There are provided the aromatic diamines 2,2-bis[(2-halo-4-aminophenoxy)-phenyl]hexafluoropropane, where the attached ortho halogen is preferably chlorine, and 4,4'-bis(4-aminophenoxy)biphenyl, as novel monomers for polyimide polymerizations. The former, when reacted with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, provides a polyimide having exceptional high-temperature performance. The latter diamine is a low-cost monomer for polyimide production.
BACKGROUND OF THE INVENTION

The invention described herein was made in the performance of work under NASA Contract No. NAS3-23274 and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958 (72 Stat. 435; 42 U.S.C. 2457).

This is a division of application Ser. No. 483,024, filed Apr. 7, 1983.

Studies have shown that the use of fiber-reinforced organic matrix resin composites in aircraft engines and nacelle structures can result in significantly improved engine performance. The weight reduction attendant to substituting plastics for metals in aircraft components and structures can result in up to a 50% fuel savings as well as significant improvement in mission performance. To date, no organic matrix resin is available for use that can provide at least 100-hour service in air at a temperature of about 700°F in pressure environments up to 10 atmospheres of compressed air, as are now being required for new advanced aircraft engines.

Linear aromatic/heterocyclic condensation polyimides as a class of polymer have found widespread application in the aerospace industry due to their toughness and flexibility, high thermal and thermo-oxidative stability, solvent resistance, and excellent mechanical properties. They may be generally characterized as the reaction products of an equimolar amount of an aromatic tetra-acid or derivative, i.e., dianhydride or diester, and an aromatic diamine. The reaction is usually run at or near ambient temperature in a high-boiling polar aprotic solvent, e.g., dimethyl formamide, dimethyl acetamide, or N-methyl-pyrrolidinone, at a solids loading of up to 40% by weight. This gives rise to an intermediate polyamide-acid, which is then concentrated and transformed to final polyimide by heating at elevated temperatures up to about 600°F, depending on whether reduced pressure is employed.

A linear condensation polyimide based upon a reaction of four-ring aromatic diamine, 2,2-bis[(4-aminophenoxy)phenyl]hexafluoropropane and pyromellitic dianhydride, as described in U.S. Pat. No. 4,111,906 to one of us, possessed promise as a matrix resin for use in jet compressor stage stator bushings at 675°F use temperature. However, the critical temperature increase from 675°F to 700°F required for the new generation of advanced aircraft engines deleteriously affects the performance of this polyimide. The only other known resin which was thought to have equal or higher promise at these high temperatures was a resin once marketed by Du Pont as NR-150B. This was a linear condensation polyimide based upon single ring aromatic diamines and 4,4'-(hexafluoroisopropylidene)dipthalic anhydride as described in U.S. Pat. No. 3,356,648; this product, however, is no longer commercially available.

We have been in quest of novel polyimide polymer systems suitable for a minumum service life of 100 hours at 644°F (700°F) in air at pressures up to 10 atmospheres.

SUMMARY OF THE INVENTION

There have been synthesized two new aromatic fourring diamines. They are 2,2-bis[(2-halo-4-aminophenoxy)phenyl]hexafluoropropane (2-X-4-BDAF) of the formula:

wherein X is a halogen, preferably chlorine, and 4,4'-(4aminophenoxy)bisphenyl (4-BPDA) of the formula:

The former provides an exceptional monomer for high-temperature-performance polyimides, especially when polymerized with 2,2-bis(3,4-dicarboxyphenoxy)hexafluoropropane dianhydride (6-FDA), while the latter has value as a novel low-cost monomer for polyimide production.

Novel polyimides in accordance with this invention provide units of the structure:

wherein Y is halogen or hydrogen, and Z is a covalent bond when Y is hydrogen and

when Y is halogen, and Z' is

The presently preferred halogen is chlorine.

The preferred polyimides are copolymers having repeating units of the structure:
Again, the preferred halogen is chlorine.

