METHOD FOR THE PREPARATION OF BIS(HALOIMIDES)

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ABSTRACT

Bis(halophthalimides) are prepared in a solvent such as ortho-dichlorobenzene or anisole, by a reaction at a temperature of at least 150°C between at least one diamine compound and at least one halophthalic anhydride in the presence of imidization catalyst. The reaction produces a vapor stream comprising solvent and water formed as a by-product of the imidization reaction. A suitable vapor handling system comprising a partial reflux condenser is used to recycle the solvent, maintain the reactant concentration, conduct the reaction at a higher temperature, and effect more efficient conversion of reactants to product bis(halophthalimides). Reaction conditions disclosed may also be used to prepare organic polyimides.
METHOD FOR THE PREPARATION OF BIS(HALOIMIDES)

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation-In-Part of U.S. patent application Ser. No. 11/022,907, entitled "Method To Prepare Bis(Haloimides)", filed 22 Dec. 2004, which is herein incorporated by reference.

BACKGROUND

[0002] In one aspect, the present invention relates to an improved method for the preparation of bis(halophthalimides) monomers useful for the preparation of polyetherimides. In a second aspect, the present invention relates to an improved method for the preparation of polyimides, including polyetherimides.

[0003] Various types of polyether polymers, such as polyetherimides, polyetherketones, and polyetherketoneketones, have become important as engineering resins by reason of their excellent properties. These polymers are typically prepared by the reaction of dihydroxyaromatic compounds, such as bisphenol A disodium salt, with dihaloaromatic compounds. For example, polyetherimides are conveniently prepared by the reaction of salts of dihydroxyaromatic compounds with bis(halophthalimides).

[0004] U.S. Pat. Nos. 5,229,482 and 5,830,974, disclose the preparation of aromatic polyether polymers in relatively non-polar solvents, using a phase transfer catalyst which is substantially stable under the polymerization conditions. Solvents disclosed in U.S. Pat. No. 5,229,482 include o-dichlorobenzene, dichlorotoluenes, 1,2,4-trichlorobenzene and diphenyl sulphone. U.S. Pat. No. 5,830,974 discloses the use of solvents such as anisole, diphenylether, and phenetole. Solvents of the same type may be used for the preparation of bis(halophthalimide) intermediates for polyetherimides.

[0005] In each of U.S. Pat. Nos. 5,229,482 and 5,830,974 the bis(halophthalimide) is introduced into the polymerization reaction as a substantially pure, isolated compound. This process step is often difficult, since solid bis(halophthalimides) are typically of very low density and fluffy, making weighing and handling burdensome. By contrast, U.S. Pat. No. 6,235,866 discloses the preparation of a slurry comprising a bis(halophthalimide). The slurry comprising the bis(halophthalimide) is prepared by reacting roughly equimolar quantities of a diamine and a halophthalic anhydride in a solvent to produce the product bis(halophthalimide) and water as a by-product. The slurry comprising the bis(halophthalimide) must be rigorously dried prior to reaction with, for example, bisphenol A disodium salt, to form a product polyetherimide. Producing a dry slurry of the bis(halophthalimide) in a solvent, for example a slurry of bis(4-chlorophthalimide) in oDCB containing less than about 10 ppm water, presents significant challenges. The reaction between the diamine and the halophthalimide is typically dried by distilling a large volume of solvent from the reaction mixture which entrains the by-product water out of the reaction mixture. This method of water removal, although effective as a means of drying the reaction mixture, is inefficient since a relatively large volume of solvent must be distilled from the reaction mixture in order to remove a relatively small amount of water. Reactions wherein by-product water is removed by distillation are characterized by long reaction times, high reaction temperatures, and the use of large volumes of solvent. Under such circumstances, the product bis(halophthalimide) is subject to an increased likelihood of degradation, and the overall process is rendered inefficient as a result of the time and expense required to distill large volumes of solvent. Further, if the diamine has a significant vapor pressure at the imidization reaction temperature (such as m-phenylene diamine), then some of the diamine may be distilled along with the solvent and water byproduct, thus upsetting the reaction stoichiometry and requiring wastewater cleanup. Thus, there is a need in the art to develop a facile process for the preparation of bis(halophthalimides) having suitable characteristics for conversion to polyetherimide polymers without isolation that overcomes the shortcomings of current synthetic methods.

BRIEF DESCRIPTION

[0006] In one aspect, the invention provides a method for preparing a bis(halophthalimide), said method comprising steps (a)-(d):

[0007] (a) contacting in a substantially water-immiscible solvent at least one halophthalic anhydride with at least one diamine to form a reaction mixture;

[0008] (b) heating the reaction mixture to form a product mixture comprising solvent and product bis(halophthalimide), and a vapor stream comprising a substantially water-immiscible solvent and water;

[0009] (c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and

[0010] (d) separating the vapor stream to provide a water-rich component and a water immiscible solvent-rich component.

[0011] In yet another aspect, the invention provides a method for preparing an organic polyimide, said method comprising steps (a)-(d):

[0012] (a) contacting in a substantially water-immiscible solvent a mixture comprising at least one dihydride and at least one diamine to form a reaction mixture;

[0013] (b) heating the reaction mixture to form a product mixture comprising the substantially water-immiscible solvent and a product organic polyimide, and a vapor stream comprising the substantially water-immiscible solvent and water;

[0014] (c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and

[0015] (d) separating the vapor stream to provide a water-rich component and a solvent-rich component.

