FIRE RESISTANT POLYAMIDE BASED ON 1-[(DIORGANOXY PHOSPHONYL)METHYL]-2,4- AND -2,6- DIAMINO BENZENE

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Notice: The portion of the term of this patent subsequent to May 6, 2003 has been disclaimed.

Related U.S. Application Data


ABSTRACT

1-[(Diorganoxyphosphonylmethyl)]2,4- and -2,6-diamino benzenes are reacted with polyacylhalides and optionally comonomers to produce polyamides which have desirable heat and fire resistance properties. These polymers are used to form fibers and fabrics where fire and flame resistance properties are important, e.g., aircraft equipment and structures.

20 Claims, No Drawings
FIRE RESISTANT POLYAMIDE BASED ON 1-[(DIORGANOXYPHOSPHONYL)METHYL]-2,4- AND -2,6- DIAMINO BENZENE

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 U.S.C. 2457).

RELATED APPLICATIONS

This application is a continuation-in-part of our commonly assigned patent application Ser. No. 522,629, filed Aug. 16, 1983, which is incorporated herein by reference. This application is also related to the following commonly assigned patent applications: U.S. Ser. No. 641,152, filed Aug. 16, 1984, which is directed to dinitrobenzene compounds of the formula:

\[(RO)_{2}P-\text{CH}2-X-Y\]

and the corresponding amines which are employed herein as monomers; U.S. Ser. No. 641,142, filed Aug. 16, 1984 which is directed to polymers and epoxy copolymers prepared from the above dinitrobenzenes; U.S. Ser. No. 641,143 now U.S. Pat. No. 4,536,565, filed Aug. 16, 1984, which is directed to polyimides and copolyimides prepared from the above dinitrobenzenes; and U.S. Ser. No. 641,147, filed Aug. 16, 1984, which is directed to maleimido and citraconimido-substituted derivatives of the above dinitrobenzenes.

FIELD OF THE INVENTION

The invention relates to fire resistant polymers derived from 1-[(diorganoxyphosphonyl)methyl]-2,4- and -2,6-diamino benzenes by reacting them with diacyl halides or with dianhydrides of higher functionality. These polymers have good fire and heat resistant properties and good mechanical properties which are useful, for example, as laminating agents for structural parts of aircraft and space vehicles.

BACKGROUND OF THE INVENTION

Certain phosphorus-containing organic compounds are known to be fire retardant when mixed with or incorporated chemically in polymers. Among such phosphorus-containing compounds are diamino compounds which can, for example, be polymerized with diacyl halides. It is known, for example, to incorporate phosphorus into 2,4-dinitrochlorobenzene by reacting the latter with diethyl phosphate resulting in 2,4-dinitro(diethoxyphosphonyl)benzene. By reducing the nitro groups a diamine is produced. However, the yield of dinitro precursor to the diamino species is low, e.g., about 11%.

Some references of the inventors which describe fire resistant polymers containing fire retardant compositions of phosphorus-containing polymers and the monomers thereof include the following:

4. J. A. Mikroyannidis and D. A. Kourtides, “Curing of Epoxy Resins with 1-[(Di(2-Chloroethoxyphosphonyl)Methyl]-2,4- and -2,6-Diaminobenzene”, National Aeronautics and Space Administration Report No. TM 84350, October 1983;
6. J. A. Mikroyannidis and D. A. Kourtides, “Synthesis and Characterization of Phosphorus Containing Polyamides and Copolyamides Based on 1-[(Di(2-Chloroethoxyphosphonyl)]Methyl]-2,4- and -2,6-Diaminobenzenes”, Proceedings of the Society for the Advancement of Materials and Process Engineering, Reno, NV (April 1984); and

This references are not considered to be prior art in the present invention.

OBJECTS OF THE INVENTION

It is an object of the invention to provide fire and heat resistant polymers which are improved with respect to one or more of the properties, limiting oxygen index (LOI), char yield, hydrophilicity and solubility.

