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(54) **PHENYLETHYNYL CONTAINING  
REACTIVE ADDITIVES**

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(73) **Assignee:** **The United States of America as represented by the United States National Aeronautics and Space Administration**, Washington, DC (US)

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C08F 238/00; C08F 4/00; C08F 251/00

(52) **U.S. Cl.** ..... **525/328.1**; 524/210; 524/600;  
524/606; 524/607; 525/262; 525/275; 525/282;  
525/285; 528/353; 528/125; 528/128; 528/171;  
528/172; 528/173; 528/174; 528/176; 528/183;  
528/185; 528/188; 528/220; 528/229; 528/350;  
528/352

(58) **Field of Search** ..... 525/328.1, 262,  
525/275, 282, 285; 524/210, 600, 606,  
607; 528/353, 125, 128, 171, 172, 173,  
174, 176, 183, 185, 188, 220, 229, 350,  
352

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\* cited by examiner

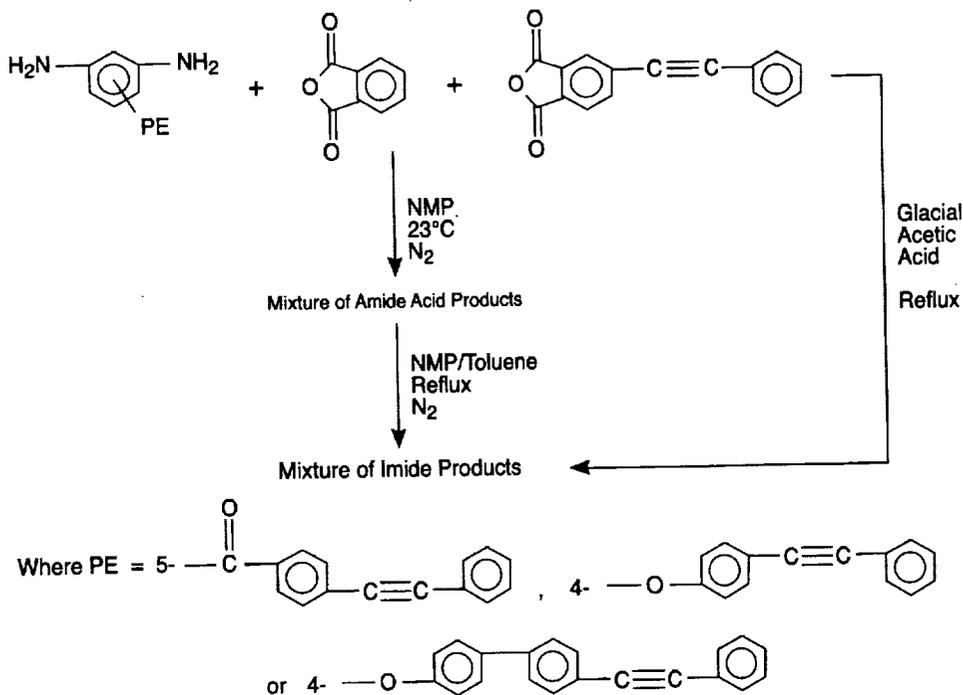
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(57) **ABSTRACT**

Phenylethynyl containing reactive additives were prepared from aromatic diamines containing phenylethynyl groups and various ratios of phthalic anhydride and 4-phenylethynylphthalic anhydride in glacial acetic acid to form the imide in one step or in N-methyl-2-pyrrolidinone to form the amide acid intermediate. The reactive additives were mixed in various amounts (10% to 90%) with oligomers containing either terminal or pendent phenylethynyl groups (or both) to reduce the melt viscosity and thereby enhance processability. Upon thermal cure, the additives react and become chemically incorporated into the matrix and effect an increase in crosslink density relative to that of the host resin. This resultant increase in crosslink density has advantageous consequences on the cured resin properties such as higher glass transition temperature and higher modulus as compared to that of the host resin.