DETAILED DESCRIPTION

[0016] The present invention may be understood more readily by reference to the following detailed description of preferred embodiments of the invention and the examples included therein. In addition, the disclosure which follows is supplemented by U.S. Pat. Nos. 5,229,482, 5,830,974; and 6,235,866 which are hereby incorporated by reference in their entirety, except that to the extent that terms defined within the incorporated references conflict with terms
defined in the present invention that the definition found in the present invention with control.

[0017] In the following specification and the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

[0018] The singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise.

[0019] “Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

[0020] The modifier “about” used in connection with a quantity is of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity).

[0021] As used herein, the term “aromatic radical” refers to an array of atoms having a valence of at least one comprising at least one aromatic group. The array of atoms having a valence of at least one comprising at least one aromatic group may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. As used herein, the term “aromatic radical” includes but is not limited to phenyl, pyridyl, furanyl, thiophenyl, naphthyl, phenylene, and biphenyl radicals. As noted, the aromatic radical contains at least one aromatic group. The aromatic group is invariably a cyclic structure having 4n+2 “delocalized” electrons where “n” is an integer equal to 1 or greater as illustrated by phenyl groups (n=1), thiophenyl groups (n=1), furanyl groups (n=1), naphthyl groups (n=2), azulenyl groups (n=2), anthracene groups (n=3) and the like. The aromatic radical may also include nonaromatic components. For example, a benzyl group is an aromatic radical which comprises a phenyl ring (the aromatic group) and a methylene group (the nonaromatic component). Similarly a tetrahydroanthrathiphyl radical is an aromatic radical comprising an aromatic group (C6H4) fused to a nonaromatic component —(CH2)n—. For convenience, the term “aromatic radical” is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, haloaromatic groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylphenyl radical is a C6 aromatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrophenyl group is a C6 aromatic radical comprising a nitro group, the nitro group being a functional group. Aromatic radicals include halogenated aromatic radicals such as 4-trifluoromethylphenyl, hexafluorosorpolonidene(4-phen-1-yloxy) (i.e., —OPh(CF3)2PhO—), 4-chloromethylphen-1-yl, 3-trifluoromethyl-2-thienyl, 3-trichloromethylphen-1-yl (i.e., 3-C6H4Ph), 4-(3-chloroprop-1-yl)phen-1-yl (i.e., 4-BrC6H4CH2CH2Ph), and the like. Further examples of aromatic radicals include 4-allyloxyphen-1-oxo, 4-amino-phen-1-yl (i.e., 4-PhNH2), 3-aminobenzyloxyphen-1-yl (i.e., NH2COPh), 4-benzoyloxyphen-1-yl, dichloromethylidene(4-phen-1-yloxy) (i.e., —OPh(CF3)2PhO—), 3-methylphen-1-yl, methylenedichlorophen-1-yl (i.e., —OPh(CF3)2PhO—), 2-ethylphen-1-yl, phenylethylphenyl, 3-formyl-2-thienyl, 2-hexyl-5-furanly, hexamethylene-1,6-bis(4-phen-1-yloxy) (i.e., —OPh(CH2)nPhO—), 4-hydroxymethylphen-1-yl (i.e., 4-HOCH2Ph), 4-mercaptopethylen-1-yl (i.e., 4-HSCH2Ph), 4-mercaptothiophen-1-yl (i.e., 4-CH2SPh), 3-methoxyphen-1-yl, 2-methoxycarbonylphen-1-yl (e.g., methyl salicyl), 2-nitromethylphen-1-yl (i.e., 2-NO2C6H4Ph), 3-trimethylsilylphen-1-yl, 4-butyldimethylsilicylphen-1-yl, 4-vinylphen-1-yl, vinylidenes(phenyl), and the like. The term “a C6 aromatic radical” includes aromatic radicals containing at least three but no more than 10 carbon atoms. The aromatic radical 1-imidazolyl (C5H4N—)— represents a C5 aromatic radical. The benzyl radical (C6H5—) represents a C6 aromatic radical. As used herein the term “cycloalkyl radical” refers to a radical having a valence of at least one, and comprising an array of atoms which is cyclic but which is not aromatic. As defined herein a “cycloalkyl radical” does not contain an aromatic group. A “cycloalkyl radical” may comprise one or more noncyclic components. For example, a cyclohexydmethyl group (C6H11CH2—) is an cycloalkyl radical which comprises a cyclohexyl ring (the array of atoms which is cyclic but which is not aromatic) and a methylene group (the noncyclic component). The cycloalkyl radical may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. For convenience, the term “cycloalkyl radical” is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, haloaromatic groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylcyclopropyl-1-yl radical is a C4 cycloalkyl radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrocyclobut-1-yl radical is a C4 cycloalkyl radical comprising a nitro group, the nitro group being a functional group. A cycloalkyl radical may comprise one or more halogen atoms which may be the same or different. Halogen atoms include, for example; fluorine, chlorine, bromine, and iodine. Cycloalkyllic radicals comprising one or more halogen atoms include 2-trifluoromethylcyclohex-1-yl, 4-bromodifluoromethylcyclooct-1-yl, 2-chlorodifluoromethylcyclohex-1-yl, hexafluoroisopropylidene-2,2-bis(cyclohex-4-yl) (i.e., C6H4(CF3)2C6H12—), 2-chloromethyldicyclohex-1-yl, 3-difluoromethylencyclocyclohex-1-yl, 4-trichloromethyldicyclohex-1-yl, 4-bromodichloromethyldicyclohex-1-ylthio, 2-bromocyclohex-1-yl, 2-bromomethylene, 1-oxo (e.g., CH3CHBrCH2CH3, C6H5—O—), and the like. Further examples of cycloalkyllic radicals include 4-allyloxyethylene-1-yl, 4-aminocyclohex-1-yl (i.e., C6H4N—), 4-cyanocarboxyl-1-yl (i.e., HCN—), 4-carboxyethylenyl (i.e., CH2CH2C=O), and the like. Further examples of cycloalkyllic radicals include 4-allyloxyethylene-1-yl, 4-aminocyclohex-1-yl, 4-cyanocarboxyl-1-yl (i.e., HCN—), 4-carboxyethylenyl (i.e., CH2CH2C=O), and the like.
4-CH₃SC₆H₄O⁻), 4-methoxycyclohex-1-yl, 2-methoxycarbonylcyclohex-1-yloxy (2-CH₂OCOC₆H₄O⁻), 4-nitromethylcyclohex-1-y (i.e., NO₂CH₂C₆H₄O⁻), 3-trimethylsilylcyclohex-1-y, 2-t-butyl(dimethyl)silylcyclooct-1-yl, 4-trimethoxysilylcyclohex-1-y (e.g., (CH₃O)₃SiCH₂C₆H₄O⁻), 4-vinylcyclohexen-1-yl, vinylidenebis(cyclohexyl), and the like. The term “a C₅-C₁₀ aliphatic radical” includes cycloalkylidene radicals containing at least three but no more than 10 carbon atoms. The cycloalkylidene radical 2-tetrahydrofuranyl (C₅H₄O⁻) represents a C₅ cycloalkylidene radical. The cyclohexylmethyl radical (C₆H₁₁CH₂⁻) represents a C₆ cycloalkylidene radical.

