This invention relates to the compositions and processes for preparing thermoset and thermoplastic polyimides derived from novel asymmetrical dianhydrides: specifically 2,3,3',4'-benzophenone dianhydride (a-BTDA), and 3,4'-(hexafluoroisopropylidene)diphthalic anhydride (a-6FDA). The a-BTDA anhydride is prepared by Suzuki coupling with catalysts from a mixed anhydride of 3,4-dimethylbenzoic acid or 2,3-dimethylbenzoic acid with 2,3-dimethylphenylboronic acid or 3,4-dimethylphenylboronic acid respectively, to form 2,3,3',4'-tetramethylbenzophenone which is oxidized to form 2,3,3',4'-benzophenonetetracarboxylic acid followed by cyclodehydration to obtain a-BTDA. The a-6FDA is prepared by nucleophilic trifluoromethylation of 2,3,3',4'-tetramethylbenzophenone with trifluoromethyltrimethylsilane to form 3,4'-(trifluoromethylmethanol)-bis(o-xylene) which is converted to 3,4'-(hexafluoroisopropylidene)-bis(o-xylene). The 3,4'-(hexafluoroisopropylidene)-bis(o-xylene) is oxidized to the corresponding tetraacid followed by cyclodehydration to yield a-6FDA.
POLYIMIDES DERIVED FROM NOVEL ASYMMETRIC DIAHYDRIDES

RELATED U.S. APPLICATION

This application is a continuation-in-part of application Ser. No. 11/378,553 filed Mar. 18, 2006 now U.S. Pat. No. 7,425,650 B1.

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 process for preparing polyimides derived from asymmetric dianhydrids namely: 2,3,3',4'-biphenyldianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), 3,4'-methylene-dipthalic anhydride (a-MDPA) and 3,4'-(hexafluoroisopropylidene)dipthalic anhydride (a-6FDA). These dianhydrides were prepared by cross-coupling dimethylphenylboronic acid and o-xylene derivatives via Suzuki coupling with various catalysts to form 2,3,3',4'-tetracarboxylic acid followed by cyclodehydration to yield a-6FDA. The a-6FDA tetracid was prepared by nucleophilic trifluoromethylation of 2,3,3',4'-tetracarboxylic acid or with trifluoromethyltrimethylsilane to form 3,4'-(trifluoromethyl)bis(o-xylene), which is converted to 3,4'-(hexafluoroisopropylidene)bis(o-xylene). The 3,4'-(hexafluoroisopropylidene)bis(o-xylene) is oxidized to the corresponding tetracarboxylic acid followed by cyclodehydration to yield a-6FDA. Thermoplastic and thermostet polyimides and co-polyimides derived from a-BTDA and a-6FDA can be made from a mixture of one or more of these dianhydrides (or the corresponding acid esters or isomide derivatives) and one or more diamine with or without a monofunctional reactive endcap (such as nadic or phenylethynyl groups) or non-reactive terminating endcap (e.g., phthalic anhydride or aniline) in stoichiometric or non-stoichiometric amounts in solvent or neat without a solvent.

BACKGROUND OF THE INVENTION

Currently, for example, asymmetrical a-BPDA is being prepared from o-xylene via an oxidative coupling reaction which essentially yields a mixture of 3,3',4,4'-biphenyl dianhydride (s-BPDA) and a minor product (2-6%) of a-BPDA. Consequently, a-BPDA is being produced in limited quantity and therefore is not commercially available in sufficient amounts, despite an enormous interest in preparing polyimides using a-BPDA. This disclosure provides alternative and more efficient processes for producing polyimides derived from asymmetrical 2,3,3',4'-biphenyl dianhydride (a-BPDA), 2,3,3',4'-benzophenone dianhydride (a-BTDA), 3,4'-methylene-dipthalic anhydride (a-MDPA) and 3,4'-(hexafluoroisopropylidene)dipthalic anhydride (a-6FDA).

