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. : 3,653,814

Government or Corporate Employee : CALTECH/JPL

Supplementary Corporate Source (if applicable) : PASADENA, CA

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

Enclosure

(NASA-Case-NPO-10830-1) VISCOELASTIC CATIONIC POLYMERS CONTAINING THE URETHANE LINKAGE Patent (NASA) 9 p CSCL 07D

Unclas 00/27 24885
FIG. 1

EFFECT OF CATIONIC GROUPS

The present invention relates to the provision of viscoelastic cationic polymers containing the urethane linkage between ordinary nitrogen and a cationic group in order to provide a material having transitional damping, mechanical strength, and electrical conductance which, upon incorporation into printed circuits and similar devices, can provide antistatic and antifogging properties. The present polymers are particularly useful in the manufacture of master plates for electrostatic, carbon toner, or photostatic printing, copying, and similar applications. Similarly, the present polymers are of significant interest in applications where adhesion, the prevention of static electricity, and the provision of prototypical activity are required. Materials having these properties have been found to be useful in the manufacture of master plates and master rolls for printing and copying, as well as in the manufacture of masters or masters for the production of printing plates, as well as in the manufacture of master rolls for the production of printing plates.

INVENTOR.
ALAN REMBAUM

BY
LINDENBERG & FREIDICK

3,655,814
US. 0.
2 Sheets-Sheet 1

U.S. CL.

74-16

BAC.

The invention relates to various polymers and to the provision of viscoelastic cationic polymers containing the urethane linkage between ordinary nitrogen and a cationic group in order to provide a material having transitional damping, mechanical strength, and electrical conductance which, upon incorporation into printed circuits and similar devices, can provide antistatic and antifogging properties. The present polymers are particularly useful in the manufacture of master plates for electrostatic, carbon toner, or photostatic printing, copying, and similar applications. Similarly, the present polymers are of significant interest in applications where adhesion, the prevention of static electricity, and the provision of prototypical activity are required. Materials having these properties have been found to be useful in the manufacture of master plates and master rolls for printing and copying, as well as in the manufacture of masters or masters for the production of printing plates, as well as in the manufacture of master rolls for the production of printing plates.

INVENTOR.
ALAN REMBAUM

BY
LINDENBERG & FREIDICK

3,655,814
US. 0.
2 Sheets-Sheet 1

U.S. CL.

74-16

BAC.
ABSTRACT OF THE DISCLOSURE

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

$$[R_1 - R_2 - Z - R_3]_n$$

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.

POLYMERIZATION OF THE URETHANE LINKAGE

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

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. Materials having conductivity within the semi-conductor range can be used with charge-transfer complexing agents. Therefore, surgical gloves formed of materials having conductivity within the semi-conductor range can be used. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying. Conductive viscoelastic rubbers would find application in forming charged master plates for graphic reproduction and ultimately for photocopying.
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 diisocyanates are N,N,N',N'-tetramethylhexahexamethylenediamine, N,N,N',N'-tetramethylda-

methyleneaniline, 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, tetramethylenbenzo-

phenone 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 H are bromo-

substituted isocyanates are reacted with diols or

similar products .are realized when tertiary amino or

dimethylaminophenyl methyl carbinal, p-dimethylamino-

phenone 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 materials is polyisocyanates (Polyisocyanate Limited) is a bromi-

nated liquid polybutadiene having a molecular weight of

about 5,000 and a functionality very near to two. Another

suitable material is HYSTL polybutadiene (HYSTL Devel-
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-cyanoquinodimethane (LITCNQ) and neutral tetra-cyanoquinodimethane (TCNQ).

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

\[ \text{REACTION 2} \]

\[
\begin{align*}
\text{OCN-R'-NCO} + 2 \text{OH-R-N(CH}_3)_2 \\
\text{CH}_3=\text{CH}_2 \text{NOCOCHR'-NOCOCH}_3 \\
\end{align*}
\]

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, 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 Solidthane-DMA (13) (Thiokol Corporation) containing three isocyanate groups per molecule (290.4 g.) was dissolved in dry benzene (1100 g.). Dry 1,3-bis(dimethylamino)-1-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/t was utilized to indicate reaction completion.

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

The stock solution (17.1 g.) was reacted at room temperature with polydibromopropylbutadiene 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 dibromopropene

The stock solution was reacted and isolated in the same way as in (1) but using 1,3-dibromopropene (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 acetone solvent. The resulting dark blue colored film was a tough flexible rubbery sheet. The room temperature resistivity found to be about \(1 \times 10^{10}\) ohm cm.

The modulus of the rubbery product is shown in FIG. 1, Curve 3.

A non-ionic Solithane was obtained by reactivating Solithane 1 and castor oil at 200° C. for 12 hours. A schematic of this material is illustrated as Curve 1, FIG. 1. The modulus temperature curves were determined by means of a modified Gehman Tester. The number of ionic links was determined by analysis of ionic 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 of 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 30° 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 containing the specimens of dibromopolybutadiene as compared to one crosslinked with dibromopropene. 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 of approximate molecular weight of 2000 (100 g. in 50 cc. of benzene) was reacted with toluene 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, 2,4-diisocyanate (DMAE) (8.9 g. in 5 cc. of benzene) was added while stirring. After standing for 4 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 in 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 VIII

Two moles of 2-dimethylaminoethanol (DMAE) were treated 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 (0.02 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. A white solid was recovered in the form of a yellow-gray rubber sheet having a shiny, slightly wrinkled surface. The product had good elasticity and a melting point of 190° C.

