United States Patent

Hergenrother et al.

[54] PHENYLETHYNYL TERMINATED IMIDE OLIGOMERS

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[58] Field of Search ................. 528/353, 125, 128, 172, 528/173, 174, 176, 183, 188, 220, 229, 350; 526/935

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ABSTRACT

Four phenylethynyl amine compounds—3 and 4-amino-phenoxy-4'-phenylethynylbenzophenone, and 3 and 4-amino-4'-phenylethynylbenzophenone—were readily prepared and were used to endcap imide oligomers. Phenylethynyl-terminated amide acid oligomers and phenylethynyl-terminated imide oligomers with various molecular weights and compositions were prepared and characterized. These oligomers were cured at 300° C. to 400° C. to provide crosslinked polyimides with excellent solvent resistance, high strength and modulus and good high temperature properties. Adhesive panels, composites, films and moldings from these phenylethynyl terminated imide oligomers gave excellent mechanical performance.

10 Claims, 1 Drawing Sheet
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PHENYLETHYNYL TERMINATED IMIDE OLIGOMERS

ORIGIN OF THE INVENTION

The invention described herein was jointly made by employees of the United States Government and during 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

The present invention relates generally to polyimides, especially imide oligomers. It relates particularly to a series of phenylethynyl-terminated imide oligomers which can be thermally cured to resins that are useful as adhesives, composite matrices, moldings, films and coatings. The invention also relates particularly to a series of amino phenylethynyl compounds used to terminate the imide oligomers.

2. Description of Related Art

Polyimides are condensation polymers that can be prepared by various routes. The most popular route involves the reaction of an aromatic dianhydride with an aromatic diamine. The intermediate polyamide acid is either thermally or chemically cyclodehydrated to form the polyimide which has a repeat unit of the general type:

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

where \( \text{Ar'} \) is a tetravalent aromatic radical, which can be as simple as 1,2,4,5-tetrasubstituted benzene, or it may be a bis-4-(o-diphenylene) having the general structure:

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

where \( \text{X} = \text{nil, 0, S, SO}_2, \text{C} = \text{O, etc.} \) \( \text{Ar'} \) 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'-oxydiphenylene, 4,4'-biphenylene, 4,4'-thiodiphenylene, 4,4'-carbonyldiphenylene, 4,4'-methylene diphenylene or any other appropriate divalent radical.


Wholly aromatic polyimides are known for their exceptional thermal, thermooxidative and chemical resistance, but are generally difficult to process as structural adhesives or composite matrices. Several polyimides such as Kapton® (DuPont), PI-2080 (Dow Chemical, licensed to Lenzing), XU-218™ (Ciba-Geigy), Ultem® (General Electric) and LaRC-TMTM (Mitsui Toatsu) are commercially available and used as fibers, films, moldings, adhesives or composite matrices.


SUMMARY OF THE INVENTION

The primary object of the present invention is to provide a series of phenylethynyl-terminated imide oligomers of various molecular weights that can be thermally cured to provide materials that are crosslinked, insoluble in common organic solvents and have excellent high temperature mechanical properties. Another object is to provide novel amino phenylethynyl compounds that can be used to terminate oligomers.

According to the present invention, the foregoing and additional objects were obtained by synthesizing phenylethynyl-terminated imide oligomers with different polymer backbones and different molecular weights. After curing 1 hour at 350° C., the resulting polymers were crosslinked and insoluble in common organic solvents. Molecular weights prepared include 3000, 6000 and 9000 g/mole. However, this should not be viewed as a limitation since essentially any molecular weight from ~500 to ~30000 g/mole is easily prepared by adjusting the monomer stoichiometry. A modified Carothers equation, \( D_p = (1+r)/(1-r) \) where \( r = \text{mo-} \)
nomer ratio and \(D_p=\) degree of polymerization, provides a means to calculate the monomer ratio necessary to produce the desired molecular weight. The general synthetic procedure is shown in the drawing wherein \(A_r\) is any diamine moiety and \(A_r'\) is any dihydride moiety. Data for theoretical number average molecular weights \((M_n)\), inherent viscosities \((\eta_{inh})\) and glass transition temperatures of uncured and cured polymers are included in Table 1. Data for the thermal stability of the cured polymer in air and nitrogen and the thin film properties are included in Table 2. Data for the titanium to titanium adhesive properties are included in Table 3. The phenylethynyl-terminated imide oligomers of the present invention are eminently suitable as adhesives, composite matrices, moldings, films and coatings.

