IMIDE OLIGOMERS ENDCAPPED WITH
PHENYLETHYL PHTHALIC ANHYDRIDES
AND POLYMERS THEREFROM

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The term of this patent shall not extend beyond the expiration date of Pat. No. 5,567,800.

Abstract

Controlled molecular weight phenylethynyl terminated imide oligomers (PETIs) have been prepared by the cyclo-dehydration of precursor phenylethynyl terminated amic acid oligomers. Amino terminated amic acid oligomers are prepared from the reaction of dianhydride(s) with an excess of diamine(s) and subsequently endcapped with phenylethynyl phthalic anhydride(s) (PEPA). The polymerizations are carried out in polar aprotic solvents such as N-methyl-2-pyrrolidinone or NN-dimethylacetamide under nitrogen at room temperature. The amic acid oligomers are subsequently cyclodehydrated either thermally or chemically to the corresponding imide oligomers. Direct preparation of PETIs from the reaction of dianhydride(s) with an excess of diamine(s) and endcapped with phenylethynyl phthalic anhydride(s) has been performed in m-cresol. Phenylethynyl phthalic anhydrides are synthesized by the palladium catalyzed reaction of phenylacetylene with bromo substituted phthalic anhydrides in triethylamine. These new materials exhibit excellent properties and are potentially useful as adhesives, coatings, films, moldings and composite matrices.

6 Claims, 2 Drawing Sheets
$$\text{Br-W} \quad \text{C=O} \quad + \quad \text{C≡C-H}$$

1. $\text{N(CH}_2\text{CH}_3\text{)}_3$/Benzene or Toluene

2. $\text{CuI} / \text{P} / (\text{P}_3)^2 \text{PdCl}_2$

$$\text{C≡C-W} \quad \text{C=O}$$

$W = \text{nil, } \text{O-O, } \text{O-O, } \text{O-O}, \text{O-O, } \text{O-O, } \text{O-C, } \text{etc.}$

**FIG. 1**
\[ \text{Ar} \cdot \text{C=CO} \cdot \text{O} \cdot \text{C=CO} \cdot \text{O} \cdot (n+1) \text{H}_2\text{N} \cdot \text{Ar}' \cdot \text{NH}_2 + 2 \text{C=CO} \cdot \text{W} \cdot \text{C=CO} \cdot \text{O} \]

\[ \rightarrow 23^\circ\text{C}/\text{N}_2/\text{APROTIC SOLVENT} \]

\[ \text{C=CO} \cdot \text{N-Ar}' \cdot \text{N-C} \cdot \text{Ar} \cdot \text{OH} \cdot \text{HO-C} \cdot \text{C=N-Ar}' \cdot \text{N-C} \cdot \text{W-C=CO} \cdot \text{O} \]

\[ \rightarrow \Delta / -\text{H}_2\text{O} \]

\[ \text{C=CO} \cdot \text{N-Ar}' \cdot \text{N-C} \cdot \text{Ar} \cdot \text{N-Ar}' \cdot \text{N-C} \cdot \text{W-C=CO} \cdot \text{O} \]

\[ n = 2.5 \text{ to } 25.5 \] (Mn(calcd) = 1500 to 12,000 g/mol)

\[ \text{Ar}' = \quad \text{etc.} \]

\[ X = \text{nil}, \text{CH}_2, \text{O}, \text{CO}, \text{CH(OH)}, \text{C(CF}_3)_2, \text{etc.} \]

\[ \text{Ar} = \quad \text{etc.} \]

\[ Y = \text{nil}, \text{O}, \text{CO}, \text{SO}_2, \text{C(CF}_3)_2, \text{etc.} \]

\[ W = \text{nil}, \quad \text{etc.} \]

**FIG. 2**
IMIDE OLIGOMERS ENDCAPPED WITH PHENYLETHYL PHTHALIC ANHYDRIDES AND POLYMERS THEREFROM

This is a continuation of application Ser. No. 08/330,773 filed on Oct. 28, 1994, now U.S. Pat. No. 5,567,800.

ORIGIN OF INVENTION

The invention described herein was made jointly in the performance of work under NASA Grant NAG 1-1251 with Virginia Commonwealth University and an employee of the United States Government. In accordance with 35 USC 202, the grantee elected not to retain title.

BACKGROUND OF INVENTION

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

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

\[
\text{Ar} = \text{Y} - \text{Ar} - \text{Y} - \text{Ar} - \text{Y} - \text{Ar} - \text{Y}
\]

where \( Y = \text{nil}, \text{O}, \text{S}, \text{SO}_2, \text{CO}, \text{C(CHO)}_2, \text{or any other appropriate divalent radical. Ar'} \text{ is a divalent aromatic radical which may be 1,3-phenylene, 1,4-phenylene, 4,4'-diphenylene, 4,4'-oxydiphenylene, 4,4'-sulfonylediphenylene, or any other appropriate divalent radical.}