**14 Claims, 5 Drawing Sheets**





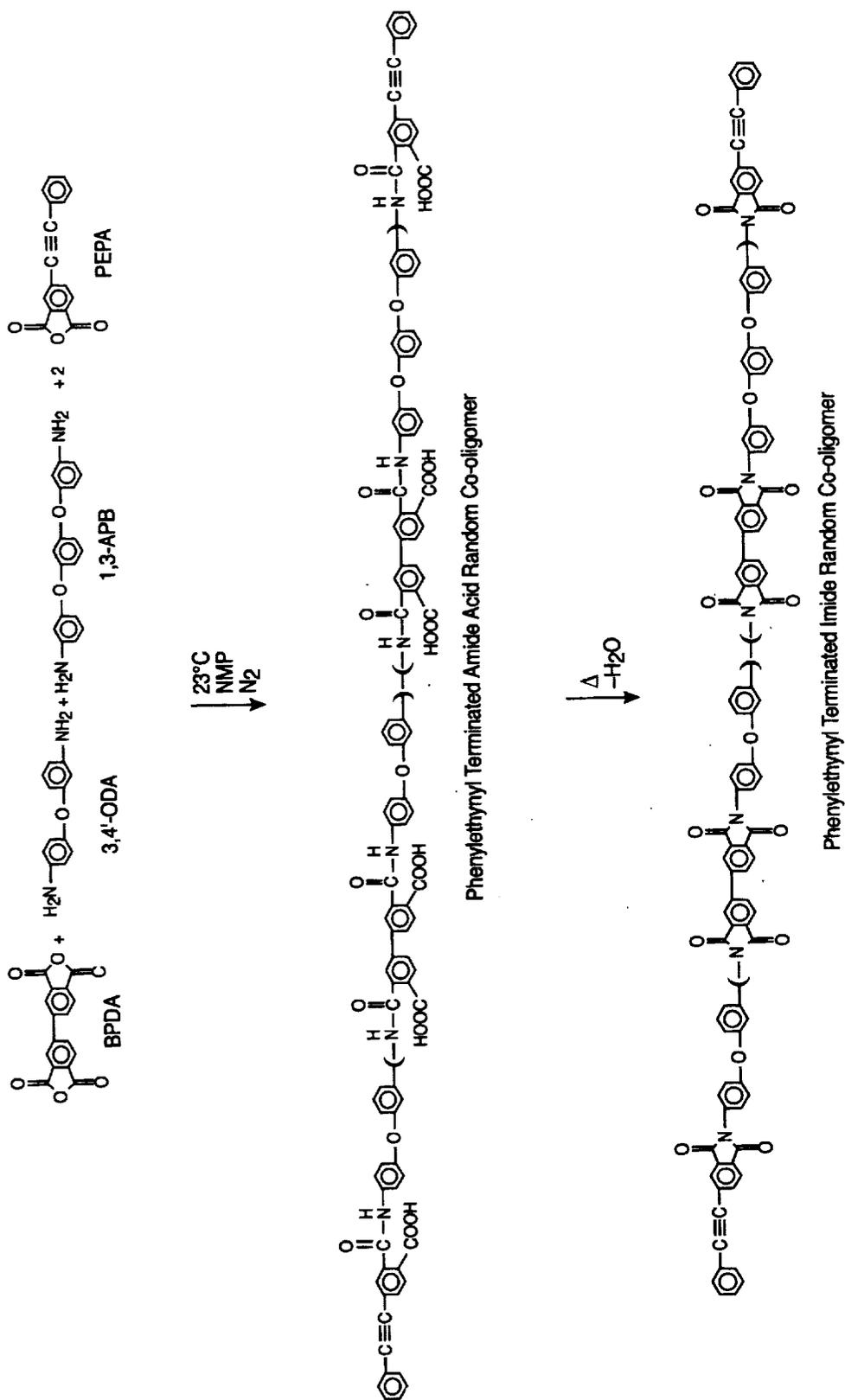


FIG. 2

Effect of PERA-1 on Melt Viscosity of PETI-5 Imide Powder

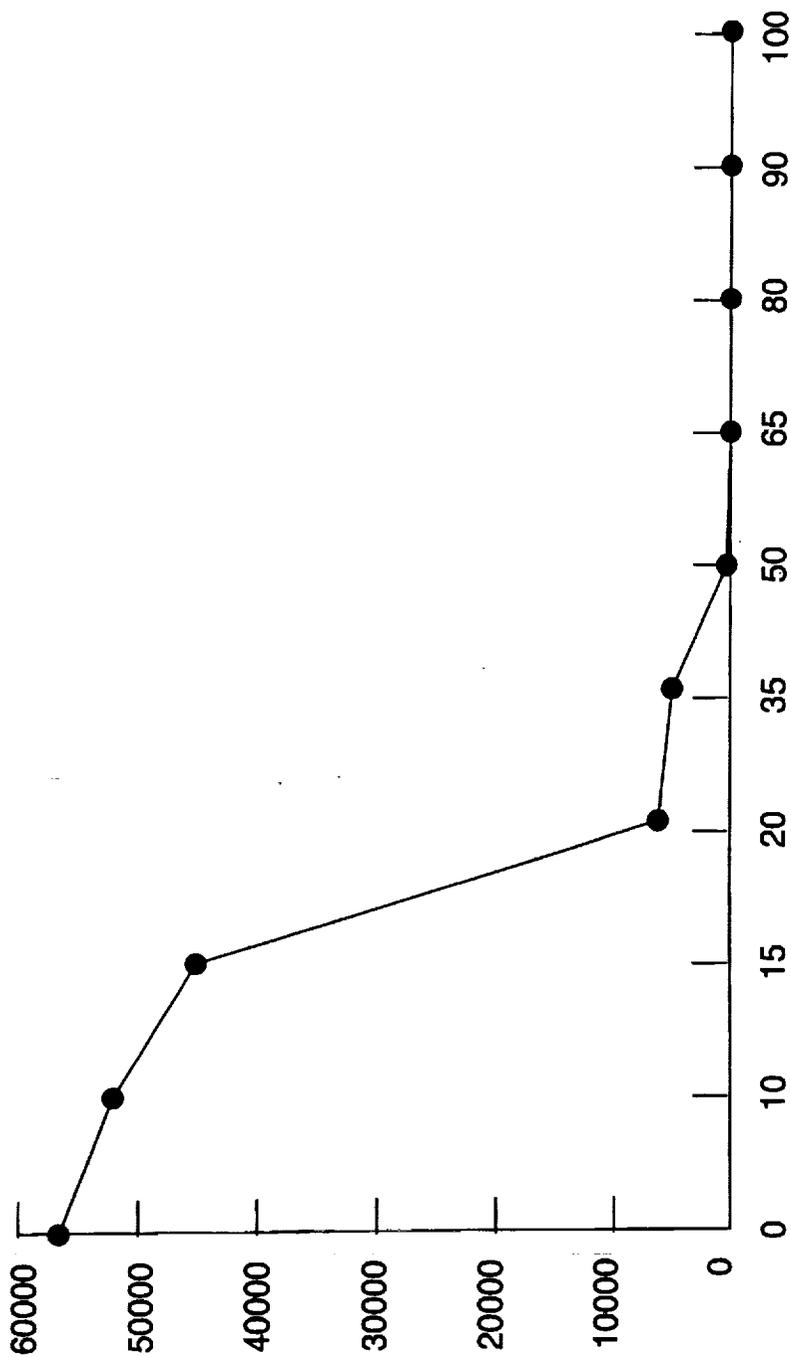


FIG. 3

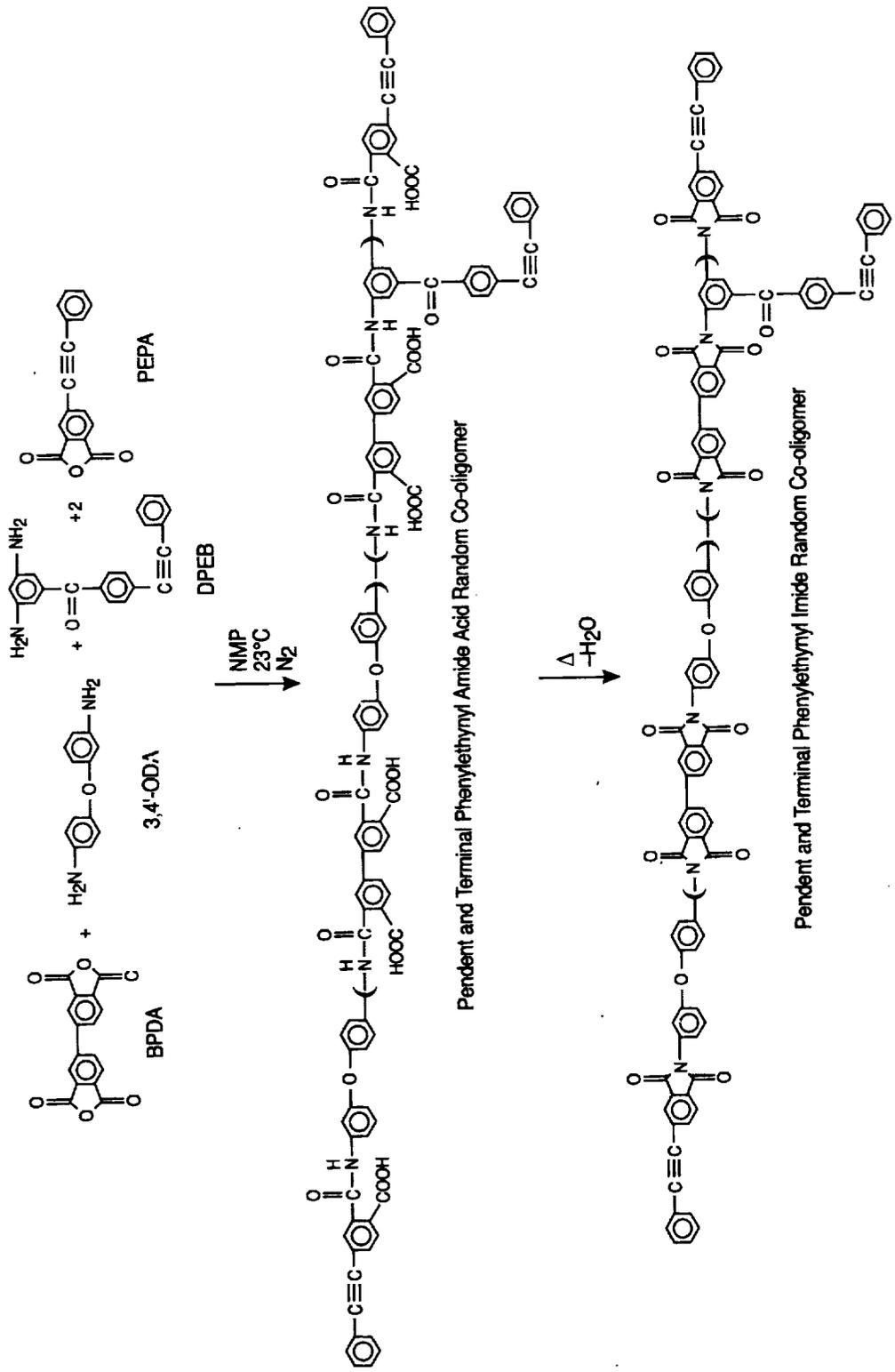


FIG. 4

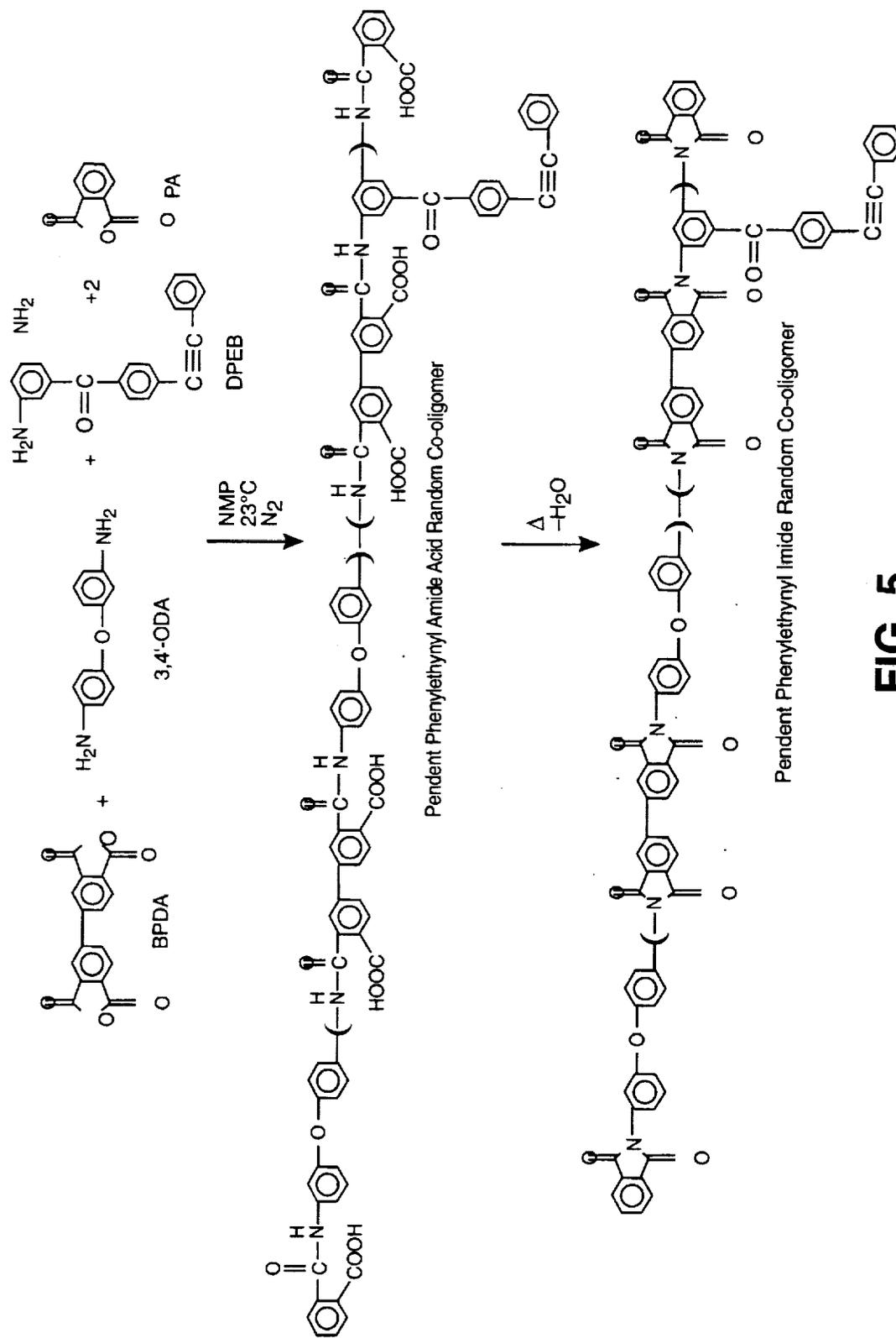


FIG. 5

## PHENYLETHYNYL CONTAINING REACTIVE ADDITIVES

### CROSS-REFERENCE

This patent application is related to commonly owned 5  
co-pending patent application Serial No. 09/310,686, filed  
Apr. 13, 1999, now U.S. Pat. No. 6,124,035.

### ORIGIN OF THE INVENTION

The invention described herein was made by employees 10  
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 therefor.

### BACKGROUND OF THE INVENTION

A variety of monomers, oligomers and polymers contain-  
ing ethynyl (acetylenic) and substituted ethynyl (i.e.,  
phenylethynyl) groups have been reported. The ethynyl  
groups in the polymer are either pendent 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  
Prepolymers" 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 have been observed for the ethynyl  
and substituted ethynyl containing materials. In general,  
thermally cured ethynyl and substituted ethynyl containing  
materials exhibit a favorable combination of physical and  
mechanical properties. Some ethynyl endcapped materials  
such as the Thermid® resins are commercially available  
(National Starch and Chemical Co., Bridgewater, N.J.  
08807). Other systems such as acetylene terminated sulfone  
have undergone extensive evaluation as matrix resins [M. G.  
Maximovich, S. C. Lockerby, F. E. Arnold and G. A.  
Loughran, *Sci. Adv. Matls. Proc. Eng. Ser.*, 23, 490 (1978)  
and G. A. Loughran, A. Wereta and F. E. Arnold, U.S. Pat.  
No. 4,131,625, December 1978 to U.S. Air Force].

Phenylethynyl containing amines have been used to ter-  
minate imide oligomers [F. W. Harris, A. Pamidimuhkala, R.  
Gupta, S. Das, T. Wu, G. Mock, *Poly. Prepr.*, 24 (2), 325,  
1983; F. W. Harris, A. Pamidimuhkala, R. Gupta, S. Das, T.  
Wu, G. Mock, *Macromol. Sci.-Chem.*, A21 (8&9), 1117  
(1984); C. W. Paul, R. A. Shultz, and S. P. Fenelli, "High  
Temperature Curing Endcaps for Polyimide Oligomers" in  
