New polyimides have been prepared from the reaction of aromatic dianhydrides with novel aromatic diamines containing carbonyl and ether connecting groups between the aromatic rings. Several of these polyimides were shown to be semi-crystalline as evidenced by wide angle x-ray diffraction and differential scanning calorimetry. Most of the polyimides form tough solvent resistant films with high tensile properties. Several of these materials can be thermally processed to form solvent and base resistant moldings.
POLYIMIDES WITH CARBONYL AND ETHER CONNECTING GROUPS BETWEEN THE AROMATIC RINGS

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).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to new polyimides formed from the reaction of aromatic dianhydrides with novel diamines containing carbonyl and ether connecting groups between the aromatic rings whereby processable, high strength, solvent, chemical and impact-resistant polyimides are obtained.

2. Description of the Related 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 which has a repeat unit of the general type

\[
\text{Ar} = \text{a tetravalent aromatic radical which can be as simple as 1,2,4,5-tetrasubstituted benzene. Ar may be a 4-bis-(o-diphenylene) having the general structure}
\]

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\text{N} \\
\end{array}
\]

where X=nil, O, S, SO₂, C==O, and Si(CH₃)₂, or Ar may be any other appropriate tetravalent radical. \(\text{Ar'}\) is a divalent aromatic radical which may be 1,3-phenylene, 1,4-phenylene, 4,4'-biphenylene, 4,4'-oxydiphenylene, 4,4'-thiodiphenylene, 4,4'-carbonyldiphenylene, 4,4'-methanidiphenylene, or any other appropriate divalent radical.

Synthesis and characterization of polyimides has been extensively reported in literature. The preparation of aromatic polyimides by reaction of an aromatic dianhydride with an aromatic diamine, followed by thermal cyclization was first reported in 1963 (G. M. Bower and repeat unit. However, experience has shown that the carbonyl to ether groups can be readily synthesized from the reaction of aromatic dianhydrides with novel diamines.

With respect to the carbonyl to ether groups, experience has shown that the polyimide acid precursor to polyimides is usually soluble and is applied as a solution to fibers or fabric. In this manner good impregnation or "wetting" of the fibers is obtained before thermal cyclodehydration to form an insoluble polyimide. An alternate method involving melt impregnation with the polyimide such as in powder form is also envisioned.

The ratio of carbonyl to ether linkages is critical toward achieving the goal of thermally processable semi-crystalline polyimides. The carbonyl and ether linkages could be incorporated into either the Ar (dianhydride) or the \(\text{Ar}'\) (diamine) portion of the polyimide repeat unit. However, experience has shown that the diamine portion is easier to modify, resulting in fewer steps than required for the synthesis of new dianhydrides. Novel diamines containing varying ratios of carbonyl and ether groups between the aromatic rings. However, the introduction of crystallinity into a polymer has long been recognized as an effective means of improving the solvent resistance and increasing the modulus. In addition, if the proper degree and type of crystallinity is attained, the material can also display extremely high toughness. A notable example is polyetheretherketone (PEEK® of Imperial Chemical Industries) which exhibits a very high fracture toughness (\(G_{fc}\) critical strain energy release rate), and is highly solvent resistant. PEEK® can also be thermally processed into moldings and composites. The carbonyl and ether connecting groups between the aromatic rings in PEEK® tend to be so stereochemically similar that the tendency toward crystalline order is greatly enhanced [T. E. Atwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, Polymer, 22, 2096 (1981)].

It would be advantageous if the benefits of PEEK® could be obtained from polyimides. Polyimides are more easily prepared and isolated than PEEK®. Additionally, special technology is required for impregnating PEEK® into fibers due to the insolubility of PEEK® in common solvents. The polyamide acid precursor to polyimides is usually soluble and is applied as a solution to fibers or fabric. In this manner good impregnation or "wetting" of the fibers is obtained before thermal cyclodehydration to form an insoluble polyimide. An alternate method involving melt impregnation with the polyimide such as in powder form is also envisioned.