A variety of monomers, oligomers and polymers containing ethyny (acetylenic) and substituted ethyny (i.e. phenylethynyl) groups have been reported. The ethynyl groups in the polymer are either pendant to the chain, in the chain, or at the chain ends. Many of these materials have been used to prepare coatings, moldings, adhesives and composites [P. M. Hergenrother, "Acetylene Terminated Prepolymer" in Encyclopedia of Polymer Science and Engineering, John Wiley and Sons, New York, Vol. 1, 61 (1985)]. Good processability by either solution casting and/or compression molding has been observed for the ethynyl and substituted ethyny containing materials. In general, thermally cured ethynyl and substituted ethynyl containing materials exhibit a favorable combination of physical and mechanical properties. Some ethyny endcapped materials such as the Thermid® resins are commercially available (National Starch and Chemical Co., Bridgewater, N.J., 08807). Phenylethynyl containing amines have been used to terminate imide oligomers [F. W. Harris, A. Pamidimuhikala, R. Gupta, S. Das, T. Wu, and G. Mock, Polym. Prep., 24 (2), 325 (1983); F. W. Harris, A. Pamidimuhikala, P. Gupta, S. Das, T. Wu, and G. Mock, J. Macromol. Sci.-Chem., A21 (8 & 9), 1117 (1984); C. W. Paul, R. A. Schultz, and S. F. Feenell, "High-Temperature Curing Endcaps For Polymide Oligomers" in Advances in Polyimide Science and Technology, (Ed. C. Feger, M. M. Khyasteh, and M. S. Htoo), Technomic Publishing Co., Inc., Lancaster, Pa., 1993, p. 220; R. G. Byrant, B. J. Jensen, and P. M. Hergenrother, Polym. Prep., 34(1), 566 (1993).


It is a primary object of the present invention to provide novel phenylethynyl phthalic anhydrides and new imide oligomers endcapped with phenylethynyl groups, as well as polymers prepared therefrom which exhibit higher elongations, higher glass transition temperatures and higher fracture toughness, as compared to similar materials.

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

Another object of the present invention is the composition of several new phenylethynyl phthalic anhydride (PEPA) endcapping reagents.

SUMMARY OF THE INVENTION

According to the present invention the foregoing and additional objects are obtained by synthesizing controlled molecular weight imide oligomers endcapped with phenylethynyl groups by different methods. First, amino terminated amic acid (AA) oligomers are prepared by the reaction of diacylhydride(s) with an excess of diamin(s) under a nitrogen atmosphere at ambient temperature in N-methyl-2-pyrrolidinone (NMP). The endcapping reagent, a phenylethynyl phthalic anhydride (PEPA), was added after the formation of the amino terminated AA oligomer. Phenylethynyl terminated amic acid have also been prepared where the PEPA endcapping reagent is added at the beginning of the reaction. The phenylethynyl terminated imide oligomers (PETIs) were prepared by cyclooldehydration of the precursor AA oligomers endcapped with phenylethynyl groups in NMP by azotropic distillation with toluene. PETIs are also prepared in N,N-dimethylacetaimide containing glacial acetic acid at elevated temperature. The AA oligomer can also be converted to the corresponding PETIs by treatment with chemical cyclodehydrating agents such as acetic anhydride. The direct preparation of PETIs has been performed in m-cresol containing isoquinoline at elevated temperature.

Phenylethynyl terminated imide oligomers are prepared by the reaction of the half alkyl ester of aromatic tetracarboxylic acids and the half alkyl ester of phenylethynyl substituted phthalic acids with aromatic dihydrides by heating in NMP. PETIs prepared by the alkyl ester route can also be prepared by heating neat or in solvents such as m-cresol. Phenylethynyl terminated imide oligomers are also prepared by the polymerization of monomeric reactants (PMR) approach by heating a mixture of a diamine and the ethyl ester derivatives of diacylhydrides and phenylethynylphthalic anhydrides.

In addition, the amino terminated AA oligomer can be cyclodehydrated to the corresponding amino terminated imide and the PEPA endcapper subsequently reacted with the soluble amino terminated imide oligomer. The imide oligomer must be soluble in order to perform thirdder endcapping reaction. Upon reaction of the amino terminated imide...
oligomer with the PEPA endcapper, the temperature is increased to effect cyclodehydration to complete imidization.

The inherent viscosities (ηinh) of the AA oligomers range from 0.16 to 0.53 dL/g. After cyclodehydration to PETIs, the ηinh range from 0.12 to 0.43 dL/g. The glass transition temperatures (Tg) of the uncured as-isolated PETIs range from 208° to 262°C. In some cases a crystalline melt temperature is observed for the uncured PETIs. The temperature of onset and peak exotherm due to reaction of the phenylethynyl group range from 371° to 414°C, and 419° to 452°C, respectively as evidenced by heating in a sealed DSC pan at a heating rate of 20°C/minute. After curing at 350°C for 1 h in a sealed DSC pan the Tg of the cured polymers ranges from 237° to 276°C.

Thermogravimetric analysis (TGA) at a heating rate of 2.5°C/min in air or nitrogen with a 5% weight loss occurring between 496°C in air and ~512°C in nitrogen. After a thermal cure (350°C for 1 h), TGA at a heating rate of 2.5°C/min of the cured polymers shows no weight loss occurring below 300°C in air or nitrogen with a 5% weight loss occurring at ~496°C in air and ~512°C in nitrogen. For a more complete understanding of the present invention, including its objects and attending benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth in detail below. This Detailed Description should be read together with the accompanying drawing, wherein:

FIG. 1 is an equation showing the preparation of phenylethynyl substituted anhydrides according to the present invention; and

FIG. 2 is an equation showing the synthesis of controlled molecular weight phenylethynyl terminated imide oligomers (PETIs) according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Phenylethynyl substituted phthalic anhydrides are prepared by the palladium catalyzed reaction of phenylacetylene with bromo substituted phthalic anhydrides as shown in the equation of 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. The general reaction sequence for the synthesis of controlled molecular weight PETIs is represented in the equation of FIG. 2.
Wherein Y is a bond or Y is a radical selected from the group consisting of

