TO: NST-44
Scientific & Technical Information Division
Attn: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,655,814

Government or Corporate Employee : PASADENA, CA

Supplementary Corporate Source (if applicable) :

NASA Patent Case No. : NPO-10,830-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES ☒ NO ☐

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "...with respect to an invention of ..."

Bonnie L. Henderson

Enclosure
FIG. 1
EFFECT OF CATIONIC GROUPS

The present invention relates to cationic polymers containing the urethane linkage which can exhibit viscoelastic properties over a wide temperature range. These polymers can be used in various applications such as in printed circuits, master plates for photocopying, devices, dust collecting plates, and the like. Furthermore, materials having this type of activity also exhibit certain damping properties that are particularly interesting in mechanical systems. Most of these polymers have been found to have a transition temperature that is sufficiently high to be useful in practical applications.

INVENTOR.
ALAN REMBAUM
FIG. 2

EFFECT OF MOLECULAR WEIGHT

TEMPERATURE, °C

INVENTOR.
ALAN REMBAUM

BY

ATTORNEYS.
ABSINTHE OF THE DISCLOSURE

A viscoelastic cationic polymer having a repeating unit of the formula:

\[ \left[ R_1 - Y - R_2 \right]_n \]

where \( Z \) is a linking condensation residue, preferably urethane and \( n \) is an integer prepared by linking reactions between monomeric starting materials including quaternary nitrogen forming coreactants and condensation residue forming coreactants.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates generally to cationic polymers and to methods of polymerizing novel monomeric mixtures. More particularly this invention relates to linear and cross-linked cationic viscoelastic polymers.

(2) Description of the prior art

Elastomeric cationic materials will find many uses. The presence of cationic moieties in the backbone will provide a product of increased conductivity which can be further enhanced by complexing the cationic centers with charge-transfer complexing agents. Materials having conductivity within the semi-conductor range can be used with charge-transfer complexing agents. Furthermore, positive quaternary charges are usual charges.

In application, Ser. No. 678,501, filed Oct. 27, 1967, a ditertiary amine material and a dihalo material. \( R_1 \) and \( R_2 \) are organic radicals such as hydrocarbyl, Z is a linking condensation residue, m, p, q, and z are integers from 1 to 10,000 and \( n \) is an integer of sufficient magnitude to provide a final solid polymer. The backbone of the repeating unit contains at least one condensation residue and at least one quaternary nitrogen atom separated and joined by organic radicals.

Polymers of Formula I are prepared by reacting a compound selected from those of the formulae:

\[ Y-R_3-Z', Y-R_4-Y \]

with a compound selected from those of the formulae:

\[ Y-R_1-Y, Y-R_2-Z' \]

where \( R_2-R_10 \) are organic radicals such as hydrocarbyl, Y is a quaternary forming moiety such as tertiary nitrogen or halogen and \( Z' \) and \( Z'' \) are coreactive condensable moieties such as hydroxy and isocyanate urethane forming groups. At least one of compounds II or III contains a Z residue or the II-II pair contains \( Z' \) and \( Z'' \) residue forming moieties.

The linking structure \( Z \) may suitably be a urethane, amide, imide, ester, or urea. Urethane linkages are preferred because of the ready availability of diverse isocyanate materials, the absence of elimination products and the ability to select and control the properties of the final prepolymer. Therefore \( Z' \) and \( Z'' \) can be selected from hydroxyl, amino, carboxyl, anhydride or isocyanate.

Compounds \( Y-R_4-Y \) and \( Y-R_3-Y \) may be a ditertiary amine material and a dichalo material. \( R_4 \) and \( R_3 \) contain at least two carbon atoms and may be of polymeric or prepolymeric length. Exemplary dichalo compounds are \( \alpha \) (alpha), \( \Omega \) (omega) alkyl or alkylamino containing at least two carbon atoms. Suitably, the bromide may be a terminal dibrominated aliphatic such as dibromomethane, dibromopropane, dibromobutane, dibromomethane, dibromohexane, dibromomethane, and similar homologs through dibromohexadecane. Dibromoacetonitrile and alkylylated aromatics such as dibromo-
xylene are also suitable. Polymers may also be formed with corresponding dichloro- and diodo-compounds. Terminal brominated polymers such as polybutadienes containing from about 20 to about 500 or more carbon atoms can also be utilized to form polymers according to the invention. As the number of carbon atoms increases, rubbery products are favored.

