This invention relates to the composition and processes for preparing thermoset polyimides derived from an asymmetric benzophenone dianhydride, namely 2,3,3',4'-benzophenone dianhydride (a-BTDA) with at least one diamine, and a monofunctional terminal endcaps. The monofunctional terminating groups include 4-phenylethynylphthalic anhydride ester-acid derivatives, phenylethyl trimellitic anhydride (PETA) and its ester derivatives as well as 3-phenylethynylaniline. The process of polyimide composite comprises impregnating monomer reactants of dianhydride or its ester-acid derivatives, diamine and with monofunctional reactive endcaps into glass, carbon, quartz or synthetic fibers and fabrics, and then stack up into laminates and subsequently heated to between 150-375°C. either at atmosphere or under pressure to promote the curing and crosslinking of the reactive endcaps to form a network of thermoset polyimides.
POLYIMIDES DERIVED FROM NOVEL ASYMMETRIC BENZOPHENONE DIANHYDRIDES

RELATED U.S. APPLICATION


ORIGIN OF INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

This invention relates to the composition and the process for preparing polyimides derived from asymmetric dianhydrides namely; 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), 3,4'-methylenediphthalic anhydride (a-MDPA) and 3,4'-(hexafluorosoropropylene)diphthalic anhydride (a-6FDA).

The prior art (U.S. Pat. No. 3,940,426, UBE Industries) describes a coupling reaction of phthalic anhydride and o-xylene to produce polyimides with interesting and novel properties for aerospace and electronic applications.

More specifically, this invention relates to the composition and process for preparing polyimides derived from intermediately cyclodehydrated to form a mixture of 2,3,3',4'-benzophenone and 2,3,3',4'-benzophenone dianhydride. In addition, the benzophenone benzene dianhydride can be reduced by hydrazine hydrate to 3,4'-methylenediphthalic anhydride which is converted to the corresponding 3,4'-methylene dibenzylic anhydride. The unique feature of this invention is that it allows for the production of a series of asymmetrical dianhydrides, not only a-BPDA, but also a-BTDA, a-MDPA and a-6FDA.

This invention particularly relates to novel compositions and processes for the preparation of polyimides derived from asymmetric dianhydrides, namely, 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 3,4'-(hexafluorosoropropylene) diaphthalic anhydride (a-6FDA). The a-BTDA was prepared by Suzuki coupling with palladium catalysts from 3,4-dimethylphenylboronic acid or 2,3-dimethylphenylboronic acid and a mixed anhydride of 2,3-dimethylbenzoic acid or 3,4-dimethylbenzoic acid to form 2,3,3',4'-tetramethylbenzophenone, which was oxidized to form 2,3,3',4'-benzophenonetetracarboxylic acid followed by cyclodehydration to obtain a-BTDA. The a-6FDA tetracarboxylic acid was isolated from 2,3,3',4'-benzophenone dianhydride with trifluoromethyltrimethylenes to form 3,4'-(hexafluorosoropropylene)-bis(o-xylene). The 3,4'-(hexafluorosoropropylene)-bis(o-xylene) is oxidized to the corresponding tetracarboxylic acid followed by cyclodehydration to yield a-6FDA.
0088120 A1 (2003) discloses a process for producing pre-dominantly 2,3,3',4'-biphenyl dianhydride (a-BPDA) with a minor amount of 3,3',4,4'-biphenyldianhydride (s-BPDA) using palladium and copper catalyst with bidentate ligand. These prior art processes all yield mixtures of asymmetrical dianhydrides together with symmetrical dianhydrides, which then requires the separation of these isomers. In comparison, this invention discloses asymmetrical coupling of dimethylphenylboronic acid with o-xylene derivatives to provide asymmetrical dianhydrides without contamination by the symmetrical dianhydrides.