- O, CO, SO₂, C(CF₃)₂,

- and

Wherein W is a bond or W is a radical selected from the group consisting of

- O - ,
- O - ,
- O - ,
- O - ,
- and

In the general structural formula above, it is especially preferred if: Ar' is a radical represented by

and Ar is a radical represented by

and Ar is a radical represented by
and W is a bond; $\text{Ar}'$ is a radical represented by

and $\text{Ar}$ is a radical represented by

and W is a bond; $\text{Ar}'$ is a radical represented by

and $\text{Ar}$ is a radical represented by

and W is a bond; $\text{Ar}'$ is a radical represented by

and $\text{Ar}$ is a radical represented by

and W is a bond; $\text{Ar}'$ is a radical represented by

and $\text{Ar}$ is a radical represented by

In another aspect, the present invention is a phenylethynyl phthalic anhydride having the general structural formula:

Wherein W is a radical selected from the group consisting of

A particularly preferred phenylethynyl phthalic anhydride according to the present invention has the following structural formula:

In another aspect, the present invention is a phenylethynyl terminated amic acid oligomer having the general structural formula:
Wherein $\text{Ar}'$ is a radical selected from the group consisting of

![Chemical structures](image1)

and

![Chemical structures](image2)

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 bond or $X$ is a radical selected from the group consisting of $\text{CH}_2, \text{O}, \text{CO}, \text{CH(OH)}_2, \text{C}(\text{CF}_3)_2$. Wherein $Y$ is a bond or $Y$ is a radical selected from the group consisting of $\text{O}, \text{CO}, \text{SO}_2, \text{C}(\text{CF}_3)_2$.

![Chemical structures](image3)

Wherein $W$ is a bond or $W$ is a radical selected from the group consisting of

![Chemical structures](image4)

Wherein $\text{Ar}$ is a radical selected from the group consisting of $\text{CH}_3, \text{O}, \text{CO}, \text{CH(OH)}_2, \text{C}(\text{CF}_3)_2$.

![Chemical structures](image5)

Especially preferred are the following specific controlled molecular weight amic acid oligomers terminated with phenylethynyl phthalimide, reference being made to the general structural formula above.

(A) wherein $\text{Ar}'$ is a radical represented by

![Chemical structures](image6)
and Ar is a radical represented by

and W is a bond;

(B) wherein Ar' is a radical represented by

and Ar is a radical represented by

and W is a radical represented by

(C) wherein Ar' is a radical represented by

and Ar is a radical represented by

and W is a bond;

(D) Ar' is a radical represented by

Ar is a radical represented by

0.75

and 0.25

and W is a bond;

(E) Ar' is a radical represented by

Ar is a radical represented by

0.25

and

0.75

and W is a bond.

In another aspect, the present invention is a process for synthesizing controlled molecular weight imide oligomers endcapped with phenylethynyl phthalimide and having the general structural formula

by cyclodehydration of precursor amic acid oligomers terminated with phenylethynyl phthalimide and having the general structural formula
wherein the cyclodehydration reaction is carried out in a polar aprotic solvent such as N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, N-cyclohexyl-2-pyrrolidinone, m-cresol, and dimethylsulfoxide; wherein the reaction is carried out with the application of heat; wherein the reaction is carried out in the presence of a member selected from the group consisting of glacial acetic acid, isoquinoline, toluene, xylenes, and herein the reaction is carried out using acetic anhydride.

In this process, advantageous results are achieved if the phenylethylnyl terminated amic acid oligomers having the general structural formula

\[
\begin{array}{c}
\text{C} \equiv \text{C} - \text{O} \\
\text{C} - \text{N} - \text{Ar' + N} - \text{C} \equiv \text{C} - \text{W} \\
\text{C} - \text{O} \\
\end{array}
\]

are prepared by reacting an excess of a diamine with a diacy chloride and phenylethylnyl phthalic anhydride. Ideally, good results are obtained if the reaction is carried out phine

In another aspect, the present invention is a process for synthesizing controlled molecular weight imide oligomers endcapped with phenylethylnyl phthalimide by reacting an amine terminated imide oligomer with phenylethylnyl phthalic anhydride to form the phenylethylnyl amic acid. Best results are achieved if the reaction is carried out under heat and pressure.

In yet another aspect, the present invention is a cured neat resin molding prepared from controlled molecular weight imide oligomer endcapped by phenylethylnyl phthalic anhydride. Especially good results are obtained if the reaction is carried out using a solution of phenylethylnyl terminated amide acid oligomer as specified above wherein the reaction is carried out in a polar aprotic solvent such as N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, N-cyclohexyl-2-pyrrolidinone, m-cresol, and dimethylsulfoxide, and the film is thermally cured in air or an inert atmosphere such as nitrogen, argon, or helium. Very good results are obtained if the film is prepared by compression molding of powders under heat and pressure.

In yet another aspect, the present invention is a cured adhesive prepared from controlled molecular weight imide oligomer endcapped by phenylethylnyl phthalic anhydride. Best results are achieved if the cure adhesive is prepared under heat and pressure.

In yet another aspect, the present invention is a cured composite prepared from controlled molecular weight imide oligomer endcapped with phenylethylnyl phthalimide and carbon/graphite fibers. Best results are achieved if the cured composite is prepared under heat and pressure.

Having generally described the invention, a more complete understanding thereof can be obtained by reference to the following examples, which are provided herein for purposes of illustration only and do not limit the invention.

Endcapper Synthesis

The following example illustrates the reaction sequence in FIG. 1 for the preparation of the endcappers.