Advances in Polyimide Science and Technology, (Ed. C.  
Feger, M. M. Khoyasteh, and M. S. Htoo), Technomic  
Publishing Co., Inc., Lancaster, Pa., 1993, p. 220; R. G.  
Bryant, B. J. Jensen, P. M. Hergenrother, *Poly. Prepr.*, 34(1),  
566, 1993]. Imide oligomers terminated with ethynyl  
phthalic anhydride [P. M. Hergenrother, *Poly. Prepr.*, 21(1),  
81, 1980], substituted ethynyl phthalic anhydride [S. Hino,  
S. Sato, K. Kora, and O. Suzuki, *Jpn. Kokai Tokyo Koho*  
Japanese Patent #63,196,564, Aug. 15, 1988; *Chem. Abstr.*,  
115573w, 110, (1989)] and phenylethynyl containing  
phthalic anhydrides have been reported. Imide oligomers  
containing pendent substituted ethynyl groups [F. W. Harris,  
S. M. Padaki, and S. Varaprath, *Poly. Prepr.*, 21(1), 3, 1980  
(abstract only); B. J. Jensen, P. M. Hergenrother and G.  
Nwokogu, *Polymer*, 34(3), 630, 1993; B. J. Jensen and P. M.  
Hergenrother, U.S. Pat. No. 5,344,982 (Sep. 6, 1994)] have  
been reported. See also J. E. McGrath and G. W. Meyer, U.S.  
Pat. No. 4,493,002 (Feb. 20, 1996), J. G. Smith, Jr. Adhesion  
Society Proceedings, Vol. 19, 29-32 (1996) and J. W.  
Connell, J. G. Smith, Jr. and P. M. Hergenrother, *Society for*  
*the Advancement of Materials and Process Engineering*  
*Proceedings*, Vol. 41, 1102-1112 (1996).

High temperature resins are used in a variety of aerospace  
and non-aerospace applications. Generally these materials  
require high pressures (>200 psi) to form adhesive bonds,  
well consolidated moldings or fiber reinforced composite  
laminates. However, there exists a need for novel high  
temperature resins that can be processed at low pressures  
and without an autoclave (i.e., under vacuum bag  
conditions—15 psi) while maintaining excellent mechani-  
cal properties.

It is a primary object of the present invention to provide  
novel phenylethynyl containing reactive additives (PERAs)  
which can be used with any phenylethynyl containing  
polymer, co-polymer, oligomers or co-oligomers to decrease  
melt flow and consequently processing pressures required to  
fabricate molded parts, adhesive bonds, and fiber reinforced  
composite parts.