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The present invention produces novel polyimides and novel diamines. These new polyimides are not obvious because the improvements over the previous polyimide preparation could not be predicted by the placement of -(CH2)_n- or -(CF2)_n- in the center of the diamines or the addition of isopropyl groups to the diamines. The use of -(CH2)_n- gave a much shorter annealing time, and the use of the -(CF2)_n- and the isopropyl groups improved the solubility of the materials. Similarly it was not apparent that replacing the carbonyl groups in the diamines with phosphine oxide would be an improvement over the old polyimide by producing a more flame resistant polyimide.

**SUMMARY OF THE INVENTION**

The present invention is a new composition of matter and concerns new polyimides and novel monomers and the process for preparing them.

One object of the present invention is to provide new polyimides that are useful as adhesives, coatings, films, membranes, and composite matrices.

Another object of the present invention is the synthesis of five new monomers which are useful in the preparation of these novel polyimides:

1. 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,6-bis(4-aminophenoxy-4'-benzoyl)hexane.
2. 1,3-bis(4-aminophenylisopropylidene-3'-phenoxy-4'-benzoyl)benzene;
3. 1,4-bis(4-aminophenylisopropylidene-4'-phenoxy-4'-benzoyl)benzene;
4. bis(4-aminophenoxy-4'-phenyl)phenyl phosphine oxide;
5. 1,4-bis(4-aminophenoxy-4'-benzoyl)butane; and
6. 1,6-bis(4-aminophenoxy-4'-benzoyl)hexane.

According to the present invention, the foregoing and additional objects are attained by synthesizing polyimides from the reaction of aromatic dianhydrides with the five new diamines, which contain carbonyl and ether connecting groups between the aromatic rings. Several of these polyimides were shown to be semicrystalline as evidenced by wide angle x-ray diffraction and differential scanning calorimetry. Glass transition temperatures ranged between 172° and 258° C., and crystalline melt temperatures were observed between 332° and 338° C. Solution cast films of several of the polyimides were tough and flexible. Tensile strengths, tensile moduli, and elongations at break ranged between 14,400 to 14,600 psi, 391,000 to 453,000 psi, and 6.1 to 23.4%, respectively at 25° C. Mechanical properties at 177° C. were also good. The polyimide from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,6-bis(4-aminophenoxy-4'-benzoyl)hexane provided a solvent resistant semicrystalline material which could be molded at 380° C. In addition, the degree of crystallinity of this polyimide could be readily altered by either quenching from a temperature above its crystalline melt temperature (332° C.), or annealing at a temperature above its glass transition temperature but below its crystalline melt temperature.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The general reaction sequence for the synthesis of the novel diamines is represented by the following equations:
The base is an alkali metal hydroxide or carbonate selected from NaOH, KOH, Na₂CO₃, K₂CO₃ and the like.

represents either 3-aminophenol or 4-aminophenol.

Other aminophenols can also be used such as

where the NH₂ and OH groups may be in the 3 or 4 position.

Additionally, several of the diamines have been prepared by reduction of the corresponding dinitro compound:

This was accomplished using either catalytic hydrogenation with an appropriate catalyst or a sulfide such as sodium sulfide.

Therefore Ar' is equivalent to either

in the following general equation for the synthesis of new polyimides:

wherein n is an integer from 4–100. The solvent is preferably N,N-dimethylacetamide, but may be other solvents such as N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidinone, m-cresol, or ether 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
added to a stirred solution of terephthaloyl chloride 

not limited to these examples.

tation and washed several times with water. The or-

sisted at 70°-80° C. for four hours. After cooling, the 

stirred at room temperature for one hour and then main-

(50.8 g, 0.25 mol) dissolved in fluorobenzene (235 ml, 

wherein Y is not a substituent or is a substituent selected 

quence of several of the polyimides. The invention is 

The following examples illustrate the reaction se-

EXAMPLE 1

Monomer Synthesis

(a) 1,4-Bis(4-fluorobenzoyl)benzene: 

Anhydrous aluminum chloride (80.0 g, 0.60 mol) was 

added to a stirred solution of terephthaloyl chloride 

(50.8 g, 0.25 mol) dissolved in fluorobenzene (235 ml, 

2.5 mol) over a 10-15 minute period. The mixture was 

stirred at room temperature for one hour and then main-

zene and the solid residue collected by filtration, 

washed with water, and dried at 100° C. The crude solid 

was recrystallized from approximately 1000 g of 

ice containing 100 ml of concentrated hydrochloric 

The resulting suspension was separated by decan-

zene (9.67 g, 0.030 mol) were added to a solution of 

C, 74.60%; H, 3.80%; F, 11.83%.