Exemplary dialdehyde amines are N,N,N',N'-tetramethylcyanoethylenediamine, N,N,N',N'-tetramethyldiacetamide, 1,2-bis-(4-pyridyl)-ethane, 1,2-bis-(2-pyridyl)-ethane, 1,2-bis-(4-pyridyl)-ethene, and N,N,N',N'-di-(4-benzylamino)ethane, tetramethylanbenzenophenone or diazine. Other di-tertiary compounds may be formed from heterocyclic compounds such as piperidine, picoline, quinoline, acridine, or phenanthridine. The amine may also be of polymer length. For example, an isocyanate terminated polybutadiene containing 20 to 200 or more carbon atoms may be reacted with two moles of a hydroxylalkyl substituted tertiary amine such as dimethylamino hydroxyethanol which will link to the polybutadiene to form a long chain di-tertiary amine. Other suitable compounds of Formula II are bromobutanol, 1-bromo, 6-cyanato hexane, bis-1,3-dimethylamino-2-propanol or 2-dimethylaminoethanol.

The butadiene polymers utilized in the process of the invention such as the dibromo or the disiocyanate polymers discussed above should contain a minimum amount, suitably below 40%, of 1,2-addition units to avoid excessive decrease in elastomeric properties. Such polybutadienes are available as liquid polymers having a molecular weight from 2,000 to 10,000. A suitable material, Polysar-rubber (Polysar Limited) is a brominated liquid polybutadiene having a molecular weight of about 6,000 and a functionality very near to two. Another suitable material is HYSTL polybutadiene (HYSTL Development Company, a subsidiary of TRW Inc., and Cores Inc.).

As discussed above at least one of the monomers is prepared as a condensation prepolymer, and preferably is based on a urethane forming reaction. For example, a polycyanoate reacted with a tertiary amino alcohol will form a polytertiary amine of the formula:

$$\text{R}^1\text{N}-\text{R}^1\text{N}-\text{R}^2\text{OCHN}-\text{R}^2\text{N}-\text{HCOOR}-\text{R}^3\text{N}$$

where R1 is lower alkyl, R2 is lower alkyl, R4 is selected from phenyl, polyphenyl, polyoxyethylene, or alkyl of 4-20 carbon atoms and q is 1 or 2.

Reaction of the polytertiary amine where q is 1 with a dibromopolybutadiene will form a linear polymer of the formula:

$$\text{R}^1\text{N}-\text{R}^1\text{N}-\text{R}^2\text{OCHN}-\text{R}^2\text{N}-\text{HCOOR}-\text{R}^3\text{N}$$

where R1 is a polybutadiene having a molecular weight from 1,000 to 10,000 and n is an integer from 2 to 500. When the alcohol contains more than one di-tertiary amino group, the corresponding reaction product will contain amino groups in excess of the number necessary to form a linear polymer and these pendant groups would be available for cross linking the polymer of the general formula:

$$\text{R}^1\text{N}-\text{R}^1\text{N}-\text{R}^2\text{OCHN}-\text{R}^2\text{N}-\text{HCOOR}-\text{R}^3\text{N}$$

where n, R1, R2, R3 and R4 have the above meanings. For example, the reaction of bis-1,3-(dimethylamino)-2-propanol and hexamethylene diisocyanate is illustrated below:

Each hydroxyl group joins an isocyanate group to form a urethane linkage. Further reaction with dibromobutane results in quaternization of the nitrogen atoms and chain extension to form a polymer having a repeating unit of the formula:

$$\text{R}^1\text{N}-\text{R}^1\text{N}-\text{R}^2\text{OCHN}-\text{R}^2\text{N}-\text{HCOOR}-\text{R}^3\text{N}$$

The isocyanate may be aliphatic aromatic, mixtures thereof or may be of polymeric length.