### SUMMARY OF THE INVENTION

According to the present invention the foregoing and  
additional objects are obtained by synthesizing amide acid  
and imide phenylethynyl reactive additives, subsequently  
adding them to phenylethynyl containing polymers,  
co-polymers, oligomers and co-oligomers in solution or by  
mixing dry imide powder of the reactive additive with  
phenylethynyl containing oligomer powder. These species  
can be combined in several different ways: as solutions of  
amide acid of the phenylethynyl containing reactive additive  
(PERA) to a solution of the phenylethynyl containing  
polymer, co-polymer, oligomer, co-oligomer; as solutions of  
the imide of the PERA to solutions of the phenylethynyl  
containing polymer, co-polymer, oligomer, co-oligomer and  
by dry mixing of the imide powder of the PERA to the dry  
powder of the phenylethynyl containing polymer,  
co-polymer, oligomer, co-oligomer. The effect of these reac-  
tive additives on the processability and properties on the  
resin systems depends upon the form of the PERA (i.e.,  
imide vs. amide acid) used.

The PERA reduce the melt viscosity of the phenylethynyl  
containing polymer, co-polymer, oligomer, and co-oligomer  
to which they are added and thereby reduce the processing  
pressures required to form the adhesive bonds, consolidated  
filled or unfilled moldings or to fabricate fiber reinforced  
composite laminates. Upon thermal cure the PERAs react  
with themselves as well as with the phenylethynyl contain-  
ing host resin and thereby become chemically incorporated  
into the resin system. The effect on mechanical properties,  
relative to those of the host resin, are dependent on the  
amount of PERA used, but typically result in higher T<sub>g</sub>s,  
higher mechanical properties such as modulus and compre-  
sive properties as well as higher retention of these mechani-  
cal properties at elevated temperatures without significantly  
reducing toughness or damage tolerance (as determined by  
compression after impact strengths of quasi-isotropic  
laminates).

### BRIEF DESCRIPTION OF THE DRAWING

For a more complete understanding of the present  
invention, including its objects and attending benefits, ref-  
erence 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 drawings, wherein:

FIG. 1 is an equation showing the preparation of phenyl-  
ethynyl reactive additives according to the present inven-  
tion.

FIG. 2 is an equation showing the preparation of Random  
Amide Acid and Imide Co-oligomers (PETI-5).

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FIG. 3 illustrates the effect of PERA-1 on the melt viscosity of PETI-5 imide powder.

FIG. 4 is an equation showing the preparation of Random Amide Acid and Imide Co-oligomers (PTPEI-1).

FIG. 5 is an equation showing the preparation of Random Amide Acid and Imide Co-oligomers (PPEI-1).

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Phenylethynyl containing reactive additives are prepared from aromatic diamines containing phenylethynyl groups and various ratios of phthalic anhydride (PA) and 4-phenylethynylphthalic anhydride (PEPA) as depicted in FIG. 1. The PERAs may be used in both the amide acid and the imide form to lower the melt viscosity of the host phenylethynyl containing resin. The PERA amide acids are prepared by reacting a diamine containing phenylethynyl groups with a mixture of PA and PEPA in N-methyl-2-pyrrolidinone (NMP) at room temperature under nitrogen. The products remain soluble in NMP. The PERA imide products are prepared from the amide acid intermediate in NMP by adding toluene and heating the mixture to reflux (~150–160° C.) under nitrogen or in one step by reacting a diamine containing phenylethynyl groups with a mixture of PA and PEPA in refluxing glacial acetic acid. The imide products are soluble in NMP up to 50% solids by weight. Since all of the products from the reaction used to prepare the PERAs contain at least one phenylethynyl group, upon thermal cure with a phenylethynyl containing host resin, the PERAs react and become chemically incorporated onto the matrix and thus cannot migrate or leach out.

Three different PERAs were prepared and evaluated. PERA-1 was prepared from 3,5-diamino-4'-phenylethynylbenzophenone and an equimolar amount of PA and PEPA in refluxing glacial acetic acid. The amide acid of PERA-1 was prepared from 3,5-diamino-4'-phenylethynylbenzophenone and an equal molar amount of PA and PEPA in NMP at 23° C. under nitrogen. PERA-2 was prepared from 3,5-diamino-4'-phenylethynylbenzophenone (1.0 mole) and PA (1.5 mole) and PEPA (0.5 mole) in refluxing glacial acetic acid. PERA-3 was prepared from 3,5-diamino-4'-phenylethynylbenzophenone (1.0 mole) and PA (0.5 mole) and PEPA (1.5 mole) in refluxing glacial acetic acid. The PERAs were added to the host resin, which can be any polymer, co-polymer, oligomer, or co-oligomer containing phenylethynyl groups, in order to reduce the melt flow and increase the ease of processability. The phenylethynyl groups of the host resin can be either pendant, terminal or in the backbone or any combination thereof. The amount of additive to bring about the desired reduction in melt viscosity was dependent on the melt viscosity of the host resin. The PERAs (both amide acid and imide forms) were typically added as solid solutions (i.e., dry powder) to a solid solution of the phenylethynyl containing host resin and were subsequently processed into the desired form.

In one aspect the present invention is the process of adding phenylethynyl reactive additives (PERAs) to phenylethynyl containing polymers, co-polymers, oligomers and co-oligomers in solution or by mixing dry imide powder of the reactive additive with the phenylethynyl containing oligomer powder in order to reduce the melt flow and increase the ease of processability.

The best results were obtained with formulations of PERA-1 and a phenylethynyl terminated amide acid co-oligomer with a calculated number average molecular weight of 5000 g/mole (designated as PETI-5). The PETI-5

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amide acid solution in NMP and imide powder were prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) (0.91 mole), 3,4'-oxydianiline (3,4'-ODA), 1,3-bis(3-aminophenoxy) benzene (1,3-APB) (0.15 mole) and 4-phenylethynylphthalic anhydride (PEPA) (0.18 mole) according to a procedure previously reported by P. M. Hergenrother and J. G. Smith, Jr., *Polymer Preprints*, 35(1), 353, 1994. The synthetic scheme is depicted in FIG. 2. PERA-1 in the imide form was physically mixed with PETI-5 imide powder in concentrations ranging from 10% to 90% by weight and the resultant formulations characterized for complex melt viscosity and thermal properties. The data is presented in Table 1.

TABLE 1

Characterization of Physically Mixed Imide Powders of PERA-1 and PETI-5					
PERA-1, Weight %	PETI-5, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured* (Melting temp.)	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
100	0	182	ND	0.1	270
90	10	182	ND	14	270
80	20	183	ND	21	373
65	35	182	ND	53	370
50	50	182	ND	500	371
35	65	183	ND	4700	372
20	80	182	273 (393)	5600	369
15	85	185	276 (390)	44700	371
10	90	183	278 (392)	52000	371
0	100	235	250 (387)	56500	371

\*Cured 1 hour at 350° C. in a sealed aluminum pan. ND = Not detected by DSC

The data in Table 1 indicates that the most drastic reduction in complex melt viscosity occurred with a PERA-1 loading of 20 weight %. Higher loading results in a continued decrease in complex melt viscosity as shown in FIG. 3. The composition containing 10 weight % PETI-5 exhibits a dramatic reduction in the temperature at which the lowest complex melt viscosity is observed, decreasing from ~371° C. to ~270° C.

The imide of PERA-1 was mixed at a 20 weight % loading with the amide acid of PETI-5 in NMP at a concentration of ~35% weight/weight. To this solution was added toluene and the mixture was heated under a Dean Stark trap to remove the water of imidization. The PETI-5 imide powder precipitated during this imidization. The mixture was poured into water and the solid isolated and dried. This material exhibited an initial thermal transition ~180° C. and a  $T_g$  of 272° C. and a melting transition of 443° C. after curing for one hour at 350° C. The minimum complex melt viscosity was 14500 poise at 367° C.