EXAMPLE 2

Monomer Synthesis

Bis-(4-aminophenoxy-4'-phenyl)phenyl phosphine oxide

4-Aminophenol (10.9 g, 0.10 mol) and bis(4-fluorophenyl)phenyl phosphine oxide (15.7 g, 0.05 mol) (used as obtained from Hoechst Celanese) were added to a solution of N,N-dimethylacetamide (100 ml) and toluene (30 ml) in a three-neck flask equipped with a Dean-

Stark trap. Powdered anhydrous potassium carbonate 

(15.2 g, 0.11 mol) was added and water was removed by 

azeotropic distillation with toluene. Toluene was re-

moved until the temperature reached 130°-140° C. The 

reaction mixture was stirred at 130°-140° C. overnight 

under a nitrogen atmosphere. The mixture was allowed 

to cool and subsequently added to water to precipitate 

a solid which was collected by filtration and dried. 

Recrystallization from 1:1 toluene-ethanol afforded bis-(4-aminophenoxy-4'-phenyl)phenyl phosphine oxide (19.2 g, 78% yield); mp 98°-102° C.; 'H NMR (CDCl3) 83.54 

(4.42 15 g, 0.006 mol) was added in small portions over 

a period of one-half to one hour to a mechanically 

stirred solution of 1,4-bis(4-aminophenylisopropylidene-4'-phenoxy-4'-benzoyl) benzene (4.4215 g, 0.0060 

mol) dissolved in N,N-dimethylacetamide (38.8 ml), 

which was maintained under a nitrogen atmosphere at 

room temperature. The polyamide acid solution (15% 

solids w/w) was stirred overnight and the inherent 

viscosity at 0.5% concentration in N,N-dimethylacetate-

mide was subsequently determined to be 0.65 dl/g at 25° 

C. The polyamide acid solution was centrifuged, the 

decantate cast onto plate glass using a doctor blade, and 

dried to a tack-free form in a dust-free chamber. The 

film on glass was then thermally converted to the poly-

imide by heating in air at 100°, 200°, and 300° C. for one 

hour at each temperature. The resulting yellow poly-

imide film (approximately 2.0 mils thick) was deter-

mined by differential scanning calorimetry to have a 

glass transition temperature at 222° C. The film as cured 

on glass was determined by wide angle x-ray diffraction 

to be amorphous. Tensile strength, tensile modulus, and 
elongation at break of this film were determined to be 

14,400 psi, 391,000 psi, and 23.4% at 25° C.; and, 7000 

psi, 241,000 psi, and 40.6% at 177° C., respectively.

Specimens of this film placed under stress were una-

fected after 72 hours immersion in solvents which in-

cluded JP-4 (jet fuel), ethylene glycol (deicing fluid), 

and tricresyl phosphate (hydraulic fluid component). 

POLYIMIDE SYNTHESIS 

Bis-(4-aminophenoxy-4'-phenyl)phenyl phosphine oxide

3,3',4,4'-Benzophenonetetracarboxylic dianhydride 

(1.9334 g, 0.0060 mol) was added in small portions over 

a period of one-half to one hour to a mechanically 

stirred solution of 1,4-bis(4-aminophenylisopropylidene-4'-phenoxy-4'-benzoyl) benzene (4.4215 g, 0.0060 

mol) dissolved in N,N-dimethylacetamide (38.8 ml), 

which was maintained under a nitrogen atmosphere at 

room temperature. The polyamide acid solution (15% 

solids w/w) was stirred overnight and the inherent 

viscosity
at 0.5% concentration in N,N-dimethylacetamide was subsequently determined to be 0.64 dl/g at 25°C. The polyamide acid solution was centrifuged, the decantate cast onto plate glass using a doctor blade, and dried to a tack-free form in a dust-free chamber. The film on glass was then thermally converted to the polyimide by heating in air at 100°-200°, and 300°C for one hour at each temperature. The resulting yellow polyimide film (approximately 2.0 mils thick) was determined by differential scanning calorimetry to have a glass transition temperature at 258°C. The film as cured on glass was determined by wide angle x-ray diffraction to be amorphous. Tensile strength, tensile modulus, and elongation at break of this film were determined to be 14,600 psi, 453,000 psi, and 6.1% at 25°C; and, 7600 psi, 253,000 psi, and 3.1% at 177°C, respectively.