BRIEF SUMMARY OF THE INVENTION

In accordance with the invention a phosphonylmethylbenzene having the general formula

\[(RO)_{2}P-\text{CH}_2-X-Y\]

is provided and is polymerized with a monomer such as an epoxide, diacylhalide, a dihydride, etc. In 1x the R groups may be the same or different and they may be aliphatic, cycloaliphatic or aromatic, preferably being lower alkyl [methyl, ethyl, propyl (n and iso), etc.] and most advantageously contain a halogen such as chlorine. X and Y are functional groups which are polymerizable with, for example, epoxy or anhydride groups and they may be the same or different. Preferably X and Y are amino groups and they will be predominantly in.
The resulting polymers combine one or more properties of heat resistance, low flammability and high char yield with good mechanical properties such as high tensile strength.

The reaction mixture may include other species such as, for example, a mixture of a diamine species of 1x, a conventional diamine such as m-phenylenediamine (MPD) or 4,4-diaminodiphenyl sulfone (DDS). These conventional species may serve to impart toughness and/or other desirable properties to the polymer.

In the present invention, a diamino compound 1:

\[
\begin{align*}
&\text{(RO)}_2\text{P} \equiv \text{CH}_2 \equiv \text{NH}_2 \\
&\text{HN} \equiv \text{NO} \equiv \text{CO} \equiv \text{(CO)}_n \equiv \text{I} \\
&\text{CH}_2\text{P} \equiv \text{OR}_2
\end{align*}
\]

is reacted with an acyl halide, \( R' - (\text{CO})_n \equiv \) having a functionality of two or more to produce a polyamide having the recurring unit:

\[
\begin{align*}
&\text{HN} \equiv \text{CO} \equiv \text{(CO)}_n \equiv \text{I} \\
&\text{CH}_2\equiv \text{P}\equiv \text{OR}_2
\end{align*}
\]

In these formula the \( R \) groups are organo phosphonyl protecting groups which are alkyl groups, aryl groups, substituted alkyls or other suitable protecting groups of the diacyl halide; \( R' \) is an organo bridging group, preferably hydrocarbons such as alkylene or arylene or alkylene, for example a 1 to 8 carbon alkylene such as methylene, ethylene, butylene, cyclohexylene, octylene and 2-ethylhexylene benzylene, phenylene, 2-ethylbenzylene phenylethylene and the like. \( X \) is a halo such as chloro or bromo. And \( n \) is a number greater than 1, such as 2, 3 or 4, especially 2.

The reaction mixture may include other species (co-monomer unit) such as, for example, a mixture of a diamine species of 1, a conventional diamine, such as m-phenylenediamine (MPD) or 4,4-diaminodiphenyl sulfone (DDS). These conventional species may serve to impart toughness and/or other desirable properties to the polymer.

The resulting polymers combine one or more properties of heat resistance, low flammability and high char yield with good mechanical properties such as tensile strength. The subject polyamides are more fire and flame resistant than conventional polyamides. These improved polyamides can be spun into fibers and yarns to produce fire-resistant fabrics, felts and other woven structures. When used as a knit or fabrics these materials have many civil, industrial and military uses including the following: industrial protective clothing, aircraft seats, bus/train seats, soft furnishings protection, hospital beds, fire blankets, flying suits, fire fighting suits and cable insulation. The fabrics made from these polymers would not yield any toxic vapors or gases when subjected to flame or extreme radiant heat.
This reduction may be carried out by any of the methods known to the art for reducing aromatic nitrates. A preferred method is catalytic reduction using molecular hydrogen and a supported catalyst such as a supported noble metal catalyst for example platinum or palladium on an inert organic oxidic support or carbon. This reduction is exothermic and can be conducted at temperatures from ambient to about 100°C and hydrogen partial pressures of from about 1 atmosphere to 20 atmospheres or more. The reaction is continued until no more hydrogen is taken up. The reduction is carried out with the dinitro compound dissolved in a non-aqueous medium, for example, a lower alkanol such as methanol or ethanol.

The acyl halide, R'-(COX)ₙ, is a polyfunctional acyl halide. That is, it has n acyl halide functions wherein n is 2 or more, but preferably 2. X is a halo, preferably chloro, and R' is an organic bridging group as described above in the Brief Summary of the Invention. Preferred acyl halides are adipoyl dichloride and isophthaloyl dichloride. These materials are commercially available.

The polymerization can be carried out in an organic liquid phase at low to moderate temperature. A representative reaction solvent is a polar aprotic solvent, for example, a lower alkanol such as methanol or ethanol.

