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/JR

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
FIG. 1

EFFECT OF CATIONIC GROUPS

The present invention relates to viscous elastic polymers and includes linear and branched polymeric mixtures and to linear and branched polymeric mixtures.

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Elastomer:
The presence of the cationic groups provides a permanent charge that can be further exploited with charge-transfer interactions. The polymers exhibit improved conductivity under the influence of the cationic groups. These materials find useful applications in printed circuit boards, master plates for photocopiers, and devices such as dust collectors. Furthermore, the presence of the cationic groups is associated with antimicrobial activity. The materials having the cationic groups also exhibit enhanced antifungal activity.

Most of the polymers described herein have been found to exhibit transition temperature damping mechanical stress. This is particularly interesting as it provides a means to characterize these materials. In applications where low damping properties are required, the present invention provides materials that meet these needs.

INVENTOR.
ALAN REMBAUM

BY
1. D. E. Freidin
FIG. 2
EFFECT OF MOLECULAR WEIGHT

TEMPERATURE, °C

INVENTOR.
ALAN REMBAUM

MODULUS, dynes/cm²

BY
Leidenburg & Freilich
ATTORNEYS.
The present invention relates generally to cationic viscoelastic polymers and to methods of polymerizing novel monomeric or polymeric 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 starting materials. 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 for forming charged layers 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 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 mechanical strength and the elasticity has not been high enough to provide elastomeric products having commercially interesting properties.

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 R" may be selected from the following materials: hydroxyl, amino, carboxyl, anhydride or isocyanate.

Compounds Y-R"-Z-Y (II) and Y-R"-Z-R' (III)

where R" and R' are organic radicals such as hydrocarbyl, 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 R" may be selected from the following materials: hydroxyl, amino, carboxyl, anhydride or isocyanate.

Compounds Y-R"-Y (Y2) and Y-R" (Y3)

may be a ditertiary amine material and a dihalo material. R" and R" may contain at least two carbon atoms and may be of polymeric or prepolymer length. Exemplary dihalo compounds are α (alpha), Ω (omega) alkyl or alkenyl bromides containing at least two carbon atoms. Suitably, the bromide may be a terminal dibrominated aliphatic such as dibromomethane, dibromopropane, dibromobutane, dibromomethane, dibromobenzene, dibromomethane, and similar homologs through dibromohexadecane. Dibromomoramics 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 tertary amines are N,N,N',N'-tetramethylethylhexamethylene diamine, N,N,N',N'-tetramethyldi-

carboxyethylamine, 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, tetramethylenim bronoz-

phenone or diazine. Other di tertary compounds may be

formed from heterocyclic compounds such as piperidine,

picoline, quinoline, acridine, or phenan-thridine. The

amine may also be of polymer length. For example, an

isocy anate 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 lamino hydroxyethanol which will link to the

polybutadiene to form a long chain di tertary amine.

Other suitable compounds of Formula H are bromo-

substituted isocyanates are reacted with diols or

di materials having a functionality very near to two. Another

suitable commercially available polyaryl polyisocyanates,

such as 3,655,814, and 3-3,655,814 phenol or, 3-bromo, n-propanol. It is understood that

benzene-1,3-diisocyanate, hexane-1,6-diisocyanate, tolylene-2,4-diisocyanate (TDI),
tolylene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate,
diphenyl-3,3'-dimethyl-4,4'-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-1,3,7-tetrasocyanate, naphthalene-1,3,7-trisocyanate,
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 isocy-

inate terminated polyoxyalkylene glycol having a molecular

weight of about 1,000, Multhane-242F (Mobay) a polyester terminated with isocyanate groups and Sol-

thane 113 (Thiokol) which is a trisocyanate derivative of glycerol and ricinoleic acid.

The halo or tertiary amino alcohol may suitably be

alkylated or reacted with an isocyanate before reaction with a

diisocyanate to form a urethane linkage. Further reaction with dibromo-

butane results in quaternization of the nitrogen atoms

and chain extension to form a polymer having a repeating

unit of the formula:

Each hydroxy group joins an isocyanate group to form a

urethane linkage. Further reaction with dibromo-

butane results in quaternization of the nitrogen atoms

and chain extension to form a polymer having a repeating

unit of the formula:
The vinylene glycol having a molecular weight of 3500 (35 g.) dissolved in benzene (86 g.). Dry 1,3-bis(dimethylamino)-2-isocyanate groups per molecule (290.4 g.) was dissolved in dry benzene (1100 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 dibromopropylcne glycol

The stock solution was reacted and isolated in the same way as in (1) but using 1,3-dibromopropylcne glycol (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 x 10^8 ohm·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 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 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 +35°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 dibromopropylcne glycol as compared to one crosslinked with dibromopropylcne. 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 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-dimethylaminohexane (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.

The product contained 5.7% of ionic bromine and could be molded at 90°C. under pressure.

EXAMPLE III

P-dimethylaminophenol (2.7 g.) was mixed with 215 g. of polyethylene glycol disiocyanate (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 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-n-bromopropylene (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'-tetramethylaminohexane (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 cationic rubber from a low molecular weight isocyanate, a typical dialkyl diamino alcohol and a high molecular weight organic dibromo compound. About 5.6 grams of hexaethylene 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 stoechiometric amounts of polypropylene glycol di-isocyanate and 2-dimethylaminooctanol in benzene solution. After eight hours standing, a roughly equimolar quantity of 1,4-dibromobutene 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 disiocyanate (TDI) and the same tetramethyl diamino alcohol and dibromopolybutadiene. A rubbery film was obtained from benzene or chloroform solutions.

