NST-44

TO: XXX/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: CALTECH/IAK

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:

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
FIG. 1

EFFECT OF CATIONIC GROUPS

The present invention relates to cationic polymers and comprises a mixture of elastomeric and amorphous materials containing the urethane linkage. The polymers are particularly useful as a viscous liquid which can be poured into or applied to a surface, and is thereafter capable of hardening and forming a solid film in a very short period of time. The term "viscous liquid" is intended to include any material which is fluid at ordinary temperatures and pressures, and which, when poured or applied to a surface, flows under the influence of gravity. The term "elastomeric" as used herein is intended to include any material which possesses the characteristics of a resilient or rubber-like material. The term "amorphous" as used herein is intended to include any material which is not crystalline or glass-like.

The inventors have found that the polymers described herein provide a powerful means for imparting properties to the printed circuit boards and the like by the mere application of the material in the form of a liquid, or by the application of a solid film of the material which has been hardened or cured. By merely immersing a printed circuit board in the liquid polymer, or by applying a solid film of the hardened polymer to the printed circuit board, the material will impart properties to the printed circuit board which are not obtained by any other means known in the art. These properties include the following:

1. The material will harden or cure at temperatures which are below the temperature at which the printed circuit board would be damaged.
2. The material will not leave any residue on the printed circuit board after it has been hardened or cured.
3. The material will not interfere with the operation of the printed circuit board.
4. The material will not adversely affect the electrical properties of the printed circuit board.
5. The material will not interfere with the mechanical properties of the printed circuit board.
6. The material will not interfere with the optical properties of the printed circuit board.
7. The material will not interfere with the chemical properties of the printed circuit board.
8. The material will not interfere with the thermal properties of the printed circuit board.
9. The material will not interfere with the biological properties of the printed circuit board.
FIG. 2

EFFECT OF MOLECULAR WEIGHT

TEMPERATURE, °C

MODULUS, dynes/cm²

INVENTOR.
ALAN REMBAUM

ATTORNEYS.
VISCOELASTIC CATIONIC POLYMERS CONTAINING THE URETHANE LINKAGE

Alan Rembauoi, Altadena, Calif., assignor to California Institute of Technology, Pasadena, Calif.
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ABSTRACT OF THE DISCLOSURE

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

\[ \left( Z - R^m - Y - R^p \right) \]

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 complexes. Materials having conductivity within the semi-conductor range can be used in printed circuits and other electronic devices. Films of these materials would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would likewise find application in electrostatic precipitation devices, dust collectors, corona-discharge shields and the like. Furthermore, positive quaternary charges are usually associated with bacteriostatic antiparasitic and fungicidal activity. Therefore, surgical gloves formed of materials having these properties would be inherently germicidal as well as resistant to build up the static electrical charges.

Most of the previously described cationic polymers have been found to be highly crystalline and the glass transition temperature range too narrow to provide significant damping characteristics. Furthermore, both the mechanical strength and the elasticity has not been high enough to provide elastomeric products having commercially interesting properties.

In application, Ser. No. 678,501, filed Oct. 27, 1967, now abandoned, a synthesis of cationic polyelectrolytes containing quaternary nitrogen centers in the backbone of the polymer chain is disclosed. These polyelectrolytes are prepared by reacting a ditertiary amine with a dihalo organic compound. Linear polymers of widely varying properties were obtained. In accordance with the invention, the elastomeric and polyelectrolytic properties of the final polymer are substantially controlled and modified by utilizing much higher molecular weight starting materials prepared by prepolymer condensation processes.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of the invention to provide a new family of viscoelastic materials.

Still further objects are to provide synthesis and manufacture of elastomeric compositions and articles containing quaternary nitrogen centers and condensation residues along the polymeric backbone thereof.

Yet another object of the invention is the provision of linear and cross-linked straight chain and block polymers having a wide damping temperature range.

Yet another object of the invention is the provision of linear and cross-linked cationic polymers having enhanced electrical conductivity when complexed by charge-transfer complexing agents.

These and other objects and many attendant advantages of the invention will become apparent as the description proceeds.