Representative polymerization temperatures are about -20°C to about +40°C with about -10°C to +20°C being preferred. Generally, the materials are used in about equimolar proportions but, as desired, either may predominate. After polymerization, the polymer is recovered, such as by precipitation or by evaporation of the reaction solvent.

As will be demonstrated, the present polymers have excellent fire resistance. They can be spun into fibers which can be used to form fabrics, to reinforce composites and the like for use where their flame and fire resistance is of high value as in aircraft interiors and the like.

The following examples will serve to illustrate the practice and advantages of the invention and are not to be construed as limiting the invention's scope.

Examples 1 to 4 illustrate the preparation of the diamines 1. Examples 5 to 12 illustrate the polymerization of diamine 1 with diacyl halides (isophthaloyl dichloride and adipoyl dichloride) and copolymerization of the same acyl chlorides with diamines 1 and other diamines.

Polymers were analyzed by proton nuclear magnetic resonance (IH-NMR) and infrared spectra, thermogravimetric analysis, differential scanning calorimetry and chemical analysis. Limiting oxygen index (LOI) was determined by the method of ASTM 2863-74.

The starting materials 3 were [(diethoxyphosphonyl)methyl]benzene (3a) and [di(2-chloroethoxyphosphonyl)methyl]benzene (3b), both of which are known compounds described in the literature.
small amount of catalyst, 10% palladium on carbon, was added. The hydrogenation was carried out as in Example 2. A solid product was obtained (1.88 g, 98%, mp 105°-109°). Recrystallizations from benzene gave an analytical sample of Ib: mp 116°-119° C. Structure was confirmed by IH-NMR and chemical analysis.

EXAMPLE 5
Preparation of a Polyamide by Reaction of la with Isophthaloyl Dichloride

Dihydrochloride salt of la (6.29 g, 19.0 mmol), DMAC (60 ml) and pyridine (6.01 g, 76.0 mmol) were placed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel and a nitrogen inlet. The mixture was stirred to dissolve the dihydrochloride salt of la and cooled to 0°-1° C. There was added dropwise dichloride (3.86 g, 19.0 mmol) in DMAC (30 ml) allowing the above solution under stirring and nitrogen atmosphere a solution of isophthaloyl dichloride (3.86 g, 19.0 mmol) in DMAC (30 ml) allowing the reaction 10 min. in cooling and then 60 min. at room temperature. The reaction mixture was poured into about 600 ml of methanol and the product precipitated was filtered, washed repeatedly with methanol and dried at 80° C. in a vacuum oven. The polymer (6.05 g, 82%) had an inherent viscosity of 0.14 dl/g in DMF (0.5% conc. at 25° C.).

EXAMPLE 6
Preparation of a Polyamide by Reaction of Ib with Isophthaloyl Dichloride

A mixture of Ib (3.28 g, 10.0 mmol), isophthaloyl dichloride (2.04 g, 10.0 mmol) and pyridine (1.59 g, 20.0 mmol) was reacted as in Example 5. The polymer (3.90 g, 85%) had an inherent viscosity 0.16 dl/g in DMF (0.5% conc. at 25° C.).

EXAMPLE 7
Preparation of a Copolyamide by Reaction of la and m-Phenylenediamine with Isophthaloyl Dichloride

Dihydrochloride salt of la (2.21 g, 6.7 mmol), dihydrochloride salt of m-phenylenediamine (6.21 g, 34.3 mmol) and pyridine (12.96 g, 163.8 mmol) were dissolved in DMAC (80 ml). Isophthaloyl dichloride (8.32 g, 41.0 mmol) dissolved in DMAC (60 ml) was added to the above solution and the mixture was reacted as in Example 5. The copolyamide (9.70 g, 90%) had an inherent viscosity 0.22 dl/g in concentrated sulphuric acid (0.5% conc. at 25° C.).

EXAMPLE 8
Preparation of a Copolyamide by Reaction of 1b and m-Phenylenediamine with Isophthaloyl Dichloride

Utilizing the same method, a copolyamide was obtained by reaction of 1b (2.91 g, 8.9 mmol) and adipoyl dichloride (8.37 g, 41.2 mmol) in the presence of pyridine (11.55 g, 84%) had an inherent viscosity 0.31 dl/g in DMF (0.5% conc. at 25° C.).

