ABSTRACT

Controlled molecular weight imide oligomers and co-oligomers containing pendent phenylethynyl groups (PEPs) and endcapped with nonreactive or phenylethynyl groups have been prepared by the cyclodehydration of the precursor amide acid oligomers or co-oligomers containing pendent phenylethynyl groups and endcapped with nonreactive or phenylethynyl groups. The amine terminated amide acid oligomers or co-oligomers are prepared from the reaction of dihydride(s) with an excess of diamine(s) and amine containing phenylethynyl groups and subsequently endcapped with a phenylethynyl phthalic anhydride or monofunctional amine. The anhydride terminated amide acid oligomers and co-oligomers are prepared from the reaction of diamine(s) and amine containing phenylethynyl group(s) with an excess of dihydride(s) and subsequently endcapped with a phenylethynyl amine or monofunctional amine. The polymerizations are carried out in polar aprotic solvents such as N-methyl-2-pyrrolidinone and N,N-dimethylacetamide under nitrogen at room temperature. The amide acid oligomers or co-oligomers are subsequently cyclodehydrated either thermally or chemically to the corresponding imide oligomers. The polymers and copolymers prepared from these materials exhibit a unique and unexpected combination of properties that includes higher glass transition temperatures after curing and higher retention of neat resin, adhesive and carbon fiber reinforced mechanical properties at temperatures up to 204°C. under wet conditions without sacrificing melt flow behavior and processability as compared to similar materials. These materials are useful as adhesives, coatings, films, moldings and composite matrices.

2 Claims, 6 Drawing Sheets
FIG. 1
\[
\text{W-Ar-C-N-Ar'}(-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'}) (-\text{N-}) (-\text{N-Ar'})\]

\[\text{FIG. 2}\]
FIG. 3
\[
\text{FIG. 4}
\]
\[ \text{FIG. 5} \]
\[
\begin{align*}
\text{Nitrogen} & \quad \text{Aprotic Solvent} \\
\overset{29^\circ C}{\text{Nitrogen}} & \quad \text{Aprotic Solvent} \\
\end{align*}
\]
DIAMINES CONTAINING PENDENT PHENYLETHYNYL GROUPS

This is a divisional of application Ser. No. 08/511,422 filed on Aug. 4, 1995, now U.S. Pat. No. 5,606,014.

ORIGIN OF THE INVENTION

This invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government or government purposes without payment of any royalties therein or thereof.

BACKGROUND OF THE INVENTION

Polyimides (PI) are heterocyclic polymers commonly prepared by the condensation reaction of an aromatic diamine with an aromatic dianhydride or derivative thereof and having a repeat unit of the general structure

\[
\text{Ar} - \text{N} - \text{Ar'}
\]

where \( \text{Ar} \) is a tetravalent aromatic radical such as 1,2,4,5-tetrasubstituted benzene. \( \text{Ar'} \) may also be a bis(o- diphenylene) having the general structure

\[
\text{Ar} - \text{N} - \text{Ar'}
\]

where \( Y = \text{nil, O, S, SO}_2, \text{CO, C(CH}_3)_2, \) or any other appropriate divalent 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'-sulfonyldiphenylene, or any other appropriate divalent radical.


This present invention constitutes new composition of matter. It concerns novel diamines containing phenylethynyl groups and new imide oligomers and co-oligomers containing pendant phenylethynyl groups. The polymers and copolymers prepared from these materials exhibit a unique and unexpected combination of properties that includes higher glass transition temperatures after curing and higher retention of neat resin, adhesive and carbon fiber reinforced mechanical properties at temperatures up to 204° C. under wet conditions without sacrificing melt flow behavior and processability as compared to similar materials.

Another object of the present invention is to provide materials that are useful as adhesives, coatings, films, moldings and composite matrices.

Another object of the present invention is the composition of several new diamines containing pendant phenylethynyl groups.

SUMMARY OF THE INVENTION

According to the present invention the foregoing and additional objects were obtained by synthesizing controlled molecular weight imide oligomers and co-oligomers containing pendant phenylethynyl groups and endcapped with phenylethynyl groups or nonreactive groups by different methods. Amide acid oligomers and co-oligomers containing pendant phenylethynyl groups (PEPAs) were prepared by the reaction of dihydride(s) with an excess of diamine(s) and diamine containing pendant phenylethynyl group(s) and endcapped with 4-phenylethynylphthalic anhydride or phthalic anhydride under a nitrogen atmosphere at room temperature in N-methyl-2-pyrroldinidine (NMP). Additionally, PEPAs were prepared by the reaction of diamine(s) and diamine containing pendant phenylethynyl group(s) with an excess of dihydride(s) and endcapped with a 3-amino-2-phenoxy-4-phenylethynylbenzophenone under a nitrogen atmosphere at room temperature in NMP. The imide oligomers and co-oligomers containing pendant phenylethynyl groups (PEPI) were prepared by cyclohydrogenation of the precursor PEPPA oligomers in NMP by azotropic distillation. The physical and mechanical properties and of PEPIs has been performed in m-erosol containing isoquinine at elevated temperature. Amide acid oligomers and co-oligomers containing pendant phenylethynyl groups can be prepared by the reaction of diamine(s) and diamine containing pendant phenylethynyl group(s) with an excess...
of di-anhydride(s) and endcapped with a non-functional amine under a nitrogen atmosphere at room temperature in NMP. Imide oligomers and co-oligomers containing pendant phenylethynyl groups can be prepared by the reaction of the half alkyl ester of aromatic tetracarboxylic acids with aromatic diamines and diamine containing pendant phenylethynyl group(s) and endcapped with the half alkyl ester of phenylethynyl substituted phthalic acid, the half alkyl ester of phthalic acid, phenylethynyl amine, or non-functional amine by heating in NMP. PEPs prepared by the alkyl ester route can also be prepared by heating neat or in solvents such as m-cresol. Imide oligomers and co-oligomers containing pendant phenylethynyl groups can be prepared by the polymerization of monomeric reactants (PMR) approach by heating a mixture of a diamine and diamine containing pendant phenylethynyl group(s) and the ethyl ester derivatives of di-anhydride(s) and endcapped with phenylethynylphthalic anhydride, monofunctional anhydride, phenylethynyl amine, or non-functional amine.

In addition, the amine terminated PEPAA oligomer or co-oligomer or the anhydride terminated PEPAA oligomer or co-oligomer can be cyclodehydrated to the corresponding amine terminated PEP or the anhydride terminated PEP oligomer or co-oligomer, respectively, and the appropriate endcapper subsequently reacted with the soluble amine terminated PEP oligomer or co-oligomer or the soluble amine terminated PEP oligomer or co-oligomer. The PEPI oligomer or co-oligomer must be soluble in order to perform this endcapping reaction. Upon reaction of the amine terminated PEP oligomer or co-oligomer or the anhydride terminated PEP oligomer or co-oligomer with the endcapper, the temperature is increased to effect cyclodehydration to complete imidization.