[0023] As used herein the term “aliphatic radical” refers to an organic radical having a valence of at least one consisting of a linear or branched array of atoms which is not cyclic. Aliphatic radicals are defined to comprise at least one carbon atom. The array of atoms comprising the aliphatic radical may include heteroatoms such as nitrogen, sulfur, silicon, selenium and oxygen or may be composed exclusively of carbon and hydrogen. For convenience, the term “aliphatic radical” is defined herein to encompass, as part of the “linear or branched array of atoms which is not cyclic,” a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example, carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylpent-1-yl radical is a C₅ aliphatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 4-nitrobut-1-yl group is a C₅ aliphatic radical comprising a nitro group, the nitro group being a functional group. An aliphatic radical may be a haloalkyl group which comprises one or more halogen atoms which may be the same or different. Halogen atoms include, for example, fluorine, chlorine, bromine, and iodine. Aliphatic radicals comprising one or more halogen atoms include the alkyl halides trifluoromethyl, bromodifluoromethyl, chlorodifluoromethyl, hexafluoroisopropylidene, chloromethyl, difluorovinylidene, trifluoromethyl, bromodichloromethyl, bromoethyl, 2-bromotrimethylene (e.g., —CH₂CHBrCH₂—), and the like. Further examples of aliphatic radicals include alkyl, aminocarboxyl (i.e., —CONH₂), carbonyl, 2,2-dicyanoisopropylidene (i.e., —CH₂C(CN)₂CH₂—), methyl (i.e., —CH₃), methylene (i.e., —CH₂—), ethyl, ethylene, formyl (i.e., —CHO), hexyl, hexamethylene, hydroxymethyl (i.e., —CH₂OH), mercaptoethyl (i.e., —CH₂SH), methylthio (i.e., —SCH₃), methylthiomethyl (i.e., —CH₂SCH₃), methoxy, methoxyethylcarbonyl (i.e., CH₂OCONH₂), nitromethyl (i.e., —CH₂NO₂), thiocarboxyl, trimethylsilyl (i.e., (CH₃)₃Si—), t-butyldimethylsilyl, 3-trimethoxysilylpropyl (i.e., (CH₃O)₃SiCH₂CH₂CH₂—), vinyl, vinylidene, and the like. By way of further example, a C₅-C₁₀ aliphatic radical contains at least one but no more than 10 carbon atoms. A methyl group (i.e., CH₃—) is an example of a C₁ aliphatic radical. A decyl group (i.e., CH₃(CH₂)₉—) is an example of a C₁₀ aliphatic radical.

[0024] As noted, in one aspect the present invention relates to the efficient preparation of bis(halophthalimides) compositions. Thus, in one embodiment the present invention relates to a method for the preparation of bis(halophthalimides) having structure I

\[
\begin{align*}
X' & \quad (R')_a \\
X'' & \quad (R')_b
\end{align*}
\]

wherein X₁ is independently in each instance, a fluorine, chlorine, bromine or iodine group; R₁ is a hydrogen, C₁-C₁₀ aliphatic radical, a C₂-C₂₀ aromatic radical, or a C₂-C₂₀ cycloalkylidene radical; Q is a C₂-C₂₀ divalent aliphatic radical, a C₂-C₄₀ divalent aromatic radical, or a C₂-C₄₀ divalent cycloalkylidene radical; “a” is independently at each occurrence an integer in a range from 1 to 4; and “b” is independently at each occurrence an integer from 0 to 3.

[0025] Bis(halophthalimides) having structure I are illustrated by 1,3-bis[N-(4-chlorophthalimido)benzene (hereinafter sometimes “CIPAMIT”). It should be noted that bis(halophthalimides) prepared from a mixture of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride are also at times referred to as “CIPAMIT”.