EXAMPLE 9
Preparation of a Polyamide by Reaction of la with Adipoyl Dichloride

la was formed "in situ" by addition of pyridine (7.24 g, 91.6 mmol) to dihydrochloride salt of la (7.58 g, 22.9 mmol) in DMAC (60 ml). Adipoyl dichloride (4.19 g, 22.9 mmol) diluted with DMAC (30 ml) was added to the above solution under stirring and nitrogen atmosphere at 0°-1° C. The mixture was subsequently stirred for 60 min. at room temperature and poured in water. The polymer precipitated was dried at 90° C. in a vacuum oven overnight. The polyamide (6.83 g, 81%) had an inherent viscosity 0.10 dl/g (0.5% conc. at 25° C.).

EXAMPLE 10
Preparation of a Polyamide by Reaction of Ib with Adipoyl Dichloride

A mixture of Ib (3.36 g, 10.3 mmol), adipoyl dichloride (1.88 g, 10.3 mmol) and pyridine (1.62 g, 20.5 mmol) was reacted as in Example 9. The polymer (3.41 g, 76%) had an inherent viscosity 0.11 dl/g in DMF (0.5L % conc. at 25° C.).

EXAMPLE 11
Preparation of a Copolyamide by Reaction of la and m-Phenylenediamine with Adipoyl Dichloride

Dihydrochloride salt of la (2.94 g, 8.9 mmol), dihydrochloride salt of m-phenylenediamine (8.78 g, 48.0 mmol) and pyridine (18.00 g, 227.6 mmol) were dissolved in DMAC (100 ml). Adipoyl dichloride (10.41 g, 56.9 mmol) diluted with DMAC (40 ml) was added to the above solution and the mixture was reacted as in Example 9. The copolyamide (11.55 g, 84%) had an inherent viscosity 0.31 dl/g in DMF (0.5% conc. at 25° C.).

EXAMPLE 12
Preparation of a Copolyamide by Reaction of 1b and m-Phenylenediamine with Adipoyl Dichloride

Similarly, a copolyamide was obtained by reaction of 1b (2.91 g, 8.9 mmol) and dihydrochloride salt of m-phenylenediamine (6.16 g, 34.00 mmol) with adipoyl dichloride (7.85 g, 42.9 mmol) in the presence of pyridine (12.16 g, 153.8 mmol). The copolyamide (9.16 g, 81%) had an inherent viscosity 0.34 dl/g in DMF (0.5% conc. at 25° C.).

The polyamides of Examples 5, 6, 9 and 10 had the following structures:

8

The diamino moiety is shown as the 2,4-diamine species (which predominates) but it will be understood that the 2,6-diamine species may be present.

The copolyamides of Examples 7, 8, 11 and 12 have structures as in Examples 5, 6, 9 and 10, respectively interspersed with the structure.
derived from the m-phenylenediamine.

Thermogravimetric (TGA) data and fire resistance data for these polymers, for a polymer of isophthaloyl dichloride and m-phenylenediamine (Polymer I) and for a polymer of adipoyl dichloride and m-phenylene diamine (Polymer II) are set forth in Tables I and II, respectively. Limiting oxygen index (LOI) data are set forth in Table III for blends of the polymer of Example 5 and Polymer I.

As will be seen from Table I, weight loss was substantially less with most of the polymers of the present invention than with conventional polymers (Polymers I and II). That is, the char yields were greater for polymers of the invention.

LOI value indicates resistance to ignition. As will be seen in Table II the LOI values of polymers of the invention were substantially greater than those of comparable Polymers I and II

Table II shows the beneficial effect on LOI of the increasing percentages of the polymers of Example 5.