4-Phenylethylnylphthalic Anhydride (4-PEPA)

A mixture of triethylamine (1000 ml) and benzene (120 ml) was heated to reflux for 3 h under a nitrogen atmosphere to remove any residual water. The mixture was cooled to room temperature and 4-bromophthalic anhydride (60.7462 g, 0.2676 mol), phenylacetylene (27.3314 g, 0.2676 mol), cuprous iodide (0.1174 g, 0.6164 mmol), triphenylphosphine (0.5070 g, 1.9329 mmol), and bis(triphenylphosphine) palladium dichloride (0.1013 g, 0.1443 mmol) were added and the mixture was heated at reflux under a nitrogen atmosphere for 20 h. The cooled reaction mixture was filtered and the precipitate added to water. The crude solid was washed several times in distilled water and dried under...
vacuum at 85°C for 1 h to afford 48.50 g (73% crude yield) of a brown powder mp (DSC, 10°C/min) 152°C (sharp). The product was recrystallized from 1:1 toluene/hexanes to afford 41.30 g (62% yield) of an orange-brown crystalline solid. mp (DSC, 10°C/min) 151°C (sharp). An exotherm with a peak of 389°C had a ΔH of 390 J/g. IR (KBr): 2206 cm⁻¹ (C=O); 1843 cm⁻¹ and 1771 cm⁻¹ (asymmetric and symmetric C=O stretch). Anal. calc. for C₆H₅O₂C: 77.42%; H: 3.14%; Found: C, 77.12%; H, 3.14%. Mass spectroscopy: m/e 248 (calc. molecular weight: 248.2414 g/mol).

4-(4-Bromophenoxy)phenylacetylene

A mixture of 4-bromophenol (21.7209 g, 0.1254 mol), 4-fluorophenylacetylene (22.9027 g, 0.1379 mol), and potassium fluoride (11.1003 g, 0.1911 mol) in sulfolane (142.34 g, 21.95% w/w) was heated at 165°–170°C for 10.5 h. The cooled light brown mixture was precipitated in water and the solid collected by filtration. The crude solid was washed with hot water, then rehydrated with water and dried. The resulting brown powder was recrystallized from 2.6:1 cyclohexane/benzene to afford 26.97 g (67% yield) of a light brown powder, mp (DSC, 10°C/min) 251°C (asymmetric and symmetric C=O stretch). Anal. calc. for C₆H₅O₂Br: C, 52.69%; H, 2.21%; Br, 25.04%; Found: C, 52.09%; H, 2.23%; Br, 25.32%. Mass spectroscopy: m/e 319.9 (calc. molecular weight: 320.1914 g/mol).

4-(4-Phenyldiphenylphenoxy)phenyloxydiphthalic Anhydride (4-PEDPOA)

A mixture of triethylamine (20.1111 g, 0.1721 mmol) and 4-(4-phenylethynylphenoxy)phthalic anhydride (9.9389 g, 0.0320 mol) and 50 ml (12.5% w/w) of N,N'-dimethylacetamide (DMAc). After dissolution, 4,4'-oxydiphthalic anhydride (9.9389 g, 0.0320 mol) and 45 ml of DMAc (15.7% w/w) were added. The solution was allowed to stir for 8 h at room temperature under a nitrogen atmosphere. 4-Phenyldiphenylphenoxydiphthalic anhydride (0.8372 g, 0.0034 mol) and 3 ml of DMAc (16.0% w/w) were added and the reaction stirred at room temperature for an additional 16 h. The inherent viscosity of the amic acid oligomeric solution (0.5% in DMAc at 25°C) was 0.36 dL/g. Glacial acetic acid (9 ml) was added to the solution and the temperature increased and maintained at ~120°C for 16 h under a nitrogen atmosphere. As cyclodehydration to the imide occurred, a precipitate formed. The mixture was cooled, the isolated precipitate was washed with hot water and warm methanol, and dried under vacuum at 160°C for 5 h to provide a tan powder (15.2 g, 93% yield). The inherent viscosity of a 0.5% solution in m-cresol at 25°C was 0.12 dL/g. The Tₓ of the uncured as-isolated oligomer was not apparent on the initial DSC scan, but Tₓ,ₛ were observed (DSC, 20°C/min) at 254°C, 285°C, and 315°C with an exotherm onset and peak at 394°C and 434°C, respectively. The Tₓ of the cured polymer (cure conditions: 350°C/1 h/flowing air) was 248°C. Unoriented thin films cast from a DMAc solution of the amic acid oligomer and cured at 100°C, 225°C, and 350°C for 1 h each in flowing air gave tensile strength, tensile modulus, and elongation at break at 23°C of 17.5 ksl, 413 ksl, and 38% and at 177°C of 9.4 ksl, 318 ksl, and 60%, respectively. The Tₓ of the cured film was 251°C.

Example 2: 3,4'-Oxydianiline and 4,4'-Oxydiphthalic Anhydride, Using 5.14 mole % Stoichiometric Offset and 10.28 mole % 4-Phenyldiphenylphenoxydiphthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PETI where Ar' is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position, and where W is equal to a nil group. The stoichiometric imbalance is 5 mole % and the endcapping reagent is 10 mole % of 4-phenylidiphenylphenoxydiphthalic anhydride.