**EXAMPLE 3**

**Monomer Synthesis**

(A) 1,4-Bis(4-fluorobenzoyl)butane

Adipoyl chloride (45.8 g, 0.25 mol) was added over a 30-45 minute period to a mechanically stirred suspension of aluminum chloride (83.3 g, 0.625 mol) in fluorobenzene (235 ml, 2.5 mol) maintained at 5°-10°C. The yellow slurry was allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto approximately 1000 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 collected by filtration, washed with water, and dried at 110°C. The crude solid was recrystallized from approximately 1000 ml of toluene to afford 57.0 g (76% yield) of 1,4-bis(4-fluorobenzoyl)butane; mp 145°-146.5°C; 'H NMR (CDCl3) δ 1.0-2.1 (m, 8H, CCH2), 3.00 (t, 4H, O=CCCH2, J=7.0 Hz), 6.9-8.3 (m, 8H, aromatic). Anal. Calcd. for C18H16F2O2: C, 71.51%; H, 5.33%; F, 9.95%; C, 71.68%; H, 5.38%; F, 12.78%.

(B) 1,4-Bis(4-aminophenoxy-4'-benzoyl)butane

4-Aminophenol (4.37 g, 0.040 mol) and 1,4-bis(4-fluorobenzoyl)butane (6.05 g, 0.020 mol) were added to a solution of N,N-dimethylacetamide (40 ml) and toluene (50 ml) in a three-neck flask equipped with a Dean-Stark trap. Powdered anhydrous potassium carbonate (6.91 g, 0.050 mol) was added and water was removed by azeotropic distillation with toluene. Toluene was removed until the temperature reached 130°-140°C. The reaction mixture was allowed to cool and subsequently added to water to precipitate a solid which was collected by filtration and dried. Recrystallization from toluene, followed by recrystallization from 1:1 N,N-dimethylformamide ethanol afforded 1,4-bis(4-aminophenoxy-4'-benzoyl)butane (2.36 g, 25% yield) as a yellow solid; mp 199°-201°C; 'H NMR (DMF-d6) δ 1.5-2.0 (m, 4H, CCH2), 2.98 (t, 4H, O=CH2C, J=7.0 Hz), 4.90 (s, 4H, NH), 6.5-8.2 (m, 16H, aromatic). Anal. Calcd. for C24H19NO2C: 74.98%; H, 5.87%; N, 5.83%. Found: C, 74.29%; H, 5.59%; N, 5.98%.

**Polymide Synthesis**

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (1.1277 g, 0.0035 mol) was added in small portions over a period of 20-30 minutes to a mechanically stirred solution of 1,4-bis(4-aminophenoxy-4'-benzoyl)butane (1.6820 g, 0.0035 mol) dissolved in N,N-dimethylacetamide (16.4 ml), which was maintained under a nitrogen atmosphere at room temperature. The polyamide acid solution (15% solids, w/w) was stirred overnight and the inherent viscosity at 0.5% concentration in N,N-dimethylacetamide subsequently determined to be 1.14 dl/g at 25°C. The polyamide acid solution was centrifuged, the decantate cast onto plate glass using a doctor blade, and dried to a tack-free form in a dust-free chamber. The film on glass was then thermally converted to the polyimide by heating in air at 100°, 200°, and 300°C for one hour at each temperature. The resulting yellow polyimide film (approximately 2.0 mils thick) was determined by differential scanning calorimetry to have a glass transition temperature at 204°C, a weak crystalline melt transition at 278°C, and a strong crystalline melt transition at 338°C. The film as cured on glass was brittle and determined by wide angle x-ray diffraction to be semi-crystalline.