Unidirectional carbon fiber (IM-7, unsized, 3k tow) prepreg was prepared by solution coating from an NMP solution (35% solids) of the imide of PERA-1 (20%)/PETI-5 amide acid (80%). The prepreg was processed into composite laminates under 50 psi whereas composite laminates of the same lay-up and number of plies fabricated from PETI-5 prepreg are typically processed under 200 psi. Laminate data is presented in Table 2. The effect of the PERA-1 concentration on the minimum melt viscosity of PETI-5 imide powder is presented graphically in FIG. 3.

TABLE 2

IM-7 Laminate Properties*		
Property	PETI-5 (200 psi processing)	PERA-1/PETI-5 20/80 (50 psi processing)
$T_g$ , ° C. (G')	270	290
Open Hole Compression Strength, Ksi		
23° C.	56.5	58.4
177° C. (wet)	46.3	46.8
Compression After Impact Strength, Ksi		
23° C.	48.0	47.2
Failure Strain, $\mu\text{in/in}$	5800	5900
Modulus, Msi	8.1	8.5

\*Normalized to 62% fiber volume

The imide of PERA-1 was also mixed at a 35 weight % loading with the amide acid of PETI-5 in NMP at a concentration of ~35% weight/weight. To this solution was added toluene and the mixture was heated under a Dean Stark trap to remove the water of imidization. The PETI-5 imide powder precipitated during this imidization. The mixture was poured into water and the solid isolated and dried. This material exhibited an initial thermal melting transition at ~149° C. and a  $T_g$  of 289° C. by DSC after curing for one hour at 350° C. in a sealed aluminum pan. PETI-5 cured under identical conditions exhibits a  $T_g$  of 250° C. and a melting transition at 387° C. The minimum complex melt viscosity was 315 poise at 371° C. This minimum complex melt viscosity is an order of magnitude lower than that observed when the two imide powders were physically mixed at the same concentration.

Favorable results were obtained from formulations of PERA-1 and an imide oligomer containing both pendent and terminal phenylethynyl groups with a calculated number average molecular weight of 5000 g/mole (designated PTPEI-1). The preparation of PTPEI-1 is presented in FIG. 4. PTPEI amide acid in NMP and imide powder were prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) (0.91 mole), 3,4'-oxydianiline (3,4'-ODA), 3,5-diamino-4'-phenylethynylbenzophenone (DPEB) (0.15 mole) and 4-phenylethynylphthalic anhydride (PEPA) (0.18 mole) according to the procedure previously reported by J. G. Smith, Jr., *Adhesion Society Proceedings*, Vol. 19, 29-32 (1996). PERA-1 in the imide form was physically mixed with imide powder of PTPEI-1 at concentrations of 10, 20, and 50% by weight and the resultant formulation were characterized for complex melt viscosity and thermal properties. The data is presented in Table 3.

TABLE 3

Characterization of Physically Mixed Imide Powders of PERA-1 and PTPEI-1					
PERA-1, Weight %	PTPEI-1, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured*	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
100	0	191, 230	ND	<1	265
50	50	197	3236	7200	368
20	80	195	322	26300	368

TABLE 3-continued

Characterization of Physically Mixed Imide Powders of PERA-1 and PTPEI-1					
PERA-1, Weight %	PTPEI-1, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured*	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
10	90	195	318	37400	361
0	100	231	307	150600	362

\*Cured for 1 hour at 350° C. in a sealed aluminum pan. ND = Not detected by DSC.

Dramatic reductions in the minimum melt viscosity were observed with only 10 weight percent of PERA-1 while the cured  $T_g$  increased substantially.

Favorable results were also obtained from formulations of PERA-1 and an imide oligomer containing pendent phenylethynyl groups with a calculated number average molecular weight of 5000 g/mole (designated as PPEI-1). The preparation of PPEI-1 is present in FIG. 5. PPEI-1 amide acid in NMP and imide powder were prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) (0.91 mole), 3,4'-oxydianiline (3,4'-ODA) (0.85 mole), 3,5-diamino-4'-phenylethynylbenzophenone (DPEB) (0.15 mole) and phthalic anhydride (PA) (0.18 mole) according to the procedure previously reported by J. W. Connell, J. G. Smith, Jr. and P. M. Hergenrother, *Society for the Advancement of Materials and Process Engineering Proceedings*, Vol. 41, 1102-1112 (1996). PERA-1 in the imide form was physically mixed with the imide powder of PPEI-1 at concentrations of 10, 20, and 50% by weight and the resultant formulations were characterized for complex melt viscosity and thermal properties. The data is presented in Table 4.

TABLE 4

Characterization of Physically Mixed Imide Powders of PERA-1 and PPEI-1					
PERA-1, Weight %	PPEI-1, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured* (Melting temp.)	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
100	0	182	ND	<1	270
50	50	149	ND	1308	369
20	80	149	270 (380)	10125	370
10	90	150	268 (379)	13400	370
0	100	209	267 (380)	60000	371

\*Cured for 1 hour at 350° C. in a sealed aluminum pan. ND = Not detected by DSC.

PERA-1/PPEI-1 formulations exhibited similar trends as PERA-1/PETI-5 and PERA-1/PTPEI-1 formulations, but to a lesser degree with respect to reductions in melt viscosity and changes in thermal properties.

Favorable results were also obtained with formulations of PERA-2 and PETI-5 imide powders. Melt viscosity and thermal properties are presented in Table 5.

TABLE 5

Characterization of Physically Mixed Imide Powders of PERA-2 and PETI-5					
PERA-2, Weight %	PETI-5, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured* (Melting temp.)	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
100	0	179, 235	ND	<1	270
50	50	178	286	50	370
20	80	180	276 (385)	20000	371
10	90	181	275 (384)	45000	370
0	100	235	250 (387)	56500	371

\*Cured for 1 hour at 350° C. in a sealed aluminum pan. ND = Not detected by DSC.

Good results were also obtained with formulations of PERA-3 and PETI-5 imide powders. Melt viscosity and thermal properties are presented in Table 6.

TABLE 6

Characterization of Physically Mixed Imide Powders of PERA-3 and PETI-5					
PERA-3, Weight %	PETI-5, Weight %	Thermal Transition Temp., ° C. Initial	Thermal Transition Temp., ° C. Cured* (Melting temp.)	Minimum Complex Melt Viscosity, poise	Temp. of Minimum Viscosity, ° C.
100	0	191, 230	ND	<1	265
50	50	197	ND	625	367
20	80	195	272 (384)	9990	369
10	90	195	269 (381)	48300	371
0	100	235	250 (387)	56500	371

\*Cured for 1 hour at 350° C. in a sealed aluminum pan. ND = Not detected by DSC.

Formulations of PERA-2/PETI-5 and PERA-3/PETI-5 exhibited similar trends with respect to initial thermal transitions, cured  $T_g$  and reduction in melt viscosity as observed with PERA-1/PETI-5 imide powder formulations.

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.

#### SYNTHESIS OF PHENYLETHYNYL CONTAINING REACTIVE ADDITIVES (PERAs)

##### EXAMPLE 1

Synthesis of PERA-1 from 3,5-diamino-4'-phenylethynylbenzophenone (1.0 mole), phthalic anhydride (1.0 mole) and 4-phenylethynylphthalic anhydride (1.0 mole)

Into a 3 L three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser was placed 3,5-diamino-4'-phenylethynylbenzophenone (187.4 g, 0.60 mole), phthalic anhydride (88.9 g, 0.60 mole), 4-phenylethynylphthalic anhydride (148.9 g, 0.60 mole) and glacial acetic acid (785 mL, 34% solids). The mixture was heated to reflux (~120° C.) to give a dark brown solution. After ~2 hours at this temperature a large amount of light tan precipitate formed making stirring impossible. Heating was continued for an additional hour and the reaction mixture

was cooled to room temperature. The product was isolated by filtration and washed three times in warm water to remove residual acetic acid. The solid was air dried for ~36 hours and subsequently placed in a forced air oven at 125° C. for 15 hours. The light tan powder (397 g, 98% of theoretical yield) exhibited a melting transition at ~182° C., and an exothermic transition due to the thermal reaction of the phenylethynyl groups beginning at 346° C. and peaking at 381° C. as determined by DSC. The heat of the reaction was ~275 J/g.