Into a flame dried 250 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (8.4413 g, 0.0422 mol) and 50 ml (14.0% w/w) N-methyl-2-pyrrolidinone (NMP). After dissolution, 4,4'-oxydiphthalic anhydride (12.4053 g, 0.0400 mol) and 50 ml of NMP (16.8% w/w) were added. The solution was allowed to stir for ~8 h at room temperature under a nitrogen atmosphere. 4-Phenyldiphenylphenoxydiphthalic anhydride (1.0758 g, 0.0043 mol) and 10 ml NMP (16.2% w/w) were added and the reaction stirred at room temperature for an additional 16 h. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.38 dL/g. Toluene (70 ml) was added to the amic acid oligomeric solution and the temperature increased and maintained at ~150°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 160 °C for 5 h to provide an off-white powder (19.46 g, 97% yield). The inherent viscosity of a 0.5% solution of the imide oligomer in m-cresol at 25 °C was 0.29 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20 °C/min) was 225 °C. T_g was 323 °C and the exothermic onset and peak occurred at 397 °C and 442 °C, respectively. The T_g of the cured polymer (cure conditions: 350 °C/1 h/static air) was 243 °C.

Example 3: 3,4'-Oxidianiline and 4,4'-Oxydiphthalic Anhydride, Using 5.14 mol % Stoichiometric Offset and 10.28 mol % 4-Phenylenephthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEI where Ar' is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position, Ar' is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position, and where W is equal to a nil group. The stoichiometric imbalance is 5.14 mol % and the endcapping reagent is 10.28 mol % of 4-phenylethynylphthalic anhydride.

Into a flame dried 250 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3,4'-oxidianiline (8.4413 g, 0.0422 mol) and 50 ml of 14.0% w/w m-cresol. After dissolution, 4,4'-oxydiphthalic anhydride (12.4053 g, 0.0400 mol), 4-phenylethynylphthalic anhydride (1.0758 g, 0.0043 mol) and 60 ml of m-cresol (15.0% w/w) were added and the reaction stirred at room temperature for 15 h. Isoquinoline (5 drops) was added to the mixture. The temperature was increased and maintained at ̃200 °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 150 °C under vacuum for 5 h to provide an off-white powder (20.0 g, 100% yield). The inherent viscosity of a 0.5% solution of the imide oligomer in m-cresol at 25 °C was 0.29 dL/g and in NMP at 25 °C was 0.33 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20 °C/min) was 219 °C with an exothermic onset and peak at 371 °C and 425 °C, respectively. The T_g of the cured polymer (cure conditions: 350 °C/1 h/DSC) was 234 °C. A sample compression molded at 350 °C/200 psi/1 h had a G IC (critical strain energy release rate of) 19.72 in lb/in² and a T_g of 234 °C.

Example 4: 3,4'-Oxidianiline and 4,4'-Oxydiphthalic Anhydride, Using 5.14 mol % Stoichiometric Offset and 10.28 mol % 4-(4-Phenylenephenoxy)phthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEI where Ar' is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position, Ar' is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position, and where W is equal to a 4-phenoxy group. The stoichiometric imbalance is 5.14 mol % and the endcapping reagent is 10.28 mol % of 4-(4-phenylethynylphenoxy)phthalic anhydride.

Into a flame dried 300 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3,4'-oxidianiline (7.2371 g, 0.0361 mol) and 50 ml of 12.3% w/w N-methyl-2-pyrrolidinone (NMP). After dissolution, 4,4'-oxydiphthalic anhydride (10.6358 g, 0.0343 mol), 4-(4-phenylethynylphenoxy)phthalic anhydride (1.2645 g, 0.0037 mol) and 45 ml NMP (14.9% w/w) were added and the reaction stirred at room temperature for 24 h. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25 °C) was 0.53 dL/g. Approximately 30 g of amic acid oligomeric solution was used to cast an unoriented thin film. Toluene (70 ml) was added to the remaining amic acid oligomeric solution and the temperature increased and maintained at ̃150 °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 240 °C for 4 h to provide a brown powder (11.90 g). The T_g of the uncured as-isolated oligomer (DSC, 20 °C/min) was 226 °C and T_g was 274 °C, 303 °C, and 325 °C. The T_g of the cured polymer (cure conditions: 350 °C/1 h/DSC) was 235 °C.

Example 5: 3,4'-Oxidianiline and 4,4'-Oxydiphthalic Anhydride, Using 5.14 mol % Stoichiometric Offset and 10.28 mol % 4-(4-Phenylenephenoxy)phthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEI where Ar' is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position, Ar' is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position, and where W is equal to a 4-phenoxy group. The stoichiometric imbalance is 5.14 mol % and the endcapping reagent is 10.28 mol % of 4-(4-phenylethynylphenoxy)phthalic anhydride.

Into a flame dried 300 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3,4'-oxidianiline (8.4413 g, 0.0422 mol) and 50 ml of 14.0% w/w m-cresol. After dissolution, 4,4'-oxydiphthalic anhydride (12.4053 g, 0.0400 mol), 4-phenylethynylphthalic anhydride (1.0758 g, 0.0043 mol) and 60 ml of m-cresol (15.0% w/w) were added and the reaction stirred at room temperature for 15 h. Isoquinoline (5 drops) was added to the mixture. The temperature was increased and maintained at ̃200 °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 150 °C under vacuum for 5 h to provide an off-white powder (20.0 g, 100% yield). The inherent viscosity of a 0.5% solution of the imide oligomer in m-cresol at 25 °C was 0.29 dL/g and in NMP at 25 °C was 0.33 dL/g. The T_g of the uncured as-isolated oligomer (DSC, 20 °C/min) was 219 °C with an exothermic onset and peak at 371 °C and 425 °C, respectively. The T_g of the cured polymer (cure conditions: 350 °C/1 h/DSC) was 234 °C. A sample compression molded at 350 °C/200 psi/1 h had a G IC (critical strain energy release rate of) 19.72 in lb/in² and a T_g of 234 °C.
Mixtures of dianhydrides have been used to alter properties as illustrated in Examples 6 and 7.

