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: PASADENA, CA
Supplementary Corporate Source (if applicable): CALTECH/IRK
NASA Patent Case No.: NPO-10,830-1

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

YES [ X ] NO [ ]

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

Bonnie L. Henderson

Enclosure

(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 the preparation of cationic polymers containing an urethane linkage between nitroaryl residues which provide a pesticidal activity. The pesticidal activity of these materials has been found to be particularly effective in printed circuits. Polymeric mixtures of these materials provide a pesticidal activity, and further contain damping mechanical properties.

Most of the materials have been found to have transition temperature damping mechanical properties; the results are shown in the diagram. The invention has been found to be particularly interesting when applied to the preparation of a pesticidal material containing urethane linkage between nitroaryl residues. The present invention is also useful for the preparation of polymeric mixtures containing urethane linkage between nitroaryl residues.
FIG. 2
EFFECT OF MOLECULAR WEIGHT

TEMPERATURE, °C

MODULUS, dynes/cm²

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3,655,814

VISCOELASTIC CATIONIC POLYMERS CONTAINING THE URETHANE LINKAGE

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ABSTRACT OF THE DISCLOSURE

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

\[ \left[ R_1 \right]_{m} \left[ R_2 \right]_{n} \]

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

ORIGIN OF THE INVENTION

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. 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 polyelectrolytes having a repeating unit of the formula:

\[ \left[ R_1 \right]_{m} \left[ R_2 \right]_{n} \]

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 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 formula:

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

and

\[ Y-R^5-Z-R^6-Z-R^7-Y \]

with a compound selected from those of the formulae:

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

and

\[ Y-R^2-Z-R^10-Z-R^8-Y \]

where \( R^2-R^{15} \) are organic radicals such as hydrocarbyl, Y is a quaternary forming moiety such as tertiary nitrogen or halo and \( Z^2 \) and \( Z^4 \) are coreactive condensable moieties such as hydroxy and isocyanate urethane forming groups. At least one of compounds II or III contains a \( Z \) residue or the II–III pair contains \( Z^2 \) 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 \( Z^2 \) and \( Z^4 \) can be selected from hydroxyl, amino, carboxyl, anhydride or isocyanate.

Compounds \( Y-R^4-Y \) (III) and \( Y-R^7-Y \) (III) may be a ditertiary amine material and a dihalo material. \( R^4 \) and \( R^7 \) contain at least two carbon atoms and may be of polymeric or prepolymeric length. Exemplary dihalo compounds are \( \alpha \) (alpha), \( \Omega \) (omega) alkyl or alkaryl bromides containing at least two carbon atoms. Suitably, the bromide may be a terminal dibrominated aliphatic such as dibromomethane, dibromopropane, dibromobutane, dibromobutene, dibromohexane, dibromomdecane, and similar homologs through dibromohexadecane. Dibromoaromatics or alkylated aromatics such as dibromo-
xylenes 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-tertiary amines are N,N,N',N'-tetrakis(dimethylamino)amine, N,N,N',N'-tetramethylenediamine, 1,2-bis-(4-pyrrolyl)-ethane, 1,2-bis-(2-pyrrolyl)-ethane, 1,2-bis-(4-pyrrolyl)-ethane, and N,N,N',N'-di-(4-benzylation)-ethane, tetramethylenephenoxophene 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 hydroxalkyl substituted tertiary amine such as dimethylenedioxyethanol which will link to the polybutadiene to form a long chain di-tertiary amine. Other suitable compounds of Formula (II) are bromo- and chloro-compounds. N,N,N',N'-tetramethylmethylenediamine is suitable for use in the invention such as the dibromo or the diisocyanate polymers discussed above. Suitable materials for this purpose are brominated polyethylene, polyaryl polyisocyanates, polybutadiene, and the like. A suitable commercially available polyaryl polyisocyanate is PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.). This material is known as PAPI-1 (The Carvin Co.).

