PHENYLETHYNYL TERMINATED IMIDE OLIGOMERS

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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

References Cited

U.S. PATENT DOCUMENTS

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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
FIG. 1

where X = nil or
PHENYLETHYNYL TERMINATED IMIDE OLGOMERS

ORIGIN OF THE INVENTION

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

\[
\begin{align*}
\text{Ar}^2 & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{Ar}^2
\end{align*}
\]

where \( \text{Ar}^2 \) 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:

\[
\begin{align*}
\text{Ar}^2 & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{Ar}^2
\end{align*}
\]

where \( X = \text{H}, \text{SO}_2, \text{C} = \text{O}, \text{etc.} \) \( \text{Ar}^2 \) may be any other appropriate tetraivalent 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'-methylenediphenylene or any other appropriate divalent radical.


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-}

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), Ulemt® (General Electric) and LaRC™- TPI (Mitsui Toatsu) are commercially available and used as fibers, films, moldings, adhesives or composite matrices.

nomer ratio and \( D_p = \text{degree of polymerization} \), 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 \( Ar \) is any diamine moiety and \( Ar' \) 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 200 \( ^\circ C \)/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 polyimides 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:

\[
\text{H}_2\text{N}-X-\text{Y}=\text{C}(\text{CF}_3)\text{H}, \text{CO}, \text{or SO}_2
\]

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

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\(^\circ\) 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-dimethylacetamide (DMAc) at 143\(^\circ\) 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 phenylethynyl endcapper react at a moderate to fast rate in air at 300\(^\circ\) to 350\(^\circ\) C. whereas analogous model compounds containing the ethynyl group react at a moderate to fast rate in air at 200\(^\circ\) to 250\(^\circ\) C. Phenylethynyl containing imide model compounds are reasonably stable at 200\(^\circ\) C. (see Example 6) whereas thynyl containing imide model compounds react at 200\(^\circ\) 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\(^\circ\) C., the resulting glass transition temperatures (Tg) are 15\(^\circ\) to 20\(^\circ\) 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 (22.6 g, 0.122 mol), 4-bromoanisole (15.3 g, 0.063 mol), phenylacetylene (6.5 g, 0.063 mol), triphenylphosphine (0.100 g), bis(triphenylphosphine)palladium (0.08 g), and copper (I) iodide (0.05 g). The mixture was heated to 85-90°C for 2 h, then cooled to room temperature and stirred for another 16 h. The mixture was poured into 1 L of acidic (HCl) water, the precipitate was collected by filtration and dried in vacuo at 60°C. Recrystallization from ethyl ether afforded 23 g (75%) of yellow-white crystals: m.p. 155-156°C. IR (KBr): 1711 cm⁻¹ (C=O); 1656 cm⁻¹ (aromatic). Mass Spec. m/z (relative intensity): M⁺, 327.34 g/mol. Anal Calcd for C₂₁H₁₃NO₃: % C = 76.84, % H = 3.94, % N = 4.38. Found: % C = 76.54 % H = 4.00 % N = 3.81.

EXAMPLE 2

Synthesis of Phenylethynylbenzophenones

In a 250 mL flask equipped with a nitrogen inlet, overhead stirring assembly, and reflux condenser were placed 4-bromoanisole (15.9 g, 0.063 mol), phenylacetylene (6.5 g, 0.063 mol), triphenylphosphine (0.15 g), bis(triphenylphosphine)palladium (0.08 g), and copper (I) iodide (0.08 g), and 100 mL of triethylamine. The mixture was heated to 85°C for 1 h, then cooled to room temperature. The resulting mixture was poured into acidic (HCl) water, the precipitate was collected by filtration and dried in vacuo at 60°C. Recrystallization from ethyl ether afforded 23 g (75%) of yellow-white crystals: m.p. 155-156°C. IR (KBr): 1711 cm⁻¹ (C=O); 1656 cm⁻¹ (aromatic). Mass Spec. m/z (relative intensity): M⁺, 327.34 g/mol. Anal Calcd for C₂₁H₁₃NO₃: % C = 76.84, % H = 3.94, % N = 4.38. Found: % C = 76.54 % H = 4.00 % N = 3.81.
EXAMPLE 3