SUMMARY OF THE INVENTION

By employing a cross-coupling reaction (Suzuki coupling) with 3,4'-dimethyl or 2,3-dimethylphenylboronic acid and 3- or 4-substituted o-xylene in the presence of catalysts, this invention produces exclusively the asymetric precursor 2,3,3',4'-tetramethyl(biphenyl). Additionally, asymmetric 2,3,3',4'-tetramethylbenzophenone can be prepared as an intermediate precursor for a-BTDA from the coupling reaction of 3,4-dimethyl or 2,3-dimethylphenylboronic acid with o-xylene in the presence carbon monoxide gas and catalysts or alternatively with a mixed anhydride of 2,3-dimethylbenzoic acid or 3,4-dimethylbenzoic acid in the presence of catalysts to form 2,3,3,4'-tetramethylbenzophenone exclusively. These precursors are subsequently oxidized to produce asymmetric tetracarboxylic acids which are converted to the corresponding asymmetric dianhydrides.

These asymmetric dianhydrides are useful in preparing polyimides which comprise an important class of polymers because of their desirable characteristics i.e. low dielectric constant, high breakdown voltage, good wear resistance, radiation resistance, inertness to solvents, good adhesion properties, hydrolytic stability, low thermal expansion, long-term stability, and excellent mechanical properties. Specifically, high temperature polyimides, are extremely valuable particularly for aerospace applications.

A unique feature of this invention is the processes for preparing novel asymmetrical dianhydrides, namely, a-BTDA and a-6FDA, without the contamination of their symmetrical isomers (s-BTDA and s-6FDA). The a-BTDA and a-6FDA can be used to formulate or prepare polyimides with low-melt viscosities without the use of high-boiling point organic solvents such as N-methyl-pyrrolidine (NMP) whereas the conventional polyimides derived from s-BTDA and s-6FDA usually provide high viscosity products.

Accordingly, it is a primary object of this invention to produce polyimides derived from asymmetrical dianhydrides, namely: 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 3,4'-hexafluorosopropilidene) diphthalic anhydride (a-6FDA).

It is another object of this invention to provide a process for preparing polyimides derived from 2,3,3',4'-biphenylenetetracarboxylic acid and 3,4'-hexafluorosopropilidene) diphthalic acid and the corresponding asymmetrical anhydrides (a-BTDA and a-6FDA).

It is another object of this invention to provide novel processes for the preparation of polyimides derived from a-BTDA and a-6FDA, and the compositions derived from said processes.
In Scheme II, a similar Suzuki cross-coupling reaction is carried out between 3- or 4-boron-substituted o-xylene (1), boron-substituted phthalic derivative (1a) or boron-substituted phthalic diester (1b), and 4- or 3-halo-substituted phthalic anhydrides, phthalic ester or phthalimidines (2), or diesters of phthalic acid respectively, to produce the coupled asymmetrical 4-(2,3-dimethylphenyl)phthalic anhydride, phthalic ester or phthalimide (3). Compound (3) can be hydrolyzed e.g. by potassium hydroxide, followed by oxidation e.g. by KMnO₄, CrO₃ and other oxidizing methods such as low or high pressure nitric acid or with catalytic oxidation in air or oxygen to afford 2,3,3',4'-biphenyltetracarboxylic acid (5), which upon dehydration e.g. with acetic anhydride or thermal cyclodehydration to yield 2,3,3',4'-biphenyl dianhydride (a-BPDA). In the presence of carbon monoxide gas, 2,3,3',4'-benzophenonetetracarboxylic acid (9) is obtained through KMnO₄ oxidation of (2,3-dimethylphenyl)-α-methylphthalic anhydride (12) after hydrolysis or from the corresponding phthalimide (11) via the Suzuki coupling of an o-xylene derivative (1) with α-halomethylphthalic anhydride or α-halomethylphthalimidine (2) with palladium or nickel catalysts. 2,3,3',4'-benzophenonetetracarboxylic acid (9) can be reduced by hydrazine to 3,4'-methylene diphthalic acid. 

**Scheme II Synthesis of Asymmetric Dianhydrides from o-xylene Derivatives**
acid (13), which upon dehydration yields 3,4'-methylene diphthalic anhydride (14) (a-MDPA). In the cross-coupling reactions, X is selected from the group consisting of a halogen e.g. Cl, F, Br, I, or OSO₂CF₃ and OSO₂CH₃Y is either (OH)₂, or (OR)₂, Z is either oxygen or nitrogen. R is CH₂, --C==O or nil. R' is a lower alkyl such as C₃H₇, and B is boron.

