
Claim 12 wherein A is

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