Examples of suitable compounds of this type include benzene-1,3-diisocyanate, hexane-1,6-diisocyanate, tolylene-2,4-diisocyanate (TDI), tolyylene-2,3-diisocyanate, diphenylmethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate, diphenyl-3,3'-dimethyl-4,4'-diisocyanate, 3-(diethyleneamino)pentane-1,5-diisocyanate, butane-1,4-diisocyanate, cyclohex-4-ene-1,2-diisocyanate, benzene-1,3,4-triisocyanate, naphthalene-1,3,5,7-tetrasiocyanate, naphthalene-1,3,7-triscyanate, toluidine-diisocyanate, isocyanate terminated prepolymers, polyaryl polyisocyanates, and the like. A suitable commercially available polyaryl polyisocyanate is a polymethylene polyphenyl isocyanate known as PAPI-1 (The Carvin Co.). This material has an average of 3 isocyanate groups per molecule and an average molecular weight of about 380.

Other commercially available higher molecular weight polyisocyanates are Adiprene 100 (Du Pont) an isocyanate terminated polyoxyalkylene glycol having a molecular weight of about 1,000, Multithane-242F (Mobay) a polyester terminated with isocyanate groups and Solithane 113 (Thiokol) which is a triscyanate derivative of glyceroi and ricinoleic acid.

The halo or tertiary amino alcohol may suitably be phenol or, 3-bromo, n-propanol. It is understood that some of glycerol and ricinoleic acid.

The prepolymer and a stirrer may be utilized to form polymers according to the invention. As the number of carbon atoms increases, rubbery products are favored.
The urethane forming step of the synthesis of the prepolymers is preferably conducted in solvent under anhydrous conditions. A diamine is dissolved in solvent and a dihalide is slowly added to the solution with stirring. The polymer forms and may be separated and worked up in numerous ways. For example, the solution may be poured and cast into a sheet by evaporating the solvent. The conductivity of the cationic sheet can be substantially enhanced by treatment with an organic charge-transfer complexing agent such as lithium tetra-cyanomethane (LiTCNQ), and neutral tetra-cyanomethane (TCNQ).

Other specific reaction schemes leading to the cationic viscoelastic polymer of Formula I are presented below.

**REACTION 2**

\[
\text{OCH} - \text{NHCOO} - \text{OH} + 2 \text{OCH} - \text{N} - \text{(CH}_3\text{)}_2 \\
\downarrow \\
\text{Br} - \text{N} - \text{Br} \\
\text{Linear Polymer}
\]

**REACTION 3**

\[
\text{OCH} - \text{NHCOO} - \text{OH} + 2 \text{OCH} - \text{N} - \text{(CH}_3\text{)}_2 \\
\downarrow \\
\text{Br} - \text{N} - \text{Br} \\
\text{Linear Polymer}
\]

**REACTION 4**

\[
\text{OCH} - \text{NHCOO} - \text{OH} + 2 \text{OCH} - \text{N} - \text{(CH}_3\text{)}_2 \\
\downarrow \\
\text{Br} - \text{N} - \text{Br} \\
\text{Linear Polymer}
\]

**REACTION 5**

\[
\text{OCH} - \text{NHCOO} - \text{OH} + 2 \text{OCH} - \text{N} - \text{(CH}_3\text{)}_2 \\
\downarrow \\
\text{Br} - \text{N} - \text{Br} \\
\text{Linear Polymer}
\]

**REACTION 6**

\[
\text{OCH} - \text{NHCOO} - \text{OH} + 2 \text{OCH} - \text{N} - \text{(CH}_3\text{)}_2 \\
\downarrow \\
\text{Br} - \text{N} - \text{Br} \\
\text{Crosslinked polymer}
\]

Reactions 1, 2, 4, 5, 6 and 7 form a polymer having a repeating unit of the formula:

\[
\text{[R}^x\text{N} - \text{R} - \text{R}^y\text{-} - \text{R} - \text{R}^z\text{]}
\]

where \(x\) and \(n\) are integers and the groups \(R, R'\) and \(R''\) are either short or long chain aliphatic or aromatic and are varied in accordance with the desired final properties. The tertiary or quaternary nitrogen atoms may be substituted with groups other than methyl such as other lower alkyl groups, aryl groups such as phenyl, aralkyl groups such as benzyl, alkaryl groups such as tolyl, cycloalkyl such as cyclohexyl or may form a portion of a heterocyclic ring such as pyridyl.