Synthesis of Phenylethylvinylamino Endcappers

Synthesis of 4-(4-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB)

In a 500 mL flask equipped with nitrogen inlet, over-head stirring assembly, Dean-Stark trap, and reflux condenser were placed 3-aminophenol (18.5 g, 0.17 mol), 4-phenylethyl-1'-4'-fluorobenzophenone (43.2 g, 0.14 mol), potassium carbonate (22.0 g, 0.16 mol), toluene (30 mL), and DMAc (200 mL). The mixture was heated to 142° C. for 8 h, then cooled to room temperature. The reaction mixture was poured into water and the resulting light yellow powder was collected by filtration. Recrystallization from water/acetone (50/50) (v) and sodium dithionite (0.5 g) afforded 51.8 g (95% yield) of a pale yellow solid: m.p. 195°-196.5° C. IR (KBr): 3463, 3356 and 3208 cm⁻¹ (NH₂); 1667.5'°-169° C. (M) of a pale yellow solid: m.p. 195°-196.5° C. IR (KBr): 3463, 3356 and 3208 cm⁻¹ (NH₂); 1667.5'°-169° C. (M). Mass Spec. m/e (relative intensity): M⁺, 297.2 (47); FW=297.36 g/mol.

Anal Calcd for C₂₁H₁₅NO₂: % C=83.60 % H=4.92 % N=3.60 Found: % C=82.80 % H=4.86 % N=3.00

4-(4-Aminophenoxy)-4'-phenylethynylbenzophenone (4-APEB)

In a 250 mL flask equipped with nitrogen inlet, over-head stirring assembly, Dean-Stark trap, and reflux condenser were placed 4-aminophenol (5.46 g, 0.05 mol), 4-phenylethyl-1'-4'-fluorobenzophenone (15.02 g, 0.05 mol), potassium carbonate (7.6 g, 0.055 mol), toluene (20 mL), and DMAc (45 mL). The mixture was heated to 150° C. for 2 h, then cooled to room temperature. The reaction mixture was poured into water and the resulting light yellow powder was collected by filtration. Recrystallization from toluene afforded the desired product: m.p. 151°-153° C. IR (KBr); 3414 and 3342 cm⁻¹ (NH₂); 3049, 1599, and 1645 cm⁻¹ (C=O); Mass Spec. m/e (relative intensity): M⁺, 389.4 (100); FW=389.44 g/mol.

Anal Calcd for C₂₇H₂₁N₂O₄: % C=81.50 % H=4.98 % N=3.39 Found: % C=80.91 % H=4.86 % N=3.39

EXAMPLE 4

Synthesis of Imide Model Compounds

Synthesis of 4-phenylethynylbenzoyl-4'-phenoxy-4''-phenylphthalimide

In a 200 mL flask equipped with a reflux condenser were placed phthalic anhydride (1.33 g, 8.9 mmol), 3-APEB (3.50 g, 8.9 mmol), and acetic acid (100 mL). The solution was stirred for 1.5 h at 23° C. and heated to reflux for 3 h. The solution was poured into 2 L of water, the precipitate was collected by filtration, washed in warm ethanol, and dried at 120° C. in vacuo to afford 4.4 g (95% yield) of a white powder: m.p. 167.5°-169° C. IR (KBr): 3040-3010 and 1602 cm⁻¹ (NH₂); 1657 cm⁻¹ (C=O). Mass Spec. m/e (relative intensity): M⁺, 297.2 (47); FW=297.36 g/mol.