The inherent viscosities (η_inh) of the PEPI oligomers and co-oligomers ranged from 0.21 to 0.65 dL/g and the η_inh of high molecular weight uncapped PEPI was 0.85 dL/g. The glass transition temperatures (T_g) of the uncured as-isolated PEPIs ranged from 200°-260° C. In some cases, a crystalline melt temperature was observed for the uncured PEPIs. The temperature of onset and peak exotherm due to reaction of the phenylethynyl group was -350° C. and -411° C., respectively. After curing at 350° C. for 1 h in a sealed DSC pan the T_g of the cured polymers ranged from 255°-313° C. (PMR) or 269°-348° C. (NMP) at a heating rate of 2.5°C/min. After curing at 350° C. in air, the cured polymers showed no weight loss occurring below 300° C. in air or nitrogen with a 5% weight loss occurring at 475° C. in air and 517° C. in nitrogen. After a thermal cure (350° C./mold/1 h), TGA at a heating rate of 2.5° C/min of the cured polymers showed no weight loss occurring below 300° C. in air or nitrogen with a 5% weight loss occurring at 495° C. in air and -510° C. in nitrogen. The tensile strength, tensile modulus, and break elongation for unoriented thin films ranged from 18.9-21.8 ksi, 457-560 ksi, and 4-20% at 23° C.; and 10.1-14.0 ksi, 290-411 ksi, and 5-34% at 177° C.; and 9.2-12.2 ksi, 267-372 ksi, and 6-30% at 200° C., respectively. The polymers prepared from these materials exhibit higher glass transition temperatures with no apparent reduction in melt flow behavior as compared to similar materials. The G_C (critical strain energy release rate) of compression molded samples of PEPIs ranged from 2.9 in lb/in² to 10.3 in lb/in². The titanium (Ti) to Ti tensile shear properties performed on PAA 2210 at 177° C. and 4100 at 177° C. The Ti to Ti tensile shear properties performed on chromic acid anodized (5V) surface treated adherends were 4300 at 23° C. and 4100 at 177° C. The flexural properties of composite panels with a unidirectional lay-up gave flexural strength and flexural modulus which ranged from 233.5-260.3 ksi and 21.08-21.52 Msi at 23° C. and 190.3-219.4 ksi and 18.73-20.58 msi at 177° C., respectively. In general, composite specimens exhibited higher mechanical properties when tested at room temperature and better retention of those properties when tested at 177° C. than similar materials.

The diamines containing pendant phenylethynyl group(s) were prepared by the palladium catalyzed reaction of phenylacetylene with bromo substituted dinitro compounds and subsequently reduced to the corresponding diamines containing pendant phenylethynyl group(s) as shown in FIG. 1. The catenation of the phenylethynyl group on the phenyl ring may be para or meta and multiple phenyl rings may have mixed connecting positions. In general, this synthetic route to diamines containing pendant phenylethynyl groups is more cost effective than other routes. The general reaction sequence for the synthesis of both uncontrolled and controlled molecular weight polymers and copolymers is represented in FIGS. 2, 3, 4, 5 and 6.

The polymers and copolymers prepared from these materials exhibit a unique and unexpected combination of properties that includes higher glass transition temperatures after curing, higher tensile moduli and higher retention of neat resin, adhesive and carbon fiber reinforced mechanical properties at temperatures up to 204° C. when wet without sacrificing melt flow behavior and processability as compared to similar materials.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic of the synthesis of diamines containing pendant phenylethynyl groups according to the present invention;

FIG. 2 is a schematic of the synthesis of controlled molecular weight amide acid and imide co-oligomers containing pendant phenylethynyl groups chain terminated with nonreactive or reactive phthalic anhydride based encapping agents according to the present invention;

FIG. 3 is a schematic of the synthesis of controlled molecular weight amide acid and imide co-oligomers containing pendant phenylethynyl groups chain terminated with nonreactive or reactive aniline based encapping agents according to the present invention;

FIG. 4 is a schematic of the synthesis of controlled molecular weight amide acid and imide oligomers containing pendant phenylethynyl groups chain terminated with nonreactive or reactive phthalic anhydride based encapping agents according to the present invention;

FIG. 5 is a schematic of the synthesis controlled molecular weight amide acid and imide oligomers containing pendant phenylethynyl groups chain terminated with nonreactive or reactive aniline based encapping agents according to the present invention;

FIG. 6 is the reaction sequence for preparation of uncontrolled molecular weight polyimide containing pendant phenylethynyl groups where R is a 4-benzoyl group and Ar is 3,3,4,4′-diphenyl ether.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Novel diamines containing pendant phenylethynyl groups were prepared according to FIG. 1 having the following chemical structure:
The best results were obtained with 3,5-diamino-4'-phenylethynylbenzophenone. Controlled molecular weight amide acid and imide co-oligomers containing pendent phenylethynyl groups and chain terminated with either nonreactive or reactive phthalic anhydride based endcapping agents were prepared according to FIG. 2. The chemical structures of these oligomers are indicated below:

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

\[
\begin{align*}
\text{-OH} & , \quad \text{CO} \quad \text{SO}_2 \quad \text{C(CF)}_3 \quad \text{isophthalyl} \\
\text{-C} & , \quad \text{C} \quad \text{N} \quad \text{Ar} \quad \text{C} \quad \text{Ar} \quad \text{N} \quad \text{Ar} \quad \text{N} \quad \text{Ar} \quad \text{C} \\
\end{align*}
\]

...wherein \( Y \) is a bond or \( Y \) is a radical selected from the group consisting of: O, CO, \( \text{SO}_2 \), isophthalyl, terephthaloyl, 1,3-diphenoxyl, and 1,4-diphenoxyl.

...wherein \( \text{Ar} \) is a member selected from the group consisting of:

...wherein \( \text{Ar} \) is a member selected from the group consisting of:
wherein the catenation is selected from the group consisting of 2,2; 2,3; 2,4; 3,3; 3,4; and 4,4 and X is a bond or X is a radical selected from the group consisting of:

\[ \text{CH}_2, \text{O}, \text{CO}, \text{CH(OH)}, \text{C(CF)}_3, \text{OC}_{C} \]

wherein W is a radical selected from the group consisting of:

\[ \text{H} \]

\[ \text{C} \equiv \text{C} \]

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

\[ \text{O} \]

\[ \text{O} \]

wherein the amount of diamine containing pendant phenyl-ethynyl groups ranges from 1-99 mole %.

Particularly good results were obtained with examples 2, 8 and 13. Polymer characterization is presented in Table 1, thin film mechanical properties are presented in Table 2, adhesive properties are presented in Table 3 and carbon fiber reinforced composite properties are presented in Table 4.