The invention will now become better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

**DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a graph of modulus (dynes/cm.) vs. temperature (°C.) illustrating the effect of cationic groups on the properties of various polymers; and

FIG. 2 is also a graph of modulus (dynes/cm.) vs. temperature (°C.) illustrating the effect of the molecular weight of the dihalo compound on the properties of the polymer.

The following examples are offered by way of illustration. It is to be understood that only preferred embodiments of the invention are illustrated, and that numerous substitutions, alterations and modifications are readily apparent to those skilled in the art and are therefore intended to be included within the scope of the invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The following experiments illustrate the effect of molecular weight and cationic center distribution on the properties of the final polymer.

**EXAMPLE I**

A. Preparation of stock solutions of Solithane-DMAP

Solithane 113 (Thiokol Corporation) containing three isocyanate groups per molecule (290.4 g.) was dissolved in dry benzene (1100 g.). Dry 1,3-bis(dimethylamino)-2-propanol (DMAP—85.2 g.) was added to this solution and the mixture was heated at 50° for 24 hours. The completion of reaction was ascertained by means of infra red spectroscopy. The disappearance of the absorption peak at 4.56μ was utilized to indicate reaction completion.

B. (1) Reaction product of stock solution with dibromometylbutadiene

The stock solution (17.1 g.) was reacted at room temperature with polydibromometylbutadiene of approximate molecular weight 3500 (35 g.) dissolved in benzene (86 g.). The reaction mixture was cast in a Teflon lined mold. The rubber thus obtained after evaporation of solvent and drying showed good damping characteristics (see FIG. 2, Curve 1).
B. (2) Reaction product of stock solution with dibromohexane

The stock solution (51.3 g.) was mixed with 1,6-dibromohexane (7.32) and a film was cast at room temperature. The mechanical properties of the dry and solvent free film are illustrated by the modulus temperature curve shown in FIG. 1, Curve 2.

B. (3) Reaction product of stock solution with dibromopropane

The stock solution was reacted and isolated in the same way as in (1) but using 1,3-dibromopropane (6.1 g.). The modulus temperature curve is shown in FIG. 2, Curve 2.

B. (4) Reaction product of (2) with TCNQ

The flexible cationic rubber sheet prepared in (2) was treated with Li-TCNQ and neutral TCNQ by boiling the sheet for a few hours with an equimolar quantity of Li-TCNQ and then treating this sheet with boiling neutral TCNQ in acetonitrile solvent. The resulting dark blue colored film was a tough flexible rubbery sheet. The room temperature resistivity was found to be about $1 \times 10^7$ ohm$^{-1}$ cm$^{-1}$. The modulus of the rubbery product is shown in FIG. 1, Curve 3.

A non-ionic Solithane specimen was obtained by reacting Solithane 113 with castor oil at 200° F. for 12 hours. The modulus of this material is illustrated as Curve I, FIG. 1. The modulus temperature curves were determined by means of a modified Gehman Tester. The number of ionogenic links was determined by analysis of iodine bromine. The effect of cationic centers on the glass transition temperature as derived from modulus temperature curves was found to be negligible in the case in which one cationic center is introduced per molecular weight of approximately 2000. However, one quaternary ammonium group per 250 molecular weight segment raised the transition temperature by about 40° C. The transition temperature is raised from about 12° C. for Solithane cured with castor oil to the 33° C. for a polymer containing one cationic link per chain segment of 250. This is raised even further when the cationic polymer is complexed with TCNQ. Thus, cationic centers present in the backbone of the polymers at relatively low concentration have a pronounced effect on the mechanical properties of the polymer.

Referring again to FIG. 2, it is also observed that there are large differences in the mechanical behavior of a Solithane 113-tertiary amine polymer crosslinked by means of dibromopolybutadiene as compared to one crosslinked with dibromopropane. The shape of the two curves, that is, the three transition temperatures of (1) and the two transitions of (2), indicate block polymer behavior. The three transitions plateaus of the polybutadiene containing product over such a wide temperature range indicate that the product will have excellent damping characteristics.