DETAILED DESCRIPTION

The present invention is directed to the formation of novel aromatic diamines for condensation reaction with monomers having reactive anhydride groups to provide polyimides. Novel aromatic diamines of greatest interest are 2,2-bis[(2-halo-4-aminophenoxy)-phenyl]hexafluoropropanes (2-X-4-BDAF) of the formula:

\[
\text{H}_2\text{N}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{H}}{\text{N}}
\]

wherein \(X\) is halogen. The presently preferred halogen is chlorine. The diamines have halogen ortho to the ether linkage and appear to protect the ether linkage against thermal degradation. Unexpectedly, surprisingly exceptional high-temperature performance has been established for the reaction product of such diamine with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropylene dianhydride (6-FDA) to form polymers having repeating units of the formula:

\[
\text{H}_2\text{N}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{H}}{\text{N}}
\]

wherein \(X\) is halogen and \(n\) is the number of repeating units in series. Such polymers have superior thermal and thermooxidative stability at temperatures of about 700°F (644° K.). Other reactive monomers may be substituted in whole or in part for the specific dianhydride, and other diamines can be used to dilute the primary diamine, but such changes have an effect on polymer properties, and, in particular, appear to detrimentally affect the polymer's oxidative resistance. For instance, substituting pyromellitic dianhydride (PMDA) of the structure:

\[
\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{H}}{\text{N}}
\]

sours, followed by solvent evaporation in vacuo, then thermally imidized in air at 473° K. (392° F.). Dimethylacetamide (DMAc) was employed as the preferred polymerization solvent and the monomers were combined at about a twenty-five-percent (25%) solids loading in the solvent. Solvent and varnish solids loading were selected because prior work employing this combination yielded the promising initial thermo-mechanical results.

A representative reaction sequence to prepare the linear condensation polyimide candidates is in accordance with the following reaction sequence for PMDA and 2-Cl-4-BDAF:
EXAMPLE 1
Preparation of 2,2-bis[(2-chloro-4-aminophenoxy)phenyl]hexafluoropropane (2-Cl-4-BDAF)

To a 1000 ml 3-necked round-bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, condenser, heating mantle, and gas inlet adapter, there was placed bis-phenol AF (112 g, 333 mmol) and sodium hydroxide (26.8 g, 670 mg-at) in dry N,N-dimethylacetamide (DMAc, distilled from calcium hydride, 500 mL) under argon atmosphere. The mixture was stirred and brought to reflux with azeotropic removal of water. After about 20 hours, the water and toluene were removed by distillation, and the temperature of the resulting dark burgundy-colored reaction mixture was lowered to 110°C. The solution of bis-phenol AF dianion was added hot (ca. 135°-140°C) over a period of 20-25 minutes to a stirred solution of 3,4-dichloronitrobenzene present in an amount of 128.6 g (670 mmol) in dry DMAc (ca. 400 mL) under argon atmosphere. Temperature of reaction under these conditions rose to about 105°-110°C. After addition was complete, the stirred mixture was heated at from about 105°-120°C for about 2 hours, then cooled to ambient temperature and poured onto 2000 mL of water. A yellowish-brown solid precipitated out and was filtered, washed with 700 mL of ethyl acetate, then treated with 200 mL of ethanol and left to recrystallize. The precipitate was filtered, washed once with ice-cold ethanol, pulverized and air-dried to yield glistening beige crystals (148 g, 229 mmol, 69% yield). Melting point was 160°C. (DSC melting point, single peak). Infrared was 1345 cm⁻¹ (−NO₂). Elemental analysis with % actual, theoretical in parentheses, was: C, 50.8%
EXAMPLE 2
Preparation of 4,4'(4-aminophenoxy)bi phenyl (4-BPDA)

To a 1000-ml 3-necked round-bottom flask equipped with magnetic stirring bar, condenser, Dean-Stark trap, thermometer, and gas inlet adapter, there was placed p,p'-biphenyl (Buffalo Color Corporation, 37.2 g, 200 mmol) in dry N,N-dimethylacetamide (DMAc, distilled from barium oxide, 250 mL) under argon atmosphere. The stirred mixture was brought to reflux with azeotropic removal of water. After the addition period, the mixture became reddish, foamy, and exothermic during addition. Temperature was maintained at 150°C. After the addition was complete and the exotherm had subsided, the mixture was filtered, and the supernatant was concentrated in vacuo at elevated temperatures to yield a beige-colored solid (21.4 g, 50 mmol) in dry N,N-dimethylacetamide (DMAc, distilled from barium oxide, 250 mL) under argon atmosphere. The stirred mixture was maintained at 150°C, cooled to room temperature and poured onto 1200 mL of water. A yellow solid was precipitated and filtered off, washed well with ice-cold ethanol, and air-dried to yield 80.8 g, or 94.4% crude. The product 4,4'-(nitrophenoxycarbonyl)hexafluorobenzene (4-BPDA) was homogeneous by analytical thin-layer chromatography (silica gel, 60:40 hexanes:benzene, Rf = 0.092). M.p. 193°-195°C (Fisher-Johns, uncorrected), 195°C (somewhat broad endotherm, differential scanning calorimetry). Determined IR was 3640 cm⁻¹ (N=H), with no trace of -NO₂ absorption. Elemental analysis (% actual, theoretical in parentheses) was: C, 56.1 (55.2); H, 3.3 (3.1); N, 5.9 (4.8); O, 7.8 (5.4); Cl, 11.5 (12.1); F, 18.3 (19.4). Amine number (meq/g; theoretical in parentheses) was 5.12 (5.43).