The prior art (U.S. Pat. No. 3,940,426, UBE Industries) process for making a-BPDA relies on oxidative coupling of o-xylene or o-phthalate with an organic acid salt of palladium under oxygen pressure to produce a mixture of symmetrical and unsymmetrical intermediates which are oxidized and cyclodehydrated to form a mixture of s-BPDA and s-BPDA. This mixture requires the additional process of separating the two isomers.

U.S. Pat. No. 4,294,976 discloses a process for preparing a mixture of biphenyltetracarboxylic acids (3,3',4,4'-isomer, 2,3,3',4'-isomer and 2,2',3,3' isomer) via an oxidative coupling of either o-xylene or o-phthalate in the presence palladium catalyst by hydrolysis. The mixture of isomeric biphenyltetracarboxylic acids were then subjected to fractionally recrystallization to obtain the corresponding 2,3,3',4'-isomer (minor amount) and 3,3',4,4'-isomer (major amount) and minute amounts of 2,2',3,3'-biphenyldianhydrids.

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'-(hexafluoroisopropylidene)dipthalic 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 and 3,4-dimethylbenzoic acid to form 2,3,3',4'-tetracarboxylic acid which was oxidized to form 2,3,3',4'-benzenonemetacarboxylic acid followed by cyclodehydration to obtain a-BTDA. The a-6FDA tetracid was prepared by nucleophilic trifluoromethylolation of 2,3,3',4'-tetracarboxylic acid with trifluoromethyltrimethylsilane to form 3,4'-(trifluoromethyl)methanol, which is converted to 3,4'- (hexafluoroisopropylidene)bis(o-xylene). The 3,4'-(hexafluoroisopropylidene)bis(o-xylene) is oxidized to the corresponding tetracarboxylic acid followed by cyclodehydration to yield a-6FDA. Thermoplastic and thermostet polyimides and co-polyimides derived from a-BTDA and a-6FDA can be made from a mixture of one or more of these dianhydrides (or the corresponding acid esters or isomide derivatives) and one or more diamine with or without a monofunctional reactive endcap (such as nadic or phenylethynyl groups) or non-reactive terminating endcap (e.g., phthalic anhydride or aniline) in stoichiometric or non-stoichiometric amounts in solvent or neat without a solvent.

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'-(hexafluoroisopropylidene)dipthalic 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 and 3,4-dimethylbenzoic acid to form 2,3,3',4'-tetracarboxylic acid which was oxidized to form 2,3,3',4'-benzenonemetacarboxylic acid followed by cyclodehydration to obtain a-BTDA. The a-6FDA tetracid was prepared by nucleophilic trifluoromethylation of 2,3,3',4'-tetracarboxylic acid with trifluoromethyltrimethylsilane to form 3,4'-(trifluoromethyl)methanol, which is converted to 3,4'-(hexafluoroisopropylidene)bis(o-xylene). The 3,4'-(hexafluoroisopropylidene)bis(o-xylene) is oxidized to the corresponding tetracarboxylic acid followed by cyclodehydration to yield a-6FDA. Thermoplastic and thermostet polyimides and co-polyimides derived from a-BTDA and a-6FDA can be made from a mixture of one or more of these dianhydrides (or the corresponding acid esters or isomide derivatives) and one or more diamine with or without a monofunctional reactive endcap (such as nadic or phenylethynyl groups) or non-reactive terminating endcap (e.g., phthalic anhydride or aniline) in stoichiometric or non-stoichiometric amounts in solvent or neat without a solvent.
U.S. Pat. No. 4,958,002 discloses a dehydration process to obtain 3,3',4,4'-biphenyl dianhydride after the corresponding 3,3',4,4'-biphenyltetraacarboxylic acid was isolated from 2,3,3',4'-biphenyltetraacarboxylic acid. U.S. Pat. No. 5,288,530 (Mitsubishi) describes a coupling reaction of phthalic anhydride to form a mixture of 2,3,3',4'-major) and 2,3,3',4'- (minor) biphial dianhydrides. U.S. Patent Publication No. 008,120 A1 (2003) discloses a process for producing pre-dominately 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 dimethoxybenzilic 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-dimethylbenzilic acid and 3- or 4-substituted o-xylene in the presence of catalysts, this invention exclusively produces asymmetrical precursors; namely, 2,3,3',4'-tetramethylbiphenyl and 2,3,3',4'-tetramethylbenzilone. These precursors are subsequently oxidized to produce asymmetric tetracarboxylic acids which are converted to the corresponding 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, such as PMR-15, are extremely valuable particularly for aerospace applications. However, making components from these polymers via prepreg process is labor intensive and expensive. Resin Transfer Molding (RTM) is a more cost-effective alternative to making aerospace components and has been successfully deployed with lower temperature polymers such as the epoxies and bismaleimides (BMI).