**EXAMPLE 4**

**Monomer Synthesis**

(A) 1,6-Bis(4-fluorobenzoyl)hexane

Suberoyl chloride (40.8 g, 0.1933 mol) was added over a 30-45 minute period to a mechanically stirred suspension of aluminum chloride (64.4 g, 0.483 mol) in fluorobenzene (181 ml, 1.93 mol) maintained at 5°-10°C. The yellow slurry was allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto approximately 1000 g of ice containing 75 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 collected by filtration, washed with water, and dried at 100°C. The crude solid was recrystallized from approximately 500 ml of toluene to afford 43.0 g (67% yield) of 1,6-bis(4-fluorobenzoyl)hexane; mp 123°-124°C; 'H NMR (DCDCl3) δ 1.0-2.1 (m, 8H, aromatic). Anal. Calcd. for C20H16F2O2: C, 72.71%; H, 6.10%; F, 11.50%. Found: C, 72.50%; H, 5.86%; F, 11.19%.

(B) 1,6-Bis(4-aminophenoxy-4'-benzoyl)hexane

4-Aminophenol (10.91 g, 0.100 mol) and 1,6-bis(4-fluorobenzoyl)hexane (16.52 g, 0.050 mol) were added to a solution of N,N-dimethylacetamide (125 ml) and toluene (50 ml) in a three-neck flask equipped with a Dean-Stark trap. Powdered anhydrous potassium carbonate (17.3 g, 0.125 mol) was added and water was removed by azeotropic distillation with toluene. Toluene was removed until the temperature reached 130°-140°C. The reaction mixture was stirred at 130°-140°C overnight under a nitrogen atmosphere. The mixture was allowed to cool and subsequently added to water to precipitate a solid which was collected by filtration and dried. Recrystallization from toluene, followed by recrystallization from 1:1 N,N-dimethylformamide ethanol afforded 1,6-bis(4-aminophenoxy-4'-benzoyl)hexane (19.9 g, 78% yield) as a yellow solid; mp 145°-146.5°C; 'H NMR (DMF-d6) δ 1.1-2.0 (m, 8H, CH2), 3.00 (t, 4H, O=CCH2, J=7.0 Hz), 5.14 (s, 4H, NH2), 6.6-8.3 (m, 16H, aromatic). Polyimide Synthesis

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (1.1612 g, 0.0050 mol) was added in small portions over a period of 20-30 minutes to a mechanically stirred...
solution of 1,6-bis(4-aminophenoxy-4'-benzoyl)hexane (2.5431 g, 0.0050 mol) dissolved in N,N-dimethylacetamide (25.1 ml), which was maintained under a nitrogen atmosphere at room temperature. The polyamide acid solution (15% solids, w/w) was stirred overnight and the inherent viscosity at 0.5% concentration in N,N-dimethylacetamide subsequently determined to be 0.86 dl/g at 25° C. The polyamide acid solution was centrifuged, the decantate cast onto plate glass using a doctor blade, and dried to a tack-free form in a dust-free chamber. The film on glass was then thermally converted to the polyimide by heating in air at 100°, 200°, and 300° C. for one hour at each temperature. The resulting yellow polyimide film (approximately 2.0 mils thick) was determined by differential scanning calorimetry to have a glass transition temperature at 172° C. and a strong crystalline melt transition at 332° C. The film as cured on glass was brittle and determined by wide angle x-ray diffraction to be semi-crystalline. The brittle polyimide film was ground to a powdered form and molded in a 1.25 inch square stainless steel mold at 380° C. under 1000 psi to give a well-consolidated molding. The fracture toughness (Kc) as obtained on miniature compact tension specimens was 395 psi/in. The moldings were not noticeably affected by common aircraft fluids such as JP-4 (jet fuel), ethylene glycol (deicing fluid), tricresyl phosphate (hydraulic fluid component), or methylene chloride (paint stripper component) after 72 hours immersion. In addition the moldings were not noticeably affected by immersion in strong base such as 30% aqueous sodium hydroxide.

Table 1 contains the chemical structures, melting points, and yields of representative difluoro compounds used in the experiments.

Table 2 contains the chemical structures, melting points, and yields of the representative diamines used in the experiments.