Example 6: 3.4'-Oxydianiline and 1,1,4,4'-Oxypthalidichloane, and 3,3,4',4'-Biphenyl Tetracarboxylic Dianhydride. Using 5.14 mole % Stoichiometric Offset and 10.28 mole % 4-Phenylethynylphthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PETI where Ar' is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position; Ar (1) is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position and Ar (2) is equal to a bis(o-diphenylene) where W is equal to a nil group located in the 4,4'-position, and where V is equal to a nil group. The ratio of dianhydrides [Ar (1):Ar (2)] is 1:1. The stoichiometric imbalance is 5.14 mole % and the endcapping reagent is 10.28 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 500 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3.4'-oxydianiline (17.1723 g. 0.0087 mol) and 100 ml of NMP (14.3% w/w). After dissolution, 4,4'-oxiphthalidichloane (12.6288 g. 0.0407 mol) and 3,3,4',4'-biphenyl tetracarboxylic dianhydride (11.9775 g. 0.0407 mol) and 100 ml of NMP (16.8% w/w) were added and the solution stirred for ~8 h at room temperature under a nitrogen atmosphere. The inherent viscosity of the amic acid oligomer solution (0.5% in NMP at 25°C) was 0.32 dL/g. Approximately 30 g of amic acid oligomer solution was used to cast an unoriented thin film. Toluene (100 ml) was added to the remaining amic acid oligomeric solution and the temperature increased and maintained at ~150°C for ~16 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, the imide oligomer remained in solution. The solution was heated for an additional 5 h at ~175°C under a nitrogen atmosphere. The mixture was cooled, the polymer precipitated in water, washed in hot water, warm methanol, and dried under vacuum at 160°C for 3 h to provide an off-white powder (35.10 g, 88% yield).

The inherent viscosity of a 0.5% solution of the imide oligomer in NMP at 25°C was 0.38 dL/g. The Tg of the uncured as-isolated imide oligomer (DSC, 20°C/min) was 239°C with an exothermic onset and peak at 371°C and 436°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/static air) was 268°C. Unoriented thin films cast from an NMP solution of the amic 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 break at 22°C of 20.2 ksi, 431 ksi, and 69% and at 177°C of 10.7 ksi, 341 ksi, and 70%, respectively. The Tg of the cured film was 262°C. A sample compression molded at 350°C/200 psi/1 h had a GC (critical strain energy release rate) of 17.66 in lb/in² and a Tg of 248°C.

Example 7: 3,4'-Oxydianiline and 1,1,4,4'-Oxypthalidichloane, and 3,3,4',4'-Biphenyl Tetracarboxylic Dianhydride. Using 7.635 mole % Stoichiometric Offset and 15.27 mole % 4-Phenylethynylphthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PETI where Ar' (1) is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position; Ar (1) is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position and Ar (2) is equal to a bis(o-diphenylene) where W is equal to a nil group located in the 4,4'-position, and where V is equal to a nil group. The ratio of dianhydrides [Ar' (1):Ar' (2)] is 1:1. The stoichiometric imbalance is 7.635 mole % and the endcapping reagent is 15.27 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 250 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3.4'-oxydianiline (10.8126 g, 0.0540 mol), 1.3-bis(3-aminophenoxy)benzene (10.0212 g, 0.0900 mol) and 100 ml of NMP (14.9% w/w). After dissolution, 4,4'-oxiphthalidichloane (12.9223 g, 0.0417 mol) and 3,3,4',4'-biphenyl tetracarboxylic dianhydride (12.2558 g, 0.0417 mol) and 100 ml of NMP (17.3% w/w) were added and the solution stirred for ~8 h at room temperature under a nitrogen atmosphere. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.32 dL/g. Approximately 28 g of amic acid oligomeric solution was used to cast an unoriented thin film. Toluene (100 ml) was added to the remaining amic acid oligomeric solution and the temperature increased and maintained at ~160°C for ~24 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, the imide oligomer remained in solution. The mixture was cooled, the polymer precipitated in water, washed in hot water, warm methanol, and dried under vacuum at 150°C for 3.5 h to provide an off-white powder (39.4 g, 94% yield). The inherent viscosity of a 0.5% solution of the imide oligomer in NMP at 25°C was 0.32 dL/g. The Tg of the uncured as-isolated imide oligomer (DSC, 20°C/min) was 222°C with an exothermic onset and peak at 372°C and 419°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/static air) was 267°C. Unoriented thin films cast from an NMP solution of the amic 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 break at 23°C of 17.9 ksi, 427ksi, and 40%, respectively at 177°C of 10.8 ksi, 344 ksi, and 63%, respectively. The Tg of the cured film was 268°C.

Mixtures of diamines have been used to alter properties as illustrated in Examples 8 and 9.