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 polycyosylicinate reacted with a tertiary amino alcohol will form a polytertiary amine of the formula:

\[
\text{R}^1 \text{N} = \text{R}^2 \text{OCHN} - \text{R}^3 \text{NHCOO} - \text{R}^4
\]

where \( \text{R}^1 \) is lower alkyd, \( \text{R}^2 \) is lower alkyd, \( \text{R}^3 \) is selected from phenyl, polyphenyl, polyoxyethylen, or alkyl of 4-20 carbon atoms and \( q \) is 1 or 2.

Reaction of the polytertiary amine with \( q = 1 \) with a dibromopolybutadiene will form a linear polymer of the formula:

\[
\text{R}^1 \text{N} = \text{R}^2 \text{OCHN} - \text{R}^3 \text{NHCOO} - \text{R}^4
\]

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

\[
\text{R}^1 \text{N} = \text{R}^2 \text{OCHN} - \text{R}^3 \text{NHCOO} - \text{R}^4
\]

where \( n, \text{R}^1, \text{R}^2, \text{R}^3 \) and \( \text{R}^4 \) have the above meanings. For example, the reaction of bis-1,3-(dimethylamino)-2-propanol and hexamethylene diisocyanate is illustrated below:

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

\[
\text{CH}_3 \text{N}-\text{CH}_3
\]

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, diphenylmethane-4,4'-diisocyanate, naphthalene 1,5-diisocyanate, diphenyl-3,3'-dimethyl-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-tetraisocyanate, naphthalene-1,3,7-trisocyanate, toluidine-diisocyanate, isocyanate terminated prepolymers, polynaryl polyisocyanates, and the like. A suitable commercially available polynaryl polyisocyanate is a polytetrahydro furyl phenyl isocyanate known as PAPI-I (The Carvin Co.). This material has an average of 3 isocyanate groups per molecule and an average molecular weight of about 380.

Other commercially available higher molecular weight polyisocyanates are Adiprene 100 (Du Pont) an isocyanate terminated polyoxyalkylene glycol having a molecular weight of about 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 an aliphatic or aromatic such as 1,3-bis(dimethylamino)-2-propanol, 2-dimethylaminomethanol, bromoethanol, p-dimethylaminophenyl methyl carbino, p-dimethylaminophenol 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 hydroxyl 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 dibalide 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 tetracyanoquinodimethane (LiTNCQ), and neutral tetracyanoquinodimethane (TCNQ).

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

REACTION 1

\[
\text{OCN-R'-NCO} + 2\text{OH-R-N-(CH}_2\text{)}_2 \rightarrow \text{[OCN-R'-NCOH-(NHCOOR-N-(CH}_2\text{)}_2]} + \text{Br-R''-Br}
\]

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 alky groups, aryl groups such as benzyl, aralkyl 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.

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

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

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

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

The flexible cationic rubber sheet prepared in (2) was treated with Li-TCNQ and neutral TCNQ by boiling the sheet for a few hours with an equimolar quantity of Li-TCNQ and then treating this sheet with boiling neutral TCNQ in acetonitrile solvent. The resulting dark blue colored film was a tough flexible rubbery sheet. The room temperature resistivity was found to be about 1 × 10^9 ohm^-1 cm^-1. The modulus of the rubbery product is shown in FIG. 1, Curve 3.

A non-ionic Solithane specimen was obtained by reacting Solithane 113 with castor oil at 200° F. for 12 hours. The modulus of this material is illustrated as Curve 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 glycol crosslinked by means of dibromopolybutadiene as compared to one crosslinked with dibromomopropane. 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-dimethylaminomethanol (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

9 Two moles of 1,3-bis-(dimethylamino)-2-propanol (DMAP) were mixed with 1 mole of Multranthene 242F to form a diterary 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 dibromobutadiene (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 wrinkling of the surface increased.

EXAMPLE X

A tetra-tertiary amine prepolymer was synthesized from 1 mole of hexamethylene disiacyanate 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 Polyisorbar rubber (5,000 molecular weight dibromobutadiene) 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 13.0 grams of Polyisorbar 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 and had a softening point above 165°C in a desiccator and yield was 29 grams.