The chemical structure, inherent viscosity of the precursor polyamide acid, glass transition temperature, and crystalline melt temperature of representative polyimides containing carbonyl and ether connecting groups are presented in Table 3.

### Table 1

<table>
<thead>
<tr>
<th>DIFLUORO COMPOUNDS</th>
<th>MELTING POINT, °C.</th>
<th>YIELD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OOC-F</td>
<td>177.5-178.5</td>
<td>81⁴</td>
</tr>
<tr>
<td>CH₃OOC-F</td>
<td>218.5-219.5</td>
<td>88⁴</td>
</tr>
<tr>
<td>CH₃OOC-F</td>
<td>124-126</td>
<td>B</td>
</tr>
<tr>
<td>CH₃OOC-F</td>
<td>165.5-167.6</td>
<td>76⁴</td>
</tr>
<tr>
<td>CH₃OOC-F</td>
<td>123-124</td>
<td>67⁴</td>
</tr>
</tbody>
</table>

⁴Yields after recrystallization from toluene.

### Table 2

<table>
<thead>
<tr>
<th>DIAMINE</th>
<th>MELTING POINT, °C.</th>
<th>YIELD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>74-80</td>
<td>78⁶</td>
</tr>
<tr>
<td>CH₃</td>
<td>129-131</td>
<td>83⁵</td>
</tr>
<tr>
<td>CH₃</td>
<td>98-102</td>
<td>83⁵</td>
</tr>
<tr>
<td>CH₃</td>
<td>199-201</td>
<td>25⁵</td>
</tr>
<tr>
<td>CH₃</td>
<td>145-146.5</td>
<td>68⁴</td>
</tr>
</tbody>
</table>

⁶Yields after recrystallization from: A, toluene; B, toluene-methanol; C, toluene-ethanol; D, N,N-dimethylformamide-ethanol.
### TABLE 3

**POLYIMIDES CONTAINING CARBONYL AND ETHER CONNECTING GROUPS**

<table>
<thead>
<tr>
<th>Ar'</th>
<th>POLYAMIDE ACID $\eta_{inh,} \text{dL/g}$</th>
<th>POLYIMIDE $T_B, ^\circ \text{C.}$</th>
<th>$T_m, ^\circ \text{C.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Polyamide 1" /></td>
<td>0.55</td>
<td>164</td>
<td>ND²</td>
</tr>
<tr>
<td><img src="image2" alt="Polyamide 2" /></td>
<td>0.65</td>
<td>222</td>
<td>ND²</td>
</tr>
<tr>
<td><img src="image3" alt="Polyamide 3" /></td>
<td>0.64</td>
<td>258</td>
<td>ND²</td>
</tr>
<tr>
<td><img src="image4" alt="Polyamide 4" /></td>
<td>1.14</td>
<td>204</td>
<td>338</td>
</tr>
<tr>
<td><img src="image5" alt="Polyamide 5" /></td>
<td>0.86</td>
<td>172</td>
<td>332</td>
</tr>
</tbody>
</table>

²Inherent viscosity of 0.5% concentration in N,N-dimethylacetamide at 25°C.

What is new and desired to be secured by Letters Patent of the United States is:

1. A high molecular weight linear polyimide having high strength, modulus, toughness, and solvent resistance, and having the general structural formula:

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

![Radicals A](image6)

(b) wherein Ar' is a radical selected from a group consisting of:

1. a radical having the structural formula:

![Radical B](image7)

wherein Y is a band or is a substituent selected from the group consisting of:

- O, S, C=O, SO₂, CH₂, C(CH₃)₂, C(CF₃)₂ and Si(CH₃)₃;

- ![Radicals C](image8)
wherein R is a radical selected from the group consisting of:

- (CH2)_n and -(CF2)_m.

wherein z is an integer between 1 and 10;

(2) a radical having the structural formula:

wherein R' is selected from the group consisting of

- and

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

O, S, CONH, SO2, CH2, C(CH3)2, and C(CF3)3;

(3) a radical having the structural formula:
4. A diamine having the general structural formula:

5. A film from a polyimide according to claim 1 which is unaffected by immersion in a strong base for up to 18 hours.