Two significant advantages of phenylethynyl-terminated imide oligomers compared to linear polyimides are better compression moldability (more flow, better consolidation under less pressure) and the ability to react forming a structure containing some crosslinks which typically increases the solvent resistance, glass transition temperature, and modulus. These properties are important for aerospace applications as films, moldings, adhesives and composites.

The advantage of phenylethynyl-terminated imide oligomers compared to polyimides containing pendant ethynyl or phenylethynyl groups is that the phenylethynyl-terminated imide oligomers have low to moderate molecular weights and therefore have lower melt viscosity for easier processing into moldings, composites and adhesive bonds.

The advantage of phenylethynyl-terminated imide oligomers compared to ethynyl-terminated polyimides is the higher reaction temperature of the phenylethynyl group compared to the ethynyl group. The phenylethynyl group begins to react at \(\sim 350^\circ\) C. (beginning of the exotherm in the DSC trace when run at 20\(^\circ\) C./min) compared to \(\sim 200^\circ\) C. for the ethynyl group. This higher reaction temperature provides a larger window to melt process these oligomers whereas ethynyl-terminated imide oligomers begin to react and, therefore are either not melt processable or have a very small window to melt process.

**BRIEF DESCRIPTION OF THE DRAWING**

For a more complete understanding of the present invention, including its primary objects and attending benefits reference should be made to the Description of the Preferred Embodiments, which is set forth in detail below. This description should be read together with the accompanying drawing, wherein the single drawing figure is an equation showing the general synthetic scheme for the preparation of phenylethynyl terminated imide oligomers according to the present invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The approach according to the present invention was to provide phenylethynyl-terminated polymides by employing any of four novel phenylethynyl amine compounds to endcap imide oligomers. By adjusting the monomer stoichiometry, the molecular weight of the resulting phenylethynyl-terminated polyimide could be controlled. The four phenylethynyl amine compounds are 3 and 4-aminophenoxy-4'-phenylethynylbenzophenone, and 3 and 4-amino-4'-phenylethynylbenzophenone, which have the following structures, respectively:

The phenylethynyl group is the functionality which reacts at elevated temperatures, while the amine group allows the compound to be incorporated into any system which reacts with an amine. Any compound having the following general structural formula can also be used as an endcapping agent:

where X is nil or a meta or para substituted phenoxy group and Y is an activating group consisting of C(CF\(_3\))\(_3\), CO, or SO\(_2\).

The phenylethynyl group has two important advantages over the ethynyl group. These are stability towards conditions of aromatic nucleophilic displacement reactions and stability at moderate temperatures (i.e. 150–250° C.). For example, when 4-phenylethynyl-4'-fluorobenzophenone was treated with a slight excess of 3 or 4-aminophenol in the presence of an alkali metal base such as potassium carbonate in a polar aprotic solvent such as N,N-dimethyacetamide (DMAc) at 143° C., 3 or 4-aminophenoxy-4'-phenylethynylbenzophenone was afforded in nearly quantitative yield. However, several attempts to make the 3-aminophenoxy-4'-ethynylbenzophenone from the 4-ethynyl-4'-fluorobenzophenone under similar reaction conditions afforded a mixture of products. In addition, imide model compounds of the phenylethylnyl endcapper react at a moderate to fast rate in air at 300° to 350° C. whereas analogous model compounds containing the ethynyl group react at a moderate to fast rate in air at 200° to 250° C. Phenylethynyl containing imide model compounds are reasonably stable at 200° C. (see Example 6) whereas thynyl containing imide model compounds react at 200° C.

When an imide oligomer terminated with these activated phenylethynyl endcappers has been cured in a steel mold for 1 hour at 200 psi and 350° C., the resulting glass transition temperatures \((T_g)\) are 15° to 20° C. higher than those of the cured imide oligomer terminated with nonactivated phenylethynyl endcappers. (See Example 7 below and the accompanying Table).

Cured imide oligomers terminated with the activated phenylethynyl endcappers offered higher use temperatures than that of cured imide oligomers from nonactivated phenylethynyl endcappers.
EXAMPLE 1

Synthesis of Bromo Benzophenones

In a 250 mL flask equipped with a nitrogen inlet, overhead stirring assembly, and reflux condenser were placed 3-nitrobenzoyl chloride (28 g, 0.15 mol), bromobenzene (100 g, 0.63 mol), and aluminum chloride (27 g, 0.20 mol). The mixture was heated for 3 h at 100°C, then cooled to room temperature and stirred for an additional 16 h. The mixture was poured into 1 L of acidic (HCl) ice water, and the organics were extracted using methylene chloride, dried over magnesium sulfate, and the solvents were removed under reduced pressure to yield a yellow powder. Recrystallization from acetone afforded 42.1 g (90% yield) of white crystals: m.p. 104°–105°C.