The viscoelastic cationic polymers according to the invention are selected from polymers having a repeating unit of the formula:

\[ \left( Z - R^m - Y - R^p \right) \]

where \( R^1 \) 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:

\[ Y - R^3 - Z^1, Y - R^4 - Y \]

\[ Y - R^3 - Z - R^6 - Z - R^5 - Y \] (II)

with a compound selected from those of the formulae:

\[ Y - R^1 - Y, Y - R^6 - Z^4 \]

\[ Y - R^2 - Z - R^10 - Z - R^8 - Y \] (III)

where \( R^2 - R^10 \) are organic radicals such as hydrocarbyl, \( Y \) is a quaternary forming moiety such as tertiary nitrogen or halo and \( Z^6 \) and \( Z^4 \) are co-reactive 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 \( Z^6 \) and \( Z^4 \) 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 \( Z^6 \) and \( Z^4 \) can be selected from hydroxyl, amino, carboxyl, anhydride or isocyanate.

Compounds \( Y - R^4 - Y \) (III) and \( Y - R^3 - Y \) (II) may be a ditertiary amine material and a dihalo material. \( R^4 \) and \( R^3 \) contain at least two carbon atoms and may be of polymeric or prepolymeric length. Exemplary dihalo compounds are \( \alpha \) (alpha), \( \Omega \) (omega) alkyl or alklyl bromides containing at least two carbon atoms. Suitably, the bromide may be a terminal dibrominated aliphatic such as dibromoethane, dibromopropane, dibromobutane, dibromomethane, dibromomethane, dibromomethane, and similar homologs through dibromhexadecane. Di bromoamnatics or alkylated 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 di tertiar y amines are N,N,N',N'-tetracycl methylethoxycycl amideine, N,N,N',N'-tertacethylene diamine, 1,2-bis ( 4-pyridyl )-ethane, 1,2-bis ( 2-pyridyl )-ethane, 1,2-bis ( 4-pyridyl )-ethan e, and N,N,N', N'-di ( 4 - benzylamino )ethane, tertacycl methylenebenzophenone 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 hydroxyalkyl substituted tertiary amine such as dimethy l e thylhydroxyethanol 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-cyano, 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 5,000 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 poliosycyanate reacted with a tertiary amino alcohol will form a polytertiary amine of the formula:

\[
\begin{align*}
N & - R_1 - O - O C H - N H - C O O - R_2 - R_3 - N = R_4 \nonumber \\
R_1 & - R_2 - R_3 - C H - N H - C O O - R_2 - R_3 - N = R_4
\end{align*}
\]

where \( R_2 \) is lower alkyl, \( R_3 \) is lower alkyl, \( R_4 \) is selected from phenyl, polyphenyl, poloxyethylen e, 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:

\[
\begin{align*}
N & - R_1 - O - O C H - N H - C O O - R_2 - R_3 - N = R_4 \nonumber \\
R_1 & - R_2 - R_3 - C H - N H - C O O - R_2 - R_3 - N = R_4
\end{align*}
\]

where \( R_1 \) 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:

\[
\begin{align*}
N & - R_1 - O - O C H - N H - C O O - R_2 - R_3 - N = R_4 \nonumber \\
R_1 & - R_2 - R_3 - C H - N H - C O O - R_2 - R_3 - N = R_4
\end{align*}
\]

where \( n, R_1, R_2, R_3 \) and \( R_4 \) have the above meanings. For example, the reaction of bis-1,3-dimethylamino)-2-propanol and hexamethylene diisocyanate is illustrated below:

\[
\begin{align*}
& \text{CH}_3 \text{N-CH}_3 \\
& \text{CH}_2 \\
& \text{CH}_2 \\
& \text{CH}_2 \\
& \text{CH}_2 \\
& \text{CH}_2 \\
& \text{CH}_3 \text{N-CH}_3
\end{align*}
\]

Each hydroxy 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:

\[
\begin{align*}
& \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{O}-\text{OCN}-\text{CH}_2 \text{C}_2-\text{NHO} \cdots -\text{CH}_2 \text{CH}_2 \text{CH}_3 \\
& \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \\
& \text{CH}_3 \text{N-CH}_3
\end{align*}
\]