EXAMPLE II

A dry benzene solution of dihydroxypropylene glycol (1.7 g.) of approximate molecular weight of 200 (100 g. in 50 cc. of benzene) was reacted with toluene disiocyanate (17.5 g. in 15 cc. of benzene) at room temperature. After standing overnight, the mixture was heated to 50° C. for two hours and then heated under reflux for five minutes.

After cooling to room temperature, 2-dimethylaminooctanol (DMAE) (8.9 g. in 5 cc. of benzene) was added while stirring. After standing for 48 hours, the reaction mixture was heated to 60° C. for 15 minutes and subsequently cooled to room temperature. At this time 1,6-dibromo hexane in benzene (12.2 g. in 5 cc. of benzene) was added. An immediate increase of viscosity was noted.

The reaction mixture was transferred into a Teflon lined pan and left in a hood. After evaporation of the solvent 110 g. of a transparent rubbery solid was obtained.
EXAMPLE IX

Two moles of 1,3-bis-(dimethylamino)-2-propanol (DMAP) were mixed with 1 mole of Multithane 242F to form a ditertiary amine adduct having a molecular weight of 1584. 9.5 grams of a 50% benzene solution of the adduct (0.003 mole) were thoroughly mixed with a solution of 30 grams of a 5000 molecular weight dibromopolybutadiene (0.006 mole) in 30 grams of chloroform. The so-formed solution was poured into a Teflon lined pan and left for evaporation in a well ventilated room. The yield was 32 grams of rubber with a non-krinkled shiny surface. The product was non-sticky and elastic and discolors by 180° C. without losing its shape. In a second batch the batches of 30 grams of a 5000 molecular weight dibromopolybutadiene in 60 ml. of benzene. The so-formed solution was poured into a Teflon lined pan and left for evaporation in a well ventilated room for 48 hours. The final yield was 32 grams of a rubbery gray sheet 21 x 10.5 x 0.2-0.3 cm.3. The product was non-sticky and had a shiny surface. The sheet was elastic and had a softening point above 165° C.

EXAMPLE X

A tetra-tertiary amine prepolymer was synthesized from 1 mole of hexamethylene diisocyanate and two moles of DMAP. 1.4 grams or 0.003 mole of the prepolymer were carefully mixed with 8.5 ml. of benzene. This solution was then thoroughly mixed with a solution of 30 grams of Polysar rubber (5,000 molecular weight dibromopolybutadiene) in 60 ml. of benzene. The so-formed solution was poured into a Teflon lined pan and left for evaporation in a well ventilated room for 48 hours. The final yield was 32 grams of a rubbery yellow-gray sheet 21 x 10.5 x 0.2-0.3 cm.3. The product was non-sticky and had a shiny surface. The sheet was elastic and had a softening point above 165° C.

EXAMPLE XI

A. Preparation of PAPI-DMAP stock solution

The synthesis was carried out under extremely dry conditions. 15.0 grams of PAPI dissolved in 33 ml. of dry benzene were added under agitation in a fine stream to 9.0 grams (0.10 percentage) of 1,3-bis-(dimethylamino)-2-propanol (DMAP). An immediate exothermic reaction was evidenced. The reaction mixture was agitated at room temperature for 72 hours. The reaction product was recovered by pouring the brown viscous mixture into 18 ml. of petroleum ether while rapidly agitating the ether. The residue was washed in 200 ml. of petroleum ether. The final washed product was dried in a desiccator and yield was 29 grams.

B. Polymerization with dibromopolybutadiene

1.7 grams of PAPI-DMAP (0.006 mole) dissolved in 8.5 ml. of benzene were thoroughly mixed with a solution of 30 grams of Polysar (dibromopolybutadiene-5,000 M.W.) in 60 ml. of benzene. The so-formed solution was poured into a Teflon lined pan and left for evaporation in a well ventilated room for 30 hours. 31 grams of a yellow-gray rubber sheet were recovered. The sheet had a non-sticky shiny surface. The softening point was above 180° C.

C. Polymerization with dibromopropane

6.2 grams (0.02 mole) of PAPI-DMAP solution was dissolved in 25 ml. of a 1/1 acetone-DMF mixture. 0.02 mole plus 3% excess. No immediate reaction took place. Agitation at room temperature for 24 hours rendered the mixture cloudy. Homogenous rubber resin conglomerates were precipitated in petroleum ether. Final yield was 12 grams after drying in a desiccator. The product was a yellow-gray, non-sticky elastomer which dissolved in a golden brown above 185° C.