### Table 1

<table>
<thead>
<tr>
<th>Oligomer (Amide acid)</th>
<th>Imide (°C)</th>
<th>% Tg,°C</th>
<th>Tg,°C</th>
<th>5% WT. Loss in air,°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imide</td>
<td>m-DLg^2</td>
<td>Dl/g (Tg), °C</td>
<td>Tg, °C</td>
<td>5% Wt. Loss in air, °C</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>----------------</td>
<td>-------</td>
<td>----------------------</td>
</tr>
<tr>
<td>1</td>
<td>0.85</td>
<td>ND</td>
<td>300</td>
<td>465</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>240</td>
<td>279</td>
<td>446</td>
</tr>
<tr>
<td>3</td>
<td>0.65</td>
<td>265</td>
<td>297</td>
<td>458</td>
</tr>
<tr>
<td>4</td>
<td>0.32</td>
<td>0.28 (217 (276))</td>
<td>255</td>
<td>451</td>
</tr>
<tr>
<td>5</td>
<td>0.31</td>
<td>0.22 (272, 286)</td>
<td>299</td>
<td>436</td>
</tr>
<tr>
<td>6</td>
<td>0.26</td>
<td>0.24 (259 (278))</td>
<td>300</td>
<td>478</td>
</tr>
<tr>
<td>7</td>
<td>0.29</td>
<td>0.22 (284)</td>
<td>283</td>
<td>495</td>
</tr>
<tr>
<td>8</td>
<td>0.32</td>
<td>0.28 (282)</td>
<td>315</td>
<td>463</td>
</tr>
<tr>
<td>9</td>
<td>0.21</td>
<td>0.41 (274)</td>
<td>310</td>
<td>463</td>
</tr>
<tr>
<td>10</td>
<td>0.28</td>
<td>0.26 (274)</td>
<td>296</td>
<td>451</td>
</tr>
<tr>
<td>11</td>
<td>0.36</td>
<td>ND</td>
<td>ND</td>
<td>446</td>
</tr>
<tr>
<td>12</td>
<td>0.30</td>
<td>ND</td>
<td>260</td>
<td>447</td>
</tr>
<tr>
<td>13</td>
<td>0.29</td>
<td>0.32 (284)</td>
<td>289</td>
<td>459</td>
</tr>
<tr>
<td>14</td>
<td>0.35</td>
<td>0.26 (243, 262)</td>
<td>310</td>
<td>499</td>
</tr>
<tr>
<td>15</td>
<td>0.33</td>
<td>0.31 (231)</td>
<td>299</td>
<td>440</td>
</tr>
<tr>
<td>16</td>
<td>0.22</td>
<td>ND</td>
<td>ND</td>
<td>402</td>
</tr>
<tr>
<td>17</td>
<td>0.31</td>
<td>ND</td>
<td>ND</td>
<td>413</td>
</tr>
</tbody>
</table>

1. Number corresponds to Example number.
2. Determined on 0.5% (w/v) NMP solutions of the amide acid at 25°C.
3. Determined by DSC at 20°C/min. *i* = as-isolated oligomer, *j* = cured sealed DSC pan/350°C/1 h.
4. Determined by TGA at 2.5°C/min.
5. ND: not detected.

### Table 2

<table>
<thead>
<tr>
<th>Oligomer (Amide acid)</th>
<th>Imide (°C)</th>
<th>Test Temp., °C</th>
<th>Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23</td>
<td>14.0</td>
<td>411</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>289</td>
<td>12.0</td>
<td>372</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>12.0</td>
<td>370</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>12.0</td>
<td>370</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>306</td>
<td>9.0</td>
<td>276</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>9.0</td>
<td>267</td>
<td>17</td>
<td></td>
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<tr>
<td>11</td>
<td>200</td>
<td>9.0</td>
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</tr>
<tr>
<td>12</td>
<td>306</td>
<td>9.0</td>
<td>267</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>301</td>
<td>20.5</td>
<td>495</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>294</td>
<td>20.5</td>
<td>495</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>296</td>
<td>20.5</td>
<td>495</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

1. Number corresponds to Example number.
2. Determined by DSC at 20°C/min on film samples cured at 100, 225, 350°C, for 1 h each, in flowing air.
TABLE 3
PRELIMINARY Ti-to-Ti TENSILE SHEAR PROPERTIES

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Property</th>
<th>Layup</th>
<th>Temp., °C</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 3,4-ODA/0.15 DPEB/BPD/PPA (Example 2)</td>
<td>PASA Jell 107 Surface Treatment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test</td>
<td>Strength, MPa</td>
<td>Cohesive Failure, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>3900</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>4100</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Property</th>
<th>Layup</th>
<th>Temp., °C</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic Acid Anodized (SV) Surface Treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>4300</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>4100</td>
<td>75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Processing conditions: 200 psi/300°C/0.5 h, then 200 psi/350°C/1 h
0.70 3,4-ODA/0.15 APB/0.15 DPEB/BFDA/PEPA (Example 13) PASA Jell 107 Surface Treatment

<table>
<thead>
<tr>
<th>Processing Conditions</th>
<th>Test Temperature, °C</th>
<th>Strength, psi</th>
<th>Failure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C/200 psi/1h</td>
<td>23</td>
<td>5000</td>
<td>50</td>
</tr>
<tr>
<td>371°C/200 psi/1h</td>
<td>23</td>
<td>4800</td>
<td>60</td>
</tr>
<tr>
<td>350°C/100 psi/1h</td>
<td>23</td>
<td>5200</td>
<td>65</td>
</tr>
<tr>
<td>350°C/200 psi/1h</td>
<td>177</td>
<td>5000</td>
<td>75</td>
</tr>
<tr>
<td>350°C/100 psi/1h</td>
<td>177</td>
<td>4500</td>
<td>100</td>
</tr>
<tr>
<td>350°C/200 psi/1h</td>
<td>200</td>
<td>4700</td>
<td>90</td>
</tr>
<tr>
<td>350°C/200 psi/1h</td>
<td>232</td>
<td>4000</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Property</th>
<th>Layup</th>
<th>Temp., °C</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 3,4-ODA/0.15 DPEB/BFDA/PEPA (Example 8)</td>
<td>PASA Jell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test</td>
<td>Strength, psi</td>
<td>Failure, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>371°C/50 psi/1h</td>
<td>23</td>
<td>2500</td>
<td>85 A</td>
<td></td>
</tr>
<tr>
<td>371°C/100 psi/1h</td>
<td>23</td>
<td>3100</td>
<td>60 A</td>
<td></td>
</tr>
<tr>
<td>371°C/200 psi/1h</td>
<td>23</td>
<td>3000</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1. 300°C/200 psi/0.5 h</td>
<td>23</td>
<td>4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. 350°C/200 psi/1.0 h</td>
<td>23</td>
<td>5000</td>
<td>80 A</td>
<td></td>
</tr>
</tbody>
</table>

Controlled molecular weight amide acid and imide co-oligomers containing pendant phenylethynyl groups and chain terminated with either nonreactive or reactive aniline based endcapping agents were prepared according to FIG. 3. The chemical structures of these oligomers are indicated below:
wherein Ar is a member selected from the group consisting of:

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

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

wherein Ar' is a member selected from the group consisting of:

wherein the catenation is selected from the group consisting of

wherein Z is a radical selected from the group consisting of:

wherein the amount of diamine containing pendent phenylethynyl groups ranges from 1-99 mole%.

The best results were obtained from example 6. Polymer characterization is presented in Table 1.

Controlled molecular weight amide acid and imide oligomers containing pendent phenylethynyl groups and chain terminated with either nonreactive or reactive phthalic anhydride based endcapping agents were prepared according to FIG. 4.

The chemical structures of these oligomers are indicated below:
wherein \( \text{Ar} \) is a member selected from the group consisting of:

\[
\begin{align*}
\text{Ar} = \text{member selected from the group consisting of:} & \\
\text{O, CO, SO, } & \\
\text{isophthaloyl, terephthaloyl, 1,3-} & \\
\text{diphenoxy and 1,4-diphenoxy.} & \\
\end{align*}
\]

wherein \( \text{W} \) is a radical selected from the group consisting of: \( \text{H} \),

\[
\begin{align*}
\text{W} = \text{radical selected from the group consisting of:} & \\
\text{H, diphenoxyl and 1,4-diphenoxyl.} & \\
\end{align*}
\]

The best results were obtained with example 17. Polymer characterization is presented in Table 1.