Anal Calcd for C₂₁H₁₅NO₂: % C=83.60 % H=4.92 % N=3.60 Found: % C=82.80 % H=4.86 % N=3.00

Synthesis of 3-amino-4'-phenylethynylbenzophenone

In a 500 mL flask equipped with a nitrogen inlet, thermometer, addition funnel, and reflux condenser were placed 3-nitro-4'-phenylethynylbenzophenone (5.16 g, 0.070 mol), 200 mL of ethanol, and 20 mL of water. The solution was heated to reflux for 4 h, then allowed to cool to room temperature. The solvent was removed under reduced pressure, and the resulting solid was washed in water, collected by filtration, and dried at 100° C. Recrystallization from ethanol afforded 5.41 g (61% yield) of a pale yellow solid: m.p. 195°-196.5° C. IR (KBr): 3224, 3340, and 3224 cm⁻¹ (NH₂); 2216 cm⁻¹ (C=O) and at 100 C. Recrystallization from ethanol afforded 5.41 g (61% yield) of a pale yellow solid: m.p. 195°-196.5° C. IR (KBr): 3224, 3340, and 3224 cm⁻¹ (NH₂); 2216 cm⁻¹ (C=O). 1H-NMR (DMF-d7): 6.28 (s, 2H amine); 6.65-7.90 (m, 13H, aromatic). Mass Spec. m/e (relative intensity): M⁺, 389.4 (100); FW=389.44 g/mol.

Anal Calcd for C₂₇H₂₁N₂O₂: % C=83.28 % H=4.92 % N=4.71 Found: % C=82.80 % H=4.86 % N=4.60

Synthesis of 4-phenylethynylbenzoyl-4'-phenoxy-4''-phenylphthalimide

In a 500 mL flask equipped with a nitrogen inlet and reflux condenser were placed sodium sulfide nonahydrate (24.02 g, 0.10 mol) and water (60 mL). The solution was heated to reflux for 4 h, then cooled to room temperature. The solvent was removed under reduced pressure, and the resulting solid was collected by filtration, washed in water, collected by filtration, and dried at 100° C. Recrystallization from ethanol afforded 5.09 g (69% yield) of a pale yellow solid: m.p. 140°-142° C. IR (KBr): 3463 3356 and 3208 cm⁻¹ (NH₂); 2217 cm⁻¹ (C=O); 1646 cm⁻¹ (C=O). Mass Spec. m/e (relative intensity): M⁺, 297.2 (47); FW=297.36 g/mol.

Anal Calcd for C₂₁H₁₅NO₂: % C=84.82 % H=5.08 % N=4.71 Found: % C=84.99 % H=5.12 % N=4.52

Synthesis of 4-aminophenylbenzophenone
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 (imidic 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 C₃₅H₂₁N₄O₄: % 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 heated at a rate of 10°C/min to 450°C. The model compounds displayed melting point maxima of 172°, 209° and 208°C with melting enthalpies of 248, 287, and 408 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) | Tg (°C.) Uncured | Tg (°C.) Cured
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂N-O-</td>
<td>0.35</td>
<td>218</td>
<td>243</td>
</tr>
<tr>
<td>H₂N-O-</td>
<td>0.41</td>
<td>226</td>
<td>242</td>
</tr>
<tr>
<td>H₂N-</td>
<td>0.36</td>
<td>220</td>
<td>228</td>
</tr>
<tr>
<td>H₂N-</td>
<td>0.37</td>
<td>213</td>
<td>223</td>
</tr>
</tbody>
</table>

*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-methylpyrrolidinone (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-diphenylene) having the general structure

where X=nil, O, S, C==O, SO₂, CH₂, C(CH₃)₂, C(CF₃)₂,
wherein Y=nil, O, S, \( \text{C} = \text{O} \), \( \text{SO}_2 \), \( \text{CH}_2 \), \( \text{C}(\text{CH}_3)_2 \), \( \text{C}(-\text{CF}_3)_2 \) etc., and mixtures thereof.

Phenylethynyl-terminated imide oligomers have a wide range of molecular weights (\( \geq 500 \) to \( \approx 20,000 \) g/mole) are readily prepared by offsetting the ratio of one monomer relative to the other by a calculated amount and adding an appropriate amount of either 3- or 4-aminophenoxy-4'-phenylethynylbenzophenone or 3- or 4-amino-4'-phenylethynylbenzophenone. Prior to curing, low molecular weight polymers have low melt viscosity and are readily processed into moldings, composites and adhesive bonds. When cured, different molecular weight polymers display different properties. For example, low molecular weight phenylethynyl-terminated imide oligomers provide a higher crosslink density than higher molecular weight phenylethynyl-terminated imide oligomers. Materials containing high crosslink density normally produce better solvent resistance, higher modulus, better high temperature properties and lower toughness than those containing low crosslink density. Therefore, the polymers can be designed with the proper combination of properties for the desired application by controlling the molecular weight. Specific examples follow.