The amide acid of PERA-1 was prepared in a 3 L three-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and drying tube using 3,5-diamino-4'-phenylethynylbenzophenone (289.4 g, 0.926 mole), phthalic anhydride (137.2 g, 0.926 mole), 4-phenylethynylphthalic anhydride (230.0 g, 0.926 mole) and NMP (1180 mL, 35% solids). Initially, the diamine was dissolved in 400 mL of NMP and the dianhydrides were added as a slurry in 250 mL of NMP. Additional NMP (350 mL) was used to rinse in all of the solids. The mixture was stirred at room temperature under nitrogen for ~72 hr (for convenience, this much time is not necessary). This solution was used to prepare formulations with various phenylethynyl containing oligomers.

##### EXAMPLE 2

Synthesis of PERA-2 from 3,5-diamino-4'-phenylethynylbenzophenone (1.0 mole), phthalic anhydride (1.5 mole) and 4-phenylethynylphthalic anhydride (0.5 mole)

Into a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser was placed 3,5-diamino-4'-phenylethynylbenzophenone (23.43 g, 75.0 mmole), phthalic anhydride (16.66 g, 112.5 mmole), 4-phenylethynylphthalic anhydride (9.31 g, 37.5 mmole) and glacial acetic acid (125 mL, 30% solids). The mixture was heated to reflux (~120° C.) to give a dark brown solution. After ~2 hours at this temperature a large amount of light tan precipitate formed making stirring impossible. Heating was continued for an additional hour and the reaction mixture was cooled to room temperature. The product was isolated by filtration and washed three times in warm water to remove residual acetic acid. The solid was air dried for ~15 hours and subsequently placed in a forced air oven at 130° C. for 6 hours. The light tan powder (45.0 g, 96% of theoretical yield) exhibited a melting transition at ~179° C. and 235° C., and an exothermic transition due to the thermal reaction of the phenylethynyl groups beginning at 346° C. and peaking at 383° C. as determined by DSC. The heat of the reaction was ~209 J/g.

##### EXAMPLE 3

Synthesis of PERA-3 from 3,5-diamino-4'-phenylethynylbenzophenone (1.0 mole), phthalic anhydride (0.5 mole) and 4-phenylethynylphthalic anhydride (1.5 mole)

Into a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser was placed 3,5-diamino-4'-phenylethynylbenzophenone (21.98 g, 70.4 mmole), phthalic anhydride (5.211 g, 35.2 mmole), 4-phenylethynylphthalic anhydride (26.20 g, 105.5 mmole) and glacial acetic acid (200 mL, 20% solids). The mixture was heated to reflux (~120° C.) to give a dark brown solution. After ~2 hours at this temperature a large amount

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of light tan precipitate formed making stirring impossible. Heating was continued for an additional hour and the reaction mixture was cooled to room temperature. The product was isolated by filtration and washed three times in warm water to remove residual acetic acid. The solid was dried in a forced air oven at 130° C. for 15 hours. The light tan powder (50.20 g, 99% of theoretical yield) exhibited a melting transition at ~191° C. and 230° C., and an exothermic transition due to the thermal reaction of the phenylethynyl groups beginning at 340° C. and peaking at 374° C. as determined by DSC. The heat of the reaction was ~281 J/g.

## EXAMPLE 4

Resin from Physical Mixture of Imide Powders of PERA-1 (10% By Weight) and PETI-5 (90% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.5 g) and PERA-1 imide powder (0.5 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 183° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 278° C. and a melting transition at 392° C. The material exhibited a minimum melt viscosity of 52,000 poise at ~371° C.

## EXAMPLE 5

Resin from Physical Mixture of Imide Powders of PERA-1 (15% By Weight) and PETI-5 (85% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.25 g) and PERA-1 imide powder (0.75 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 185° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 276° C. and a melting transition at 390° C. The material exhibited a minimum melt viscosity of 44,700 poise at ~371° C.

## EXAMPLE 6

Resin from Physical Mixture of Imide Powders of PERA-1 (20% By Weight) and PETI-5 (80% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.0 g) and PERA-1 imide powder (1.0 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 182° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 273° C. and a melting transition at 393° C. The material exhibited a minimum melt viscosity of 5600 poise at ~371° C.

## EXAMPLE 7

Resin from Physical Mixture of Imide Powders of PERA-1 (35% By Weight) and PETI-5 (65% By Weight)

Into a plastic vial was placed PETI-5 imide powder (3.25 g) and PERA-1 imide powder (1.75 g). The two solids were

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physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 183° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited no  $T_g$  or melting transition by DSC. The material exhibited a minimum melt viscosity of 4700 poise at ~372° C.

## EXAMPLE 8

Resin from Physical Mixture of Imide Powders of PERA-1 (50% By Weight) and PETI-5 (50% By Weight)

Into a plastic vial was placed PETI-5 imide powder (2.5 g) and PERA-1 imide powder (2.5 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 182° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited no  $T_g$  or melting transition by DSC. The material exhibited a minimum melt viscosity of 500 poise at ~371° C.

## EXAMPLE 9

Resin from Physical Mixture of Imide Powders of PERA-1 (65% By Weight) and PETI-5 (35% By Weight)

Into a plastic vial was placed PETI-5 imide powder (1.75 g) and PERA-1 imide powder (3.25 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 182° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited no  $T_g$  or melting transition by DSC. The material exhibited a minimum melt viscosity of 53 poise at ~371° C.

## EXAMPLE 10

Resin from Physical Mixture of Imide Powders of PERA-1 (80% By Weight) and PETI-5 (20% By Weight)

Into a plastic vial was placed PETI-5 imide powder (1.0 g) and PERA-1 imide powder (4.0 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 183° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited no  $T_g$  or melting transition by DSC. The material exhibited a minimum melt viscosity of 21 poise at ~373° C.

## EXAMPLE 11

Resin from Physical Mixture of Imide Powders of PERA-1 (90% By Weight) and PETI-5 (10% By Weight)

Into a plastic vial was placed PETI-5 imide powder (0.5 g) and PERA-1 imide powder (4.5 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further

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mix the solids. The material exhibited an initial thermal transition by DSC at 182° C. The material was cured for one hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited no  $T_g$  or melting transition by DSC. The material exhibited a minimum melt viscosity of 14 poise at -270° C.

## EXAMPLE 12

Resin from Mixture of Imide Powder of PERA-1 (20% By Weight) and PETI-5 Amide Acid (80% By Weight)

PETI-5 amide acid solution (7397.0 g of solution=2588.9 g of amide acid, 35% solids in NMP) was placed in a large metal container and a solution of PERA-1 (647.2 g, 35% solids in NMP) was added. The two solutions were stirred at room temperature under nitrogen for ~16 hours. The resulting homogenous solution exhibited a Brookfield viscosity of 8700 centipoise. This solution was used to prepare unidirectional carbon fiber (IM-7, unsized, 3k tow) prepreg. The prepreg was subsequently used to prepare laminates in a vacuum press and in an autoclave using the following processing cycle. The laminates were heated under vacuum at 250° C. and held for one hour to remove volatiles and affect imidization. Pressure (50 psi) was subsequently applied and the laminate heated to 371° C. and held for one hour. The laminate was cooled to room temperature under pressure and vacuum. Laminates processed under this cycle were well consolidated and void-free as evidenced by ultrasonic inspection. Mechanical properties of the composite laminates are presented in Table 2.