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 provide polyimides derived from asymmetric dianhydrides, namely; 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 3,4'-hexafluoroisopropylidene) diphthalic anhydride (a-6FDA).

It is another object of this invention to provide a process for preparing polyimides derived from 2,3,3',4'-benzophenonetetraacarboxylic acid and 3,4'-hexafluoroisopropylidene diphthalic anhydride and the corresponding asymmetric 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.

It is another object of this invention to provide processes for preparing asymmetrical tetracarboxylic acids and the corresponding dianhydrides (a-BTDA and a-6FDA) useful in producing polyimides having lower-melt viscosities and high glass transition temperatures (T<sub>g</sub>).

It is a further object of this invention to provide processes for the preparation of polyimides derived from the synthesis of a-BTDA and a-6FDA obtained by cross-coupling dimethylphenilboronic acid with substituted o-xylens to produce asymmetric precursors which are further reacted to form the corresponding tetracarboxylic acids and subsequently converted to the corresponding asymmetric dianhydrides.

These and other objects will become more apparent from a further and more detailed description of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Polyimides are derived from dianhydrides illustrated in the reactions in Scheme I. The asymmetric dianhydrides are obtained by cross-coupling o-xylene derivatives (I) and (II), if (I) is a 3-horon substituted o-xylene, then (II) is a 4-substituted o-xylene, or if (I) is a 4-horon substituted o-xylene, then (II) is a 3-substituted o-xylene derivative. 2,3,3',4'-biphenyl dianhydride (a-BPDA) is prepared by cross-coupling (I) and (II), where X is selected from the group consisting of Cl, Br, SO<sub>2</sub>Cl, SO<sub>3</sub>CF<sub>3</sub>, OSO<sub>2</sub>CH<sub>3</sub>, and Y is (OH)<sub>2</sub>, or (OR)<sub>2</sub>, where R is a lower alkyl group such as CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or i-Pr, in order to form the asymmetrical 2,3,3',4'-tetramethylbiphenyl (III) in a common organic solvent, e.g. toluene, N,N-dimethylformamide (DMF), dimethoxyethane (DME), 1,4-dioxane, tetrahydrofuran (THF), anisole, or aqueous solution with or without phase transfer catalysts in the presence of palladium or nickel catalysts, either with or without co-catalysts or co-ligands, such as Pd(PPh<sub>3</sub>)<sub>2</sub>, Pd(OAc)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, Pd(dba)<sub>2</sub>[P(t-Bu)]<sub>2</sub>, Pd(dba)<sub>2</sub>[P(t-Bu)]<sub>2</sub>PHBF<sub>4</sub>, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>(dppe), NiCl<sub>2</sub>(dppb), and their corresponding polymer bound palladium or nickel catalysts.