The dianhydrides prepared by these processes are particularly useful in preparing polyimides from one or more of a combination of reactants comprising dianhydrides selected from the group consisting of 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), and 3,4'-methylene diphthalic anhydride (a-MDPA), with at least one multifunctional amine, such as diamines, and an endcap that can be melt-processed at temperatures between 232-270\degree C. (450-520\degree F.), without any solvent. The imide oligomers of this reaction have low-melt viscosities of 1-60 poise at 260-280\degree C. These imide oligomers are amenable to RTM, VARTM or resin infusion processes at 260-280\degree C., and then cured at 343-375\degree C. to produce high quality polymer matrix composites comprising carbon, glass, quartz or synthetic fibers for use at temperatures ranging up to about 288-343\degree C. (550-650\degree F.).
The preferred polyimides of this invention are derived from anhydrides specifically illustrated in Schemes III and IV, which provides novel processes for preparing asymmetrical 2,3,3',4'-benzophenone dianhydride (a-BTDA) and asymmetrical 3,4'-(hexafluoroisopropylidene)diphthalic anhydride (a-6FDA) without the complicated process of separating isomers. The 2,3,3',4'-benzophenone dianhydride (a-BTDA) is prepared by employing the cross-coupling of specific pair of dimethylphenylboronic acid with a mixed anhydride of dimethylbenzoic acid, generated in situ or prepared externally, to obtain the intermediate 2,3,3',4'-tetramethylbenzophenone (4). The mixed dianhydride can be prepared by reacting 3,4-dimethylbenzoic acid or 2,3-dimethylbenzoic acid with either a dialkyl dicarbonate, alkyl chloroformate, alkyl acid halides (acid chloride preferred) or alkyl dianhydrides where the alkyl groups includes primary, secondary and tertiary alkyl groups of C₁-C₆. The catalysts for the cross-coupling reaction includes, but is not limited to Pd(PPh₃)₄, Pd(PPh₃)₂Cl₂, Pd(PCy₃)₂, Pd(OAc)₂, PdCl₂ (CH₃CN), and Pd(dba)₂(p-t-Bu)_². The co-catalysts or co-ligands include but not limited to PPh₃, PCy₃, P(o-MeOC₆H₄), P(o-Tol)₃, and 1,1'-bis(diphenylphosphino)ferrocene (DPPF). Other additives used in the cross-coupling reaction can include water, NaI, NaF, Na₂CO₃, KI, KF, K₂CO₃, K₃PO₄ and N,N'-dicyclohexylcarbodiimide (DCC).
R = primary, secondary or tertiary lower alkyl groups C1-C6
(R' = R or OR)

1) CF₃Si(CH₃)₃
2) Hydrolysis

Oxidation

(a) CF₃CF₂O

CH₃CF₂OH

Oxidation

(a-BTDA)

CH₃CF₂O

HOOCCF₃

COOH

(a-6FDA)

HOOCCF₃

COOH

Ac₂O

HOOCCF₃

COOH

Ac₂O
The 2,3,3',4'-tetramethylbenzophenone is reacted with tris(2,3,3,4,4,5,5,6,6-nonfluorohexyl)posilane, and further converted to 3,4'-hexafluoroisopropylidene)bis-o-xylene (8). Alternatively, 3,4'-hexafluoroisopropylidene)bis-o-xylene (8) is also prepared from two different routes as shown in Scheme IV. A) Via the coupling of either 2-(3,4-dimethylphenyl)-hexafluoro-2-propanol (a) or 2-(2,3-dimethylphenyl)-hexafluoro-2-propanol (b) with respective trialkylsilane derivatives of o-xylene (c) and (d). B) By converting (a) and (b) to their corresponding halides (e) and (f) and then coupled with 3- or 4-substituted o-xylene.

The 2,3,3',4'-tetramethylbenzophenone (4) and 3,4'-hexafluoroisopropylidene)bis-o-xylene (8) are oxidized by potassium permanganate (KMnO₄), chromium trioxide (CrO₃), or by other oxidation methods, such as nitric acid oxidation, or catalytic oxidation in air or oxygen in the presence of catalysts to obtain the corresponding 2,3,3',4'-benzophenone tetracarboxylic acid (5) and 3,4'-hexafluoroisopropylidene)dipthalic acid (9), respectively. The tetracarboxylic acids (5) and (9) are subsequently reacted with either acetic anhydride or propionic dianhydride, or thermally cyclodehydrated to obtain the corresponding 2,3,3',4'-benzophenone dianhydride (a-BTDA) or 3,4'-hexafluoroisopropylidene)dipthalic anhydride (a-6FDA).

