METHYL SUBSTITUTED POLYIMIDES CONTAINING CARBONYL AND ETHER CONNECTING GROUPS

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Appl. No.: 589,571
Filed: Sep. 28, 1990

Int. Cl. 5 ........................ C08G 69/26; C08G 8/02; C08G 79/02
U.S. Cl. ......................... 528/353; 528/128; 528/172; 528/185; 528/352; 564/315; 564/328; 564/422; 564/440; 564/442; 564/443; 564/502; 564/418

Field of Search ................ 528/125, 128, 172, 185, 528/353, 352, 229; 564/315, 328, 428, 440, 442, 443, 502; 556/418

References Cited
U.S. PATENT DOCUMENTS
4,820,791 4/1989 Hergenrother et al. .............. 528/125

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ABSTRACT

Novel polyimides have been prepared from the reaction of aromatic dihydrides with novel aromatic diamines having carbonyl and ether groups connecting aromatic rings containing pendant methyl groups. The methyl substituted polyimides exhibit good solubility and form tough, strong films. Upon exposure to ultraviolet irradiation and/or heat, the methyl substituted polyimides crosslink to become insoluble.

7 Claims, No Drawings
METHYL SUBSTITUTED POLYIMIDES CONTAINING CARBONYL AND ETHER CONNECTING GROUPS

ORIGIN OF THE INVENTION

The invention described herein was jointly 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, as amended, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

CROSS-REFERENCE

This application is related to our co-pending application Ser. No. 07/433,812, filed Nov. 9, 1989, entitled "Polyimides with Carbonyl and Ether Connecting Groups Between the Aromatic Rings."

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to polyimides. It relates particularly to soluble, thermally-processable polyimides with high glass transition temperatures and good mechanical properties. These polyimides can crosslink either thermally or photolytically to yield insoluble polymer networks. It also relates to novel monomers used in the preparation of these polyimides.

2. Description of the Prior Art

Polyimides are condensation polymers commonly synthesized by the reaction of aromatic dianhydrides with aromatic diamines. The intermediate polyamide acid is either thermally or chemically cyclodehydrated to form the polyimide as depicted in Equation (1).

\[
\begin{align*}
\text{(1)} & \\
\text{Polyamide Acid} & \\
\text{Polyimide} & \\
\end{align*}
\]

where \(X=\text{nil, O, S, SO}_2, \text{C}=\text{O, Si(CH}_3)_2\), and the like, or \(\text{Ar}\) may be any other appropriate tetravalent radical. \(\text{Ar}^+\) is a divalent aromatic radical which may be 1,3,5-triphenylene, 1,4-phenylene, 4,4'-biphenylene, 4,4'-oxydiphenylene, 4,4'-thiodiphenylene, 4,4'-carbonyldiphenylene, 4,4'-methanedi phenylene, or any other appropriate divalent radical.


Typically the polyamic acid precursors are soluble in the reaction medium, a polar aprotic solvent such as N,N-dimethylacetamide, N,N-dimethylformamide, N-methylpyrrolidinone, dimethyl sulfoxide, or other solvents such as diglyme. Upon ring closure the resulting polyimide usually becomes insoluble in the previously mentioned solvents. Consequently, all solution processing, for example, prepregging, film casting, fiber spinning, and coating application, is normally done with the polyamide acid. Soluble high molecular weight polyimides are rare and limited to cases where solubilizing groups are incorporated to reduce chain regularity or where the effect of the aromatic polyimide moiety is diluted by the presence of more flexible groups. For example, XU-218, an amorphous polyimide commercially available from Ciba-Geigy, is soluble in N,N-dimethylacetamide due to incorporation of an asymmetric 1,3,3-trimethyl-1-phenylindene group into the polyimide backbone. The incorporation of oxyethylene units into polyimide backbones has resulted in material which are soluble in N-methylpyrrolidinone [F. W. Harris, A. J. Karnavas, S. Das, C. N. Curcurus, and P. M. Hergenrother, Polymeric Materials: Science and Engineering Preprints, 54, 89 (1986)].

The addition of methyl groups onto an aromatic ring of a polyimide chain has been found in some instances to be an effective means of disrupting the regularity of the chain and increasing the glass transition temperature of the polyimide [F. W. Harris and S. H. S. Lien, Polymeric Materials: Science and Engineering Preprints, 60, 197 (1989)].

A primary object of the present invention is to provide new polyimides that are especially useful as coatings, films, membranes, photoresists, and insulators.