**EXAMPLE 8**

The following example illustrates the synthesis of a phenylethynyl-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 dianhydride (ODPA) (5,000 mmole, 1,5511 g), 4-(4-aminophenoxy)-4'-phenylethynylbenzophenone (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 followed by heating at reflux (\( \approx 195^\circ \text{C} \)) 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 \( \eta_{\text{in}} \) resulting phenylethynyl-terminated polyimide had an inherent viscosity of 0.20 dL/g in m-cresol at 25°C. Additional properties for this polymer are listed in Tables 1, 2 and 3.

**TABLE 1**

<table>
<thead>
<tr>
<th>Theory Mn, g/mole</th>
<th>Endcapper</th>
<th>Polyimide Characteristics</th>
<th>DSC Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td></td>
</tr>
<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>6000</td>
<td>3-APEB</td>
<td>0.22</td>
<td>208</td>
</tr>
<tr>
<td>6000</td>
<td>4-APEB</td>
<td>0.22</td>
<td>208</td>
</tr>
<tr>
<td>9000</td>
<td>3-APEB</td>
<td>0.36</td>
<td>220</td>
</tr>
<tr>
<td>9000</td>
<td>4-APEB</td>
<td>0.41</td>
<td>222</td>
</tr>
</tbody>
</table>

*Thermally imidized in m-cresol at \( \approx 195^\circ \text{C} \) for 4 h with isoquinoline catalyst.

*After curing 1 h each at 100, 225 and 350°C.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Tensile, psi</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>439</td>
<td>558</td>
</tr>
<tr>
<td>100</td>
<td>491</td>
<td>6.5</td>
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<tr>
<td>150</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>436</td>
<td>19.6</td>
</tr>
<tr>
<td>300</td>
<td>478</td>
<td>455</td>
</tr>
</tbody>
</table>

*Heating rate of 2.5°C/min in flowing air or nitrogen.

*Cured at 195°C for 4 h.

**TABLE 2**

<table>
<thead>
<tr>
<th>Theoretical Mn, g/mole</th>
<th>Endcapper</th>
<th>Polyimide Characteristics at 5% Weight Toluene</th>
<th>Tensile, psi</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>3-APEB</td>
<td>443</td>
<td>488</td>
<td>23</td>
</tr>
<tr>
<td>3000</td>
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**TABLE 3**

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<th>Test Temperature, °C</th>
<th>Shear Strength, psi</th>
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<td>3000 h/177°C</td>
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*Chevron Hytest IV hydraulic fluid.

**EXAMPLE 9**

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) (4,619 mmole, 0.9250 g), 4,4'-oxydiphthalic dianhydride (ODPA) (5,000 mmole, 1,5511 g), 4-(4-aminophenoxy)-4'-phenylethynylbenzophenone (4-APEB) (0.7762 mmole, 0.3023 g, 2% excess), 3,4'-oxydianiline (ODA) (4.619 mmole, 0.9250 g), 4,4'-oxydiphthalic dianhydride (ODPA) (5,000 mmole, 1,5511 g), 4-(4-aminophenoxy)-4'-phenylethynylbenzophenone (4-APEB) (0.7762 mmole, 0.3023 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 (\( \approx 195^\circ \text{C} \)) 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-ter-
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'-phenylethynylbenzophenone (3-APEB) (5.260 55 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 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 $\eta_{inh}$ 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 TM-PETI-1.

EXAMPLE 13

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) (18.97 mmole, 3.7992 g), 4,4'-oxydiphthalic dihydride (ODPA) (20.00 mmole, 6.2045 g), 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB) (2.056 mmole, 0.8007 g), m-cresol (55 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 $\eta_{inh}$ 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 TM-PETI-1.