EXAMPLE VIII

Two moles of 2-dimethylaminooctanol (DMAE) were reacted with one mole of PAPI to form a DMAE/PAPI adduct having a molecular weight of 226.5. 4.5 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. Then at room temperature in a dry box for a week. 31 grams of polymer was recovered in the form of a yellow-gray rubbery sheet having a shiny, slightly wrinkled surface. The product had good elasticity and a melting point of 190°C.
EXAMPLE IX
Two moles of 1,3-bis-(dimethylamino)-2-propanol (DMAP) were mixed with 1 mole of Multranthae 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 bath the reaction mixture was doubled and the air bubbles in the presence decreased but the knitting 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 mls. of benzene. This solution was then thoroughly mixed with a solution of 30 grams of Polyar, diisocyanate 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 0.2-0.5 cm. The product was non-sticky and had a shiny surface. The sheet was elastic and had a softening point above 185° 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 of Polyar, diisocyanate rubber (10% molecular excess) 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 Polyar, 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 of 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 (0.02 mole plus 3% excess) of 1,6-diisocyanatohexane in DMF. No immediate reaction of 1,3-dibromopropane took place. As 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 discolors to 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 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 discolors to 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 (5,000 M.W.) was added to the resulting viscous liquid with agitation. Slow agitation was continued for five minutes and a nearly 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 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) of 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 (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. Multithane-DMAP addition compound
The synthesis was again conducted under extremely dry conditions. 25.8 grams of Multithane 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 was a 50% solution in benzene.

Ring 9.7 g. of the 50% solution in benzene described 75.

Agitation was continued for 16 hours at ambient temperature. Liquid was added dropwise under stirring to a solution of 33 g. of dry benzene. The resulting, fairly viscous liquid was added drop-wise, under stirring to a solution of 25.6 g. of Adiprene L-100 containing 4.1% isocyanate groups and having a molecular weight of 5,000 were dissolved in 60 g. of solvent.

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-sticky, 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 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 groups and having a molecular weight of 1,024.

**EXAMPLE XVI**

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 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 softening 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 6.35%. 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 under 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 into a Teflon coated mold. After evaporation of benzene a rubbery sheet was obtained.

**EXAMPLE XIX**

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

The reaction product obtained as described above (6.6 g.) was intimately mixed with 1,4-dibromobutane (0.93 g. in 50 ml. of benzene) and the mixture was placed in a shallow mold. A rubbery 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.

**EXAMPLE XX**

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 infra red spectrophotometry. The reaction product is a viscous yellow liquid.

**EXAMPLE XXX**

Conversion of A to a tertiary amine prepolymer

The reaction product obtained as described above (6.6 g.) was intimately mixed with 1,4-dibromobutane (0.93 g. in 50 ml. of benzene) and the mixture was placed in a shallow mold. A rubbery 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.

**EXAMPLE XXXI**

Copolymerization of B with dibromobutene

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 IR. 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 (132 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.

**EXAMPLE XXXII**

E. Complexing D with TCNQ

1. cm.² of this film was immersed in a methanol solution of lithium tetracyanoquinoimethane (0.1% by weight). The resulting dark colored film after drying had a resistivity equal to $5 \times 10^{8}$ ohm cm.

**EXAMPLE XXXIII**

F. Reaction of D with heparin

1. cm.² 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.
rubbery, elastic, and transparent 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 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 was dissolved in acetonitrile 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 have 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 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:

\[ R^1 - N^+ - C \equiv \text{OCH}_2 - R^2 - N^+ - C \equiv \text{OCH}_2 - R^3 - N^+ - C \equiv \text{OCH}_2 - R^4 - N^+ - C \equiv \text{OCH}_2 - R^5 \]

where \( R^1 \) is a polybutadiene having a molecular weight from 1,000 to 10,000, \( R^2 \) is lower alkyl, \( R^3 \) is selected from phenyl, polyphenyl, polyoxyethylene and alkyl of 4-20 carbon atoms and \( n \) is an integer from 2 to 50.

2. A polymer according to claim 1 in which \( R^2 \) is methyl.

3. A polymer according to claim 2 in which \( R^3 \) is propyl.

4. A polymer according to claim 2 in which \( R^4 \) 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:

\[ R^1 - N^+ - C \equiv \text{OCH}_2 - R^2 - N^+ - C \equiv \text{OCH}_2 - R^3 - N^+ - C \equiv \text{OCH}_2 - R^4 - N^+ - C \equiv \text{OCH}_2 - R^5 \]

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, polyoxyethylene 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 in which \( R^3 \) is ethyl.

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

(a) reacting at least two moles of tertiary amino alkanol with a diisocyanate in solvent under anhydrous conditions to form a polymeric amine of the formula:

\[ R^1 - N^+ - C \equiv \text{OCH}_2 - R^2 - N^+ - C \equiv \text{OCH}_2 - R^3 - N^+ - C \equiv \text{OCH}_2 - R^4 \]

where \( R^1 \) is lower alkyl; \( R^2 \) is alkyl of 1 to 10 carbon atoms; \( R^3 \) is alkyl of 4-20 carbon atoms, phenyl and polyoxyethylene and \( q \) is an integer from 1 to 2;

(b) dissolving the polymeric 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:

\[ R^1 - N^+ - C \equiv \text{OCH}_2 - R^2 - N^+ - C \equiv \text{OCH}_2 - R^3 - N^+ - C \equiv \text{OCH}_2 - R^4 \]

where \( R^1 \) is polybutadiene and \( n \) is an integer from 2-500; and

(c) reacting said material with tetracyanoquinodimethane to form a complex having a higher conductivity than \( n \) said material.

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

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

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