Another object of the present invention is to provide soluble, thermally processable polyimides with high...
glass transition temperatures and good mechanical properties which can crosslink to yield insoluble polymer networks.

Another object of the present invention is the synthesis of two new monomers which have utility in the production of the above polyimides: 1,3-bis(3-methyl-4-aminophenoxy-4'-benzoyl)benzene and 1,3-bis(3,5-dimethyl-4-aminophenoxy-4'-benzoyl)benzene.

SUMMARY OF THE INVENTION

According to the present invention, novel polyimides are prepared by the reaction of aromatic dianhydrides with novel aromatic diamines containing carbonyl and ether groups connecting aromatic rings containing pendant methyl groups. The novel aromatic diamines are prepared by the reactions of 3-methyl-4-aminophenol and 3,5-dimethyl-4-aminophenol with bis(4-fluorobenzoyl) terminated compounds in the presence of potassium carbonate. Polyimides prepared according to the present invention are generally amorphous, and when the polyamide acids are converted to the corresponding polyimides under conditions which prevent thermal crosslinking, the resulting polyimides are much more soluble than similar polyimides which do not contain methyl substituents. Upon exposure to ultraviolet radiation or temperature > 275°C in air, the methyl substituted polyimides according to the present invention crosslink to form insoluble polymer networks.

Accordingly, a soluble polyimide according to the present invention may be applied as a coating, film, insulator, photosresist, etc., and rendered insoluble and resistant to chemical attack by crosslinking the polymer chains, either thermally or photolytically. The methyl groups are understood to provide a labile functionality for photolytic crosslinking, which process is apparently enhanced by the presence of carbonyl groups in the polymer chain.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The general reaction sequence in Equation (2) for the synthesis of novel diamines according to the present invention is represented by the following equations:

\[
\text{C} = \text{C} \text{R} \text{C} = \text{R} \text{C} + 2 \text{NH}_2 \text{OH} \text{R} \text{R}' \text{R}'' \text{OH}
\]

where:
- \( R \) is selected from the group of aliphatic or aromatic radicals consisting of:
- \( \text{NH}_2 \) and \( \text{OH} \) groups may be in the 3 or 4 position and \( R' \) and \( R'' \) are ortho to the \( \text{NH}_2 \) group.

Additionally, novel diamines according to the present invention are prepared by reduction of the corresponding dinitro compound.
Therefore $Ar'$ is equivalent to either

\[
\begin{align*}
\text{or}
\end{align*}
\]

in equation (3) for the synthesis of new polyimides according to the present invention.

\[
\begin{align*}
\text{(3) } m\text{-Q-l}_{y}=^{*}
\end{align*}
\]

where \(n\) is an integer from 4-100. The solvent is preferably N,N-dimethylacetamide (DMAc), but may be other solvents such as N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidinone (NMP), m-cresol, or other solvents such as diglyme.

Cyclodehydration is accomplished chemically or by heating the intermediate polyamide acid at temperatures exceeding 150° C.

$Ar$ is selected from a group of radicals consisting of

\[
\begin{align*}
\text{where } Y = \text{nil, } O, \text{ S, } \text{C}==\text{O}, \text{SO}_2, \text{CH}_2, \text{C(CH}_3)_2, \text{C(CF}_3)_2, \text{Si(CH}_3)_3 \text{ or mixtures thereof.}
\end{align*}
\]

The following examples illustrate monomer synthesis and the reaction sequence for the synthesis of several of the polyimides described according to the present invention.

**EXAMPLES**

I. Monomer Synthesis

(A) 1,3-Bis(4-fluorobenzoyl)benzene

Anhydrous aluminum chloride (160.0 g, 1.20 mol) was added to a stirred solution of isophthaloyl chloride (101.5 g, 0.50 mol) dissolved in fluorobenzene (480.5 g, 5.0 mol) over a five to ten minute period. The mixture was stirred at room temperature for one hour and then maintained at 70°-80° C for four hours. After cooling,
the reaction mixture was poured onto approximately 2000 g of ice containing 100 mL of concentrated hydrochloric acid. The resulting suspension was separated by decantation and washed several times with water. The organic layer was distilled to remove excess fluorobenzene and the solid residue was collected by filtration, washed with water, and dried at 100° C. The crude solid was recrystallized from approximately 1000 mL of toluene to afford 130.5 g (81% yield) of 1,3-bis(4-fluorobenzoyl)benzene; m.p. 177.5°-178.5° C.; 1H NMR (CDCl3) δ 6.8-8.3 (m, 12H, aromatic). Anal. Calcld. for C20H12F2O2: C, 74.53%; H, 3.75%; F, 11.79%. Found: C, 74.53%; H, 3.59%; F, 11.42%.