Controlled molecular weight amide acid and imide oligomers containing pendant phenylethynyl groups and chain terminated with either nonreactive or reactive aniline based endcapping agents were prepared according to FIG. 5. The chemical structures of these oligomers are indicated below:
wherein $Ar$ is a member selected from the group consisting of:

- $H, \text{CO}, \text{SO}$,
- $2,2'$-isophthalaldehyde, $1,3'$-isophthalaldehyde, $1,4'$-isophthalaldehyde.

wherein $Ar'$ is a member selected from the group consisting of:

- diphenoxy and 1,4-diphenoxyl.
wherein \( R \) is a radical selected from the group consisting of:

\[
\begin{align*}
1 & \quad \begin{array}{c}
\text{R} \quad \text{selected from the group consisting of}:
\end{array} \\
2 & \quad \begin{array}{c}
\text{-C} \\
3 & \quad \begin{array}{c}
\text{-0}
\end{array} \\
4 & \quad \begin{array}{c}
\text{-N}
\end{array} \\
5 & \quad \begin{array}{c}
\text{-SO}_2
\end{array} \\
6 & \quad \begin{array}{c}
\text{-CO}
\end{array} \\
7 & \quad \begin{array}{c}
\text{C(CF}_3)_2
\end{array} \\
8 & \quad \begin{array}{c}
\text{isophthaloyl}
\end{array} \\
9 & \quad \begin{array}{c}
\text{terephthaloyl}
\end{array} \\
10 & \quad \begin{array}{c}
\text{1,3-}
\end{array} \\
11 & \quad \begin{array}{c}
\text{diphenoxy}
\end{array} \\
12 & \quad \begin{array}{c}
\text{1,4-}
\end{array} \\
13 & \quad \begin{array}{c}
\text{diphenoxy}
\end{array}
\end{align*}
\]

The best results were obtained with example 16. Polymer characterization is presented in Table 1. Unencapped, uncontrolled molecular weight poly(amide acid)s and polyimides containing pendent phenylethynyl groups were prepared according to FIG. 6. The chemical structures of the polymers are indicated below:

Diamine Synthesis

The following example illustrates the reaction sequence in FIG. 1 for the preparation of the diamine, 3,5-diamino-4'-(phenylethynyl)benzophenone.

**3,5-Dinitro-4'-bromobenzophenone**

To a flame dried 3 necked 3 L round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, condenser and acid trap was charged 3,5-dinitrobenzoyl chloride (99.00 g, 0.429 mol) and bromobenzene (2000 mL). Anhydrous aluminum chloride (73.40 g, 0.550 mol) was added as a powder in several portions over a 40 minute period at ambient temperature. The addition of aluminum chloride was complete, the temperature was increased to ~65 °C. and maintained for ~24 h. The solution was cooled to ambient temperature and added to a rapidly stirred acidic solution (hydrochloric acid 500 mL and 6600 mL distilled water). A yellow tacky solid separated from solution and was recovered by vacuum filtration. The tacky solid was washed with methanol, recovered by vacuum filtration and dried at 100 °C. for 2 h in flowing air to afford 107.60 g (71%) of a yellow solid. The crude solid was recrystallized from toluene to afford 90.1 g (60%) of a yellow crystalline solid, mp (DSC, 10 °C/min)=179 °C. Anal. calcd. for C₁₁H₉N₂O₅Br: C, 44.47%; H, 2.00%; N, 7.98%; Br, 22.75%; Found: C, 44.26%; H, 1.75%; N 8.0%; Br, 22.98%. 

wherein \( \text{Ar} \) is a member selected from the group consisting of:

\[
\begin{align*}
1 & \quad \begin{array}{c}
\text{Ar} \quad \text{selected from the group consisting of:}
\end{array} \\
2 & \quad \begin{array}{c}
\text{O}
\end{array} \\
3 & \quad \begin{array}{c}
\text{CO}
\end{array} \\
4 & \quad \begin{array}{c}
\text{SO}_2
\end{array} \\
5 & \quad \begin{array}{c}
\text{C(CF}_3)_2
\end{array} \\
6 & \quad \begin{array}{c}
\text{isophthaloyl}
\end{array} \\
7 & \quad \begin{array}{c}
\text{terephthaloyl}
\end{array} \\
8 & \quad \begin{array}{c}
\text{1,3-}
\end{array} \\
9 & \quad \begin{array}{c}
\text{diphenoxy}
\end{array} \\
10 & \quad \begin{array}{c}
\text{1,4-}
\end{array} \\
11 & \quad \begin{array}{c}
\text{diphenoxy}
\end{array}
\end{align*}
\]

wherein \( \text{Y} \) is a bond or \( \text{Y} \) is a radical selected from the group consisting of:

O, CO, SO₂, C(CF₃)₂, isophthalyl, terephthaloyl, 1,3-diphenoxy and 1,4-diphenoxy.
The reaction mixture was allowed to warm to room temperature. A cooled solution of stannous chloride dihydrate (78.4 g, 0.35 mol) was added dropwise while maintaining the temperature between -10°C. After the addition, the ice bath was removed and the reaction mixture allowed to warm to room temperature.

3,5-Dinitro-4'-phenylethynylbenzophenone

To a flame dried 3 necked 2 L round bottom flask equipped with nitrogen inlet, mechanical stirrer and condenser was charged 3,5-dinitro-4'-bromobenzophenone (101.0 g, 0.288 mol), triethylamine (1.0 L), cuprous iodide (0.24 g, 1.26 mmol), triphenylphosphine (32.32 g, 0.157 mol), and phenylacetylene (0.316 mol). The temperature was increased to 85°C and maintained for -12 h. After -2 hr, the solid precipitate was very thick making stirring difficult. The mixture was cooled to ambient temperature and the crude solid recovered was recrystallized from toluene (1 L) to afford 104.0 g (97%) of a yellow powder, mp 130-131°C. Final yield was 83.5 g (78%). Anal. calcd for C30H18BrNO5: C, 67.73%; H, 3.55%; N, 7.67%; Found: C, 67.64%; H, 3.25%; N, 7.52%; C, 67.64%; H, 3.55%; N 7.67%.

3,5-Diamino-4'-phenylethynylbenzophenone

To a 1 L Erlenmeyer flask equipped with a magnetic stirrer was charged 3,5-dinitro-4'-phenylethynylbenzophenone (19.6 g, 0.053 mol) and 1,4-dioxane (450 mL). The orange solution was cooled to -10°C. The mixture was stirred for 1 h in flowing air to afford 16.0 g (98%) of a brown solid. The crude product was recrystallized from toluene to afford 10.9 g (65.6%) of a yellow powder, mp (DSC, 10°C/min) 156°C. Anal. calcd. for C30H18N4O5: C, 80.74%; H, 5.16%; N, 8.97%; Found: C, 80.73%; H, 5.10%; N 8.98%.

EXAMPLE 1

1.0 3,5-Diamino-4'-phenylethynylbenzophenone and 1.0 4,4'-Oxydiphthalic Anhydride with no Endcapping Agent

The following example illustrates the reaction sequence in FIG. 6 for the preparation of the uncontrolled high molecular weight PEPI where R is a 4-benzoyl group and Ar is 3,3',4,4'-diphenylether and the monomer stoichiometry is 1.0 to 1.0.

Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,5-diamino-4'-phenylethynylbenzophenone (2.0069 g, 0.0064 mol) and 6 mL of N,N-dimethylacetamide (DMAc). After dissolution, 4,4'-oxydiphthalic anhydride (1.9931 g, 0.0064 mol) and DMAc (10 mL) were added to give a final concentration of 20.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the poly(amide acid) solution 0.5% in DMAc at 25°C was 0.85 dL/g. Approximately 7 g of poly(amide acid) solution was used to cast an unoriented thin film. Toluene (30 mL) was added to the remaining poly(amide acid) solution and the temperature increased and maintained at -150°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the polymer precipitated. The polyamide powder was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a tan powder (2.3 g, 43% yield). The Tg of the uncured as-isolated polymer (DSC, 20°C/min) was 273°C and the exothermic onset and peak occurred at 340°C and 419°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was not detectable by DSC. Unoriented thin film cast from the DMAc solution of the poly(amide acid) and cured at 100, 225, and 350°C. 1 h each in flowing air did not exhibit a Tg by DSC. The Tg by thermomechanical analysis (TMA) at a heating rate of 5°C/min was 300°C. Polymer characterization is presented in Table 1.

EXAMPLE 2

0.85:0.15 3,3'-Oxydianiline and 3,5-Diamo-4'-phenylethynylbenzophenone and 0.9093 3,3',4,4'-Biphenyltetraacarbonyl Dianhydride. Using 9.07 mole % Stoichiometric offset and 18.14 mole % Phthalic Anhydride (Calculated: Mn=5000 g/mol)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight
where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a hydrogen atom.

The ratio of diamines \([\text{Ar'}:\text{R}]\) is 0.85:0.15. The stoichiometric imbalance is 9.07 mole % and the endcapping reagent is 18.14 mole % of phthalic anhydride.

The T,<sub>n</sub> of the cured film was 279<sup>0</sup>C. A sample compression molded at 300<sup>0</sup>C./200 psi/0.5 h then 350<sup>0</sup>C./200 psi/1 h had a G<sub>IC</sub> (critical strain energy release rate) of 6.2 in lb/in<sup>2</sup> and a T<sub>n</sub>.

INTO a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.7220 g, 0.0186 mol), 3,5-diamino-4'-phenylethynylbenzophenone (1.0246 g, 0.0033 mol) and 9 mL N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 4,4'-biphenyldiacarboxylic dianhydride (5.8502 g, 0.0199 mol), and phthalic anhydride (0.5924 g, 0.0040 mol) in 10 mL of NMP was added and washed in with an additional 7 mL of NMP to afford a 30.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25<sup>0</sup>C.) was 0.33 dL/g. Approximately 11 g of amide acid oligomeric solution was used to cast an unoriented thin film. The reaction vessel was fitted with a moisture trap and toluene (40 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180<sup>0</sup>C. for ~16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230<sup>0</sup>C. for 4 h to provide a brown powder (6.9 g, 66% yield). The T<sub>n</sub> of the uncured as-isolated oligomer (DSC, 20<sup>0</sup>C./min) was 240<sup>0</sup>C. with a very slight T<sub>n</sub> at 325<sup>0</sup>C. and the exothermic onset and peak occurred at 340<sup>0</sup>C. and 423<sup>0</sup>C., respectively. The T<sub>n</sub> of the cured polymer (cure conditions: 350<sup>0</sup>C./1 h/sealed pan) was not detected by DSC. Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100<sup>0</sup>C., 225<sup>0</sup>C., and 350<sup>0</sup>C. for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23<sup>0</sup>C. of 21.8 ksi, 600 ksi, and 4% and at 177<sup>0</sup>C. of 14.0 ksi, 411 ksi, and 5% and at 200<sup>0</sup>C. of 12 ksi, 372 ksi, and 6%, respectively. The T<sub>n</sub> of the cured film was 279<sup>0</sup>C. A sample compression molded at 300<sup>0</sup>C./200 psi/0.5 h then 350<sup>0</sup>C./200 psi/1 h had a G<sub>IC</sub> (critical strain energy release rate) of 6.2 in lb/in<sup>2</sup> and a T<sub>n</sub>.

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a hydrogen atom.

The ratio of diamines \([\text{Ar'}:\text{R}]\) is 0.85:0.15. The stoichiometric imbalance is 2.4 mole % and the endcapping reagent is 4.8 mole % of phthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (2.8765 g, 0.01436 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.7919 g, 0.00253 mol) and 10.1 mL N-methyl-2-pyrrolidinone (NMP). After dissolution, 4,4'-biphenyltetra carboxylic dianhydride, (4.8530 g, 0.0165 mol), and phthalic anhydride (0.1201 g, 0.00081 mol). NMP (10.0 mL) was used to wash in the solid to afford a 30.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.645 dL/g. Approximately 7.1 g of amide acid oligomeric solution was used to wash the unoriented thin film. The reaction vessel was fitted with a moisture trap and toluene (40 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a brown powder (6.0 g, 75% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 265°C. and the exothermic onset and peak occurred at 340°C and 423°C, respectively. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 297°C by DSC. Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23°C of 16.3 ksi, 473 ksi, and 4%. The T_g of the cured film was not detectable by DSC. Polymer characterization is presented in Table 1.

EXAMPLE 4

0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 0.9093 3,3',4,4'-Biphenyltetra carboxylic Dianhydride. Using 9.07 mole % Stoichiometric offset and 18.14 mole % Phthalic Anhydride (Calculated (M)_w=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a hydrogen atom. The ratio of diamines [Ar':R]=0.90:0.10. The stoichiometric imbalance is 8.97 mole % and the endcapping reagent is 17.94 mole % of phthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with, nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (4.8752 g, 0.0243 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.8450 g, 0.0027 mol) and 10 mL N-methyl-2-pyrrolidinidone (NMP). After dissolution, a slurry of 4,4'-biphenyltetrahydroxylic dianhydride (7.2451 g, 0.0246 mol) and phthalic anhydride (0.7188 g, 0.0049 mol) in 10 mL of NMP was added and washed in with an additional 10 mL of NMP to afford a 30.6% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.32 dL/g. Approximately 13 g of amide acid oligomeric solution was used to cast an unoriented thin film. The reaction vessel was fitted with a moisture trap and toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for ~16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a yellow powder (8.91 g, 70% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.28 dL/g. The T_g of the uncured as-isolated oligomer (DSC. 20°C/min) was 217°C with a T_m at 276°C. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 255°C with a T_m at 369°C. The T_g of the cured film was 259°C with a T_m at 367°C. Polymer characterization is presented in Table 1.

EXAMPLE 5

0.70:0.30 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 0.9093 3,3',4,4'-Biphenyltetrahydroxylic Dianhydride. Using 9.07 mole % Stoichiometric offset and 18.14 mole % Phthalic Anhydride (Calculated (M)_w=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a hydrogen atom. The ratio of diamines [Ar':R] is 0.70:0.30. The stoichiometric imbalance is 9.38 mole % and the endcapping reagent is 18.76 mole % of phthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.5721 g, 0.0178 mol), 3,5-diamino-4'-phenylethynylbenzophenone (2.3882 g, 0.0076 mol) and 10 mL N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 4,4'-biphenylyltracarboxylic dianhydride (6.7947 g, 0.0231 mol), and phthalic anhydride (0.7081 g, 0.0048 mol) in 10 mL of NMP was added and washed in with an additional 10 mL of NMP to afford a 30.3% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25° C.) was 0.31 dL/g. Approximately 11 g of amide acid oligomeric solution was used to cast an unoriented thin film. The reaction vessel was fitted with a moisture trap and toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at ~180° C. for ~16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230° C. for 4 h to provide a brown powder (8.93 g, 71% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25° C.) was 0.22 dL/g. The Tg of the uncured as-isolated oligomer (DSC, 20° C/min) was 230° C. with Tg's at 272° and 286° C. The Tg of the cured polymer (cure conditions: 350° C/1 h/sealed pan) was 293° C.

Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°, 225°, and 350° C. for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23°C. of 23.5 ksi, 563 ksi, and 8%; at 177°C. of 12.7 ksi, 370 ksi, and 6% and at 200°C. of 12.2 ksi, 370 ksi, and 9%, respectively. The Tg of the cured film was 289° C. Polymer characterization is presented in Table 1 and thin film mechanical properties are presented in Table 2.

EXAMPLE 6

0.85:0.15 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 3,3',4,4'-Biphenylyltracarboxylic Dianhydride. Using 9.07 mole % Stoichiometric offset and 18.14 mole % 3-Aminophenoxy-4-phenylethynylbenzophenone (Calculated (M),=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 3 for the preparation of the controlled molecular weight PEPI where Ar is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and Z is a phenoxy-4-phenylethynylbenzophenone group located in the 3 position. The ratio of diamines [Ar'-R] is 0.85:0.15. The stoichiometric imbalance is 9.07 mole % and the endcapping reagent is 18.14 mole % of 3-aminophenoxy-4-phenylethynylbenzophenone.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.8826 g, 0.0194 mol), 3,5-diamino-4'-phenylethynylbenzophenone (1.0689 g, 0.0034 mol), 3-aminophenoxy-4'-phenylethynylbenzophenone (1.7723 g, 0.0046 mol) and 10 mL (39.4% w/w) N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (7.3809 g, 0.0251 mol) in 10 mL (41.7% w/w) of NMP was added and washed in with an additional 11 mL of NMP to afford a 30.6% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.26 dL/g. Approximately 10.85 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 220°C. For 1.5 h to provide a tan powder (10.06 g. 76% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.24 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 209°C. With a T_m at 278°C. and the exothermic onset and peak occurred at 359°C and 406°C, respectively. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 300°C. An unoriented thin film cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air was phase separated. The T_g of the cured film was 299°C. Polymer characterization is presented in Table 1.

**EXAMPLE 7**

0.75:0.15:0.10 3,4'-oxydianiline, 1,3-bis(3-aminophenoxy)benzene and 3,5-Diamino-4'-phenylethynylbenzophenone, and 3,3',4,4'-Biphenyltetraarylatecarboxylic Dianhydride, Using 9.22 mole % Stoichiometric offset and 18.44 mole % 4-Phenylethynylphthalic Anhydride (Calculated (M_w)=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PELP, where A (1) is 3,4'-diphenyether and A (2) is 1,3-phenoxypyphenyl and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a phenylethynyl group located in the 4 position. The ratio of diaminnes [Ar (1):Ar (2):R] is 0.75:0.15:0.10. The stoichiometric imbalance is 9.22 mole % and the endcapping reagent is 18.44 mole % of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three-necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (2.9030 g, 0.0145 mol), 1,3-bis(3-aminophenoxy)benzene (0.8476 g, 0.0029 mol), 3,5-diamino-4'-phenylethynylbenzophenone (6.6038 g, 0.0019 mol) and 20 mL (17.4% w/w) of m-cresol. After dissolution, a slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (5.1627 g, 0.0175 mol) and 4-phenylethynylphthalic anhydride (0.8848 g, 0.0036 mol) in 20 mL (22.6% w/w) of m-cresol was added and washed in with an additional 15 mL of m-cresol to afford a 15.5% (w/w) solution. The reaction mixture was stirred at room temperature for -16 h. The tan opaque solution was warmed to -100° C. for 0.75 h to effect dissolution of the oligomer. The solution was cooled to -50° C. and isoquinoline (9 drops) was added to the mixture. The temperature was increased and maintained at -205° C. for -6.5 h under a nitrogen atmosphere. The mixture was cooled, the oligomer precipitated in methanol, washed in warm methanol, and dried at 230° C. under vacuum for 1 h to provide a light yellow powder (9.7 g, -100% yield). The inherent viscosity of a 0.5% (w/v) solution of the imide oligomer in m-cresol at 25° C. was 0.26 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20° C/min) was 226° C. with an exothermic onset and peak at 359° C. and 425° C., respectively. The T_g of the cured polymer (cure conditions: 350° C/1 h/sealed pan) was 286° C. Unoriented thin films cast from a m-cresol solution of the amide acid oligomer cured at 100°, 225°, and 350° C. for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23° C. of 18.9 ksi, 495 ksi, and 12%; at 177° C. of 10.8 ksi, 301 ksi, and 34%; and at 200° C. of 9.2 ksi, 276 ksi, and 25%, respectively. The T_g of the cured film was 290° C. A sample compression molded at 275° C./200 psi/0.5 h then 350° C./200 psi/1 h had a G_{nc} (critical strain energy release rate) of 10.3 in lb/in². Polymer characterization is presented in Table 1 and thin film mechanical properties are presented in Table 2.

EXAMPLE 8

0.85±0.15 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 3,3',4,4'-Biphenyltetracarboxylic Dianhydride. Using 9.07 mole % Stoichiometric offset and 18.14 mole % 4-Phenylethynylphthalic Anhydride (Calculated (M)_a=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a phenylethynyl group located in the 4 position. The ratio of diamines [Ar'R] is 0.85±0.15. The stoichiometric imbalance is 9.07 mole % and the endcapping reagent is 18.14 mole % of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.722 g, 0.0186 mol), 3,5-diamino-4'-phenylethynylbenzophenone (1.0246 g, 0.0033 mol) and 4-phenylethynylphthalic anhydride (0.9847 g, 0.0040 mol) in 9 mL (42.4% w/w) of NMP. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.32 dL/g. Approximately 10 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at −180°C for 16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 220°C for 1.5 h to provide a tan powder (7.94 g, 74% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 226°C. with a T_m of 243°C and the exothermic onset and peak occurred at 348°C and 406°C, respectively. The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.28 dL/g. The T_g of the cured film was 318°C. A sample compression molded at 300°C/200 psi/0.5 h then 371°C/200 psi/1 h had a G_c (critical strain energy release rate) of 2.9 in lbf/in² and a T_g of 312°C. Flexural properties of composite panels prepared from prepreg of example 8 on IM-7 fiber processed at 250°C/50 psi/1 h then 371°C/200 psi/1 h with a unidirectional lay-up gave flexural strength and flexural modulus at 23°C of 233.5 ksi and 21.08 Msi, respectively.

**EXAMPLE 9**

0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 3,3',4,4'-Biphenyltetra-carboxylic Dianhydride, Using 8.97 mole % Stoichiometric offset and 17.94 mole % 4-Phenylethynylphthalic Anhydride (Calculated (\(M_\text{w}=5000 \text{ g/mole}\))

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a phenylethynyl group located in the 4 position. The ratio of diamines \([\text{Ar}'] (1)\) and \([\text{Ar}'] (2)\) is 0.90:0.10. The stoichiometric imbalance is 8.97 mole % and the endcapping reagent is 17.94 mole of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.9211 g, 0.0196 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.6797 g, 0.0022 mol) and 8 mL (35.8% w/w) N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4', 4'-biphenyltetra carboxylic dianhydride (5.8273 g, 0.0198 mol) and 4-phenylethynylphthalic anhydride (0.9690 g, 0.0040 mol) in 8 mL (45.1% w/w) of NMP was added and washed in with an additional 9 mL of NMP to afford a 30.6% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.21 dL/g. Approximately 10.5 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclo-dehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 220°C for 1.5 h to provide a tan powder (7.00 g, 66% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.41 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 223°C with a T_m at 274°C and the exothermic onset and peak occurred at 350°C and 412°C, respectively. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 310°C. Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23°C of 20.5 ksi, 495 ksi, and 20%; at 177°C of 12.1 ksi, 296 ksi, and 27% and at 200°C of 10.7 ksi, 299 ksi, and 30%, respectively. The T_g of the cured film was 306°C. Polymer characterization is presented in Table 1 and thin film mechanical properties are presented in Table 2.

