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

In accordance with the procedures agreed upon by Code GP-4 and Code NHB, the enclosed NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No.: 3,538,053
Government or Corporate Employee: California Institute of Technology, Pasadena, CA
Supplementary Corporate Source (if applicable): JPL
NASA Patent Case No.: NPO-10,557

NOTE - Is this an invention made by a corporate employee of a NASA contractor? YES [X] NO [ ]

If "YES" is checked, 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..."

Elizabeth A. Carter

Enclosure

(NASA-Case-NPO-10557) NUCLEAR ALKYLATED PYRIDINE ALDEHYDE POLYMERS AND CONDUCTIVE COMPOSITIONS THEREOF Patent (NASA) 3 p

CSCL 07C

00/27 05409
The background of the invention

The present invention relates to novel polymers and to conductive compositions incorporating the same. More particularly, the invention relates to solid and polymerizable compositions and to methods of synthesizing and utilizing such polymers.

Description of the prior art

Recently, solid nitrogen-containing polymers with poly-electrolyte properties have been synthesized. These polymers are of considerable interest due to the discovery of the pseudo-metallic behavior of certain heterocyclic organic salts. The polymers are of interest since being organic in nature, they provide greater resistance to radiation and cosmic rays than that exhibited by conventional inorganic crystalline conductors.

The available poly-electrolyte nitrogen-containing polymers suffer from complex processing with specially prepared starting materials and the conductivity and heat stability have not been particularly high. It would be desirable to prepare polymers having conductivity approaching that of inorganic semiconductors that could be prepared from readily available low-cost materials and under mild and simple synthesis conditions and procedures. These and other objects and attendant advantages of the invention will be apparent as the description proceeds.

According to the invention, polymers of the formulae:

\[
\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}
\]

are prepared by reacting in the presence of catalyst an alky!ated pyridine aldehyde of the formulae:

![Chemical structure]( attachment: chemical_structure.png)

where \( n \) is an integer greater than 2 and \( R' \) is aromatic or aliphatic. The pyridine groups are linked by olefinic groups between 2-, 4-, or 6-nuclear alkylated 2-, 3-, or 4-pyridine aldehyde or quaternary derivatives thereof to form a polymer of the formulae:

\[
\begin{align*}
\text{CH} = \text{CH} & \quad \text{or} \quad \text{CH} = \text{CH} \\
& \quad \text{or} \quad \text{CH} = \text{CH}
\end{align*}
\]

where \( n \) is an integer greater than 2 and \( R' \) is aromatic or aliphatic.

According to the invention, polymers of the formulae:

\[
\begin{align*}
\text{CHO} & \quad \text{and} \quad \text{CHO} \\
& \quad \text{and} \quad \text{CHO}
\end{align*}
\]

are prepared by reacting in the presence of catalyst an alky!ated pyridine aldehyde of the formulae:

![Chemical structure]( attachment: chemical_structure.png)

where \( R \) is a lower alkyl of 1 to 5 carbon atoms, \( n \) is an integer greater than 2 and preferably an integer from 10 to 1000 or more, and \( R' \) is a quaternizing moiety selected from the group consisting of aliphatic and aromatic moieties and preferably is lower alkyl, aryl, lower alkenyl or lower aralkyl.

The aldehyde group may be on any of the five ring carbon positions. The alky! group (R) must be positioned on one of the remaining four carbon positions in which it is activated by the ring nitrogen atom. For example, when the aldehyde is in the 2-position, the alky! group can be in the 4- or 6-position. When the aldehyde is in the 3-position, the alky! can be in the 2-, 4-, or 6-position, and when the aldehyde is in the 4-position, the alky! may be in the 2- or 6-position. Thus the olefin (-\( \text{CH} = \text{CH} \)) group will bridge repeating pairs of pyridine molecules between 2-, 4-, 2-, 3-, 4-3, 3-6 or 4-6 positions.

Exemplary pyridine carboxaldehydes for use in the process of the invention are 6-methyl-2-pyridine-carboxaldehyde, 4-methyl-2-pyridine-carboxaldehyde, and 2-methyl-4-pyridine-carboxaldehyde. The polymerization catalyst may be either acidic or basic and is of the class that induces the activated R (alkyl) and an aldehyde moiety from a pair of pyridine carboxaldehyde molecules to eliminate water to form a bridging olefin group. The pyridine aldehyde monomers are reacted in presence of the catalyst until a solid resin or polymeric product is obtained. In the case of the first aforementioned non-quaternized pyridine carboxaldehyde monomeric materials, the reaction is suitably conducted with heating and stirring at temperatures about 140° C. for a period of one-half to 24 hours or more until a polymer is obtained. The catalyst may be an acid or acid anhydride. A preferred catalyst is acetic anhydride but other catalysts such as phosphorus pentoxide or zinc chloride are also effective in forming polymers according to the invention. Polymerization of the quaternized compounds is catalyzed by organic bases such as pyridine or piperidine. When acetic anhydride is utilized, it may be used as the solvent for the polymerization.