Anal Calcd for C13HsNO3Br: % C = 51.01 % H = 2.63 % N = 4.58 % Br = 26.01 Found: % C = 50.08 % H = 2.82 % N = 4.45 % Br = 25.81

Synthesis of 4-bromo-4'-nitrobenzophenone

In a 250 mL flask equipped with a nitrogen inlet, overhead stirring assembly, and reflux condenser were placed 4-bromo-3'-nitrobenzophenone (15.31 g, 0.050 mol), phenylacetylene (5.62 g, 0.055 mol), triphenylphosphine (0.08 g), bis(triphenylphosphine)palladium (0.11 mol), and aluminum chloride (100 g, 0.63 mol), and aluminum chloride (17.3 g, 0.13 mol). The mixture was heated for 3 h at 100°C, then cooled to room temperature and stirred for an additional 16 h. The mixture was poured into 1 L of acidic (HCl) ice water, and the organics were extracted using methylene chloride, dried over magnesium sulfate, and the solvents were removed under reduced pressure to yield a yellow powder. Recrystallization from acetone afforded 29.2 g (85% yield) of yellow crystals: m.p. 123°–124°C, (Lit. 122°C).

EXAMPLE 2

Synthesis of Phenylethynylbenzophenones

Synthesis of 4-fluoro-4'-phenylethynylbenzophenone

In a 250 mL flask equipped with a nitrogen inlet, overhead stirring assembly, and reflux condenser were placed 4-methylbenzene (117 g, 1.2 mol) and 4-bromobenzoyl chloride (39.8 g, 0.181 mol). The mixture was cooled to 0°C and aluminum chloride (27 g, 0.20 mol) was added. The mixture was stirred for 15 minutes at 23°C, followed by heating to reflux for 4 h. The reaction was then cooled to 23°C and stirred for 16 h. The resulting slurry was poured into 2 L of acidic (HCl) water. The organics were extracted with methylene chloride, and dried over magnesium sulfate. The slurry was filtered and the methylene chloride was removed under reduced pressure to yield an off white powder. Recrystallization from ethanol afforded 13.73 g (47% yield) of white crystals: m.p. 185°–186°C. IR (KBr) 3086 cm⁻¹ (aromatic); 2209 cm⁻¹ (C=C); 1654, 1612 cm⁻¹ (w); and 1601 cm⁻¹ (aromatic C-H). Mass Spec. m/e (relative intensity): M⁺, 327.1 (53%); FW=327.34 g/mol.

Anal Calcd for C21H13FO: % C = 76.54 % H = 4.26 % N= 4.02

Synthesis of 4-nitro-4'-phenylethynylbenzophenone

In a 250 mL flask equipped with a nitrogen inlet and reflux condenser were placed 4-fluoro-4'-nitrobenzenophenone (19.3 g, 0.063 mol), phenylacetylene (6.5 g, 0.063 mol), triphenylphosphine (0.15 g), bis(triphenylphosphine)palladium (0.11 chloride (0.08 g), copper (I) iodide (0.08 g), and 100 mL of triethylamine. The mixture was heated to 50°–60°C. Copper (I) iodide (0.050 g), and additional 50 mL of triethylamine were added. The reaction was heated to reflux for 2 h, then cooled to room temperature. The resulting precipitate was collected by filtration, washed with acidic (HCl) water, and dried at 100°C. Recrystallization from 1-butanol afforded 9.5 g (47% yield) of white crystals: m.p. 185°–186°C. IR (KBr) 3086 cm⁻¹ (aromatic); 2209 cm⁻¹ (C=C); 1654, 1612 cm⁻¹ (C-O); and 1601 cm⁻¹ (aromatic C-H).

Anal Calcd for C21H13NO3: % C = 77.05 % H = 4.00 % N= 4.28 Found: % C = 76.54 % H = 4.26 % N= 4.02

Synthesis of 3-nitro-4'-phenylethynylbenzophenone

In a 250 mL flask equipped with a nitrogen inlet and reflux condenser were placed 4-bromo-3'-nitrobenzenophenone (17.3 g, 0.063 mol), phenylacetylene (6.5 g, 0.063 mol), triphenylphosphine (0.15 g), bis(triphenylphosphine)palladium (0.11 chloride (0.08 g), copper (I) iodide (0.08 g), and 100 mL of triethylamine. The mixture was heated to 65°C for 16 h, then cooled to room temperature. The resulting mixture was poured into acidic (HCl) water, the precipitate was collected by filtration, washed with acidic (HCl) water, and dried at 110°C. Recrystallization from toluene afforded 13.73 g (85% yield) of white crystals: m.p. 195°–196°C. IR (KBr) 3086 cm⁻¹ (aromatic); 2212 cm⁻¹ (C=C); 1656 cm⁻¹ (C=C); and 1602 cm⁻¹ (aromatic C-H). Mass Spec. m/e (relative intensity): M⁺, 327.1 (53%); FW=327.34 g/mol.