Example 8: 0.85:0.15 3,4'-Oxydianiline and 1,3-bis(3-aminophenoxy)benzene, and 3,3',4',4'-Biphenyl Tetracarboxylic Dianhydride. Using 9.02 mole % Stoichiometric Offset and 18.04 mole % 4-phenylethynylphthalic anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PETI where Ar' (1) is equal to a diphenylene where X is an oxygen atom located in the 3,4'-position and Ar (2) is equal to a bis(o-diphenylene) where Y is an oxygen atom located in the 4,4'-position and Ar (2) is equal to a bis(o-diphenylene) where W is equal to a nil group located in the 4,4'-position and Ar (2) is equal to a nil group. The ratio of dianhydrides [Ar' (1):Ar' (2)] is 1:1. The stoichiometric imbalance is 9.02 mole % and the endcapping reagent is 18.04 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 250 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3.4'-oxydianiline (10.8126 g, 0.0540 mol), 1,3-bis(3-aminophenoxy)benzene (18.0309 g, 0.0900 mol) and 100 ml of NMP (14.9% w/w). After dissolution, 4,4'-oxiphthalidichloane (12.9223 g, 0.0417 mol) and 3,3,4',4'-biphenyl tetracarboxylic dianhydride (12.2558 g, 0.0417 mol) and 100 ml of NMP (17.3% w/w) were added and the solution stirred for ~8 h at room temperature under a nitrogen atmosphere. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.32 dL/g. Approximately 28 g of amic acid oligomeric solution was used to cast an unoriented thin film. Toluene (100 ml) was added to the remaining amic acid oligomeric solution and the temperature increased and maintained at ~160°C for ~24 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, the imide oligomer remained in solution. The mixture was cooled, the polymer precipitated in water, washed in hot water, warm methanol, and dried under vacuum at 150°C for 3.5 h to provide an off-white powder (39.4 g, 94% yield). The inherent viscosity of a 0.5% solution of the imide oligomer in NMP at 25°C was 0.32 dL/g. The Tg of the uncured as-isolated imide oligomer (DSC, 20°C/min) was 222°C with an exothermic onset and peak at 372°C and 419°C, respectively. The Tg of the cured polymer (cure conditions: 350°C/1 h/static air) was 267°C. Unoriented thin films cast from an NMP solution of the amic 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 break at 23°C of 17.9 ksi, 427 ksi, and 40%, and at 177°C of 10.8 ksi, 344 ksi, and 63%, respectively. The Tg of the cured film was 268°C.
(2.7857 g, 0.0095 mol) and 90 ml of NMP (12.8% w/w). After dissolution, 3,3',4,4'-biphenyl tetracarboxylic dianhydride (17.0049 g, 0.0175 mol) and 25 ml of NMP (37.8% w/w) were added and the reaction stirred at room temperature for 20 h. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.27 dL/g. Approximately 25 g of amic acid oligomeric solution was used to cast an unoriented thin film. Toluene (70 ml) was added to the remaining amic acid oligomeric solution and the temperature increased and maintained at ~180°C for ~24 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, a precipitate formed. The mixture was cooled, the oligomer washed in hot water, warm methanol, and dried under vacuum at 240°C for 4 h to provide a yellow powder (38.4 g, 78% yield). The 4-phenylethynylphthalic anhydride (10.1079 g, 0.0407 mol) and 58.06 mole of NMP (120 ml total NMP). The mixture was stirred overnight at room temperature under nitrogen. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.16 dL/g. Toluene (70 ml) was added to the amic acid oligomeric solution and the temperature increased and maintained at ~180°C for ~24 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, a precipitate formed. The mixture was cooled, the oligomer washed in hot water, warm methanol, and dried under vacuum at 240°C for 4 h to provide a yellow powder (38.4 g, 98% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 262°C and the T_g was 341°C. The T_g of the uncured polymer (cure conditions: 360°C/1 hr) was 276°C. A sample compression molded at 350°C/150 psi/1 hr had a G_{IC} (critical strain energy release rate) of 27.4 in J/m².

Example 9: 0.7050.25 3,4'-Oxydianiline and 1,3-bis(3-aminophenoxy)benzene, and 3,3',4,4'- Benzophenone Tetracarboxylic Dianhydride, Using 29.03 mole % Stoichiometric Offset and 58.06 mole % 4-Phenylethynylphthalic Anhydride

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the controlled molecular weight PEIT where Ar(1) is equal to a diphenylene where X is an oxygen atom located in the 3.4'-position and Ar(2) is equal to a diphenylene where X is a 1,3-dioxybenzene and Ar is equal to a bis(o-diphenylene) where Y is a carbonyl group located in the 4.4'-position, and where W is equal to a naphthyl group. The ratio of diamines [Ar(1):Ar(2)] is 0.75:0.25. The stoichiometric imbalance is 29.03 mole % and the endcapping reagent is 58.06 mole % of 4-phenylethynylphthalic anhydride.

Into a flame dried 250 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and drying tube were placed 3,4'-oxydianiline (10.5323 g, 0.0256 mol), 1,3-bis(3-aminophenoxy)benzene (5.1256 g, 0.0175 mol) and 25 ml of NMP (37.8% w/w). After dissolution, a slurry of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (16.0382 g, 0.0498 mol) and 4-phenylethynylphthalic anhydride (10.1079 g, 0.0407 mol) in 50 ml of NMP (33.6% w/w) were added to the stirred solution. An additional 45 ml of NMP was used to rinse in the anhydrides. The solids content was 25.2% w/w (120 ml total NMP). The mixture was stirred overnight at room temperature under nitrogen. The inherent viscosity of the amic acid oligomeric solution (0.5% in NMP at 25°C) was 0.16 dL/g. Toluene (70 ml) was added to the amic acid oligomeric solution and the temperature increased and maintained at ~180°C for ~24 h under a nitrogen atmosphere. As the amic acid oligomer was cyclodehydrated to the imide, a precipitate formed. The mixture was cooled, the oligomer washed in hot water, warm methanol, and dried under vacuum at 240°C for 4 h to provide a yellow powder (38.4 g, 98% yield). The T_g of the uncured as-isolated oligomer (DSC, 20°C/min) was 262°C and the T_g was 341°C. The T_g of the cured polymer (cure conditions: 360°C/1 hr/static air) was 276°C.