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), tolylene-2,3-diisocyanate, diphenylenemethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate, diphenyl-3,3'-dimethyl-1,4'-diisocyanate, diphenyl-3,3'-dimethoxy-4,4'-diisocyanate diethyl ether, 3-(diethylamino)-pentane-1,5-diisocyanate, butane-1,4-diisocyanate, cyclohex-4-ene-1,2-diisocyanate, benzene-1,3,4-trisocyanate, naphthalene-1,3,5,7-tetrasocyanate, naphthalene-1,3,7-trisocyanate, tetra-2,2,4-trimethylpentane-1,3,5,7-tetrasocyanate, and the like. A suitable commercially available polyarylic polyisocyanate is polystyrene polyisocyanate 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 Aldiprene 100 (Dur Pont) an isocyanate terminated polyoxyalkylene glycol having a molecular weight of about 1000, Multithane-242F (Mobay) a polyester terminated with isocyanate groups and Solithane 113 (Thiokol) which is a trisocyanate derivative of glycerol and ricinoleic acid.

The halo or tertiary amino alcohol may suitably be aliphatic or aromatic such as 1,3-bis (dimethylamino)-2-propanol, 2-dimethylaminoethanol, bromoethanol, p-dimethylaminophenyl methyl carbinol, p-dimethylo naminophenol or, 3-bromo, n-propanol. It is understood that similar products are realized when tertiary amino or bromo substituted isocyanates are reacted with diols or when carboxyl, amino or other reactive functional groups are substituted for the isocyanate or hydroxy groups on the illustrative compounds discussed above.
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 dihalo 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-cyanoquinodimethane (LITCN), and neutral tetra-cyanoquinodimethane (TCNQ).

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

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

\[
\text{OCN-R-NCO} + \text{NH}_2-R' + \text{H}_2\text{O} \rightarrow \text{OCN-R-NHCOO-R'-NHCONH-R'-NCO} + 2 \text{H}_2\text{O}
\]

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.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of modulus (dynes/cm.\(^2\)) 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.\(^2\)) 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 4.56 μ was utilized to indicate reaction completion.

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

The stock solution (17.1 g.) was reacted at room temperature with polydibromobutadiene 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).
The reaction mixture was transferred into a Teflon lined pan, placed in a ventilated hood. After 24 hours a transparent, strong rubbery sheet was obtained.

**EXAMPLE V**

This example illustrates the preparation of a soluble, non-crosslinked cationic rubbery material. Example I was repeated using stoichiometric amounts of polypropylene glycol di-isocyanate and 2-dimethylaminoethanol in benzene solution. After eight hours standing, a roughly equimolar quantity of 1,4-dibromobutane was added directly to the benzene solution, with agitation. Evaporation of the solvent in a Teflon lined tray gave a transparent rubbery sheet.

**EXAMPLE VII**

Example V was repeated using commercially available toluene di-isocyanate (TDI) and the same tetramethyl diaminohexane and dibromopolybutadiene. A rubbery film was obtained from benzene or chloroform solutions.

**EXAMPLE VIII**

Two moles of 2-dimethylaminoethanol (DMAE) were reacted with one mole of PAPI to form a DMAE/PAPI adduct having a molecular weight of 2200. The mixture was heated for 1 hour at 60°C and left standing for 24 hours. A portion of the resultant viscous product (11.5 g.) was reacted at room temperature with dibromobutene (1.9 g.) dissolved in benzene (50 cc.). The reaction product was cast on a Teflon sheet. After evaporation of the solvent, a rubbery film was obtained.

**EXAMPLE IV**

Solithane 113 (145 g.) was intimately mixed with dry 1,3-bromopropylene (82 g.). The mixture was heated at 50°C for two hours and left standing at room temperature for 24 hours. About 15.2 g. of a viscous reaction product was obtained. A 1.4 g. portion of the purified product was then dissolved in 10 ml. of benzene and to this solution 30 g. of dibromopolybutadiene was then added. The latter organic dibromo compound has a fairly linear backbone, terminal bromine groups and a molecular weight of about 5000. After stirring, the mixture was poured into a Teflon lined molds, and allowed to stand and evaporate overnight. The product upon removal from the mold was found to be a translucent, flexible rubbery sheet with a glass transition temperature of about 80°C.

The condition of the dry benzene or toluene di-isocyanate solutions was aging in an action co-solvent. A suspension of the product in a dry nitrogen atmosphere.

**EXAMPLE XVI**

This example illustrates the preparation of a soluble, non-crosslinked cationic rubbery material. Example I was repeated using commercially available toluene di-isocyanate (TDI) and the same tetramethyl diaminohexane and dibromopolybutadiene. A rubbery film was obtained from benzene or chloroform solutions.