TABLE I

<table>
<thead>
<tr>
<th>Polymer</th>
<th>TGA DATA OF POLYAMIDES</th>
<th>400° C.</th>
<th>500° C.</th>
<th>700° C.</th>
<th>500° C.</th>
<th>700° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 5</td>
<td>Weight Loss in Nitrogen, Percent</td>
<td>11</td>
<td>21</td>
<td>27</td>
<td>17</td>
<td>26</td>
</tr>
<tr>
<td>Ex. 6</td>
<td>Weight Loss in Air, Percent</td>
<td>26</td>
<td>35</td>
<td>43</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>Ex. 7</td>
<td>Weight Loss in Air, Percent</td>
<td>5</td>
<td>22</td>
<td>29</td>
<td>4</td>
<td>22</td>
</tr>
<tr>
<td>Ex. 8</td>
<td>Weight Loss in Air, Percent</td>
<td>14</td>
<td>27</td>
<td>41</td>
<td>12</td>
<td>71</td>
</tr>
<tr>
<td>Polymer I</td>
<td>Weight Loss in Air, Percent</td>
<td>10</td>
<td>30</td>
<td>43</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>Ex. 9</td>
<td>Weight Loss in Air, Percent</td>
<td>7</td>
<td>46</td>
<td>50</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>Ex. 10</td>
<td>Weight Loss in Air, Percent</td>
<td>35</td>
<td>48</td>
<td>50</td>
<td>34</td>
<td>45</td>
</tr>
<tr>
<td>Ex. 11</td>
<td>Weight Loss in Air, Percent</td>
<td>9</td>
<td>43</td>
<td>46</td>
<td>6</td>
<td>32</td>
</tr>
<tr>
<td>Ex. 12</td>
<td>Weight Loss in Air, Percent</td>
<td>27</td>
<td>47</td>
<td>50</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>Polymer II</td>
<td>Weight Loss in Air, Percent</td>
<td>8</td>
<td>64</td>
<td>67</td>
<td>5</td>
<td>53</td>
</tr>
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</table>

TABLE II

<table>
<thead>
<tr>
<th>Polymer</th>
<th>FIRE-RESISTANCE OF POLYAMIDES</th>
<th>P. percent</th>
<th>Cl. percent</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 7</td>
<td>1.44</td>
<td>0</td>
<td>52.0</td>
<td></td>
</tr>
<tr>
<td>Ex. 8</td>
<td>2.09</td>
<td>5.14</td>
<td>52.6</td>
<td></td>
</tr>
<tr>
<td>Polymer I</td>
<td>0.0</td>
<td>0</td>
<td>46.4</td>
<td></td>
</tr>
<tr>
<td>Ex. 11</td>
<td>1.52</td>
<td>0</td>
<td>45.0</td>
<td></td>
</tr>
<tr>
<td>Ex. 12</td>
<td>2.04</td>
<td>4.84</td>
<td>45.7</td>
<td></td>
</tr>
<tr>
<td>Polymer II</td>
<td>0.0</td>
<td>0</td>
<td>49.6</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III

<table>
<thead>
<tr>
<th>Phosphorus in Phosphorus index of Blends of Polymers of Example 5 and Polymer I</th>
<th>0.24</th>
<th>0.48</th>
<th>0.95</th>
<th>1.46</th>
<th>1.90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer of Example 5 in blend, percent</td>
<td>1.75</td>
<td>7.90</td>
<td>15.00</td>
<td>23.00</td>
<td>30.00</td>
</tr>
</tbody>
</table>

It will, therefore, be apparent that new and useful polymers have been provided.

While the present invention has been described with reference to specific embodiments thereof, it will be understood by those skilled in this art that various changes may be made and that equivalent steps may be substituted without departing from the true spirit and scope of the present invention. All such modifications or changes are intended to be included within the scope of the following claims.

We claim:

1. A polymer having the recurring unit:

   \[
   \text{NH-CO-R(CO)}_{n-1}^- \]

   wherein the R groups are independently selected from alkyls, substituted alkyls or aryls and the second NH is in the 4-position, the 6-position or both the 4-position and the 6-position relative to the phosphonyl methyl group; with an acyl halide of the formula:

   \[
   \text{R'}(\text{COX})_n \]

   wherein R' is a hydrocarbon bridging group, X is halogen and n is 2 to yield a polyamide having the recurring group

   \[
   \text{NH-CO-R(CO)}_{n-1}^- \]
11. (b) thereafter recovering the polyamide.
12. The method of claim 11 wherein the R' groups are lower alkyl.
13. The method of claim 12 wherein the R groups are lower alkyl.
14. The method of claim 13 wherein the R groups are halo alkyl.
15. The method of claim 13 wherein the R groups are ethyl.
16. The method of claim 14 wherein the R groups are 2-chloroethyl.
17. The method of claim 12 wherein R' is an arylene group.
18. The method of claim 12 wherein the acyl halide is isophthaloyl dichloride.
19. The method of claim 12 wherein R' is an alkylene group.
20. The method of claim 12 wherein the acyl halide is adipoyl dichloride.