B. Polymerization with dibromobutadiene

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 Polyisorbar (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 ml. of a 1/1 acetone-DMF mixture were quickly added under agitation to 4.1 grams (0.02 mole plus 3% excess). No immediate reaction of 1,3-dibromopropanol took place. Agitation at room temperature for 24 hours rendered the mixture cloudy. Homogenous rubber resin conglomerates were precipitated in petroleum ether. Final yield was 12 grams after drying in a desiccator. The product was a yellow-gray, non-sticky elastomer which 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 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 disiocyanate (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 almost clear liquid resulted, the few bubbles that formed disappeared after several minutes. The reaction mixture was then carefully transferred into polyethylene pans. After evaporation of the solvent for 48 hours, the material was removed from the pan and dried for 24 hours. A brownish, almost opaque rubber sheet was obtained. The sheet was elastic, bubble free, non-sticky and had a smooth dull surface.

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

EXAMPLE XIII

A. Preparation of an addition compound with hexane disiocyanate

5.0 grams (0.03 mole) of 1,6-dioxyanotetrahexane 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 (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 polystyrene 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. Multranthene-DMAP addition compound

The synthesis was again conducted under extremely dry conditions. 25.8 grams of Multranthene 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 polystyrene 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.
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 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 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-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 polynsilylene polymer terminated with isocyante groups and the resultant polymer formed by reaction with a dibromo compound. The particular prepolymer utilized was Adiprene L-100 containing 4.1% isocyante 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-0.06 mole) in 60 grams 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 drop-wise 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. After almost clear, colorless fairly viscous liquid was then slowly poured into a glass pan in the bubbles for forming by poured, eliminating 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 (Thiokoll 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 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 3 moles of bis-1,3-dimethylamino-2-propanol (0.497 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 (0.548 g.) at 60° C. for 26 hours. The rate of reaction was followed by observing the disappearance of absorption peak at 4.4 microns. The resulting reaction product was a colorless viscous liquid.

C. Copolymerization of B with dibromobutene

The reaction product obtained as described above (6.6 g.) was intimately mixed with 1,4-dibromobutene (0.93 g. in 58 ml. of benzene) and the mixture was placed in a shallow metal 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 J.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 cm.² of this film was immersed in a methanol solution of lithium tetracyano quinodimelhane (0.1% by weight). The resulting dark colored film after drying had a resistivity equal to 5×10⁴ ohm cm.

F. Reaction of D with heparin

1 cm.² of the same film was kept for 2 hours in a methanol-tetrhydrofuran-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.
except covered until about 5 minutes. most clear, colorless to a light yellow rubbery, elastic, to turn brown and

raring, eliminated except covered until

ianol at 50° C. for

rubbery, elastic, at ambient tempera-

ito a Teflon coated

lybutadiene of ap-

uxture was placed in

mine prepolymer

approximately molec-

ical toluene di-

on an analyzer and

followed by I.R. The re-

on a dye (Azure A) test.

followed by infra red reaction was followed by means of I.R. The reaction

rubbery sheet was

in a methanol solu-

amine prepolymer

braided as described

 amino-2-propanol. The rate of reaction

ance of absorbing

reaction product is

rubber butadiene

rubber

in a Teflon coated

rubber prepolymer

mately mixed with 3-

at 50° C. for 24

N. The re-

in a methanol solu-

amine prepolymer

in a solution of sodium he-

for 2 hours in a

sodium he-

in a solution of sodium he-

propion 45:45:1) with water contained

D. A polymer according to claim 2 in which R 1 is methyl.

D. A polymer according to claim 6 in which R 3 is methyl.

D. A polymer according to claim 6 in which R 2 is ethyl.

D. A polymer according to claim 6 complexed with tetracyanoquinodimethane.

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

D. A method according to claim 10 in which the

References Cited

UNITED STATES PATENTS

2,955,108 10/1960 Omietanski 260—205

3,036,998 5/1962 Rudner 260—775

3,294,752 12/1966 Wilkinson 260—775

3,321,415 5/1967 Hennig et al. 260—29.2

3,388,087 6/1968 Dieterich et al. 260—29.2

3,397,184 8/1968 Heylolkamp et al. 260—77.5

3,415,768 12/1968 Dieterich et al. 260—29.2

FOREIGN PATENTS

912,491 4/1962 Great Britain 260—77.5

1,006,151 9/1965 Great Britain 260—77.5

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