Anal Calcd for C21H13NO3: % C = 77.05 % H = 4.00 % N= 4.28 Found: % C = 76.84 % H = 3.94 % N= 3.81.

\[
\text{PdCl}_2(\text{PPh}_3)_2 + \text{X} = \text{F}, \text{NO}_2
\]
mixture was allowed to cool to room temperature. The dried at 100 °C in vacuo to afford 2.5 g (95% yield) of
water and allowed to dry. Recrystallization from etha-
ture. The reaction mixture was poured into water and
the resulting light yellow powder was collected by filtra-
Recrystallization from water/acetone (50/50) (v) and
sodium dithionite (0.5 g) afforded 51.8 g (95% yield) of
the desired product: m.p. 151°-153° C. IR (KBr); 3463, 3356 and 3208 cm−1 (NH2); 3049, 2216 cm−1 (aromatic C-H); 1645 cm−1 (aromatic C=O); Mass Spec. m/e (relative intensity): M+ 389.4 (100); FW = 389.44 g/mol.
Analog Calcd for C27H19N02: % C = 83.28 % H = 4.92 % N = 3.60 Found: % C = 82.80 % H = 4.86 % N = 3.00 syn

**EXAMPLE 3**

**Synthesis of 4-(4-aminophenoxy)-4' -phenylethynylbenzophenone (4-APEB)**

In a 500 mL flask equipped with a reflux condenser, sodium dithionite (0.5 g) was added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
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added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
added over a 45 minute period. The mixture was heated was poured into 1 L of water, and the precipitate was
added over a 45 minute period.
Synthesis of 4-phenylethynylbenzoyl-3-phenylphthalimide

In a 100 mL flask equipped with a reflux condenser were placed 3-amino-4'-phenylethynylbenzophenone (2.97 g, 0.010 mol), phthalic anhydride (1.48 g, 0.010 mol), and glacial acetic acid (50 mL). The mixture was heated to reflux for 16 h, then cooled to room temperature. The resulting precipitate was collected by filtration, washed with acetic acid and water and dried at 100°C. Recrystallization from 1-butanol afforded 3.50 g (82% yield) of a white solid: m.p. 195°-195.5°C. IR (KBr) 2214 cm⁻¹ (C≡C), 1727 cm⁻¹ (imide C=O), and 1654 cm⁻¹ (C=O). Mass Spec. m/e (relative intensity): M⁺, 427.4 (6); FW=427.46 g/mol. Anal Calcd for C₃₉H₂₁N₂O₄: % C=80.91 % H=4.07 % N=2.70 Found: % C=78.88 % H=4.06 % N=2.31

EXAMPLE 5

4-Phenylethynylbenzoyl-4'-phenoxy-3''-phenylphthalimide, 4-phenylethynylbenzoyl-4'-phenoxy-4''-phenylphthalimide, and 4-phenylethynylbenzoyl-4'-phenylphthalimide were individually placed in a DSC cell and held at a rate of 10°C/min to 450°C. The model compounds displayed melting point maxima of 172°, 209° and 208° C. with a melting enthalpies of 101,109, and 107 J/g respectively. The exothermic onsets occurred at 354°, 347°, and 319° C. with maximum onsets at 415°, 402°, and 399° C. and curing enthalpies of 248, 287, and 408 J/g respectively. These compounds were also held at 350°C for 1 h. The resulting DSC thermograms of these thermally treated compounds displayed an absence of both melting points and exothermic peaks.

EXAMPLE 6

4-Phenylethynylbenzoyl-4'-phenoxy-3''-phenylphthalimide, 4-phenylethynyl-benzoyl-4'-phenoxy-4''-phenylphthalimide, and 4-phenylethynylbenzoyl-4'-phenylphthalimide were individually placed in a DSC cell and held at 200°C for 20 h. The melting enthalpies of these compounds were 90.7, 73.2, and 95.7 J/g respectively indicating that 9%, 68%, and 89% of the starting material remained intact.
EXAMPLE 7
Synthesis of a 9000 g/mol phenylethynyl-terminated imide oligomer
In a 250 mL flask equipped with a nitrogen inlet, overhead stirring assembly, and reflux condenser were placed 3,4'-ODA (3.7992 g, 0.019 mol), ODPA (6.2045 g, 0.200 mol), and the appropriate endcapper (0.8007 mol), m-cresol (54 g), and isoquinoline (0.2 g). The solution was stirred at 23°C for 16 h, and heated to reflux for 3.5 h. The reaction was cooled to 23°C and poured into stirring methanol. The white precipitate was collected by filtration, extracted with methanol for 48 h and dried in vacuo at 180°C for 10 h to yield 9.2 g (98%) of white powder.