EXAMPLE 10
0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'- phenylethynylbenzophenone, and 3,3',4',4'-Benzophenonetetracarboxylic Dianhydride. Using 9.48 mole % Stoichiometric offset and 18.96 mole % 4-Phenylethynylphthalic (Anhydride (Calculated (M)_r=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 3,3',4',4'-benzophenone and W is a phenylethyln group located in the 4 position. The ratio of diamines [Ar':R] is 0.90:0.10. The stoichiometric imbalance is 9.48 mole % and the endcapping reagent is 18.96 mole % of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.9229 g, 0.0196 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.6800 g, 0.0022 mol) and 10 mL (30.8% w/w) N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (6.3494 g, 0.0197 mol) and 4-phenylethynylphthalic anhydride (1.0245 g, 0.0041 mol) in 8 mL (47.2% w/w) of NMP was used to wash in the solid to afford a 30.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.28 dL/g. Approximately 10.5 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at ~180°C for ~16 h under a nitrogen atmosphere. As cyclo-dehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 220°C for 1.5 h to provide a tan powder (7.43 g, 65% yield). The Tg of the uncured as isolated oligomer (DSC, 20°C/min) was 269°C and the exothermic onset and peak occurred at 352°C and 399°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 296°C. An unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air was brittle and broke on the plate. The Tg of the cured film was 296°C. Polymer characterization is presented in Table 1.

EXAMPLE 11

0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and Pyromellitic Dianhydride. Using 7.57 mole % Stoichiometric offset and 15.14 mole % 4-Phenylethynylphthalic Anhydride (Calculated (Mm)=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEP1 where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group and Ar is 1,2,4,5-tetrasubstituted benzene, and W is a phenylethynyl group located in the 4 position. The ratio of diamines [Ar':R] is 0.90:0.10. The stoichiometric imbalance is 9.48 mole % and the endcapping reagent is 18.96 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.7846 g, 0.0189 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.6560 g, 0.0021 mol) and 11.0 mL N-methyl-2-pyrrolidinone (NMP). After dissolution, pyromellitic dianhydride, (4.2337 g, 0.01941 mol), and 4-phenylethynylphthalic anhydride (0.7893 g, 0.00318 mol). NMP (10.0 mL) was used to wash in the solid to afford a 30.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.36 dL/g. Approximately 10.5 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at ~180°C for ~16 h under a...
nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a brown powder (6.3 g, 76% yield). The T_g of the uncured as-isolated oligomer (DSC, 20° C/min) was not detected by DSC. The exothermic onset and peak occurred at 340° C and 423° C, respectively. The T_g of the cured polymer (cure conditions: 350° C/1 h/sealed pan) was not detectable by DSC. The T_g of the cured film was 260° C by DSC. Polymer characterization is presented in Table 1.

EXAMPLE 13

0.70:0.15:0.15 3,4'-Oxydianiline, 1,3-bis(3-amino phenox)benzene and 3,5-Diamino-4'- phenylethynylbenzophenone, and 3,3',4,4'-Biphenyltetracarboxylic Dianhydride, Using 9.33 mole % Stoichiometric offset and 18.66 mole % 4-Phenylenylyphthalic Anhydride (Calculated (M_w)=5000 g/mole).

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPl where Ar' is 3,4'- diphenylether and R is a 4-benzoyl group and Ar is 3,3',4,4'-diphenylether and W is a phenylethynyl group located in the 4 position. The ratio of diamines [Ar':R] is 0.90:0.10. The stoichiometric imbalance is 9.3 mole % and the endcapping reagent is 18.6 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.2439 g, 0.0162 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.5623 g, 0.0018 mol) and 12.0 mL N-methyl-2-pyrolidine (NMP). After dissolution, 4,4'-oxydiphthalic dianhydride, (5.0645 g, 0.0163 mol), and 4-phenylethynylphthalic anhydride (0.8311 g, 0.00334 mol), NMP (10.0 mL) was used to wash in the solid to afford a 30.0% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25° C) was 0.30 dL/g. Approximately 6.4 g of amide acid oligomeric solution was used to cast an unoriented thin film. The reaction vessel was fitted with a moisture trap and toluene (40 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at ~180° C for ~16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer began to precipitate. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a brown powder (6.6 g, 75% yield).
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (3.3565 g, 0.0168 mol), 1,3-bis(3-aminophenoxy)benzene (1.0501 g, 0.0036 mol), 3,5-diamino-4'-phenylethynylbenzophenone (1.1220 g, 0.0036 mol) and 10 mL of N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4,4'-biphenyltetraacarboxylic dianhydride (6.3881 g, 0.0217 mol) and 4-phenylethynyl phthalic anhydride (1.1092 g, 0.0045 mol) in 9 mL (22.6% w/w) of NMP was added and washed in with an additional 10 mL of NMP to afford a 30.28% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25° C.) was 0.29 dL/g. Approximately 12.6 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180° C. for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer precipitated in solution. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230° C. for 2 h to provide a brown powder (8.07 g, 66% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25° C.) was 0.32 dL/g. The Tg of the uncured as-isolated oligomer (DSC, 20° C./min) was 224° C. with a Tg at 284° C. and the exothermic onset and peak occurred at 363° C. and 416° C., respectively. The Tg of the cured polymer (cure conditions: 20.4 ksi, 492 ksi, and 15%; at 177° C. of 11.2 ksi, 307 ksi, and 24% and at 200° C. of 9.9 ksi, 285 ksi, and 28%, respectively. The Tg of the cured film was 301° C. A sample compression molded at 371° C./200 psi for 1 h had a Gc (critical strain energy release rate) of 6.2 in lb/in². Polymer characterization is presented in Table 1, thin film mechanical properties are presented in Table 2 and adhesive properties are presented in Table 3.

Mixtures of dianhydrides were used to alter properties as illustrated in Examples 14 and 15.

**EXAMPLE 14**

| Stoichiometric offset | 0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 0.85:0.15 3,3',4,4'-Benzophenonetetraacarboxylic Dianhydride and 4,4'-Oxydiphthalic Anhydride. Using 9.02 mole % 4-Phenylethynylphthalic Anhydride (Calculated (\( M_n \))=5000 g/mole) |

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzyol group; Ar (1) is 3,3',4,4'-diphenylether and Ar (2) is 3,3',4,4'-benzophenone and W is a phenylethynyl group located in the 4 position. The ratio of diamines [Ar (1):Ar' (2)] is 0.90:0.10 and the ratio of dianhydrides [Ar (1):Ar (2)] is 0.15:0.85. The stoichiometric imbalance is 9.02 mole % and the endcapping reagent is 18.04 mole % of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (4.6046 g, 0.0230 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.7981 g, 0.0026 mol) and 9 mL (36.8% w/w) N-methyl-2-pyrrolidione (NMP). After dissolution, a slurry of 3,3',4,4'-biphenyltetraacarboxylic dianhydride (5.8134 g, 0.0198 mol), 4,4'-oxydipthalic anhydride (1.0817 g, 0.0035 mol) and 4-phenylethynylphthalic anhydride (1.1436 g, 0.0046 mol) in 10 mL (43.4% w/w) of NMP was added and washed in with an additional 11 mL of NMP to afford a 30.3% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.35 dL/g. Approximately 10.6 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for ~16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer remained in solution. As the mixture was cooled, a precipitate formed. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 220°C for 1.5 h to provide a brown powder (9.47 g, 76% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.26 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was not detected with T_g < 243°C and 262°C. The exothermic onset and peak occurred at 320°C and 391°C, respectively.