The quaternary analogues of the polymer described above can be prepared by quaternization of the pyridine
3

carboxaldehyde monomer. The quaternization reaction proceeds by direct addition of quaternization reagents to the pyridine carboxaldehyde. Suitable quaternization reagents are the halides or sulfates of the desired quaternary moiety such as methyl iodide, allyl, or lower aralkyl iodides or sulfates such as methyl iodide or dimethyl sulfate.

It has further been discovered according to the invention that the quaternary pyridine derivative readily undergoes polymerization with mild alkaline catalyst in aqueous solution. The base-catalyzed polymerization proceeds at room temperature to form a black polymer having low specific resistivities of about 1 X 10^8 ohm-cm. The quaternary derivative obtained with dimethyl sul fate is found to be a black water-soluble polymer while that obtained with methyl iodide is found to be water-insoluble. The quaternized polymers may also be obtained by quaternization of the first described polymer with quaternization reagents. More severe conditions are required to quaternize the final polymer, heating and stirring with reflux being utilized to form the analogous products.

Compositions of even higher conductivity can be prepared by forming polymeric analogues of organic charge transfer complexes with a negative organic charge transfer complexing agent. For example, the polymeric quaternary pyridinium polymer of the invention, (P)+n, can be combined with a salt of 7,7,8,8-tetracyanoquinodimethane (TCNQ) to form products believed to have the structure (P)+ (TCNQ)n where n represents the number of quaternary nitrogen centers in the polymer. The mechanism of electronic transporters or pseudo-metallic behavior of the polymeric salts is not well understood. The salts have also been found to exhibit even higher electrical conductivity in the presence of neutral cyano compounds such as neutral TCNQ. On addition of neutral TCNQ, the resistivity of the product is further lowered, probably caused by increased electron delocalization. These charge transfer complexes are formed by dissolving the polymer and the TCNQ in mutual solvents such as methanol. The resulting precipitate is filtered and dried to form the desired charge transfer complex.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will now be illustrated by the following detailed examples of practice. It is to be understood that these examples are offered by way of illustration only and are not intended in any way to limit the invention.

Example I

Seventy-three grams of purified 6-methyl-2-pyridine-carboxaldehyde were added to 200 cc. of acetic anhydride. The mixture was heated with stirring at reflux for about 18 hours. The mixture was rendered basic with aqueous potassium hydroxide and stirred for one hour. The solid material that formed was removed by filtration and was washed in 1500 cc. of distilled water. The solid polymers was reprecipitated by potassium hydroxide, refiltered, and vacuum dried for two days at 50° C. to yield 64.04 grams of solid (87.89% yield). The polymer forms a black film on vacuum dried for two days at 50° C. to yield 64.04 grams (87.89% yield). The polymer is believed to have the structure indicated below:

\[
\begin{array}{c}
\text{CH} \equiv \text{CH} \\
\text{C}_2 \text{H}_5
\end{array}
\]

Sixty-one grams of the polymer were dissolved in 200 cc. of methanol and were passed through an alumina column to yield three fractions which were vacuum evaporated, and dried in an oven at 50° C. for 18 hours. The first fraction of about 9 grams exhibited shrinking at 265° C. with little change noted through 330° C. A second fraction of about 18.5 grams shrank at about 310° C. with again little change through 330° C. The third fraction of about 16.5 grams exhibited little change with no charring evident through 330° C.

The quaternary polymers can be prepared by quaternization of the polymer of Example I with typical quaternization reagents such as dimethyl sul fate or methyl iodide.

Example II

Ten grams of the polymer of Example I were reacted with a stoichiometric excess of dimethyl sul fate. The weight of the final product demonstrates a quantitative uptake of dimethyl sul fate to form a quaternary polymer of the formula:

\[
\begin{array}{c}
\text{CH} \equiv \text{CH} \\
\text{C}_2 \text{H}_5
\end{array}
\]

When methyl iodide was substituted for the dimethyl sul fate, a water-insoluble polymer was formed in high yield. The quaternary polymer can also be prepared by pre-quaternization of the pyridine aldehyde monomers. With the quaternized monomers, it has been discovered that the polymerization reaction will proceed under very mild conditions of room temperature and mild alkali such as 25% alkali metal hydroxide or 1% of piperidine.