**EXAMPLE VII**

Example V was repeated using commercially available toluene di-isocyanate (TDI) and the same tetramethyl diaminohexane and dibromopolybutadiene. A rubbery film was obtained from benzene or chloroform solutions.

**EXAMPLE VIII**

Two moles of 2-dimethylaminoethanol (DMAE) were reacted with one mole of PAPI to form a DMAE/PAPI adduct having a molecular weight of 222.6. 5.3 grams of a 50% benzene solution of DMAE/PAPI (0.012 mole) were thoroughly mixed with a mixture of 30 grams of dibromopolybutadiene (0.006 mole) in 45 grams of benzene. The so formed solution was poured into a teflonized pan and left for evaporation in a well ventilated room for 24 hours. 31 grams of polymer was recovered in the form of a transparent, strong rubbery sheet.

**EXAMPLE III**

P-dimethy1aminophenol (2.7 g.) was mixed with 215 g. of polypropylene glycol diisocyanate (approximate molecular weight, 2200). The mixture was heated for 1 hour at 60°C and left standing for 24 hours. A portion of the resultant viscous product (11.5 g.) was reacted at room temperature with dibromobutene (1.9 g.) dissolved in benzene (50 cc.). The reaction product was cast on a Teflon sheet. After evaporation of the solvent, a rubbery film was obtained.

**EXAMPLE II**

A dry benzene solution of dihydroxypropylene glycol of approximate molecular weight of 2000 (100 g. in 50 cc. of benzene) was reacted with tolulene diisocyanate (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-dimethylaminoethanol (DMAE) (8.9 g. in 5 cc. of benzene) was added while stirring. After standing for 48 hours, the reaction mixture was heated to 80°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 (DMPA) were mixed with one mole of Multathane 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 180° C. without losing its shape. In a second batch the coloring content was doubled and the air bubbles in the presence decreased but the wrinkling of the surface increased.

EXAMPLE X

A tetra-tertiary amine prepolymer was synthesized from 1 mole of hexamethylene disiocyanate and two moles of DMAP, 1.4 grams or 0.003 mole of the prepolymer were carefully mixed with 8.5 mls. of benzene. This solution was then thoroughly mixed with a solution of 30 grams of Polyisorb 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. 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 8.0 grams (a 10% molecular excess) of 1,3-bis(dimethylamino)-2-propanol (DMPA). 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 Polysyr (dibromobutadiene-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 dissolved in 25 mls. of a 1/1 acetone-DMF mixture were quickly added under agitation to 4.1 grams (0.002 mole plus 3% excess) of dibromopropane. A tetra-tertiary amine prepolymer was added directly into a Teflon lined pan and left for evaporation in a well ventilated room for 24 hours. A shiny, slightly krinkled elastic and a melting point of 180° C. was formed. 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 XII

A. Preparation of an addition compound with hexane disiocyanate

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 (DMPA). No exotherm was evidenced and agitation was continued overnight. A gray-white very viscous, homogeneous 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 XIII

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. The reaction mixture was then carefully transferred into a polyethylene pan. After evaporation of the solvent for 48 hours, the material was removed from the pan and dried overnight. A brownish, almost opaque rubber sheet was obtained. The sheet was elastic, bubble free, non-sticky and had a smooth dull surface.

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 homogeneous 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. non-elastic 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 XIV

A. Multrathane-DMAP addition compound demonstration

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 homogeneous 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.
25.8 grams of Multithane 242F (0.02 mole) were mixed with 25.8 grams of dry benzene under extremely dry conditions resulting in a homogeneous mixture which was stirred for 16 hours until a viscous, gray-white, opaque liquid was obtained. The liquid was then added drop-wise with stirring into a mixture of 6.0 g. of 1,3-bis-(dimethylamino)-2-propanol (0.04 mole plus 3% excess) in 5.6 g. of dry benzene. No spontaneous reaction took place. Agitation was continued at room temperature for 16 hours with a slight increase in viscosity. The mixture was diluted with 100 g. of benzene and added in a fine stream under agitation to a mixture of 100 g. of polydibromobutadiene (5,000 molecular weight-0.02 mole) in 35 g. of benzene.