The preparation of asymmetrical BTDA and a-6FDA presents a successful and economical synthesis of asymmetrical 2,3,3',4'-benzophenone dianhydride (a-BTDA) that can be formulated into low-melt viscosity polyimide resins (10-30 poises) that are amenable to low-cost resin transfer molding (RTM) process. Since a-BTDA is an isomer of s-BTDA used in PMR-15, essentially, this invention will afford an RTMable PMR-15 without health hazards associated with PMR-15 composites manufacturing.

Additionally, the intermediate 2,3,3',4'-tetramethylbenzophenone also can be used to make asymmetrical 6F-dianhydride. This process can produce asymmetrical 6F-dianhydride (a-6FDA) to yield low viscosity 6F-polyimide resins adaptable to RTM process with potential 30% savings in manufacturing cost. Since this invention can produce novel a-BTDA and a-6FDA exclusively, it is essentially capable of producing a new class of thermoplastic and thermoset polyimides that have the potential of making colorless polyimides for optical and electronic applications.
The thermoplastic polyimides of this invention are prepared from dianhydrides or the ester-acid derivatives thereof selected from the group consisting essentially of:

(a) 
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{Z} \\
\text{O} \\
\text{N} \\
\text{A} \\
\text{O} \\
\text{O}
\end{array}
\]

and

(b) 
\[
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{O} \\
\text{Z} \\
\text{O} \\
\text{I} \\
\text{I} \\
\text{OR}
\end{array}
\]

with at least one multifunctional amine, e.g. diamines, in the equivalent stoichiometric ratio or an excess of either the dianhydride or the amine in solvents, such as N-methyl-2-pyrrolidinone (NMP) to form polyamic-acid intermediate, which are then cyclodehydrated at temperatures between 120-200° C. to thermoplastic polyimides having the formula:

or

wherein Z is (CF₃)₂C, C—O, R is a lower alkyl of 1-6 carbons, B is a dianhydride or its acid-ester derivative other than the dianhydrides (a) or (b) as shown in the above formulas, \((BA)_n\) is the product of B and A, n is equal to 1-100, m is equal to 0-100, and when m=0, it is a homopolymer, and when m is greater than 0, it is a copolymer.

In the above formulas, A is a diamine containing an organic divalent radical consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane, or aromatic groups linked through bridging atoms or groups. The preferred structure of A is selected from the group consisting essentially of

wherein \(R_1, R_2, R_3, R_4\) are selected from the group consisting of:

wherein \(R_i\) and \(R_j\) are alkyl groups, and \(R''\) is an alkyl, alkoxy, halogen, CF₃, phenyl or phenoxo radical.

The preferred multifunctional amines are the diamines including: meta-phenylenediamine, para-phenylenediamine, 2,2-bis(4-aminophenyl) hexafluoropropane, 2,2-bis(4-aminophenyl)propane, 4,4'-oxydianiline, 3,4'-oxydianiline, 4,4'-methylenediamine, 3,4'-methylenedianoline, 3,3'-diaminodianiline, 4,4'-diaminobenzophenone, 3,3'-diaminobenzophenone, 3,3'-diaminobenzophenone, 3,3'-diaminoazobenzene, 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 4,4'-diaminophenylsulfone, 3,4'-diaminophenylsulfone, 4,4'-(1,3-phenylene-bis[1-methyllethylene]), 3,3'-diaminobenzofuran, 4,4'-[1,4-phenylene-bis(1-methyllethylene)], 3,3'-diaminobenzofuran, 4,4'-bis(4-aminophenoxy)-biphenyl, 2,2-bis[4-(aminophenoxy)phenyl]propane, and mixtures thereof.