[0026] Bis(halophthalimides) of the invention are typically prepared by the amidation reaction between a halophthalic anhydride and a diamine. There is no particular limitation on the diamine component. Any diamine compound may be employed and used according to the method of this invention. Typically, the diamine compound comprises at least one compound having structure II:

\[
H₂N-Q-NH₂
\]

wherein Q is a C₂-C₂₀ divalent aliphatic radical, a C₂-C₄₀ divalent aromatic radical, or a C₂-C₄₀ divalent cycloalkylidene radical. Suitable aliphatic diamine compounds represented by structure II (Q is a C₂-C₂₀ divalent aliphatic radical) include ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, and 1,10-diaminodecane. Suitable aromatic diamine compounds represented by structure II (Q is a C₂-C₄₀ divalent aromatic radical) include 1,4-diaminonaphthalene, 2,6-diaminonaphthalene, 4,4'-diaminobiphenyl, 2,4-diaminotoluene, 2,6-diaminotoluene, 2-methyl-4,6-diethyl-1,3-phenylenediamine, 5-methyl-4,6-diethyl-1,3-phenylenediamine, 1,3-diamino-4-isopropylbenzene, and the like. Suitable cycloalkylidene diamine compounds represented by structure II (Q is a C₂-C₂₀ divalent cycloalkylidene radical) include trans-1,2-diaminocyclopetane, trans-1,4-(bis aminoethyl)cyclohexane, and the like.

[0027] In one embodiment, the diamine compound is selected from the group consisting of 4,4'-oxydianiline (ODA, CAS No. 110-80-4), bis(4-aminophenyl)sulfone, meta-phenylenediamine, and para-phenylenediamine and mixtures thereof. In an alternate embodiment, the diamine compound is selected from the group consisting of 4,4'-oxydianiline (ODA, CAS No. 110-80-4) and bis(4-aminophenyl)sulfone. In yet another embodiment, the diamine compound is 4,4'-oxydianiline. In yet still another embodiment, the diamine compound is bis(4-aminophenyl)sulfone.
In one embodiment of the invention, the diamine compound is selected from the group represented by structures III and IV:

![Chemical structures](image)

wherein R and R are independently at each occurrence a halogen atom, a nitro group, a cyano group, a C₂₋₅ₐliphatic radical, a C₅₋₆ aliphatic radical, or a C₃₋₅ aromatic radical; and “n” and “m” are independently integers ranging from 0 to 4. Examples of suitable diamines having structure III or structure IV are metaphenylenediamine, para-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, 2-methyl-4,6-diethyl-1,3-phenylenediamine, 5-methyl-4,6-diethyl-1,3-phenylenediamine, 1,3-diamino-4-isopropylbenzene, 1,4-diamino-3-isopropylbenzene, and mixtures thereof.

In another embodiment, the solvent has a boiling point of at least 150°C. The prevailing reaction conditions include the temperature and pressure at which the amidation reaction is carried out. In one embodiment, the amidation reaction is carried out under superatmospheric pressure (i.e., the pressure is greater than 1 atmosphere). In another embodiment, the solvent is a water-immiscible solvent.

In yet another embodiment, the solvent is capable of forming azeotropic mixtures with water. Ortho-dichlorobenzene (oDCB) is frequently the solvent of choice for the reaction.

With respect to the amounts of halophthalic anhydride and diamine employed, it is in certain embodiments preferable to have an excess of the halophthalic anhydride in the reaction mixture. Typically, 2.01 to 3.0 molar equivalents of the halophthalic anhydride with respect to the diamine compounds are employed. In one embodiment, 2.01 to 2.5 molar equivalents of the halophthalic anhydride with respect to the diamine compound are employed.

In some embodiments an amidation catalyst may be added to the reaction mixture. Suitable amidation catalysts are known in the art. They include salts of organophosphorus acids, particularly phosphinates such as sodium phenylphosphinate (SPhP) and heterocyclic amines such as 4-dimethylaminopyridine (DMAP). Organic and inorganic acids may also be used to catalyze this reaction. Suitable organic acids include chlorophthalic acid, phthalic acid, and acetic acid. Sodium phenylphosphinate is a preferred catalyst in certain embodiments. The catalyst, when added, may be added before the diamine compound has been added, after the diamine compound has been added, or together with the diamine compound.

Typically, Step (b) of the method of the present invention comprises heating the reaction mixture to a temperature of at least 100°C, optionally in the presence of an amidation catalyst. Typically the reaction mixture is heated to a temperature of at least 150°C, in one embodiment in a range from about 150°C to about 250°C, and in another embodiment in a range from about 175°C to about 230°C. It should be noted that the reaction mixture may be heated at atmospheric pressure, subatmospheric pressure, or superatmospheric pressure. When superatmospheric pressures are employed, the pressure is typically up to about 5 atmospheres, to facilitate the conversion of starting materials to product bis(halophthalimide).

In one embodiment the contacting of the at least one halophthalic anhydride with at least one diamine in a solvent may be conducted for a period of time sufficient to obtain the desired degree of conversion to the bis(halophthalimide). In various embodiments the contact time depends upon a number of factors including, but not limited to, the amounts of the at least one halophthalic anhydride and the at least one diamine employed. In a particular embodiment the contact time is greater than about 1 hour. In one embodiment the contact time is for about 1.5 hours to about 30 hours. Appropriate contact times depend upon reaction temperatures and the nature of the reactants, and this may be determined by one skilled in the art, without undue experimentation.