EXAMPLE 3
Preparation of Polymers

The following procedure is typical preparation for a 2,2'-bis[2-chloro-4-aminophenox y]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxypheny l)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

There were also formed by the procedure, 4-BPDA/6-FDA and 4-BPDA/PMDA polymers.

Isothermal Thermo-Oxidative Stability Assessment

There were also formed by the procedure, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

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The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

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The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

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The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.

The polymers, 2,2'-bis[2-chloro-4-aminophenoxy]phenyl]hexafluoropropane and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dia nhydride reactions to yield and imidized to form a 2,2'-bis[4,4'-BDAF/6-FDA polymer.
would be expected to show a tendency to form micro-cracks in the molded resin causing a loss in structural integrity. Data for weight loss at 166 hours and 240 hours is included solely for purposes of completion as it can be seen from the Table that at these extreme oxidative environmental conditions the performance of all of the tested candidates has deteriorated to where the desired performance cannot be achieved.

As shown in Table I, our novel 2-Cl-4-BDAF/6-FDA polyimide surprisingly had a weight loss of only 13.0% after 109 hours in air at 700°F. This is particularly unexpected in view of the 24.4% weight loss of the 4-BDAF/6-FDA control. Thus, the weight-loss data given in Table I establish 2-Cl-4-BDAF/6-FDA to be a thermally superior polyimide. The 2-Cl-4-BDAF/PMDA polyimide displayed good thermal stability.

Conversely, the two resins prepared from the 4-BPDA diamine, namely, 4-BPDA/PMDA and 4-BPDA/6-FDA, clearly were not suitable for consideration for service at 644°K (700° F.).

What is claimed is:
1. 2,2-bis[(2-halo-4-aminophenoxy)phenyl]hexa-fluoropropane.
2. 2,2-bis[(2-chloro-4-aminophenoxy)phenyl]hexa-fluoropropane.

<table>
<thead>
<tr>
<th>Polyimide Candidate</th>
<th>40 hours</th>
<th>109 hours</th>
<th>166 hours</th>
<th>240 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-BDAF/PMDA Control (Neat Resin Disc)</td>
<td>1.3</td>
<td>5.4</td>
<td>10.3</td>
<td>19.3</td>
</tr>
<tr>
<td>4-BDAF/PMDA Control (Powder)</td>
<td>4.2</td>
<td>21.5</td>
<td>44.6</td>
<td>69.3</td>
</tr>
<tr>
<td>4-BDAF/6-FDA Control (Powder)</td>
<td>6.5</td>
<td>24.4</td>
<td>43.1</td>
<td>65.3</td>
</tr>
<tr>
<td>2-Cl-4-BDAF/PMDA (Powder)</td>
<td>4.6</td>
<td>28.7</td>
<td>62.3</td>
<td>89.7</td>
</tr>
<tr>
<td>2-Cl-4-BDAF/6-FDA (Powder)</td>
<td>4.4</td>
<td>13.0</td>
<td>39.9</td>
<td>58.2</td>
</tr>
<tr>
<td>CBPDA/PMDA</td>
<td>53.0</td>
<td>98.1</td>
<td>98.9</td>
<td>99.0</td>
</tr>
<tr>
<td>CBPDA/6-FDA (Powder)</td>
<td>60.0</td>
<td>92.5</td>
<td>99.5</td>
<td>99.6</td>
</tr>
</tbody>
</table>

**TABLE I**

SUMMARY OF ISOTHERMAL AGING AT 644° K. (700° F.) IN AIR

Weight Loss as a Function of Isothermal Aging in Air at 644° K.