In the tables which follow, oligomer and polymer characterization is presented in Table 1; unoriented thin film properties are presented in Table 2; adhesive properties are presented in Table 3; and composite properties are presented in Table 4.

### Table 1

**OLIGOMER and POLYMER CHARACTERIZATION**

<table>
<thead>
<tr>
<th>Imide (Mₐ)</th>
<th>Acid</th>
<th>Imide</th>
<th>Imide²</th>
<th>C-Imide</th>
<th>C-Imide²</th>
<th>Temp. of 5% (\Delta T_g)</th>
<th>Wt. Loss, °C</th>
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<td>237</td>
<td>508</td>
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<td>265</td>
<td>253</td>
<td>487</td>
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<tr>
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<td>0.28</td>
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<td>248</td>
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<tr>
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<td>—</td>
<td>262</td>
<td>276</td>
<td>276</td>
<td>451</td>
</tr>
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</table>

*Imide-1: ODPA/3,4'-ODA/PEPA
Imide-2: 3,1: ODPA/BPDA/3,4'-ODA/PEPA
Imide-3: 1,1: ODPA/BPDA/3,4'-ODA/PEPA
Imide-4: 1,3: ODPA/BPDA/3,4'-ODA/PEPA
Imide-5: ODPA/3,4'-ODA/PEPA
Imide-6: BPDA/3,5'-ODA/3,4'-ODA/PEPA
Imide-7: BPDA/3,1: 3,4'-ODA/PEPA

**Inherent viscosity determined on 0.5% (w/v) NMP solution at 25°C.**

**Inherent viscosity determined on 0.5% (w/v) m-cresol solution at 25°C.**

**T_g and T_i of as-isolated oligomers (Imide) by DSC at a heating rate of 20°C/min.**

**Powdered samples after hold at 350°C C/1 h/static air, C-Imide: cured imide powder.**
### TABLE 2

<table>
<thead>
<tr>
<th>Calcd((M_1)) (g/mol)</th>
<th>T&lt;sub&gt;c&lt;/sub&gt; C</th>
<th>Test Temp., °C</th>
<th>Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
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<td>23</td>
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<td>17.9</td>
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<tr>
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<td>23</td>
<td>177</td>
<td>15.3</td>
<td>407</td>
<td>5</td>
</tr>
</tbody>
</table>

1-Inside-1: ODPA/3,4'-ODA/PEPA
2-Inside-2: ODPA/3,4'-ODA/PEPA
3-Inside-3: ODPA/3,4'-ODA/PEPA
4-Inside-4: ODPA/3,4'-ODA/PEPA
5-Inside-5: ODPA/3,4'-ODA/PEPA
6-Inside-6: ODPA/3,4'-ODA/PEPA
7-Inside-7: ODPA/3,4'-ODA/PEPA

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Layup</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;, °C</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Strength, ksi</td>
<td>Unidirectional</td>
<td>23</td>
<td>310</td>
</tr>
<tr>
<td>Flexural Modulus, ksi</td>
<td>Unidirectional</td>
<td>23</td>
<td>20.4</td>
</tr>
<tr>
<td>Short Beam Shear</td>
<td>Unidirectional</td>
<td>23</td>
<td>16.4</td>
</tr>
</tbody>
</table>

We claim:
1. A phenylethynyl terminated amic acid oligomer having the formula

![Chemical formula](attachment:chemical_formula.png)

and being selected from the group consisting of:

### TABLE 4

<table>
<thead>
<tr>
<th>Property</th>
<th>Layup</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;, °C</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Strength, ksi</td>
<td>Unidirectional</td>
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<tr>
<td>Flexural Modulus, ksi</td>
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<tr>
<td>Short Beam Shear</td>
<td>Unidirectional</td>
<td>23</td>
<td>16.4</td>
</tr>
</tbody>
</table>

We claim:
1. A phenylethynyl terminated amic acid oligomer having the formula

![Chemical formula](attachment:chemical_formula.png)
wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar}\text{ in the formula is}
\end{array}
\]

and

W in the formula is a bond;

wherein Ar in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W in the formula is

\[
\begin{array}{c}
\text{W in the formula is a bond;}
\end{array}
\]

wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W in the formula is

\[
\begin{array}{c}
\text{W in the formula is a bond;}
\end{array}
\]

wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W in the formula is

\[
\begin{array}{c}
\text{W in the formula is a bond;}
\end{array}
\]

wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W in the formula is

\[
\begin{array}{c}
\text{W in the formula is a bond;}
\end{array}
\]

wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W is a bond; and

wherein Ar in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W is a bond;

and

W in the formula is

\[
\begin{array}{c}
\text{W in the formula is a bond;}
\end{array}
\]

wherein Ar' in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W is a bond; and

wherein Ar in the formula is

\[
\begin{array}{c}
\text{Ar in the formula is}
\end{array}
\]

and

W is a bond.

2. A cured polymer prepared from the phenylethynyl terminated amic acid oligomer of claim 1.

3. A cured film prepared from the phenylethynyl terminated amic acid oligomer of claim 1.

4. A cured neat resin molding prepared from the phenylethynyl terminated amic acid oligomer of claim 1.

5. A cured adhesive prepared from the phenylethynyl terminated amic acid oligomer of claim 1.

6. A composite prepared from the phenylethynyl terminated amic acid oligomer of claim 1.

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