In the various embodiments of the present invention, the reaction mixture formed by contacting in a substantially water-immiscible solvent at least one halophthalic anhydride with at least one diamine is heated to form a product mixture and a vapor stream. The reaction mixture is typically heated in a reaction vessel equipped with a vapor handling system comprising a partial reflux condenser.
ing the reaction mixture affords a product mixture comprising the substantially water-immiscible solvent and at least one product bis(halophthalimide), and a vapor stream comprising the substantially water-immiscible solvent and water. Water is produced as a by-product in the condensation reaction of the diamine with the haloephthalic anhydride. Known methods for the preparation of bis(halophthalimides) typically remove the water formed as a by-product in the amidization reaction by azeotropic distillation. As noted, this method of water removal is inefficient since most solvent-water azeotropes contain substantial amounts of solvent. Typically, a relatively large volume of solvent must be distilled in order to remove a relatively small volume of water. The Table below illustrates the behavior and composition of some common water-solvent azeotropes. It should be noted that even with an azeotrope such as the water-dOCB azeotrope which comprises substantially more water than solvent (62.7% water, 37.3% dOCB) a large volume of solvent must be distilled from the reaction mixture in order to produce a slurry of the bis(halophthalimide) comprising less than about 10 ppm water. By “large volume of solvent” it is meant that between 5 and 15 units of dO CB solvent must be distilled from the reaction mixture for every unit of water removed in order to produce a slurry comprising less than about 10 ppm water.

<table>
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<tr>
<th>Component A</th>
<th>Component B</th>
<th>Boiling Point A, °CN</th>
<th>Boiling Point B, °CN</th>
<th>Water Wt. % H₂O</th>
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<td>180</td>
<td>99</td>
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</tbody>
</table>

It has been discovered that more efficient removal of water from the reaction mixture may be achieved by the use of a partial reflux condenser as a component of a suitable vapor handling system. The vapor stream produced as the reaction mixture is heated is introduced into the vapor handling system. The partial reflux condenser is typically maintained at a temperature below the boiling point of the solvent under the prevailing conditions and above the boiling point of water under the prevailing conditions, which results in the separation of the vapor stream to provide a water-rich component (as vapor) and a solvent-rich component (as liquid reflux). The solvent-rich component may be condensed in the vapor handling system and returned to the reaction vessel. In instances in which the partial reflux condenser communicates directly with the reaction vessel, as in for instance Example 1 of this disclosure, such that vapor condensing in the partial reflux condenser is returned directly to the reaction vessel, the solvent rich component is said to be “refluxed back into the reaction vessel”. Typically the temperature of the partial reflux condenser ranges from about 100°C to about 150°C under atmospheric pressure which is a temperature high enough for water vapor to pass through without condensing and low enough for the solvent to condense within the partial reflux condenser. The water-rich component of the vapor stream, which emerges from the partial reflux condenser may be condensed in a secondary condenser. The water and any accompanying solvent may be separated, for example in a decanter, if desired. The solvent accompanying the water-rich component may optionally be returned to the reaction vessel. In an amidization reaction, the amount of water in the water-rich component is limited to the water of reaction. Therefore the amount of solvent in this stream is often quite small. In one embodiment the water-rich component emerging from the partial reflux condenser comprises both water and the solvent, the solvent comprising less than about 50 percent by weight of the water-rich component emerging from the partial reflux condenser. In one embodiment the water-rich component comprises between about 5 and about 98 percent by weight water. In yet another embodiment the water-rich component comprises between about 25 and about 98 percent by weight water. Typically, the vapor stream introduced into the vapor handling system comprises between about 5 ppm and about 40 percent by weight water. In one embodiment the vapor stream comprises between about 15 and about 35 percent by weight water. In another embodiment, for example in the preparation of I,3-bis[N-(4-chlorophthalimidom)]benzene, the vapor stream comprises between about 5 ppm and about 5 percent by weight water.

The use of a partial reflux condenser provides several advantages during the amidization reaction. The reaction may be conducted at higher temperature, such as a temperature close to the boiling point of the solvent employed for the reaction. A partial reflux condenser allows for the condensation of the solvent back to the reaction medium while any other low boiling components of the vapor stream are evaporated out of the reaction flask. This is in direct contrast to a vapor handling system that utilizes a short path condenser wherein the solvent boils out of the reaction flask and is condensed into a collector that is separate from the reaction vessel. Thus, in a vapor handling system involving the use of short path condenser, it is often difficult to maintain sufficient solvent in the reaction flask as the reaction temperature approaches the boiling point of the solvent. As a consequence, amidization reactions run with a vapor handling system comprising a short path condenser need to be conducted at temperatures well below the solvent boiling point. In the preparation of organic polyimides a major drawback of conducting reactions at lower temperatures is that the viscosity of the reaction mixture is at times
very high such that efficient mixing is not achieved. Thus, the use of a partial reflux condenser for imidization reactions enables the use of higher temperatures, efficient utilization of solvent, faster reaction times, efficient removal of volatile by-products, and higher efficiency of conversion of reactants to products.