Thermal Properties of a 9000 g/mol Imide Oligomer Synthesized from ODPA and 3,4'-ODA Using Several Phenylethynyl Endcaps

| Endcap | ηinh (dL/g)² | Tg (°C.) Uncured | Tg (°C.) Cured
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Endcap" /></td>
<td>0.35</td>
<td>218</td>
<td>243</td>
</tr>
<tr>
<td><img src="image2" alt="Endcap" /></td>
<td>0.41</td>
<td>226</td>
<td>242</td>
</tr>
<tr>
<td><img src="image3" alt="Endcap" /></td>
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<td>220</td>
<td>228</td>
</tr>
<tr>
<td><img src="image4" alt="Endcap" /></td>
<td>0.37</td>
<td>213</td>
<td>223</td>
</tr>
</tbody>
</table>

* ηinh measured in m-cresol at 25°C using a conc. of 0.5 g/dL.
* Cured in a mold at 350°C for 1 hour at 200 psi.

The general reaction scheme for the phenylethynyl-terminated imide oligomers is shown in the Drawing where n is an integer from 1–100 repeat units. The solvent can be N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF) or m-cresol. Ar' can be as simple as 1,2,4,5-tetrasubstituted benzene, or it may be a bis-4-(o-diphenyl) having the general structure

where X = nil, O, S, C=O, SO₂, CH₂, C(CH₃)₂, C(CF₃)₂,
properties for this polymer are listed in Tables 1, 2 and 3.

**TABLE 1**

<table>
<thead>
<tr>
<th>Mn, g/mole</th>
<th>Endcapper</th>
<th>Polyimide</th>
<th>DSC Tg, °C</th>
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<tr>
<td>3000</td>
<td>3-APEB</td>
<td>0.12</td>
<td>173</td>
</tr>
<tr>
<td>3000</td>
<td>4-APEB</td>
<td>0.20</td>
<td>195</td>
</tr>
<tr>
<td>3000</td>
<td>5-APEB</td>
<td>0.22</td>
<td>208</td>
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<td>3000</td>
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<td>220</td>
</tr>
<tr>
<td>3000</td>
<td>4-APEB</td>
<td>0.41</td>
<td>222</td>
</tr>
</tbody>
</table>

aThermally imidated in m-cresol at -195°C for 4 h with isoquinoline catalyst
bAfter curing 1 h each at 100, 225 and 350°C

**TABLE 2**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mn, g/mole</th>
<th>3-APEB</th>
<th>4-APEB</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 5% Weight Loss, °C</td>
<td></td>
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<tr>
<td>25</td>
<td>443</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>48 h soak</td>
<td>439</td>
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<td>502</td>
<td>19.3</td>
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**TABLE 3**

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<th>Test Conditions</th>
<th>Molding</th>
<th>Exposure</th>
<th>Test Temperature, °C</th>
<th>Shear Strength, psi</th>
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<td>23</td>
<td>4730</td>
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<tr>
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<tr>
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<td>50</td>
<td>48 h soak</td>
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<td>5410</td>
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<td>none</td>
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<tr>
<td>9000</td>
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<tr>
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<td>3890</td>
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</tbody>
</table>

The following example illustrates the synthesis of a phenylethylnyl-terminated imide oligomer with theoretical number average molecular weight of 3000 g/mole. 3,4'-Oxydianiline (ODA) (4.268 mmole, 0.8546 g), 4,4'-oxydiphthalic dihydride (ODPA) (5.000 mmole, 1.5511 g), 4-(4-aminophenoxo)-4'-phenylethylnylbenzophenone (4-APEB) (1.494 mmole, 0.5819 g, 2% excess), m-cresol (14 g), and isoquinoline (0.2 g) were added to a 100 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25°C for 16 h by heating at reflux (195°C) for 4 h. After cooling, the reaction was poured into methanol, washed in boiling methanol and dried at 110°C for 72 h to afford an off-white solid in >95% yield. The % solids resulting phenylethynyl-terminated polyimide had an inherent viscosity of 0.20 dL/g in m-cresol at 25°C. Additional
EXAMPLE 10