EXAMPLE 14

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'-phenylethynylbenzophenone (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 to form an insoluble yellow precipitate. After cooling, the reaction was poured into methanol, washed in boiling methanol and dried at 110 °C for 72 h to afford a light yellow solid in >95% yield. The resulting phenylethynyl-terminated polyimide was insoluble in m-cresol. The initial Tg by DSC was 205 °C and the oligomer displayed a melting point (Tm) with a maximum at 384 °C. The wide angle X-ray diffraction pattern also indicated the oligomer was crystalline. The material displayed a final Tg of 278 °C and no Tm after heating to 450 °C and cooling directly to room temperature.

EXAMPLE 15

The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 9000 g/mole. Meta-phenylenediamine (m-PDA) (34.70 mmole, 3.6845 g), isophthaloyldiphenyl anhydride (IDPA) (36.70 mmole, 15.6449 g), 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB) (4.000 mmole, 1.5578 g), N-methylpyrrolidinone (NMP) (140 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 followed by adding acetic acid (14 g) and heating at reflux (~130 °C) for 5 h. After cooling, the reaction was poured into water, washed in boiling methanol and dried at 110 °C for 72 h to afford
a white solid in >95% yield. The resulting phenylethynyl-terminated polyimide was insoluble in NMP. The initial Tg by DSC was 245°C and a final Tg of 263°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 9000 g/mole. This material has the same chemical composition as that in Example 13 and is designated LARC-TM-PETI-1. Examples of various solvents for 2 weeks at ambient temperature. The following example illustrates the synthesis of a phenylethynyl-terminated imide oligomer with theoretical number average molecular weight of 9000 g/mole. The initial Tg by DSC was 227°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) (30.00 mmole, 8.8267 g), 4,4'-oxydiphthalic dianhydride (ODPA) (36.70 mmole, 10.797 g), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) (30.00 mmole, 8.8267 g), 4-(3-aminophenoxo)-4'-phenylethylnylbenzophenone (3-APEB) (4.5012 mmole, 1.7529 g), 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 16 h to form the phenylethynyl-terminated polyamide acid 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 polyimide 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 18**

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-aminophenoxo)-4'-phenylethylnylbenzophenone (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 followed by adding toluene (20 g) and heating at 165°C for 8 h. After cooling, the reaction was poured into water, washed in boiling methanol and dried at 180°C for 10 h to afford a yellow solid in >95% yield. The resulting phenylethynyl-terminated imide oligomer had a white solid in >95% yield. The resulting phenylethynyl-terminated imide oligomer had \( \eta_{	ext{sp.}} = 0.41 \text{dL/g} \) 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 creasible, with a Tg of 245°C. The film was not noticeably affected by immersion for 48h 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**

Unoriented thin films were prepared in the following manner. NMP solutions (~30% solids) of the phenylethynyl terminated amide acid oligomers were centrifuged, the decantate doctorred 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°C, 225°C and 350°C for 1 h each. Thin film tensile properties were determined according to ASTM D882. LARC™-PETI-1 films gave tensile strength, tensile modulus and elongation at break at 25°C of 17,600 psi, 425,000 psi and 424% and at 177°C of 7400 psi, 284,000 psi and 76%, 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 multi-ple wraps around a standard paper clip. Films from LARC™-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
and 0.010 in. by heating at 350° C. according to ASTM D-1783.

Cured panels were cut into 1 in. wide specimens and tested for:

1. Climbing drum peel panels were fabricated using E-glass (Al100 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.

2. Unidirectional prepregs (tapes) were prepared by coating 112 E-glass (Al100 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° C. and 225° C. for 1 h each.

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-1. 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 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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<th>Flexural St., KSI (Modulus, Msi)</th>
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<td>177</td>
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<td>23</td>
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</table>

We claim:
1. A phenylethynyl terminated oligomer having the general structure:

```
Ar-O-C-N-X-C-N-O-Ar
```

wherein Ar is any diamine moiety Ar' is any dihydride 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.
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:

![Chemical Structures](image1)

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂.

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.

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

![Chemical Structures](image2)

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂.

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

![Chemical Structures](image3)

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂.

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

![Chemical Structures](image4)

wherein Y is a bond, or Y is selected from the group consisting of O, S, C=O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂.

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

![Chemical Structures](image5)
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 phenylthynyl 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