EXAMPLES 1-2

General Procedure with Partial Reflux Condenser

A 450 mL Parr autoclave equipped with a sight window, a temperature control system, a pressure gage, a dual 4-blade impeller, an inlet for a nitrogen purge, and a partial reflux condenser, which was cooled with a recirculating oil bath. The partial reflux condenser was an open 1/2" outer diameter (o.d.) stainless steel tube 12" long, jacketed with a 1/2" o.d. stainless steel tube, through which oil from the recirculating oil bath flowed. This recirculating oil bath was held at 102° C. while the Parr reactor was operated at ambient pressure, and at 135-140° C. while the Parr reactor was held at 26.5 psig. The vapor stream leaving the partial reflux condenser passed through a secondary condenser, which was cooled with chilled water at 10° C. The condensate from the partial reflux condenser flowed by gravity back into the Parr autoclave. The system pressure was maintained by a back-pressure regulator, which vented to the atmosphere. Condensate from the secondary condenser was collected in a Jerguson® sight glass, which could be observed and drained as needed. The Parr autoclave was charged with 21.8657 grams (g) of 3-chlorophthalic anhydride, 14.898 g of diaminodiphenyl sulfoxide (DDS) (2.006 mole 3-CIPA per mole DDS, i.e. 0.3 mole % excess of 3-CIPA vs. DDS), 100.0 milliliters (ml.) ortho-dichlorobenzene (oDCB), 0.2219 grams of phthalic anhydride, and 42.2 milligrams (mg) sodium phenylphosphinite (SPP) catalyst, under an inert nitrogen atmosphere, and then the vessel was heated to 180° C. under ambient pressure. The Parr autoclave was sight glass. This glass was periodically drained (while maintaining a liquid seal). After a prespecified duration, the reactor was cooled to ambient temperature, and sampled. The conversion of amine groups to imide groups was measured by HPLC. No DDS was detected in any samples.

COMPARATIVE EXAMPLE 1

General Procedure with Short-Path Condenser

The Parr autoclave described above was fitted with a water-cooled short-path condenser (in place of the partial reflux condenser) and the reaction was conducted as noted above. The short-path condenser comprised a 3/8" o.d. stainless steel tube 12" in length, which was jacketed with a 1/2" stainless steel tube. The jacket was cooled with a recirculating water bath, which was held at 10° C. The condensate from this condenser was not returned to the Parr autoclave. The condensate was collected in a sight glass (under pressure). This sight glass was periodically drained (while maintaining a liquid seal) and dry oDCB was pumped into the reactor in order to maintain the reactor level. The condenser was vented through a backpressure regulator to the atmosphere.

Table 1 summarizes the results of these experiments. In example 2A, the reaction was conducted and then the reactor was cooled and sampled. The reactor was then reassembled. The reaction was resumed and conducted at 230° C. to form example 2B. The formulation was the same for all reactions. Examples 1 and 2 operated under a vigorous reflux. With comparative example 1, it was difficult to maintain the reactor level because of the rapid distillation of oDCB.

Examples 1-2 results show that the partial condenser permits operation at 230° C. without distilling a significant amount of oDCB. Further, the reaction rate is not decreased by the use of a partial condenser.

<table>
<thead>
<tr>
<th>Example</th>
<th>Condenser</th>
<th>H N2</th>
<th>hours</th>
<th>ml. oDCB</th>
<th>ml. oDCB</th>
<th>ml. oDCB</th>
<th>% amine conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>Partial Reflux</td>
<td>22</td>
<td>3.7</td>
<td>2.15</td>
<td>0</td>
<td>90.66</td>
<td></td>
</tr>
<tr>
<td>Example 2A</td>
<td>Partial Reflux</td>
<td>60</td>
<td>4.4</td>
<td>0.2</td>
<td>0</td>
<td>90.74</td>
<td></td>
</tr>
<tr>
<td>Example 2B</td>
<td>Partial Reflux</td>
<td>60</td>
<td>7.9</td>
<td>15</td>
<td>0</td>
<td>90.84</td>
<td></td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>Short Path</td>
<td>30</td>
<td>7.0</td>
<td>290</td>
<td>290</td>
<td>99.81</td>
<td></td>
</tr>
</tbody>
</table>

1 Standard cubic centimeters per minute
2 Added during reaction
3 Determined by HPLC

TABLE 1

<table>
<thead>
<tr>
<th>Example</th>
<th>Condenser</th>
<th>H N2</th>
<th>hours</th>
<th>ml. oDCB</th>
<th>ml. oDCB</th>
<th>% amine conversion</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>15</td>
<td>0</td>
<td>90.84</td>
</tr>
<tr>
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<td>290</td>
<td>290</td>
<td>99.81</td>
</tr>
</tbody>
</table>