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 9000 g/mole. 3,4'-Oxydianiline (ODA) (50.00 mmole, 10.0123 g), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) (47.37 mmole, 15.2642 g), 4-(3-aminophenoxy)-4'-phenylethylybenzophenone (3-APEB) (5.260 mmole, 2.0485 g), m-cresol (155 g), and isoquinoline (2 g) were added to a 250 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25 °C for 16 h followed by heating at reflux (≈195 °C) for 4 h. After cooking, the reaction was poured into methanol, washed in boiling methanol and dried at 110 °C for 72 h to afford an off-white solid in >95% yield. The resulting phenylethynyl-terminated polyimide had η_{inh} of 0.36 dL/g in m-cresol at 25 °C. A film cast from m-cresol solution of this oligomer and cured 1 h at 350 °C was tough and finger nail creasible. The film was completely insoluble and did not swell when soaked for 48 h in DMAc and completely insoluble but swelled slightly (≈5% increase in area) when soaked for 48 h in methylene chloride. Additional properties for this polymer are listed in Tables 1, 2 and 3. This material has been designated LARC™-PETI-1.

EXAMPLE 11

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 6000 g/mole. 3,4'-Oxydianiline (ODA) (18.48 mmole, 3.7001 g), 4,4'-oxydiphthalic dianhydride (ODPA) (20.00 mmole, 6.2045 g), 4-(3-aminophenoxy)-4'-phenylethylybenzophenone (3-APEB) (3.044 mmole, 1.1855 g), m-cresol (85 g) and isoquinoline (0.2 g) were added to a 100 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25 °C for 16 h followed by heating at reflux (≈195 °C) for 4 h. After cooling, the reaction was poured into methanol, washed in boiling methanol and dried at 110 °C for 72 h to afford an off-white solid in >95% yield. The resulting phenylethynyl-terminated polyimide had η_{inh} of 0.22 dL/g in m-cresol at 25 °C. Additional properties for this polymer are listed in Tables 1, 2 and 3.
Nyl-terminated polyimide was insoluble in NMP. The initial Tg by DSC was 226°C and a final Tg of 235°C was measured after 1 h at 350°C.

EXAMPLE 16

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 6000 g/mole. 3,4-Oxydianiline (ODA) (24.974 mmole, 5.0010 g), 1,3-bis(3-aminophenoxy)benzene (APB) (2.7749 mmole, 0.5112 g), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) (30.00 mmole, 8.8267 g), 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB) (4.5012 mmole, 1.7529 g), N-methylpyrrolidinone (NMP) (65 g) were added to a 250 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25°C for 16 h to form the phenylethynyl-terminated polyamide acid oligomer. After cooling, the reaction was poured into water, 3,4'-Oxydianiline (ODA) (42.69 mmole, 8.5432 g), 4,4'-oxydiphthalic dianhydride (ODPA) (30.00 mmole, 8.5432 g), 4,4'-oxydiphthalic dianhydride (ODPA) (45.00 mmole, 13.9599 g), 3-amino-4'-phenylethynylbenzophenone (4.620 mmole, 1.3738 g) and N-methylpyrrolidinone (NMP) (54 mL) were added. The mixture was stirred for 8 h. After cooling, the reaction was poured into water, washed in boiling methanol and dried at 110°C for 72 h to afford a yellow solid in >95% yield. The resulting phenylethynyl-terminated polyamide acid oligomer was insoluble in NMP. The initial Tg by DSC was 230°C and a final Tg of 252°C was measured after 1 h at 350°C.

EXAMPLE 17

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 9000 g/mole. 3,4'-Oxydianiline (ODA) (77.29 mmole, 15.478 g), 4,4'-oxydiphthalic dianhydride (ODPA) (36.70 mmole, 11.384 g), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) (36.70 mmole, 10.797 g), 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB) (7.81 mmole, 3.041 g), N-methylpyrrolidinone (NMP) (95 g) were added to a 250 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25°C for 16 h to form the phenylethynyl-terminated polyamide acid oligomer followed by adding toluene (40 mL) and heating at 160°C for 24 h. After cooling, the reaction was poured into water, washed in boiling methanol and dried at 110°C for 72 h to afford a yellow solid in >95% yield. The resulting phenylethynyl-terminated polyamide acid oligomer had \( \eta_{in} = 0.41 \text{ dL/g in m-cresol} \) at 25°C. The initial Tg by DSC was 226°C and a final Tg of 235°C was measured after 1 h at 350°C. This powder could be compression molded at 350°C under 200 psi to give a well consolidated, void free molding which was tough and solvent resistant. The air cured film was tough and creasable, with a Tg of 245°C. The film was not noticeably affected by immersion for 48 h in either methylene chloride or DMAc. At 25°C, the tensile strength, tensile modulus and elongation at break were 18,500 psi, 424,500 psi and 53%, respectively. At 177°C, these properties were 8,600 psi, 279,500 psi and 65%, respectively.