In order to let the bubbles formed by the mixture escape the material was left covered for approximately 1 hour during which time reaction took place. The mixture became so viscous that it was impossible to transfer the contents of the beaker into the glass pans without bubble formation, the material stiffening almost immediately. The covered pans were left at room temperature for evaporation of the solvent for 16 hours. Beige colored 0.2 cm. thick rubber sheets were obtained. The sheets were non-elastic, elastic, and had a shiny surface. The product starts to soften at 160°.

When the molar ratio of the Multithane-DMAP-polydibromobutadiene was changed from 1:2:2 as above to 1:2:1 under the same conditions the softening point was reduced to 100° C. and the product had poor elasticity.

The following example illustrates the preparation of a prepolymer based on a polyoxyethylene polymer terminated with isocyanate groups and the resultant polymer formed by reaction with a dibromo compound. The particular prepolymer utilized was Adiprene L-100 containing 4.1% isocyanate groups and having a molecular weight of 1,024.

25.6 g. of Adiprene L-100 (0.025 mole) were mixed with 25.6 g. of dried benzene. The resultant fairly viscous liquid was added drop-wise, under stirring, to a solution of 3.8 g. of DMAP (0.025 mole plus 3%) in 3.6 g. of dry benzene. No spontaneous reaction took place. Agitation at room temperature was continued for 16 hours. Only a slight increase in viscosity was observed. 14 g. of this 50% benzene solution (0.06 mole) was added under stirring to a solution of 30 g. of dibromopolybutadiene (5,000 molecular weight) in 60 g. of chloroform. After five minutes the bubbles had disappeared. No visible changes were observed. The colorless-clear fairly viscous liquid was then carefully poured into a glass pan and the bubbles formed by pouring eliminated with a spatula. The solvent was evaporated under a hood and the residue OD heating at 50° for 12 hours. The rate of reaction was followed by infra red spectrophotometry. At the end of this time the solution was mixed with 3 moles of dibromopolybutadiene of approximate molecular weight 5,000 dissolved in 3,000 ml. of benzene. The mixture was poured into a Teflon coated mold. After evaporation of benzene a rubbery sheet was obtained.

EXAMPLE XVII

Under extremely dry conditions Adiprene L-167 was reacted with DMAP. Adiprene L-167 has a molecular weight of about 662 based on an isocyanate content of 63.5%. 33 g. of Adiprene L-167 (0.05 mole) were mixed with 33 g. of dry benzene. The resulting, fairly viscous liquid was added dropwise under stirring to a solution of 7.5 g. of DMAP (0.05 mole plus 3% excess) in 7.1 g. of dry benzene. No spontaneous reaction was evident. Agitation was continued for 16 hours at ambient temperature. A slight change of viscosity was observed. The product was a 50% solution in benzene.

30 g. (0.006 mole) of polydibromobutadiene having a molecular weight of 5,000 were dissolved in 60 g. of chloroform. Into this solution was then added under stirring 9.7 g. of the 50% solution in benzene described above (0.06 mole). The mixture was kept covered until bubbles had disappeared which required about 5 minutes. No visible changes were observed. The almost clear, colorless fairly viscous liquid was then slowly poured into a glass pan and the bubbles formed by pouring eliminated with the aid of a spatula. The mixture soon stiffened. The solvent was evaporated at a hood at ambient temperature for 48 hours. The final product was a clear, light yellow sheet about 0.5 cm. thick and was rubbery, elastic, shiny and smooth. The product began to turn brown and soften at 175° C.

EXAMPLE XVIII

One mole of Solithane 113 (Thiokol Co.) dissolved in dry benzene (30% solution by weight) was reacted with 3 moles of bis-1,3-dimethylamino-2-propanol at 50° C. for 12 hours. The rate of reaction was followed by infra red spectrophotometry. At the end of this time the solution was mixed with 3 moles of dibromopolybutadiene of approximate molecular weight 5,000, dissolved in 3,000 ml. of benzene. The mixture was poured onto a Teflon coated mold. After evaporation of benzene a rubbery sheet was obtained.

EXAMPLE XIX

A. Synthesis of diisocyanate prepolymer

Dihydroxy polypropylene glycol of approximate molecular weight 2,000 was reacted with commercial toluene diisocyanate (49.07 g.) at 60° C. for 26 hours to form a viscous liquid.

The completion of reaction was established by infra red spectrophotometry (disappearance of absorption peak at 2.9 microns).