Example III

2.5 grams of 6-methyl-2-pyridine-carboxaldehyde were reacted at 25° C. with 2.6 grams of dimethyl sul fate in ether. 20 cc. of a 25% KOH aqueous solution were added to an aqueous solution of the resulting quaternary compound, and a black water-soluble polymer resulted. When methyl iodide was utilized as the quaternization reagent, the resulting polymer was water-insoluble.

The specific resistance of the black water-soluble quaternary polymer was measured and found to be about 1 X 10^8 ohm-cm. A quantity of the quaternary polymer was dissolved in aqueous methanol and a molar equivalent amount of lithium-TCNQ was added to the solution of polymer. The specific resistance of the composition was lowered to 1 X 10^7 ohm-cm. This conductivity is comparable to that of some conventional inorganic semiconductors.

Thus, a new class of conductive organic polymeric compositions have been provided by the invention. These compositions can be used in the fabrication of conductive coatings, anisotropic materials and as conductive heat-resistant compounds for use in the fabrication of electronic components. Polymers can be formed from soluble starting material at very low polymerization temperatures, thus rendering the polymers readily adaptable to the preparations of films, molded structures and coatings. The polymeric compositions of the invention exhibit a high conductivity compared to other polymers and organic complexes and materials. The conductivity in some of the products approaches that of inorganic semi-conductors, and inorganic metal compounds, they appear to be more radiation and cosmic ray resistant than typical inorganic crystal materials. Moreover, the polymers of the invention which are soluble in methanol can readily be fabricated into thermally stable films of relatively high conductivity by casting a solution of the polymer in methanol onto a surface and evaporating the methanol. Furthermore, the polymers are synthesized from readily available low-cost starting materials and thus would appear to be considerably less expensive than any known family of conductive organic 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, all without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A method of synthesizing a solid polymer comprising the steps of:
   condensing in the presence of a catalyst selected from the group consisting of zinc chloride and acetic anhydride a nuclear alkylated pyridine aldehyde of the formula:
   \[
   \begin{array}{c}
   \text{HCC} \\
   \text{CHO}
   \end{array}
   \]
   where \( R \) is lower alkyl of 1 to 5 carbon atoms until a solid polymer of the formula:
   \[
   \begin{array}{c}
   \text{CH}=\text{CH} \\
   \text{R}
   \end{array}
   \]
   is obtained where \( n \) is an integer greater than 2 and the \(-\text{CH}=\text{CH}-\) olefinic group is positioned between 2-4, 2-6, 2-3, 3-4, 3-6, or 4-6 positions on a pair of molecules.

2. A method according to claim 1 in which said pyridine aldehyde is 2-, 4-, or 6-methyl-pyridine-2-, 3-, or 4-carboxaldehyde.

3. A method according to claim 2 in which said aldehyde is selected from the group consisting of 6-ethyl-2-pyridine-carboxaldehyde, 4-methyl-2-pyridine-carboxaldehyde and 2-methyl-4-pyridine-carboxaldehyde.

4. A method according to claim 1 wherein said catalyst is acetic anhydride.

5. A method of synthesizing a polymer comprising the steps of:
   condensing at low temperature in the presence of a mild alkali catalyst a nuclear alkylated pyridine aldehyde of the formula:
   \[
   \begin{array}{c}
   \text{HCC} \\
   \text{CHO}
   \end{array}
   \]
   \( R' \) is a quaternizing moiety selected from the group consisting of lower alkyl, aryl, lower alkenyl and lower aralkyl until a solid polymer of the formula:
   \[
   \begin{array}{c}
   \text{CH}=\text{CH} \\
   \text{R'}
   \end{array}
   \]
   is obtained where \( n \) is an integer greater than 2 and the \(-\text{CH}=\text{CH}-\) olefinic group is positioned between 2-4, 2-6, 2-3, 3-4, 3-6, or 4-6 positions on a pair of molecules.

6. A method according to claim 5 wherein said catalyst is selected from potassium hydroxide, pyridine and piperidine.

7. A polymer having a specific resistivity of no more than \( 10^9 \) ohm-cm, of the formula:
   \[
   \begin{array}{c}
   \text{CH}=\text{CH} \\
   \text{R'}
   \end{array}
   \]

References Cited
UNITED STATES PATENTS
3,422,071 1/1969 Thomson.

OTHER REFERENCES

WILLIAM H. SHORT, Primary Examiner
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U.S. Cl. X.R.