EXAMPLE 19

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 9000 g/mole. This material has the same chemical composition as is in Example 13 and is designated LARC \textsuperscript{TM}-PET-1. 3,4'-Oxydianiline (ODA) (42.69 mmole, 8.5432 g), 4,4'-oxydiphthalic dianhydride (ODPA) (45.00 mmole, 13.9599 g), 3-amino-4'-phenylethynylbenzophenone (4.620 mmole, 1.3738 g) and N-methylpyrrolidinone (NMP) (54 mL) were added to a 250 mL three neck flask equipped with a mechanical stirrer, condenser and nitrogen inlet. The reaction was stirred at 25°C for 24 h. A film was cast from a portion of this solution and cured 1 h at 350°C in air. Toluene (50 mL) was added to the rest of the solution and water was removed by azeotropic distillation using a Dean-Stark trap. Toluene was removed and the mixture diluted to a concentration of 15% (w/w) by the addition NMP (61 mL). The mixture was heated at 183°-191°C for 2 h. The precipitated imide oligomer/NMP mixture was poured into methanol, collected by filtration, extracted with methanol for 48 h and dried under vacuum at 220°C to afford an off-white solid in >98% yield. The resulting phenylethynyl-terminated imide oligomer had \( \eta_{inh} = 0.32 \text{ dL/g in m-cresol} \) at 25°C. The initial Tg by DSC was 225°C and a final Tg of 233°C was measured after 1 h at 350°C.

EXAMPLE 20

Unoriented thin films were prepared in the following manner. NMP solutions (\( \approx 30\% \) solids) of the phenylethynyl terminated amide acid oligomers were centrifuged, the decaantate doctored onto clean, dry plate glass and dried to a tack free form in a low humidity chamber. The films on glass were dried in flowing air at 100°, 225° and 350° for 1 h each. Thin film tensile properties were determined according to ASTM D882. LARC \textsuperscript{TM}-PETI-1 films gave tensile strength, tensile modulus and elongation at break at 25°C of 17,600 psi, 225,000 psi and 25%, respectively. The air cured film had a Tg of 249°C. Solvent resistance was determined on stressed (0.2 x 2 in x 0.002 in) film strips immersed in various solvents for 2 weeks at ambient temperature. The specimens were secured in a circular form by multiple wraps around a standard paper clip. Films from LARC \textsuperscript{TM}-PETI-1 exhibited excellent resistance to ethylene glycol, methylthyl ketone, jet fuel, hydraulic fluid and toluene.

EXAMPLE 21

Molded specimens were prepared in the following manner. Powdered imide oligomers (approximately 8.5
EXAMPLE 22

LARC™-PETI-1 adhesive specimens were prepared in the following manner. Adhesive tape was prepared by coating 112 E-glass (A100 finish) cloth with phenylethynyl terminated amic acid (PETAA) solution in NMP and drying at a final temperature of 250° C. to a volatile content of approximately 0.7%. Several coats were required to obtain adequate tape thickness. Titanium (Ti-6Al-4V) with a Pasagel 107™ surface treatment was primed with the corresponding PE-TAA/NMP solution, and dried at 100° and 225° C. for 1 h each. The volatile contents of the tapes varied from 31 to 34% by weight. Small composites (3 in. x 6 in. x 8 to 16 plies) were fabricated in a stainless steel mold by heating to 350° C. under 200 psi and holding at 350° C. under 200 psi for 1 h. Larger laminates (6 in. x 6 in. x 16 to 32 plies) were fabricated in an autoclave by heating to 350° C. under 200 psi and holding for 1 h at 350° C. under 200 psi.

The composite panels were ultrasonically scanned (C-scanned) to show no voids, cut into specimens and tested for flexural properties according to ASTM D790, short beam shear strength according to ASTM D2344, and compression strength according to ASTM D3410 Procedure B.