The polyimides terminated with reactive or non-reactive endcaps are prepared from at least one dianhydride and its acid-ester derivatives selected from the group consisting of:
and react with at least one multifunctional amine e.g. diamine, H₂N-A-NH₂, in an equivalent stoichiometric ratio or off-set stoichiometry, and with a reactive or non-reactive terminal endcap having a preferred but not limited to a formula selected from the group consisting of:

with solvents, such as N-methyl-2-pyrrolidinone or an alcohol such as methanol or ethanol, or without a solvent at high temperature in the melt, to form polyimide oligomers having the formula:
wherein Z is (CF₃)₂C or C==O, R is a lower alkyl of C₁-C₆ carbons, R* is alkyl, alkoxy, halogen, CF₃, substituted or unsubstituted phenyl or phenoxy radical. B is a dianhydride or its acid-ester derivative selected from either of the above formulas (a) or (b) together with one other dianhydride or its ester-acid derivative. (AB)n is the product of A and B, n is equal to 1-100, x is equal to 0 or 1.0 and y is equal to 0 or 1.0. However, when x is 0 then y is 1, and when x is 1 then y should be 0.

In the preferred formulas, A is a diamine containing an organic divalent radical consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane; or aromatic groups linked through bridging atoms or groups. The preferred structure of A includes the following:

20 (I) Synthesis of Asymmetric Compounds

In a preferred embodiment, a polyimide derived from the 2,3,3',4'-benzophenone dianhydride (a-BTDA) diester diacid has the following structure:

with an effect amount of at least one diamine (H₂N-A-NH₂), and a monofunctional terminal endcap in organic solvents to form polyimides having a formula selected from the group consisting of:
wherein A is an organic divalent radical of a diamine \([\text{H}_2\text{N}-\text{A-NH}_2]\), R is a low alkyl of 1-6 carbon, B is a second dianhydride or its ester-acid derivatives consisting of the following structure other than 2,3,3',4'-benzophenone dianhydride (a-BTDA):

where n is equal to 1-100, and m is equal to 1-100. The polyimides of claim 1 wherein the terminal monofunctional endcap is selected from the group consisting of:

where R is low alkyl of 1-7 carbon, and R" is an alkyl, alkoxy, halogen. The polyimides of claim 1 wherein a diamine \((\text{H}_2\text{N}-\text{A-NH}_2)\) containing an organic divalent radical A, is consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane, or aromatic groups linked through bridging atoms or groups. The preferred structure of divalent radical A is selected from the group consisting of:
Synthesis of 2,3,3',4'-benzophenonetetracarboxylic acid (5)

2,3,3',4'-tetrachlorobenzophenone (2.0 g, 8.4 mmol) and potassium permanganate (5.3 g, 33.6 mmol) were mixed in 25 ml of water and heated to reflux under nitrogen for 2 hours. The reaction mixture turned purple. The reaction mixture was cooled to room temperature and the brown MnO₂ precipitate was filtered and removed. The aqueous solution was evaporated to dryness to afford 2.5 g (90%) of the desired tetraacid.

Synthesis of 2,3,3',4'-benzophenone dianhydride (6)

2,3,3',4'-benzophenone tetracarboxylic acid (4) (3.7 g, 10 mmol) was suspended in the minimum amount of acetic anhydride (3 g, 2.7 ml) and heated to reflux for 4 hours. The reaction mixture was cooled to room temperature. The corresponding dianhydride precipitated out and was collected and washed with ether to remove traces of acetic acid before drying under vacuum to afford 2.9 g (90%) of a-BTDA.

(II) Synthesis of Thermoplastic Polyimides

EXAMPLE 2

A solution of 2,3,3',4'-benzophenone dianhydride (3.22 g, 10 mmol) and 2,2-bis(4-aminophenyl)hexafluoropropane (3.34 g, 10 mmol) in 31 g of dry N-methyl-2-pyrrolidinone (NMP) was stirred at room temperature under nitrogen overnight. Then the resulting polyamic acid solution was imidized by heating at 150 ⁰C. for 2 hours. The solution was cooled down and then precipitated into ethanol to afford fibrous polyimide.

EXAMPLE 3

A solution of 3,4'-((hexafluoropropylidene)diphthalic anhydride (4.44 g, 10 mmol) and p-phenylenediamine (1.08 g, 10 mmol) in 50 g of dry N-methyl-2-pyrrolidinone (NMP) was stirred at room temperature under nitrogen overnight. Then the resulting polyamic acid solution was imidized by heating at 150 ⁰C. for 2 hours. The solution was cooled down and then precipitated into ethanol to afford fibrous polyimide.