## EXAMPLE 13

Resin from Mixture of Imide Powder of PERA-1 (35% By Weight) and PETI-5 Amide Acid (65% By Weight)

PETI-5 amide acid solution (4051.0 g of solution=1417.9 g of amide acid, 35% solids in NMP) was placed in a large metal container and a solution of PERA-1 (777.0 g, 40% solids in NMP) was added. The two solutions were stirred at room temperature under nitrogen for ~16 hours. The resulting homogenous solution exhibited a Brookfield viscosity of 3000 centipoise. This solution was used to prepare unidirectional carbon fiber (IM-7, unsized, 3k tow) prepreg. The prepreg was subsequently used to prepare laminates in a vacuum press and in an autoclave using the following processing cycle. The laminates were heated under vacuum at 250° C. and held for one hour to remove volatiles and affect imidization. Pressure (50 psi) was subsequently applied and the laminate heated to 371° C. and held for one hour. The laminate was cooled to room temperature under pressure and vacuum. Laminates processed under this cycle were well consolidated and void-free as evidenced by ultrasonic inspection. Due to low resin content in the prepreg (~28-30%), mechanical properties were not determined.

## EXAMPLE 14

Resin from Mixture of Imide Powder of PERA-1 (50% By Weight) and PETI-5 Amide Acid (50% By Weight)

PETI-5 amide acid solution (1818.0 g of solution=727.2 g of amide acid, 40% solids in NMP) was placed in a large metal container and a solution of PERA-1 (724.2 g, 30% solids in NMP) was added. The two solutions were stirred at

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room temperature under nitrogen for ~6 hours. The resulting homogenous solution exhibited a Brookfield viscosity of ~1000 centipoise. This solution was used to prepare unidirectional carbon fiber (IM-7, unsized, 3k tow) prepreg. The prepreg was subsequently used to prepare laminates in a vacuum press and in an autoclave using the following processing cycle. The laminates were heated under vacuum at 300° C. and held for one hour to remove volatiles and affect imidization. Pressure (25 psi) was subsequently applied and the laminate heated to 371° C. and held for one hour. The laminate was cooled to room temperature under pressure and vacuum. Laminates processed under this cycle were well consolidated and void-free as evidenced by ultrasonic inspection. Unidirectional laminates (6"×6", 12 plies thick) were fabricated in an autoclave under 1-15 psi. The laminates appeared well consolidated, however ultrasonic inspection revealed poor to moderate consolidation even though excessive resin flow was evident.

## EXAMPLE 15

Resin from Amide Acid of PERA-1 (20% By Weight) and PETI-5 Amide Acid (80% By Weight)

PETI-5 amide acid solution (7490 g of solution=2621.5 g of amide acid, 35% solids in NMP) was placed in a large metal container and a solution of PERA-1 (1855 g, 35% solids in NMP) was added. The two solutions were stirred at room temperature under nitrogen for ~16 hours. The resulting homogenous solution exhibited a Brookfield viscosity of ~6800 centipoise. This solution was used to prepare unidirectional carbon fiber (IM-7, unsized, 3k tow) prepreg. The prepreg was subsequently used to prepare laminates in a vacuum press and in an autoclave using the following processing cycle. The laminates were heated under vacuum at 250-300° C. and held for one hour to remove volatiles and affect imidization. Pressure (50 psi) was subsequently applied and the laminate heated to 371° C. and held for one hour. The laminate was cooled to room temperature under pressure and vacuum. Laminates processed under this cycle were well consolidated and void-free as evidenced by ultrasonic inspection. Adhesive properties are presented in Table 4.

## EXAMPLE 16

Resin from Physical Mixture of Imide Powders of PERA-1 (10% By Weight) and PTPEI-1 (90% By Weight)

Into a plastic vial was placed PTPEI-1 imide powder (0.50 g) and PERA-1 imide powder (4.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 196° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 318° C. PTPEI-1 exhibits a  $T_g$  of 307° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 37400 poise at -361° C. PTPEI exhibited a minimum complex melt viscosity of 150600 poise at -362° C.

## EXAMPLE 17

Resin from Physical Mixture of Imide Powders of PERA-1 (20% By Weight) and PTPEI-1 (80% By Weight)

Into a plastic vial was placed PTPEI-1 imide powder (1.0 g) and PERA-1 imide powder (4.0 g). The two solids were

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physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 150° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 322° C. PTPEI-1 exhibits a  $T_g$  of 307° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 26300 poise at ~368° C. PTPEI exhibited a minimum complex melt viscosity of 150600 poise at ~362° C.

## EXAMPLE 18

Resin from Physical Mixture of Imide Powders of PERA-1 (50% By Weight) and PTPEI-1 (50% By Weight)

Into a plastic vial was placed PTPEI-1 imide powder (2.50 g) and PERA-1 imide powder (2.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 150° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 326° C. PTPEI-1 exhibits a  $T_g$  of 307° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 7200 poise at ~368° C. PTPEI exhibited a minimum complex melt viscosity of 150600 poise at 362° C.

## EXAMPLE 19

Resin from Physical Mixture of Imide Powders of PERA-1(10% By Weight) and PPEI-1 (90% By Weight)

Into a plastic vial was placed PPEI-1 imide powder (4.50 g) and PERA-1 imide powder (0.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 150° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 379° C. PPEI-1 exhibits a  $T_g$  of 267° C. and a melting transition at 379° C. PPEI-1 exhibits a  $T_g$  of 267° C. and a melting transition of 380° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 13,400 poise at ~370° C. PPEI exhibited a minimum complex melt viscosity of 60,000 poise at ~371° C.

## EXAMPLE 20

Resin from Physical Mixture of Imide Powders of PERA-1 (20% By Weight) and PPEI-1 (80% By Weight)

Into a plastic vial was placed PPEI-1 imide powder (4.0 g) and PERA-1 imide powder (1.0 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 149° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 270° C. and a melting transition at 380° C. PPEI-1 exhibits a  $T_g$  of 267° C. and a melting transition of 380° C. after curing for one hour in a sealed aluminum pan. The material exhibited a minimum

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complex melt viscosity of 10,125 poise at ~370° C. PPEI exhibited a minimum complex melt viscosity of 60,000 poise at 371° C.

## EXAMPLE 21

Resin from Physical Mixture of Imide Powders of PERA-1 (50% By Weight) and PPEI-1 (50% By Weight)

Into a plastic vial was placed PPEI-1 imide powder (2.50 g) and PERA-1 imide powder (2.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 149° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, no  $T_g$  or melting transition was detected by DSC. PPEI-1 exhibits a  $T_g$  of 267° C. and a melting transition of 380° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 1308 poise at ~369° C. PPEI exhibited a minimum complex melt viscosity of 60,000 poise at ~371° C.

## EXAMPLE 22

Resin from Physical Mixture of Imide Powders of PERA-2 (10% By Weight) and PETI-5 (90% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.50 g) and PERA-2 imide powder (0.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 181° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 275° C. and a melting transition at 384° C. PETI-5 exhibits a  $T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 45,000 poise at ~370° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 23

Resin from Physical Mixture of Imide Powders of PERA-2 (20% By Weight) and PETI-5 (80% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.0 g) and PERA-2 imide powder (1.0 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 180° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 276° C. and a melting transition at 385° C. PETI-5 exhibits a  $T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 20,000 poise at ~371° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 24

Resin from Physical Mixture of Imide Powders of PERA-2 (50% By Weight) and PETI-5 (50% By Weight)

Into a plastic vial was placed PETI-5 imide powder (2.50 g) and PERA-2 imide powder (2.50 g). The two solids were

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physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 178° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 286° C. and no melting transition was detected. PETI-5 exhibits a  $T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 50 poise at ~370° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 25

Resin from Physical Mixture of Imide Powders of PERA-3 (10% By Weight) and PETI-5 (90% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.50 g) and PERA-3 imide powder (0.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 195° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 269° C. and a melting transition at 381° C. PETI-5 exhibits a  $T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 48,300 poise at ~371° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 26

Resin from Physical Mixture of Imide Powders of PERA-3 (20% By Weight) and PETI-5 (80% By Weight)

Into a plastic vial was placed PETI-5 imide powder (4.0 g) and PERA-3 imide powder (1.0 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 195° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, the material exhibited a  $T_g$  at 272° C. and a melting transition at 384° C. PETI-5 exhibits a  $T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 9990 poise at ~369° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 27

Resin from Physical Mixture of Imide Powders of PERA-3 (50% By Weight) and PETI-5 (50% By Weight)

Into a plastic vial was placed PETI-5 imide powder (2.50 g) and PERA-2 imide powder (2.50 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The material exhibited an initial thermal transition by DSC at 197° C. The material was cured for 1 hour at 350° C. in a sealed aluminum pan. Upon reheating, no  $T_g$  or melting transition was detected. PETI-5 exhibits a

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$T_g$  of 250° C. and a melting transition of 387° C. after curing for one hour at 350° C. in a sealed aluminum pan. The material exhibited a minimum complex melt viscosity of 625 poise at ~367° C. PETI-5 exhibited a minimum complex melt viscosity of 56,500 poise at ~371° C.