3 Standard cubic centimeters per minute
4 Added during reaction
5 Determined by HPLC

EXAMPLE 3A

meta-Phenylenediamine (mPD) Imidization

meta-Phenylenediamine (mPD) imidizations were conducted in an electrically heated 3-Liter glass round-bottom flask equipped with a Teflon paddle impeller operating at 400 rpm. The bottom of the Teflon paddle was about 12.7 millimeters above the bottom of the vessel. The reactor was fitted with either a glass short-path condenser (cooled with 10° C. coolant) or with a glass partial reflux condenser cooled with 105° C. oil. The reactor was purged with 30 sec nitrogen for the duration of each reaction. When the
vapor handling system comprised a partial reflux condenser, the vapor stream leaving the partial reflux condenser was condensed in a secondary condenser, which was cooled with 10° C. cooling water, and the condensate from the partial reflux condenser was returned to the reactor vessel by gravity. The secondary condenser was vented to the atmosphere via a bubbler that contained mineral oil. When the reactor was fitted with a short-path condenser, the condensate was not returned to the vessel, but was collected in a round-bottom flask, which was vented to the atmosphere through a bubbler that contained mineral oil. The reactor was insulated, but provision was made to observe the agitation, particularly the top surface. The reaction flask was charged with 230.38 grams 4-CIPA, oDCB, and 260 milligrams SPP catalyst. A total of 68.35 grams of molten mPD was added over a period of 90 minutes under agitation. The reaction was operated under refluxing oDCB for 4.8 hours and the conversion of amine to imide was 99.76%. The condensate from the secondary condenser was clear and did not darken on exposure to air over a period of 24 hours, which was cooled with a 10° C. circulating water bath. The condensate was collected in a flask, which was vented through a mineral oil bubbler to the atmosphere. The reactor was preheated to 165° C. under a nitrogen purge and agitation. A total of 68.35 grams of molten mPD was added over a period of 90 minutes, while the reactor was maintained at 165° C. After only 30 mL mPD was added (46% of total mPD), the top of the reactor showed no fluid motion, and had the consistency of a thick paste. It was observed that because of the shear thinning behavior of the material, the impeller simply cut a path through the reaction mixture, leaving the bulk of the mixture stagnant. This behavior persisted throughout the remainder of mPD addition. This reaction was considered to be a failure. In an effort to improve the mixing, the temperature was increased to 180° C. However, even after 4 hours at 180° C., the reaction mass was still largely stagnant. The condensate turned black over a period of less than 1 hour on exposure to air, which indicated that the condensate contained mPD.

![Image]

**TABLE 2**

<table>
<thead>
<tr>
<th>Example</th>
<th>Condenser Type</th>
<th>Temp, °C</th>
<th>mL oDCB</th>
<th>wt % Solids</th>
<th>hrs at Temperature</th>
<th>mL oDCB distilled</th>
<th>% Monoamine Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example 2</td>
<td>short-path</td>
<td>165</td>
<td>1200</td>
<td>15</td>
<td>—</td>
<td>65</td>
<td>—^</td>
</tr>
<tr>
<td>Example 3A</td>
<td>partial (reflux)</td>
<td>181</td>
<td>1200</td>
<td>15</td>
<td>4.8</td>
<td>11</td>
<td>99.76</td>
</tr>
<tr>
<td>Example 3B</td>
<td>partial (reflux)</td>
<td>180</td>
<td>1200</td>
<td>15</td>
<td>20.5</td>
<td>11</td>
<td>99.78</td>
</tr>
<tr>
<td>Example 4</td>
<td>partial (reflux)</td>
<td>181</td>
<td>1110</td>
<td>20</td>
<td>8.9</td>
<td>17</td>
<td>100</td>
</tr>
</tbody>
</table>

^reagent surface completely stagnant after 30 mL mPD addition—no motion at surface

indicating that the condensate was free of mPD. The reaction proceeded smoothly, with no significant thickening of the reaction mass. The top surface of the reaction showed no signs of stagnation.

**EXAMPLE 3B**

[0043] The reaction of Example 3A was continued for an additional 16 hours at a temperature of 180° C. (just below reflux), and then sampled again after a total 20.5 hours. The mixing was steady and smooth for the entire reaction, with no evidence of any stagnation at the top surface or along the vessel walls. The amine conversion was 99.78% after a total of 20.5 hours of operation. As with example 3A, the condensate from the secondary condenser was clear and did not darken over a period of 24 hours, indicating the absence of mPD in the condensate.

**EXAMPLE 4**

[0044] Example 3A was repeated a higher solids loading (20 wt %). No mixing issues were observed. The reaction showed no stagnation at the top surface or along the vessel walls. The amine conversion was 100% after 8.9 hours under refluxing conditions. The condensate from the secondary condenser was clear and did not darken over a period of 24 hours, indicating the absence of mPD in the product.

**COMPARATIVE EXAMPLE 2**

[0045] The reactor of example 3 was fitted with a glass short path condenser in place of the partial reflux condenser, [0046] Comparative Example 2 shows that the mPD imidization has a tendency to agglomerate and thicken at 165° C., but shows good mixing at 180-181° C. when the mPD was added to the reaction mixture at the reflux temperature. In addition, the imidization reaction mixture was subject to shear thinning (Comparative Example 2), which introduced severe limitations on mixing (the relatively high shear rate in the vicinity of the impeller caused the impeller to slide through the mixture without effective mixing). It is hypothesized that amic acid intermediates may cause the reaction mixture to thicken. Since the amic acids are reactive intermediates, it is believed that the amic acid concentration is lower at 180-181° C. than at 165° C. In addition, the partial reflux condenser enabled operating at the oDCB boiling point with negligible oDCB distillation. It is also noted that the reaction went to completion in a reasonable time with the partial reflux condenser configuration. Example 4 showed that mPD imidization may also be conducted at 20 wt % solids at 181° C. without any problems associated with stirring of the reaction mixture.

[0047] Further, mPD is somewhat volatile. It was observed that when the mPD imidization was conducted with a short-path condenser configuration, the aqueous phase of the distillate became black within 1 hour, which means that mPD was distilled along with the water and oDCB. This is not desirable, because any mPD that distills alters the CIPA/mPD stoichiometry. Further, the mPD-containing distillate must be treated prior to being recycled or disposed of. In contrast, both phases of the distillate were
clear and did not show any sign of darkening for 24 hours after the reaction was complete for all mPD imidizations run with a partial reflux condenser.

[0048] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

1. A method for preparing a bis(halophthalimide), said method comprising steps (a)-(d):
   (a) contacting in a substantially water-immiscible solvent at least one halophthalic anhydride with at least one diamine to form a reaction mixture;
   (b) heating the reaction mixture to form a product mixture comprising the substantially water-immiscible solvent and a product bis(halophthalimide), and a vapor stream comprising the substantially water immiscible solvent and water;
   (c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and
   (d) separating the vapor stream to provide a water-rich component and a solvent-rich component.