Compound (III) is oxidized by potassium permanganate (KMnO<sub>4</sub>), chromium trioxide (CrO<sub>3</sub>), or by other oxidation methods such as low or high pressure nitric acid oxidation, catalytic oxidation, in air or in oxygen to form the 2,3,3',4'-biphenyltetraacarboxylic acid (IV), which upon dehydration e.g. by acetic anhydride or thermal dehydration, yields 2,3,3',4'-biphenyl dianhydride a-BPDA (V). Alternatively, compounds (I) and (II) are cross-coupled with carbon monoxide gas in the presence of the Pd or nickel catalysts to form the asymmetrical 2,3,3',4'-tetramethylbenzilone (VI), which is further oxidized e.g. by KMnO<sub>4</sub>, CrO<sub>3</sub>, nitric acid oxidation, or with other known catalytic oxidation methods in air or in oxygen to form 2,3,3',4'-benzononetetraacarboxylic acid (VII) which is then dehydrated by acetic anhydride or thermally cycled to yield 2,3,3',4'-benzononetetraacarboxylic acid a-BPDA (VIII). Alternatively, 2,3,3',4'-benzophenonetetraacarboxylic acid (VII) is reduced by hydrazine to form 3,4'-methylenediphthalic acid (IX), which upon dehydration e.g. by acetic anhydride yields 3,4'-methylenediphthalic anhydride (X) a-MPDA.
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 phthalimides (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, Cr₂O₃ 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'-biphenyl tetracarboxylic acid (5), which upon dehydration e.g. with acetic anhydride or thermal cyclodehydration to yield 2,3,3',4'-biphenyl dianhydride (α-BPDA). In the presence of carbon monoxide gas, 2,3,3',4'-benzophenone dianhydride (10), (α-BTDA) is produced by similar routes from compounds (1) and (2) via compounds (7), (8) and (9) as shown in this reaction.

Alternatively, 2,3,3',4'-benzophenonetetracarboxylic acid (9) is obtained through KMnO₄ oxidation of (2,3-dimethylphenyl)-α-methylphthalic acid (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-halomethylphthalimide (2) with palladium or nickel catalysts. 2,3,3',4'-benzophenone tetracarboxylic acid (9) can be reduced by hydrazine to 3,4'-methylene di-phthalic acid.
Scheme II Synthesis of Asymmetrical Dianhydride between o-Xylene Derivative and Phthalic Anhydride or Phthalimide Derivatives

\[ R' \text{ nil, CH}_3, \text{ C}_2\text{H}_5, \text{ Pr} \]

(Pd Catalyst)

\[ X = \text{Cl, Br, I, OSO}_2\text{CF}_3, \text{ OSO}_2\text{CH}_3 \]

Y = (OH)\(_2\), (OR')\(_2\)

Z is either oxygen or nitrogen.

R is CH\(_2\)- or nil.

R' is a lower alkyl such as C\(_1\), C\(_2\), 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'-biphenyldianhydride (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° C. (450-520° F.), without any solvent. The imide oligomers of this reaction have low-melt viscosities of 1-60 poise at 260-280° C. These imide oligomers are amenable to TRM, VARTM or resin infusion processes at 260-280° C. to product high quality polymer composites comprising carbon, glass, quartz or synthetic fibers for use at temperatures ranging up to about 550° to 650° 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'-hexafluorotrisopropylidene)diphthalic anhy-
dride (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 C<sub>r</sub>-C<sub>6</sub>. The catalysts for the cross-coupling reaction includes, but is not limited to Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Pd(PCy<sub>3</sub>)<sub>2</sub>, Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub> (CH<sub>3</sub>CN), and Pd(dba)<sub>2</sub>(t-Bu)<sub>2</sub>. The co-catalysts or co-ligands include but not limited to PPh<sub>3</sub>, PCy<sub>3</sub>, P(p-MeOC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, P(o-Tol)<sub>3</sub>, and 1,1'-bis(diphenylphosphino)ferrocene (DPPF). Other additives used in the cross-coupling reaction can include water, NaI, NaF, Na<sub>2</sub>CO<sub>3</sub>, KI, KF, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub> and N,N'-dicyclohexylcarbodiimide (DCC).

Scheme III Synthesis of a-BTDA and a-6FDA

Additives can be water, KI, KF, K<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, NaI, NaF, N,N'-dicyclohexylcarbodiimide (DCC)

Additives can be water, KI, KF, K<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, NaI, NaF, N,N'-dicyclohexylcarbodiimide (DCC)
Scheme IV Alternative Synthesis of a-6FDA