## EXAMPLE 28

Synthesis of a phenylethynyl terminated amide acid and imide co-oligomer with a calculated number average molecular weight of 1,000 g/mole using 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 0.5552 mole), 1,3-bis(3-aminophenoxyphenyl)benzene (1,3-APB, 0.52 mole), 9,9-bis(4-aminophenyl)fluorene (FDA, 0.33 mole), 3,5-diamino-4'-phenylethynyl benzophenone (DPEB, 0.15 mole) and 4-phenylethynylphthalic anhydride (PEPA, 0.8896 mole).

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer and nitrogen inlet/outlet was placed 1,3-APB (2.8263 g, 0.0097 mole), FDA (2.1379 g, 0.0061 mole), DPEB (0.8712 g, 0.0028 mole) and 10 mL N-methyl-2-pyrrolidinone (NMP). Once dissolved, a slurry of BPDA (3.0371 g, 0.0103 mole) and PEPA (4.1058 g, 0.0165 mole) in 9 mL of NMP was added and rinsed in with an additional 10 mL of NMP to afford a solids content of 30.2%. The mixture was stirred overnight under nitrogen (all solids had dissolved at this point). Toluene was then added (60 mL) and the reaction flask was fitted with a Dean Stark trap and reflux condenser. The mixture was heated via an oil bath to 185° C. and held overnight. The toluene was removed from the system via the Dean Stark trap (the reaction temperature eventually reached ~205° C. during the toluene removal) and the reaction solution was allowed to cool to room temperature. The solution was poured into water in a blender to precipitate the oligomer. The solid was isolated by filtration, washed in warm water (by placing in a large beaker and stirring) two times. The solid was allowed to air dry overnight and further dried in a forced air oven at ~130° C. for ~8 hours to give a quantitative yield of a tan powder. The powder exhibited an initial  $T_g$  of 162° C. and  $T_m$  of 21° C. and a  $T_g$  of 362° C. after curing for 1 hour at 371° C. The powder exhibited a complex melt viscosity of 185 poise at 250° C., this viscosity was stable at 250° C. for the duration of the experiment (1 hour). The powder exhibited a complex melt viscosity of 40 poise at 280° C., this viscosity was stable at 280° C. for the duration of the experiment (2 hours). A neat resin molding, approximately 1.5 inches in diameter and 25 mils thick, was fabricated by heating the powder in an aluminum pan to 371° C. for 1 hour in air. Based on a qualitative test of the molding, it was moderately tough.

## EXAMPLE 29

Resin from Physical Mixture of Imide Powders of PERA-1 (10% By Weight) and PTPEI Described Above (90% By Weight)

Into a plastic vial was placed PTPEI (305-91-087) imide powder (2.67 g) and PERA-1 imide powder (0.30 g). The two solids were physically mixed with a spatula for 10 minutes. The cap was placed on the vial and the vial shaken repeatedly to further mix the solids. The powder exhibited an initial  $T_g$  of 160° C. and  $T_m$  of 196° C. and a  $T_g$  of 340° C. after curing for 1 hour at 371° C. The powder exhibited a complex melt viscosity of 90 poise at 250° C., this viscosity was stable at 250° C. for the duration of the experiment (1 hour). The powder exhibited a complex melt

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viscosity of 35 poise at 280° C., this viscosity was stable at 280° C. for the duration of the experiment.

A carbon fiber laminate (10 inches by 24 inches, 36 plys thick, 44/44/12 layup) was fabricated from this material by a resin infusion process. The laminate was well-consolidated and contained low void content. Specimens were machined from the laminate and tested for open hole tension strength and open hole compression strength at temperatures ranging from room temperature to 600° F. The material exhibited excellent properties at both room temperature with good retention of strengths up to temperatures of 600° F.

While the invention has been described in terms of its preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

We claim:

1. A process for reducing melt flow and increasing ease of processability of a host phenylethynyl containing polymer, which comprises:

adding phenylethynyl reactive additives to said host phenylethynyl containing polymer, wherein the phenylethynyl reactive additives have a molecular weight less than approximately 1000 g/mol and are selected from the group consisting of amide acid phenylethynyl reactive additives and imide phenylethynyl reactive additives.

2. The process of claim 1, wherein the phenylethynyl containing host polymer is prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride, 3,4'-oxydianiline, 1,3-bis(3-aminophenoxy)benzene, and 4-phenylethynylphthalic anhydride.

3. The process of claim 1, wherein the phenylethynyl containing host polymer is prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride, 3,4'-oxydianiline, 3,5-diamino-4'-phenylethynylbenzophenone, and 4-phenylethynylphthalic anhydride.

4. The process of claim 1, wherein the phenylethynyl containing host polymer is prepared from 3,4,3',4'-biphenyltetracarboxylic dianhydride, 3,4'-oxydianiline, 3,5-diamino-4'-phenylethynylbenzophenone and phthalic anhydride.

5. The process of claim 1, wherein the phenylethynyl containing host polymer is prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride, 1,3-bis(3-aminophenoxyphenyl)benzene, 9,9-bis(4-aminophenyl)

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fluorene, 3,5-diamino-4'-phenylethynylbenzophenone and 4-phenylethynylphthalic anhydride.

6. A process for reducing melt flow and increasing ease of processability of a host phenylethynyl containing polymer, which comprises:

adding phenylethynyl reactive additives to said host phenylethynyl containing polymer, wherein the phenylethynyl reactive additive is prepared from 3,5-diamino-4'-phenylethynylbenzophenone, and equal molar amounts of phthalic anhydride and 4-phenylethynylphthalic anhydride.

7. A process for reducing melt flow and increasing ease of processability of a host phenylethynyl containing polymer, which comprises:

adding phenylethynyl reactive additives to said host phenylethynyl containing polymer, wherein the phenylethynyl reactive additive is prepared from 1 mole of 3,5-diamino-4'-phenylethynylbenzophenone, 1.5 moles of phthalic anhydride and 0.5 moles of 4-phenylethynylphthalic anhydride.

8. A process for reducing melt flow and increasing ease of processability of a host phenylethynyl containing polymer, which comprises:

adding phenylethynyl reactive additives to said host phenylethynyl containing polymer, wherein the phenylethynyl reactive additive is prepared from 1 mole of 3,5-diamino-4'-phenylethynylbenzophenone, 0.5 moles of phthalic anhydride and 1.5 moles of 4-phenylethynylphthalic anhydride.

9. The process of claim 1, wherein the phenylethynyl containing host polymer is a co-polymer.

10. The process of claim 1, wherein the phenylethynyl containing host polymer is an oligomer.

11. The process of claim 1, wherein the phenylethynyl containing host polymer is a co-oligomer.

12. The process of claim 1, wherein the phenylethynyl containing host polymer is in solution and the phenylethynyl reactive additive is in an amide acid solution.

13. The process of claim 1, wherein the phenylethynyl containing host polymer is in solution and the phenylethynyl reactive additive is in an imide solution.

14. The process of claim 1, wherein the phenylethynyl containing host polymer is a dry powder and the phenylethynyl reactive additive is a dry imide powder.

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