B. Conversion of A to a tertiary amine prepolymer

46.96 grams of the viscous liquid obtained as described in I were heated with bis-1,3-dimethylamino-2-propanol (5.48 g.) at 60° C. for 24 hours. The rate of reaction was followed by observing the disappearance of absorption peak at 4.4 microns. The resulting reaction product is 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 colored 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 a polarizer.

D. Copolymerization with di bromopropylene

Solithane 113 (1 mole) was intimately mixed with 3-bromo-a-propanol (3 moles) and kept at 60° C. for 24 hours. The rate of reaction was followed by I.R. The reaction product is a yellow viscous liquid at 60° C. The viscous yellow liquid obtained (19.4 g.) was intimately mixed with the liquid obtained as described in B (13.2 g.) and with benzene (100 ml.). The solution was evaporated at a hood and the residue on heating at 50° C. for 5 hours yielded a rubbery film.

E. Complexing D with TCNQ

1 cm² of this film was immersed in a methanol solution of lithium tetracyanoquinodimethane (0.1% by weight). The resulting dark colored film after drying had a resistivity equal to 5×10⁸ ohm cm.

F. Reaction of D with heparin

1 cm² of the same film was kept for 2 hours in a methanol-tetrahydrofuran-water solution of sodium 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 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 reprecipitated 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 hydroxide (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 dissolved in acetone yielding a transparent gel. The dry heparinized polymer is slightly soluble in tetrahydrofuran and gives a very pronounced positive Azure A test.

The cationic viscoelastic materials of the invention having a wide damping temperature range from about -100° C. to about 150° C., will find ready use in aircraft parts which quite often encounter such temperature extremes during service. The glycol based materials are found to be hydrophilic. Thus the materials of the invention combine the properties and advantages of the cationic centers with elastomeric physical behavior further in combination with fire resistance, hydrophilicity and other useful effects.

The cationic centers can also function as attachment sites to substrates such as a rocket motor case propellant particles and in general to negatively charged surfaces. The elastomers of the invention can include various fillers, dyes or pigments well known in the art and further improvement in properties can be expected. The viscoelastic materials can be utilized to mold, coat, extrude or otherwise form articles in film, sheet or other configurations. The unique combination of properties will provide many new areas of utilization for elastomeric materials.

It is to be realized that only preferred embodiments of the invention have been disclosed and that numerous substitutions, alterations and modifications are permissible without departing from the scope of the invention as defined in the following claims.

What is claimed is:
1. A viscoelastic cationic polymer of the formula:
   \[ \text{R}^1 - \text{N}^+ - \text{R}^2 - \text{OCCH}_3 - \text{R}^3 - \text{NCH}_2 - \text{R}^4 \]
   where \( \text{R}^1 \) is polybutadiene and \( n \) is an integer from 1 to 250; and reacting said material with tetracyanoquinodimethane to form a complex having a higher conductivity than said material.

11. A method according to claim 10 in which the alkyl is selected from 1,3-bis-(dimethylamino)-2-propanol and 2-dimethylaminoethanol.

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4. A polymer according to claim 2 in which \( \text{R}^1 \) is a polybutadiene containing less than 40% 1,2-addition units.
5. A polymer according to claim 1 complexed with tetracyanoquinodimethane.
6. A polymer having a repeating unit of the formula:
   \[ \text{R}^1 - \text{N}^+ - \text{R}^2 - \text{OCCH}_3 - \text{R}^3 - \text{NCH}_2 - \text{R}^4 \]
   where \( \text{R}^1 \) is polybutadiene containing a molecular weight from 1,000 to 10,000, \( \text{R}^2 \) is lower alkyl, \( \text{R}^3 \) is lower alkyl, \( \text{R}^4 \) is selected from phenyl, polyphenyl, polyoxyethylene and alkyl of 4-20 carbon atoms and \( n \) is an integer from 2 to 300.
7. A polymer according to claim 6 in which \( \text{R}^3 \) is methyl.
8. A polymer according to claim 6 in which \( \text{R}^2 \) is ethyl.
9. A polymer according to claim 6 in which \( \text{R}^4 \) is complexed with tetracyanoquinodimethane.
10. A method of forming a cationic, viscoelastic polymer comprising the steps of:

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MAURICE J. WELSH, Primary Examiner
M. I. MARQUIS, Assistant Examiner
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