-continued

(a) H₂C

(b) H₂C

or

or

HX

X = halogen

Y = Li, MgX, ZnX, Al X₂, B(OH)₂, B(OR)₂, Ti, Sn

(c) CH₃

(d) R₃Si

(e) CH₃

(f) CH₃

(g) CH₃
The 2,3,3',4'-tetramethylbenzophenone is reacted with trifluoromethyltetramethylsilane \( \text{CF}_3\text{Si(CH}_3\text{)}_3 \) and further converted to 3,4'-hexafluoroisopropylidenebis-o-xylene (8). Alternatively, 3,4'-hexafluoroisopropylidenebis-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'-hexafluoroisopropylidenebis-o-xylene (8) are oxidized by potassium permanganate (KMnO\(_4\)) or by other oxidation methods, such as nitric acid oxidation, or by 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'-hexafluoroisopropylidenephthalic 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-phthalic 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 poise) that are amenable to low-cost resin transfer molding (RTM) process. Because 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's 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:

\[
\begin{align*}
\text{(a)} & \quad \text{O} & \quad \text{O} & \quad \text{Z} \\
\text{(b)} & \quad \text{RO} & \quad \text{OHO} & \quad \text{O} & \quad \text{Z} & \quad \text{Z} & \quad \text{OR} & \quad \text{O}
\end{align*}
\]

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:
herein Z is (CF₃)₂C—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 R₁, R₂, R₃, R₄ are selected from the group consisting essentially of

wherein R₅ and R₆ are alkyl groups of 1-6 carbons, and R'₅ is an alkyl, alkoxy, halogen, CF₃, phenyl or phenoxy 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, 3,3′-methylenediamine, 4,4′-diaminobenzophenone, 3,3′-diaminobenzophenone, benzidine, 2,2′-dimethylbenzidine, 2,2′-bis(trifluoromethyl) benzidine, 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 4,4′-diaminophenylsulfone, 3,4′-diaminosulfone, 4,4′-[1,3-phenylene-bis(1-methylethylidene)], 3,3′-diaminosulfone, 4,4′-[1,4-phenylene-bis(1-methylethylidene)], 3,3′-diaminobenzophenone, 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:

reacted 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:
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:

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 R₁, R₂, R₃, R₄ are selected from the group consisting of:

EXAMPLE 1

Synthesis of 2,3,3',4'-tetramethylbenzophenone (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), 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°C overnight to become a viscous reaction mixture. 20 ml of water was added to dissolve the heterogeneous reaction mixture, and dioxane was evaporated to dryness. The aqueous solution was extracted with 20 ml of ethyl acetate, dried over anhydrous magnesium sulfate and then evaporated to dryness. The crude
product was purified by silica gel column chromatography eluted by hexane/ethyl acetate 20:80 to afford 2.0 g (33%) of the product.

**Synthesis of 2,3,3',4'-benzophenonetetracarboxylic acid (5)**

2,3,3',4'-tetramethylbenzophenone (2.0 g, 8.4 mmol) and potassium permanganate (10.3 g, 33.6 mmol) were mixed in 25 ml of water in a 100 ml round-bottom flask and the reaction mixture turned purple. The reaction mixture was heated at 150°C. overnight. The reaction mixture was cooled down 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 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 anhydride (4.44 g, 10 mmol) in 31 g of dry N-methyl-2-pyrrolidinone (NMP) were stirred at room temperature under nitrogen overnight. The resulting polyamic acid precipitated out and was collected and washed with ether to remove trace of acetic acid before drying under vacuum to afford 2.9 g (90%) of a-BTDA.

**EXAMPLE 3**

A solution of 3,4'-oxydianiline (8.0 g) and 4-phenylethynylphthalic anhydride (9.92 g) in 26.64 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'-methyleneedianiline in 20.37 g of methanol was mixed with the diester diacid solution with stirring. The resulting 50% monomer solution as painted onto unidirectional carbon fibers or fabrics. The prepregs were allowed to be air-dried. The polyimide prepregs can be staged at 150°C. and then cured at 315°C. for 2 hours to form the polyimide carbon fiber composites.

**EXAMPLE 4**

A solution of 2,3,3',4'-benzophenonetetracarboxylic acid (4) (3.7 g, 10 mmol) was suspended in 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 trace of acetic acid before drying under vacuum to afford 1.75 g (90%) of 2,3,3',4'-benzophenone dianhydride (6).