(B) 1,3-Bis(3-methyl-4-aminophenoxy-4'-benzoyl)benzene (1,3-BMABB)

3-Methyl-4-aminophenol (24.6 g, 0.20 mol) was dissolved in a solution of DMAc (100 mL) and toluene (50 mL) in a three-neck flask equipped with a Dean-Stark trap. Powdered anhydrous potassium carbonate (34.5 g, 0.25 mol) was added and the reaction temperature was increased to remove water by azeotropic distillation. Toluene was removed until the temperature reached 130° C. 1,3-Bis(4-fluorobenzoyl)benzene (32.24 g, 0.10 mol) was then added and the reaction mixture stirred at about 140° C. overnight under a nitrogen atmosphere. The mixture was allowed to cool and subsequently added to water to precipitate a light brown solid which was collected by filtration and dried (50 g, 94% crude yield). Two recrystallizations from an ethanol/toluene mixture afforded 1,3-bis(3-methyl-4-aminophenoxy-4'-benzoyl)benzene (30 g, 62% yield) as a light tan crystalline solid; m.p. 131°-132° C.; 1H NMR (CDCl3) δ 2.17 (s, 6H, CH3), 3.62 (s, 4H NH2), 6.5-8.2 (m, 18H, aromatic). Anal. Calcld. for C36H30N2O4: C, 77.27%; H, 5.57%; N, 5.34%; Found: C, 77.27%; H, 5.57%; N, 5.24%.

(C) 3,5-Dimethyl-4-Aminophenol

A diazoniunm salt solution was prepared by slowly adding a cold solution of sodium nitrate (75.90 g, 1.10 mol) and water (400 mL) to a solution of aniline (93.13 g, 1.00 mol), concentrated hydrochloric acid (500 mL) and water (500 mL) cooled to 5°-10° C. The cold diazoniunm salt solution was added slowly (30-40 minutes) with stirring to a solution of 3,5-dimethylphenol (122.17 g, 1.00 mol) in water (1.2 L) containing sodium hydrosulfide (80.0 g, 2.0 mol) in a 4-L beaker at 5°-10° C. The reaction mixture was allowed to warm to ambient temperature. The red-orange solid of 3,5-dimethyl-4-phenylazophenol was collected by filtration, dried and recrystallized twice from methanol-water to afford 32.24 g (32.24% yield) as a white solid; m.p. 180.5°-182.5° C.; 1H NMR (DMSO-d6) δ 2.10 (s, 6H, CH3), 5.32 (s, 2H, NH2), 5.32 (s, 1H, OH), 6.45 (s, 2H, aromatic).

II. Poly(amide Acid) Synthesis

Polyamide acids were prepared at a concentration of 15% solids content (w/w) by the addition of a stoichiometric amount of an appropriate dianhydride [3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), or 4,4'-oxydiphthalic anhydride (ODPA)] to a mechanically stirred solution of a diamine according to the present invention in DMAc under a nitrogen atmosphere at ambient temperature. The resulting polyamide acid solutions were stirred overnight at ambient temperature under nitrogen, and inherent viscosities at 0.5% concentration in DMAc at 25° C. were subsequently determined. See Table I.

III. Chemical Conversion of Polyamide acid to Polyimide

A solution of acetic anhydride (7 mL) pyridine (7 mL) and DMAc (10 mL) was added slowly to a stirred solution (about 26 mL) of polyamide acid (2 g) in DMAc (7% solids content) at ambient temperature under nitrogen. After complete addition, the solution was stirred for one hour at ambient temperature and then overnight at temperatures as high as 120° C. under nitrogen. In the case of the BTDA/1,3-BMABB and PMDA/1,3-BMABB polymers, the polymer precipitated during the heating period. The reaction mixture was poured into methanol and the solid collected by filtration, washed with methanol and subsequently dried in vacuo at 200° C. overnight. The inherent viscosities of the chemically imidized PMDA/1,3-BMABB, BTDA/1,3-BMABB and ODPA/1,3-BMABB polyimides in NMP at 0.5% concentration at 25° C. were 0.45, 0.60, and 0.81 dL/g, respectively. The inherent viscosities of the chemically imidized PMDA/1,3-BDABB, BTDA/1,3-BDABB, and ODPA/1,3-BDABB polyimides were 0.39, 0.32, and 0.29 dL/g, respectively in NMP. See Table II.
IV. Preparation of Polyimide in m-Cresol