EXAMPLE 4

To a solution of 3,4'-((hexafluoropropylidene)diphthalic anhydride (4.44 g, 10 mmol) and 2,2'-bis(trifluoromethyl) benzidine (3.2 g, 10 mmol) in 43.3 g of m-cresol, 5 drops of isoquinoline was added. The reaction mixture was heated to reflux under nitrogen to afford a very viscous solution. The solution can be poured into ethanol solution to afford polyimide fibers or can be spun into high strength, high modulus polyimide fibers.

(III) Synthesis of Thermoset Polyimides

EXAMPLE 5

A solution of 2,3,3',4'-benzophenone dianhydride (12.88 g) and 4-phenylethynylphthalic anhydride (9.92 g) in 26.64 g of methanol was heated to reflux for 1 hour to convert them into the corresponding diester diacid, and then 3,4'-methyleneedianiline (11.76 g) in 10 g of methanol was added. The solution was concentrated to dryness in a hot plate and then staged at 150 ⁰C. for 1 hour to afford a polyimide powder.

EXAMPLE 1

Synthesis of 2,3,3',4'-tetrachlorobenzophenone (4)

To a 250 ml 3-necked round-bottom flask, 2,3-dimethylphenylboronic acid (3.6 g, 24 mmol), 3,4-dimethylbenzoic acid (3.0 g, 20 mmol), and a selected palladium catalyst (0.6 mmol), dimethyl dicarbonate (2.7 g, 30 mmol) and potassium carbonate (6.22 g, 45 mmol) were mixed with 150 ml of dry dioxane. The reaction mixture was heated at 80 ⁰C. overnight to become a viscous reaction mixture. 20 ml of water was added to dissolve the heterogeneous reaction mixture, and the reaction mixture was heated at 90 ⁰C. overnight. The reaction mixture turned brown, and the brown MnO₂ precipitate was filtered and removed. The aqueous solution was evaporated to dryness to afford 2.0 g (33%) of the product.
EXAMPLE 6

A solution of 2,3,3',4'-benzophenone dianhydride (22.17 g) and nacid anhydride anhydride (10.93 g) in 6.68 g of methanol was heated to reflux for 1 hour to make a 50% solution of the corresponding diester acid. After cooling the solution down to room temperature, 20.37 g of 4,4'-methylenedianiline in 20.37 of methanol was mixed with the diester diancid solution with stirring. The resulting 50% monomer solution as painted onto unidirectional carbon fibers or fabrics. The prepgs were allowed to be air-dried. The polyimide prepgs can be staged at 50% C. and then cured at 315° C. for 2 hours to form the polyimide carbon fiber composites.

EXAMPLE 7

A solution of 3,4'-(hexafluoroisopropylidene)dipthalic anhydride (17.99 g) and 4-phenylethynylphthalic anhydride (2.23 g) in 24.32 g of absolute ethanol was heated to reflux for 1 hour to form the corresponding diester diacid. Then p-phenylenediamine (4.86 g) in 4.86 g of ethanol was added at room temperature to form a 50% solution. The resulting 50% monomer solution as painted onto unidirectional carbon fibers or fabrics. The prepgs were allowed to be air-dried. The polyimide prepgs can be staged at 150° C. and then cured at 315° C. for 2 hours to form the polyimide carbon fiber composites.

EXAMPLE 8

A mixture of 3,4'-(hexafluoroisopropylidene)dipthalic anhydride (8.88 g), 4-phenylethynylphthalic anhydride (9.92 g) and 3,4'-oxydianiline (8.0 g) were mixed well and then the reaction mixture was heated in an oven at between 200-280° C. for 1 hour to melt all the monomers into forming a polyimide resin with low-melt viscosity (10-30 poise). The low-melt resins can be injected into carbon fiber perform by resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM) or resin infusion process to form light-weight carbon fiber composites.

An additional embodiment of the invention is provided by way of the following two examples.