EXAMPLE III

P-dimethylaminophenol (2.7 g.) was mixed with 215 g. of polystyrene 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 (11.3 g.) was reacted at room temperature with dibromobutene (1.9 g.) dissolved in benzene (50 cc.). The reaction mixture 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-n-bromopropanol (42 g.). The mixture was heated at 50° C. for two hours and left standing at room temperature for 24 hours. N,N,N',N'-tetramethylenedihexane (25.8 g.) in benzene (100 g.) was then added to the mixture which was made homogeneous by mechanical stirring. The viscous solution was transferred to 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, neutral, anionic rubber sheet that contains a low molecular weight isocyanate, a typical dialkyldiamino alcohol and a high molecular weight organic dibromo compound. About 5.6 grams of hexamethylene di-isocyanate was added slowly with agitation to 9.6 grams of bis-1,3-(dimethylamino) 2-propanol in a flask and allowed to react at room temperature for 24 hours. About 15.2 grams of a viscous reaction product was obtained. A 1.4 gram 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 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.

EXAMPLE VI

This example illustrates the preparation of a soluble, non-crosslinked cationic rubbery material. Example I was repeated using stoichiometric amounts of polypolyethylene glycol di-isocyanate and 2-dimethylaminoethanol in benzene solution. After eight hours standing, a roughly equimolecular 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 tolulene di-isocyanate (TDI) and the same tetramethyl di-amino alcohol and dibromopolybutadiene. A rubber film was obtained from benzene or chloroform solutions.

EXAMPLE IX

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 Multranthane 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 chloroform content was doubled and the air bubbles in the surface decreased but the krinkling of the surface increased.

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 (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 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 9.0 grams of Polysear Rubber (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 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 (5000 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 ml. of a 1/1 acetone-DMF mixture were quickly added under agitation to 4.1 grams (0.002 mole plus 3% excess) of 1,6-dibromopropane. No immediate reaction was seen. Agitation at room temperature for 24 hours plus storage for 72 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 discolored 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. 4.7 grams (0.01 mole of a suspension of polydibromobutadiene (5000 M.W.) was added to the resulting viscous liquid with agitation. Slow agitation was continued for five minutes and almost clear liquid resulted, the few bubbles that formed disappearing 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 continuing 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, homogeneous liquid was obtained with crystalline particles separating after two weeks.

B. Polymerization of A with polydibromobutadiene

25 grams (0.005 mole) of polydibromobutadiene (5000 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 homogeneous liquid was spread in a thin layer over the pan. The solvent was evaporated at room temperature over a 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.
EXAMPLE XV

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, grayish-white opaque liquid was obtained. The liquid was then added drop-wise with stirring to 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 resultant 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-shiny, elastic, and had a shiny surface. The product starts to soften at 160°C.

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 polyether 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 and having a molecular weight of 1,024.

EXAMPLE XVI

25.6 g. of Adiprene L-100 (0.0025 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 (0.0025 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-0.02 mole) 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 at ambient temperature for 48 hours. The final product was a clear, light yellow sheet approximately 0.5 cm. thick, exhibiting good elasticity. The product had a shiny and smooth surface and become brownish-golden and softened at 185°C.

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 63.3%. 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 were eliminated with the aid of a spatula. The mixture soon stiffened. The solvent was evaporated in a hood at a 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 into 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 24 hours to form a viscous liquid.

The completion of reaction was established by infrared 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 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-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 viscous yellow 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 solvent was evaporated in 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 X 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.
kept covered until about 5 minutes. Most clear, color-fully poured into a molder in inverted, eliminated, 

The ambient temperature is a clear, light yellow, rubbery, thicken, to turn brown and 

clear at 50°C. for 5 hours. A benzene soluble rubbery transparent sheet was obtained.

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.

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 precipitated 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 heparin polymer washed in aceton yields 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 birefringence, hydropeliphilic 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:

$$R^1_-N^-R^1-OCHN-R^1-RHOCOOR^1-N^-R^1$$

where $R^1$ is a polybutadiene having a molecular weight from 3,000 to 5,000, $R^2$ is lower alkyl, $R^3$ is lower alkyl, $R^4$ is selected from phenyl, polyphenyl, polyoxyalkylene and alkyl of 4-20 carbon atoms and $n$ is an integer from 2 to 500.

2. A polymer according to claim 1 in which $R^3$ is methyl.

3. A polymer according to claim 2 in which $R^2$ is propyl.

4. A polymer according to claim 2 in which $R^1$ 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:

$$\left( R^1-R^1 \right)$$

where $R^1$ is polybutadiene having a molecular weight from 1,000 to 10,000, $R^2$ is lower alkyl, $R^3$ is lower alkyl, $R^4$ is selected from phenyl, polyphenyl, polyoxyalkylene and alkyl of 4-20 carbon atoms and $n$ is an integer from 2 to 500.

7. A polymer according to claim 6 in which $R^3$ is methyl.

8. A polymer according to claim 6 in which $R^2$ is ethyl.

9. A polymer according to claim 6 with tetracyanoquinodimethane.

10. A method of forming a cationic, viscoelastic polymer comprising the steps of:

11. A method according to claim 10 in which the polybutadiene has a molecular weight from 1,000 to 10,000 to form a solid elastomeric, polyquaternary material of the formula:

$$\left( R^1-R^1 \right)$$

where $R^1$ is lower alkyl; $R^2$ is alkyl of 1 to 10 carbon atoms; $R^3$ is selected from alkyl of 4-20 carbon atoms, phenyl and polyoxyalkylene and $q$ is an integer from 1 to 2;

dissolving the polytertiary amine in solvent and slowly adding to the solution a dibromopolybutadiene having a molecular weight from 1,000 to 10,000 to form a solid elastomeric, polyquaternary material of the formula:

$$\left( R^1-R^1 \right)$$

where $R^1$ is polybutadiene and $n$ is an integer from 2-500; and

12. A method of forming a complex having a higher conductivity than said material.

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