The following procedure was used to prepare a polyimide in m-cresol. BTDA (1.9334 g, 0.0060 mol) was added to mechanically stirred solution of 1,3-BDABB (3.3400 g, 0.0060 mol) in m-cresol (27.7 mL) and toluene (30 mL). Isoquinoline (eight drops) was added, and the temperature of the solution was gradually increased. Water was removed by azeotropic distillation with toluene under an atmosphere of flowing nitrogen.

Excess toluene was removed and the reaction mixture was maintained at 180°-185° C. for three hours. The polyimide remained in solution on cooling to room temperature.

A small amount of the solution was added to methanol to precipitate a yellow solid, which was washed with methanol and dried at 200° C. in vacuo overnight. The inherent viscosity at a concentration of 0.5% in 25° C. m-cresol was 0.30 dl/g. A transparent orange film 30 mil thick was cast from an NMP polyamide acid solution of Example I1. The films on glass were then converted to the polyimide by heating in air at 100°, 200°, and 300° C. in air. The chemical imidization temperature was 221° C. The film was then exposed to ultraviolet radiation from a Xenon arc lamp operating over a range of 200-2000 nm at 0.21 watts/cm² for a period of 100 hours. The exposed film was then insoluble in hot NMP and m-cresol, and the glass transition temperature had risen to 224° C.

A thin film (1.7 mils thick) of the ODPA/1,3-BMABB polyimide was cast from an NMP solution of the chemically imidized powder and dried under vacuum to a maximum temperature of 240° C. The tough, flexible film readily dissolved in NMP and m-cresol with slight warming. The glass transition temperature was 221° C. The film was then exposed to ultraviolet radiation from a Xenon arc lamp operating over a range of 200-2000 nm at 0.21 watts/cm² for a period of 100 hours. The exposed film was then insoluble in hot NMP and m-cresol, and the glass transition temperature had risen to 224° C.

VI. Ultraviolet Irradiation

A thin film (2.4 mils thick) of the BTDA/1,3- BMABB polyimide was exposed to ultraviolet radiation from a Xenon arc lamp operating over a range of 200-2000 nm at 0.21 watts/cm² for a period of 100 hours. The exposed film was then insoluble in hot NMP and m-cresol, and the glass transition temperature had risen to 232° C., and the film was insoluble in m-cresol after heating.

The present invention has been described in detail and with respect to certain preferred embodiments thereof. As is understood by those of skill in the art, variations and modifications in this detail may be effected without any departure from the spirit and scope of the present invention, as defined in the hereto appended claims.

What is claimed is:

1. A high molecular weight linear polyimide having high strength and toughness and a degree of solubility in organic solvents, which polyimide can be induced to crosslink or chain extend to form an insoluble polymer network, the polyimide having the general structural formula:

TABLE II

<table>
<thead>
<tr>
<th>Designation</th>
<th>ηm (dl/g)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA/1,3-BMABB</td>
<td>0.45</td>
<td>[330, 347]</td>
<td></td>
</tr>
<tr>
<td>BTDA/1,3-BMABB</td>
<td>0.60</td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>ODPA/1,3-BMABB</td>
<td>0.81</td>
<td>209</td>
<td></td>
</tr>
<tr>
<td>PMDA/1,3-BDABB</td>
<td>0.39</td>
<td>258</td>
<td></td>
</tr>
<tr>
<td>BTDA/1,3-BDABB</td>
<td>0.32</td>
<td>232</td>
<td></td>
</tr>
<tr>
<td>ODPA/1,3-BDABB</td>
<td>0.29</td>
<td>224</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III