The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 310°C. Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°, 225°, and 350°C for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23°C. Of 19.8 ksi, 250 ksi, and 11% and at 200°C of 10.7 ksi, 290 ksi, and 11%, respectively. The T_g of the cured film was 294°C. Polymer characterization is presented in Table 1 and thin film mechanical properties are presented in Table 2.

**EXAMPLE 15**

0.90:0.10 3,4'-Oxydianiline and 3,5-Diamino-4'-phenylethynylbenzophenone, and 0.70:0.30 3,3',4,4'-Benzophenonetetraacarboxylic Dianhydride and 4,4'-Oxydipthalic Anhydride. Using 9.06 mole % Stoichiometric offset and 18.12 mole % 4-Phenylethynylphthalic Anhydride (Calculated \( M_w = 5000 \) g/mole)

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEPI where Ar' is 3,4'-diphenylether and R is a 4-benzoyl group; Ar (1) is 3,3',4,4'-diphenylether and Ar (2) is 3,3',4,4'-biphenyl and W is a phenylethynyl group located in the 4 position. The ratio of diamines [Ar (1):Ar (2)] is 0.90:0.10 and the ratio of dianhydrides [Ar (1):Ar (2)] is 0.36:0.70. The stoichiometric imbalance is 9.06 mole % and the endcapping reagent is 18.12 mole % of 4-phenylethynylphthalic anhydride.
Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (4.6301 g, 0.0231 mol), 3,5-diamino-4'-phenylethynylbenzophenone (0.8025 g, 0.0026 mol) and 10 mL (34.5% w/w) N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (4.8118 g, 0.0164 mol), 4,4'-oxydiphenylalicyclic anhydride (2.1744 g, 0.0070 mol) and 4-phenylethynylphthalic anhydride (1.1556 g, 0.0047 mol) in 10 mL (44.1% w/w) of NMF' was added and washed in with an additional 10 mL of NMP to afford a 30.5% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.33 dL/g. Approximately 10.9 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for 16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, the oligomer remained in solution. As the mixture was cooled, a precipitate formed. The oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a brown powder (7.98 g, 63% yield). The inherent viscosity of the imide oligomer (0.5% in m-cresol at 25°C) was 0.31 dL/g. The Tg of the uncured as-isolated oligomer (DSC, 20°C/min) was 277°C. With a Tm at 260°C and the exothermic onset and peak occurred at 340°C and 419°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was 299°C. Unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at 23°C of 19.5 ksi, 457 ksi, and 16%; at 177°C of 10.1 ksi, 291 ksi, and 20% and at 200°C of 9.2 ksi, 299 ksi, and 12%, respectively. The Tg of the cured film was 296°C. Polymer characterization is presented in Table 1 and thin film mechanical properties are presented in Table 2.

**EXAMPLE 16**

3,5-Diamino-4'-phenylethynylbenzophenone and 3,3',4,4'-Biphenyltetracarboxylic dianhydride. Using 10.80 mole % Stoichiometric offset and 21.60 mole % 3-Aminophenoxy-4-phenylethynylbenzophenone (Calculated (M)_n=5000 g/mole)

The following example illustrates the reaction sequence in FIG. 5 for the preparation of the controlled molecular weight PEPI where Ar is 1,3-diphenylene, R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and Z is a phenoxo-4'-phenylethynylbenzophenone group located in the 3 position. The stoichiometric imbalance is 10.80 mole % and the endcapping reagent is 21.60 mole % of 3-aminophenoxy-4-phenylethynylbenzophenone.
oligomeric solution (0.5% in NMP at 25°C) was 0.22 dL/g. Approximately 10.84 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a tan powder (2.27 g, 40% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was not detected by DSC and the exothermic onset and peak was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a tan powder (2.27 g, 40% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was not detected by DSC and the exothermic onset and peak occurred at 299°C and 368°C, respectively. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was not detected by DSC. The unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air was brittle. The T_g of the cured film was not detected by DSC. Polymer characterization is presented in Table 1.

EXAMPLE 17

3,5-Diamino-4'-phenylethynylbenzophenone and 3, 3',4,4'-Biphenyltetracarboxylic Dianhydride, Using 10.80 mole % Stoichiometric offset and 21.60 mole % 4-Phenylethynylphthalic Anhydride (Calculated (M_w=5000 g/mole)

The following example illustrates the reaction sequence in equation 4 for the preparation of the controlled molecular weight PEPI where R is a 4-benzoyl group and Ar is 3,3',4,4'-biphenyl and W is a phenylethynyl group located in the 4 position. The stoichiometric imbalance is 10.80 mole % and the endcapping reagent is 21.60 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 100 mL three necked round bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,5-diamino-4'-phenylethynylbenzophenone (2.8499 g, 0.0091 mol) and 4 mL (40.8% w/w) of N-methyl-2-pyrrolidinone (NMP). After dissolution, a slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (2.3944 g, 0.0081 mol) and 4-phenylethynylphthalic anhydride (0.4892 g, 0.0020 mol) in 4 mL (41.1% w/w) of NMP was added and washed in with an additional 5 mL of NMP to afford a 29.9% (w/w) solution. The reaction was stirred at room temperature for 24 h under nitrogen. The inherent viscosity of the amide acid oligomeric solution (0.5% in NMP at 25°C) was 0.21 dL/g. Approximately 9.95 g of amide acid oligomeric solution was used to cast an unoriented thin film. Toluene (60 mL) was added to the remaining amide acid oligomeric solution and the temperature increased and maintained at -180°C for -16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the oligomer was washed in hot water, warm methanol, and dried under vacuum at 230°C for 4 h to provide a brown powder (1.75 g, 32% yield). The T_g of the uncured isolated oligomer (DSC, 20°C/min) was not detected by DSC and the exothermic onset and peak occurred at 299°C and 376°C, respectively. The T_g of the cured polymer (cure conditions: 350°C/1 h/sealed pan) was not detected by DSC. The unoriented thin films cast from a NMP solution of the amide acid oligomer cured at 100°C, 225°C, and 350°C for 1 h each in flowing air was brittle. The T_g of the cured film was not detected by DSC. Polymer characterization is presented in Table 1.

Oligomer and polymer characterization is presented in Table 1, unoriented thin film properties are presented in Table 2, preliminary titanium (Ti) to Ti tensile adhesive properties are presented in Table 2, and preliminary composite properties are presented in Table 4.

What is claimed is:

1. A diamine containing pendant phenylethynyl groups having the following general structure:
2. The diamine containing pendent phenylethynyl groups of claim 1 wherein R is equal to:

![Chemical Structure](attachment:chemical STRUCTURE.png)