D. Polymerization with 1,6-dibromohexane

6.2 grams (0.02 mole) of PAPI-DMAP dissolved in 25 ml. of a 1/1 acetone-DMF mixture were quickly added under agitation to 5.0 grams (0.02 mole plus 3% excess) of 1,6-dibromohexane. No immediate reaction was seen. Agitation at room temperature for 24 hours gave no observable change. The reaction mixture was transferred to teflonized dishes for evaporation of solvent in well ventilated rooms. Final product was in the form of yellow-brown, non-elastic particles. Product does not melt or soften below 205° C. and discolors towards a golden brown from above 180° C.

EXAMPLE XII

50 grams (0.01 mole) of the reaction product of 2 moles of DMAP and one mole of toluene diisocyanate (TDI) were thoroughly mixed with 100 grams of CCl4. 47. grams (0.01 mole of a suspension of polydibromobutadiene (5,000 M.W.) was added to the resulting viscous liquid with agitation. Slow agitation was continued for five minutes and then almost clear liquid resulted, the few bubbles that formed disappeared after several minutes. The reaction mixture was then carefully transferred into polyethylene pans. After evaporation of the solvent for 48 hours, the material was removed from the pan and dried for 24 hours. A brownish, almost opaque rubber sheet was obtained. The sheet was elastic, bubble-free, non-sticky and had a smooth dull surface.

The reaction was repeated utilizing 75 grams (0.015 mole) of polydibromobutadiene in 150 grams of CCl4 and 7.0 grams of the TDI-DMAP complex in 148 grams of CCl4. Ten rubber sheets approximately 10 by 20 cm. and 18 by 18 cm. were obtained.

EXAMPLE XIII

A. Preparation of an addition compound with hexane diisocyanate

5.0 grams (0.03 mole) of 1,6-diisocyanatohexane was carefully mixed with 9.0 grams (0.06 mole plus 3% excess) 1,3-bis-(dimethylamino)-2-propanol (DMAP). No exotherm was evidenced and agitation was continued overnight. A gray-white very viscous, homogenous liquid was obtained with crystalline particles separating after two weeks.

B. Polymerization of A with polydibromobutadiene

25 grams (0.005 mole) of polydibromobutadiene (5,000 M.W.) were mixed into 75 grams CCl4. A mixture of 1.2 grams (0.0025 mole) of the adduct from A in 23 grams of CCl4 was added to the adduct mixture while stirring. The resulting, slightly viscous mixture was left standing, covered for several minutes in order to let bubbles disappear and then carefully transferred into a polyethylene pan. Solvent was evaporated at room temperature for 72 hours. 25 grams of a golden brown, clear, thick rubber sheet 8 x 8 cm. with good elasticity and a shiny, smooth, bubble-free surface was obtained.

EXAMPLE XIV

A. Multrathane-DMAP addition compound

The synthesis was again conducted under extremely dry conditions. 25.8 grams of Multrathane 242F (0.02 mole) was mixed with a magnetic stirrer bar until a gray-white, opaque homogeneous mixture was obtained. While agitation continued, a mixture of 6.0 grams of DMAP (0.04 mole plus 3% excess) in excess 5.6 grams of dried benzene was added in one portion. A small further amount of dry benzene was added when increased viscosity made agitation difficult. The reaction was not exothermic.

B. Polymerization with polydibromobutadiene

10 grams of polydibromobutadiene (0.002 mole) was mixed with 6.4 grams of a 50% benzene solution of A (0.002 mole) in a polyethylene pan. The resulting very viscous and homogenous liquid was spread in a thin layer over the pan. The solvent was evaporated at room temperature over one week. 12 grams of an 8 cm. by 8 cm. thin rubber sheet was obtained.

The following example demonstrates the effect of proportions on the properties of the final product.
A slight change of viscosity was observed. The product 70
chloroform. Into this solution was then added under stir-
tation was continued for 16 hours at ambient temperature.