<table>
<thead>
<tr>
<th>Polymide</th>
<th>Temp (°C)</th>
<th>Tensile Yield (ksi)</th>
<th>Tensile Strength (ksi)</th>
<th>Tensile Modulus (ksi)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTDA/1,3- BMABB</td>
<td>25</td>
<td>14.9</td>
<td>22.0</td>
<td>147</td>
<td>63</td>
</tr>
<tr>
<td>1,3-BMABB</td>
<td>177</td>
<td>5.5</td>
<td>7.8</td>
<td>215</td>
<td>82.7</td>
</tr>
<tr>
<td>PMDA/1,3-BBMABB</td>
<td>25</td>
<td>11.2</td>
<td>17.4</td>
<td>472</td>
<td>6.3</td>
</tr>
<tr>
<td>ODPA/1,3-BMABB</td>
<td>25</td>
<td>11.0</td>
<td>19.9</td>
<td>504</td>
<td>6.6</td>
</tr>
<tr>
<td>ODPA/1,3-BDABB</td>
<td>177</td>
<td>5.0</td>
<td>7.4</td>
<td>254</td>
<td>42.4</td>
</tr>
<tr>
<td>BTDA/1,3-BDABB</td>
<td>25</td>
<td>11.2</td>
<td>15.8</td>
<td>406</td>
<td>12.9</td>
</tr>
<tr>
<td>ODPA/1,3-BDABB</td>
<td>177</td>
<td>7.5</td>
<td>9.5</td>
<td>295</td>
<td>20.2</td>
</tr>
<tr>
<td>ODPA/1,3-BDABB</td>
<td>25</td>
<td>7.6</td>
<td>13.5</td>
<td>326</td>
<td>19.2</td>
</tr>
</tbody>
</table>

TABLE III-continued

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>Conversion Method</th>
<th>Solvent 1</th>
<th>Solvent 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTDA/1,3-BMABB</td>
<td>Thermal</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>PMDA/1,3-BMABB</td>
<td>Chemical</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>BTDA/1,3-BDABB</td>
<td>Thermal</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>PMDA/1,3-BDABB</td>
<td>Chemical</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>ODPA/1,3-BDABB</td>
<td>Thermal</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

1 Thermal = polyamic acid film converted to polyimide by heating for one hour each at 100, 200, and 300° C. in air.
2 Chemical = polyamic acid treated with acetic anhydride at 120° C. for 18 hours followed by drying at 200° C. for 18 hours.
3 Solids content 3-5%. I = insoluble, S = soluble.
4 Prepared solutions of 15% solids content (w/v) upon warming.
(a) wherein Ar is a radical selected from the group consisting of:

whereIn Y is a bond or is a substituent selected from the group consisting of:

O,S,C=O,SO₂,CH₂,C(CH₃)₂,C(CF₃)₂,Si(CH₃)₂

(b) wherein Ar' is a radical having the structural formula selected from the group consisting of:

whereIn R is a radical selected from the group consisting of:

-(CH₃)₂−, −(CF₂)ₘ−,
wherein \( Y \) is a bond or is a substituent selected from the group consisting of:

\[
\text{O, S, C==O, SO}_2\text{C(CH}_3\text{)}_2, \text{C(F)}_2\text{H}_2, \text{Si(OR)}_3;
\]

wherein \( x \) is an integer between 1 and 10;

wherein \( R' \) is \( \text{CH}_3 \); and

wherein \( R'' \) is either \( \text{H} \) or \( \text{CH}_3 \).

3. A diamine having the general structural formula:

\[
\text{R'} \quad \text{H}_2\text{N} \quad \text{C} \quad \text{O} \quad \text{R''} \\
\text{H}_3 \quad \text{C} \quad \text{O} \quad \text{R'} \\
\text{H}_2 \text{N} \quad \text{C} \quad \text{O} \quad \text{R''}
\]

wherein \( R \) is a radical selected from the group consisting of:

\[-(\text{CH}_2)_x-, -(\text{CF}_2)_x-\].

wherein \( Y \) is a bond or is a substituent selected from the group consisting of:

\[
\text{O, S, C==O, SO}_2\text{C(CH}_3\text{)}_2, \text{C(F)}_2\text{H}_2, \text{Si(OR)}_3;
\]

wherein \( x \) is an integer between 1 and 10;

wherein \( R' \) is \( \text{CH}_3 \); and

wherein \( R'' \) is either \( \text{H} \) or \( \text{CH}_3 \).

4. A high molecular weight linear polyimide according to claim 1, which has been thermally crosslinked to form insoluble polymer networks therein.

5. A high molecular weight linear polyimide according to claim 1, which has been photolytically crosslinked to form insoluble polymer networks therein.

6. A thermally crosslinked high molecular weight linear polyimide according to claim 4 in the form of a film which has been thermally cured in air.

7. A thermally crosslinked high molecular weight linear polyimide according to claim 5 in the form of a film which has been exposed to ultraviolet radiation.