We claim:

1. A phenylethynyl terminated oligomer having the general structure:

\[
\text{Ar}-(\text{O})_{2}\text{Ar'}
\]

wherein Ar is any diamine moiety Ar' is any dianhydride moiety, x is a member selected from the group consisting of: a bond, a meta-substituted phenoxy group and a para-substituted phenoxy group; y is a member

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**Flatwise Sandwich Tensile Strength**

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>23° C.</td>
<td>27</td>
</tr>
<tr>
<td>23° C. after 72 h water boil</td>
<td>10.5</td>
</tr>
<tr>
<td>23° C. after 48 h soak, jet fuel</td>
<td>9.5</td>
</tr>
<tr>
<td>150° C.</td>
<td>2.5</td>
</tr>
<tr>
<td>150° C. after 72 h water boil</td>
<td>2.5</td>
</tr>
<tr>
<td>177° C.</td>
<td>2.25</td>
</tr>
<tr>
<td>177° C. after 72 h water boil</td>
<td>2.25</td>
</tr>
<tr>
<td>177° C. after 500 h at 177° C, air</td>
<td>2.25</td>
</tr>
</tbody>
</table>

---

**Unidirectional IM-7 Laminate Properties of LARC™-PETI-1**

<table>
<thead>
<tr>
<th>Test Temperature, °C</th>
<th>Flexural St. KSI (Modulus, Msi)</th>
<th>Short Beam Shear St., KSI</th>
<th>Compressive St., KSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>21.7</td>
<td>16.2</td>
<td>197</td>
</tr>
<tr>
<td>177</td>
<td>27</td>
<td>8.0</td>
<td></td>
</tr>
</tbody>
</table>

---

**Climbing Drum Peel Strength**

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Strength, in. lb/in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-54° C.</td>
<td>33.4</td>
</tr>
<tr>
<td>23° C.</td>
<td>32.9</td>
</tr>
<tr>
<td>177° C.</td>
<td>38.8</td>
</tr>
</tbody>
</table>

---

**Unidirectional prepregs (tapes) were prepared by coating unsized IM-7 carbon/graphite fiber on a tape machine with 30% NMP solutions of the PETAA of LARC™-PETI. The volatile contents of the tapes varied from 7 to 12% and were controlled by the residence time and temperature of an in-line furnace in the tape machine. Resin content in the tapes (minus volatiles) varied from 31 to 34% by weight. Small composites (3 in. x 6 in. x 8 to 16 plies) were fabricated in a stainless steel mold by heating to 350° C. under 200 psi and holding at 350° C. under 200 psi for 1 h. Larger laminates (6 in. x 6 in. x 16 to 32 plies) were fabricated in an autoclave by heating to 350° C. under 200 psi and holding for 1 h at 350° C. under 200 psi. The composite panels were ultrasonically scanned (C-scanned) to show no voids, cut into specimens and tested for flexural properties according to ASTM D790, short beam shear strength according to ASTM D2344 and compression strength according to ASTM D3410 Procedure B.

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The composite panels were ultrasonically scanned (C-scanned) to show no voids, cut into specimens and tested for flexural properties according to ASTM D790, short beam shear strength according to ASTM D2344 and compression strength according to ASTM D3410 Procedure B.
selected from the group consisting of: C(CF₃)₂, Co and SO₂; n is 1–100; and the number average molecular weight of the phenyl ethynyl terminated imide oligomer is between about 500 and 20,000 g/mole.

2. A phenylethynyl terminated imide oligomer according to claim 1 wherein Ar is a diamine moiety selected from the group consisting of:

wherein Y is a bond, or Y is selected from the group consisting of 0, S, C=O, SO₂, CH₂, C(CH₃)₂, and

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22

C(CF₃)₂; and Ar' is a dianhydride moiety selected from the group consisting of:

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and

5. A phenylethynyl terminated imide oligomer according to claim 2, wherein

wherein Ar is — and

25

4. A phenylethynyl terminated imide oligomer according to claim 2, wherein

wherein Ar is — and

30

3. A phenylethynyl terminated imide oligomer according to claim 2, wherein the number average molecular weight is between about 3,000 and 9,000 g/mole.

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6. A phenylethynyl terminated imide oligomer according to claim 2, wherein

wherein Ar is — and

40

45

10

15

20

50

60

65

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and

wherein Ar is — and

wherein Ar' is — and

7. A phenylethynyl terminated imide oligomer according to claim 2, wherein
8. A phenylethynyl terminated imide oligomer according to claim 2, wherein

9. An adhesive prepared from a phenylethynyl terminated imide oligomer according to claim 1.

10. An adhesive prepared from the phenylethynyl terminated imide oligomer according to claim 4.
CERTIFICATE OF CORRECTION

PATENT NO.: 5,412,066
DATED: May 2, 1995
INVENTOR(S): Paul M. Hergenrother, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 21, line 1:

After "C(CF₃)₂," delete "Co" and insert ---CO--- in lieu thereof.

Signed and Sealed this Seventh Day of November, 1995

Attest:

BRUCE LEHMAN
Attesting Officer
Commissioner of Patents and Trademarks