No spontaneous reaction was evident. Agi-
with 33 g. of dry benzene. The resulting, fairly viscous 05
weight of about 662 based on an isocyanate content of
6.35%; 33 g. of Adiprene-L-167 (0.05 mole) were mixed
and become brownish-golden and softening at 185° C.

elasticity. The product had a shiny and smooth surface

solvent was evaporated under a hood at ambient tempera-
ture for 48 hours. The final product was a clear, light yel-

nary weight-0.06 mole) in 60 grams of chloroform. After

a solution of 30 g. of dibromopolybutadiene (5,000 molec-
benzene solution (0.06 mole) was added under stirring to

reduced to 100° C. and the product had poor elasticity.

formed by reaction with a dibromo compound. The par-
uclear weight 2,000 was reacted with commercial toluene di-

Dihydroxy polypropylene glycol of approximate molecu-

B. Conversion of A to a tertiary amine prepolymer

solids were destroyed which was indicated by infra red spectrophotometry (disappearance of absorption peak at 2.9 microns). The resulting reaction product was a colorless viscous liquid.

C. Copolymerization of B with dibromobutene

The reaction product obtained as described above (6.6 g.) was intimately mixed with 1,4-dibromobutene (0.93 g. in 50 ml. of benzene) and the mixture was placed in a shallow mold. A transparent colorless film was formed within 15 minutes. The rubbery film was dried in a vacuum oven at room temperature for 24 hours. It exhibited strong birefringence between an analyzer and polarizer.

D. Copolymerization with dibromopropylene

Solithane 113 (1 mole) was intimately mixed with 3-

2

of this film was immersed in a methanol solu-
tion of lithium tetracyano quinodimethane (0.1% by weight). The resulting dark colored film after drying had a resistivity equal to 5 x 10 ohm cm.

E. Complexing D with TCNQ

1 cm² of this film was immersed in a methanol solu-
tion of lithium tetrayano quinodimethane (0.1% by weight). The resulting dark colored film after drying had a resistivity equal to 5 x 10 ohm cm.

F. Reaction of D with heparin

1 cm² of the same film was kept for 2 hours in a methanol-tetrayano quinodimethane solution of heparin (2% by weight) (solvents in proportion 45:45:1). The film after thorough washing with water contained heparin as evidenced by means of a dye (Azure A) test.

G. The final product was a colorless viscous liquid.

H. The reaction product was a colorless viscous liquid.

I. The final product was a colorless viscous liquid.

J. The final product was a colorless viscous liquid.
The product obtained as described in B (6.6 g.) was intimately mixed with m-dibromolylene (1.32 g. in 50 ml. of benzene). A clear transparent film cast was formed in the hood within 15 minutes.

H. The product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

I. The reaction product obtained as described in H (12.63 g.) was intimately mixed with 1,3-dibromo propane (1.48 g. in 100 cc. of benzene) in a Teflon lined mold. After slow evaporation of solvent, the mixture was heated at 60° C. for 5 hours. A benzene soluble rubbery transparent sheet was obtained.

J. The reaction product obtained as described in H (0.005 mole) dissolved in 30 ml. benzene was intimately mixed with 1,4-dibromobutene (0.005 mole in 20 ml. of benzene). The mixture was poured into a Teflon coated mold. After evaporation of solvent and drying, a transparent rubbery film was obtained. The film was soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

K. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

L. The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

M. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

N. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

O. The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

P. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

Q. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

R. The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

S. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

T. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

U. The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

V. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

W. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

X. The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

Y. The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.

Z. The polymer (1 g.) obtained as described in Example J was dissolved in methanol (100 cc.) with sodium heparin (0.29 g. in 20 ml. methanol/water, 1:1 mixture). The white precipitate which formed was washed with water four times in order to remove unreacted heparin and sodium bromide. The product was subsequently washed with methanol three times. The heparinized polymer swelled in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in methanol, tetrahydrofuran and acetone. The film was dissolved in acetone and recrystallized with n-hexane.

The rate of reaction was followed by means of I.R. The reaction product obtained as described in A (112.5 g.) was intimately mixed with 2-dimethylamino ethanol (8.55 g.) and heated at 60° C. for 17 hours. The rate of reaction was followed by means of I.R. The reaction product is a clear viscous liquid.

The dry polymer could be molded under pressure at 50-100° C. to give a desired shape.