EXAMPLE 9

2,3,3',4'-benzophenone dianhydride (23.7 g) and 4-phenylethynylphthalic anhydride (18.3 g) were mixed with methanol and heated to reflux to make a 50% solution containing the corresponding 2,3,3',4'-benzophenonetetracarboxylic diester diacid and 4-phenylethynylphthalic methyl ester acid. Then m-phenylenediamine (11.9 g) was added to the above solution at room temperature. The resultant monomer reactant solution was used to coat onto the surface of carbon or glass fibers or fabrics to make prepgs. The prepgs were stacked up to form laminates and placed in an autoclave or vacuum bags and heated 300-371° C. and under 100-200 psi pressure for 2 hours to remove alcohol and cure the laminates into composites with glass transition temperature (T_g) of 332° C., which upon postcure at 343° C. (650° F.) for 16 hr afforded a T_g of 371° C.

EXAMPLE 10

2,3,3',4'-benzophenone dianhydride (15.5 g) and 4-phenylethynylphthalic anhydride (6 g) were mixed with methanol and heated to reflux to make a 50% solution containing the corresponding 2,3,3',4'-benzophenonetetracarboxylic diester diacid and 4-phenylethynylphthalic methyl ester monoacid. Then m-phenylenediamine (3.2 g) and 3,4'-oxydianiline (6.0 g) were added to the above solution at room temperature. The resultant monomer reactant solution were used to coat onto the surface of carbon or glass fibers or fabrics to make prepgs. The prepgs were stacked up to form laminates and placed in an autoclave or vacuum bags and heated 300-371° C. and under 100-200 psi pressure for 2 hours to remove alcohol and cure the laminates into composites with glass transition temperature (T_g) of 332° C., which upon postcure at 343° C. (650° F.) for 16 hr afforded a T_g of 371° C.

While this invention has been described by a number of specific examples, it is obvious that there are other variations and modification that can be made without departing from the spirit and scope of the invention as set forth in the appended claims.

The invention claimed:

1. Polyimide derived from the 2,3,3',4'-benzophenone dianhydride (a-BTDA) diester diacid having the following structure:
wherein A is an organic divalent radical of a diamine \([H_2N-A-NH_2]\), R is a low alkyl of 1-6 carbon, B is a second dianhydride or its ester-acid derivatives consisting of the following structure other than 2,3,3',4'-benzophenone dianhydride (α-BTDA):

where n is equal to 1-100, and m is equal to 1-100.

2. The polyimides of claim 1 wherein the terminal monofunctional endcap is selected from the group consisting of:

where R is low alkyl of 1-7 carbon, and R" is an alkyl, alkoxy, halogen.

3. The polyimides of claim 1 wherein a diamine \([H_2N-A-NH_2]\) containing an organic divalent radical A, is consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane, or aromatic groups linked through bridging atoms or groups. The preferred structure of divalent radical A is selected from the group consisting of:
wherein R₁, R₂, R₃, R₄ are selected from the group consisting of:

\[
\begin{align*}
\text{CH}_2 - \text{(CH}_2\text{)}_n - \text{O} - \text{C} - \\
\text{CF}_3 - \text{CH}_3 - R_5 - R_5 \\
\text{C} - \text{C} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{O} - \\
\text{CF}_3 - \text{CH}_3 - R_6 - R_6 \\
\text{O} - \text{O} - \text{O} - \text{S} - \text{S} - \\
\text{O} \quad \text{or} \quad \text{(CF}_2\text{)}_n \\
\end{align*}
\]

wherein R₅ and R₆ are alkyl groups, and R₇ is an alkyl, alkoxy, halogen, CF₃, phenyl or phenoxy group.

4. The polyimides of claim 1 wherein either the diamine or the dianhydride is in excess of the stoichiometric ratio.

5. The polyimides of claim 1 wherein more than one diamine selected from the list in claim 3 are used to prepare co-polyimides.

6. The polyimide of claim 1 wherein the preferred lower alkyl alcohol solvents are consisting of methanol, ethanol, isopropyl alcohol and primary, secondary and tertiary butyl alcohol.

7. The polyimide claim 1 wherein the monofunctional terminating group is phenylethynyl trimellitic anhydride (PET?) and its corresponding acid ester derivatives.

8. The polyimide claim 1 wherein the monofunctional terminating group is 3-phenylethynylaniline.

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