2. The method of claim 1 wherein said bis(halophthalimide) has structure I

   ![Structure I](image)

wherein \( X \) is independently in each instance, a fluorine, chlorine, bromine or iodine group; \( R^1 \) is a hydrogen, \( C_1-C_{20} \) aliphatic radical, a \( C_2-C_{20} \) aromatic radical, or a \( C_2-C_{20} \) cycloaliphatic radical; \( Q \) is a \( C_2-C_{20} \) divalent aliphatic radical, a \( C_2-C_{20} \) divalent aromatic radical, or a \( C_2-C_{20} \) divalent cycloaliphatic radical; “a” is independently at each occurrence an integer in a range from 1 to 4; and “b” is independently at each occurrence an integer from 0 to 3.

3. The method of claim 1 wherein said halophthalic anhydride is 4-chlorophthalic anhydride, 3-chlorophthalic anhydride, 4-fluorophthalic anhydride, 3-fluorophthalic anhydride, 4,5-dichlorophthalic anhydride, 3,6-dichlorophthalic anhydride, or a mixture comprising at least two of the foregoing.

4. The method of claim 1 wherein the at least one diamine has structure II

   ![Structure II](image)

wherein \( Q \) is a \( C_2-C_{20} \) divalent aliphatic radical, a \( C_2-C_{40} \) divalent aromatic radical, or a \( C_2-C_{20} \) divalent cycloaliphatic radical.

5. The method of claim 1 wherein the at least one diamine is selected from the group consisting of 4,4'-oxydianiline, and bis(4-aminophenyl)sulfone.

6. The method of claim 1 wherein said diamine is selected from the group consisting of aromatic diamines III and diamines IV

   ![Structures III and IV](image)

wherein \( R^2 \) and \( R^3 \) are independently at each occurrence a halogen atom, a nitro group, a cyano group, a \( C_1-C_{20} \) aliphatic radical, a \( C_2-C_{40} \) aromatic radical, or a \( C_4-C_{20} \) cycloaliphatic radical; and “m” and “n” are independently integers in a range from 0 to 4.

7. The method of claim 6 wherein the aromatic diamine is selected from the group consisting of meta-phenylene diamine and para-phenylene diamine.

8. The method of claim 1 wherein the solvent has a boiling point at atmospheric pressure of at least 110°C.

9. The method of claim 1 wherein the solvent is selected from the group consisting of chlorobenzene, ortho-dichlorobenzene, anisole, toluene, ortho-xylene, meta-xylene, para-xylene, mesitylene, phenetole, veratrole, and mixtures of the foregoing solvents.

10. The method of claim 1 wherein step (b) comprises heating the reaction mixture to at least about 150°C.

11. The method of claim 1 wherein the reaction mixture further comprises an imidization catalyst.

12. The method of claim 11 wherein the imidization catalyst comprises sodium phenylphosphinate.

13. The method of claim 1 wherein the halophthalic anhydride, and the diamine when taken together are present in an amount corresponding to an initial solids content of the reaction mixture in a range from about 5% to about 25% by weight.

14. The method of claim 1 wherein said contacting is carried out in a reaction vessel, wherein the solvent-rich component is refluxed back into the reaction vessel.

15. A method for preparing a bis(chlorophthalimide), said method comprising steps (a)-(d):
   (a) contacting in a substantially water-immiscible solvent a mixture comprising at least one chlorophthalic anhydride and at least one diamine to form a reaction mixture;
   (b) heating the reaction mixture to form a product mixture comprising said solvent and at least one product bis(chlorophthalimide), and a vapor stream comprising the substantially water-immiscible solvent and water;
   (c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and
   (d) separating the vapor stream to provide a water-rich component and a solvent-rich component.

16. The method of claim 15 wherein the solvent-rich component is refluxed back into the reactor.
17. A method for preparing a bis(chlorophthalimide), said method comprising steps (a)-(d):

(a) contacting in a solvent comprising ortho-dichlorobenzene a mixture comprising at least one chlorophthalic anhydride, meta-phenylene diamine, and para-phenylene diamine to form a reaction mixture;

(b) heating the reaction mixture to form a product mixture comprising said solvent and product bis(chlorophthalimide) and a vapor stream comprising ortho-dichlorobenzene and water;

(c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and

(d) separating the vapor stream to provide a water-rich component and an ortho-dichlorobenzene-rich component.

18. The method of claim 17 wherein the solvent-rich component is refluxed back into the reactor.

19. A method for preparing an organic polyimide, said method comprising steps (a)-(d):

(a) contacting in a substantially water-immiscible solvent a mixture comprising at least one dianhydride and at least one diamine to form a reaction mixture;

(b) heating the reaction mixture to form a product mixture comprising the substantially water-immiscible solvent and a product organic polyimide, and a vapor stream comprising the substantially water-immiscible solvent and water;

(c) introducing the vapor stream into a vapor handling system comprising a partial reflux condenser; and

(d) separating the vapor stream to provide a water-rich component and a solvent-rich component.

20. The method of claim 19 wherein the solvent comprises ortho-dichlorobenzene.

21. The method of claim 19 wherein the mixture further comprises an imidization catalyst.

22. The method of claim 21 wherein the imidization catalyst comprises sodium phenyl phosphinate.