**Synthesis of Thermoset Polyimide and Composites**

**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'-methyl-enedianiline (11.76 g) in 10 g of methanol was added. The solution was concentrated to dryness in a hot plate and then staged at 80°C. for 1 hour to afford a polyimide powder.

**EXAMPLE 6**

A solution of 2,3,3',4'-benzophenone dianhydride (22.17 g) and n-acid 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'-methyleneedianiline in 20.37 g of methanol was mixed with the diester diacid solution with stirring. The resulting 50% monomer solution as painted onto unidirectional carbon fibers or fabrics. The prepregs were allowed to be air-dried. The polyimide prepregs can be staged at 150°C. and then cured at 315°C. for 2 hours to form the polyimide carbon fiber composites.
and approximate stoichiometric amount of at least one multifunctional amine to form thermoplastic polyimides having a formula selected from the group consisting of:

R is a lower alkyl radical having 1 to 6 carbon, A is a divalent organic radical of a diamine (H₂N-A-NH₂), (BA)_m is the reaction product of dianhydride B or its ester acid derivative with a diamine (H₂N-A-NH₂), n has the value of 1-100, and m has the value of 1-100.

2. The polyimides of claim 1 wherein at least one of the multifunctional amines is a diamine wherein the diamine and dianhydride is in a stoichiometric ratio of 1 to 1.

3. The polyimides of claim 1 wherein at least one of the multifunctional amines is a diamine wherein the diamine or dianhydride is in excess of the stoichiometric ratio.

4. The polyimides of claim 2 wherein the diamine (H₂N-A-NH₂) contains an organic divalent radical A, consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane, or aromatic groups linked through bridging atoms or groups.

5. Polyimides of claim 4 wherein the structure of divalent radical A is selected from the group consisting of:
and endcap B'-\(AB'_n\)-A-endcap copolymer

wherein A is an organic divalent radical of a diamine [H\(_2\)N-A-NH\(_2\)]\(_3\), Z is C\((CF_3)_2\), R is a low alkyl of 1-6 carbon, \(B'_n\) is a dianhydride or the ester-acid derivatives selected from one of the group consisting of:

\[
\text{(a)}\quad R\text{O}O\quad O\quad O\quad OH
\]

and a second dianhydride \(B\) or its ester-acid derivatives other than (a) and (b) and consisting of:

\[
\text{(b)}\quad R\text{O}O\quad O\quad OR\quad OH
\]

(\(AB'_n\))\(_n\) is the reaction product of A and \(B'_n\), n is equal to 1-100, x is equal to zero or one, and y is equal to zero or one.

7. The polyimides of claim 5 wherein the terminal multifunctional endcap is selected from the group consisting of:

\[
\text{endcap}\quad A\quad \text{endcap,}
\]

with at least one multifunctional amine, and a terminal endcap to form polyimide having a formula selected from the group consisting of:

\[
\text{endcap}\quad A\quad \text{endcap,}
\]

\[
\text{endcap}\quad A\quad \text{endcap,}
\]
8. The polyimides of claim 6 wherein the diamine \( \text{H}_2\text{N-} \cdot \text{A-NH}_2 \) contains an organic divalent radical \( Z \), consisting of aliphatic, cycloaliphatic, heterocyclic, siloxane, or aromatic groups linked through bridging atoms or groups.

9. Polymides of claim 8 wherein the structure of divalent radical \( A \) is selected from the group consisting of:

where \( R \) is low alkyl of 1-6 carbon, and \( R'' \) is an alkyl, alkoxy, halogen.

10. The polyimide of claim 7 wherein at least one the multifunctional amines is a diamine, and either the diamine or dianhydride is in excess of the stoichiometric ratio.

11. The polyimides of claim 6 wherein the polymer is a copolymer having the formula:

wherein \( R_5 \) and \( R_6 \) are alkyl groups, and \( R'' \) is an alkyl, alkoxy, halogen, \( \text{CF}_3 \), phenyl or phenoxy group.

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