

METHOD TO PREPARE BIS(HALOIMIDES)

BACKGROUND OF THE INVENTION

This invention relates to an improved method for the preparation of bis(halophthalimides), monomers useful for the preparation of polyetherimides.

Various types of polyethers, such as polyetherimides, polyethersulfones, polyetherketones, and polyetheretherketones, 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).

U.S. Pat. Nos. 5,229,482 and 5,830,974, disclose the preparation of aromatic polyethers 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, dichlorotoluene, 1,2,4-trichlorobenzene and diphenyl sulfone. 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.

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. U.S. Pat. No. 6,235,866 teaches a method of slurry preparation of bis(halophthalimides) by the reaction between diamine compounds and halophthalic anhydride, in equimolar proportions and use of that slurry as such to prepare polyether polymers. But in the disclosed process, considerable caking of the product bis(halophthalimides) occurs, rendering the product difficult to isolate as a pure slurry, resulting in unacceptable levels of residual starting material in the polymer. Also, the presence of water in the resulting product has a deleterious effect on the molecular

weight of the polymer. If proper stoichiometric balance between the diamine and the halophthalic anhydride is not maintained, several undesirable by-products remain in the slurry which limit the molecular weight of the polymer, and/or result in polymers with amine end groups. 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 which overcomes the shortcomings of current synthetic methods.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a method for preparing a bis(halophthalimide), said method comprising:

- (A) preparing a mixture comprising at least one halophthalic anhydride and at least one solvent,
- (B) adding to the mixture formed in step (A) at least one diamine, to form a reaction mixture, said reaction mixture being characterized by “an initial molar ratio of halophthalic anhydride to diamine”;
- (C) heating the reaction mixture formed in step (B) to a temperature of at least 100°C, optionally in the presence of an imidization catalyst;
- (D) analyzing the reaction mixture formed by the combination of steps (A)-(C) to determine the initial molar ratio of halophthalic anhydride to diamine; and
- (E) performing one step selected from the group consisting of:
 - (i) adding anhydride or diamine to the mixture formed by the combination of steps (A)-(C) to achieve a “corrected molar ratio” of halophthalic anhydride to diamine, said corrected molar ratio being in a range between about 2.01 and about 2.3, and heating to a temperature of at least 100°C to obtain a bis(halophthalimide) product mixture that is substantially free of water; and
 - (ii) heating to a temperature of at least 100°C the reaction mixture formed by the combination of steps (A)-(C) to obtain a bis(halophthalimide) product mixture that is substantially free of water.

DETAILED DESCRIPTION OF THE INVENTION

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 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:

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

“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.

As used herein the term “integer” means a whole number which includes zero. For example, the expression “n is an integer from 0 to 4” means “n” may be any whole number from 0 to 4 including 0 and 4. Similarly, the expression “an integer ranging from 1 to 4 inclusive” means an integer in a range from 1 to 4, said range including the integer 1 and the integer 4.

As used herein the term “aliphatic radical” refers to a radical having a valence of at least one comprising a linear or branched array of atoms which is not cyclic. The array may include heteroatoms such as nitrogen, sulfur, silicon, selenium and oxygen or may be composed exclusively of carbon and hydrogen. Aliphatic radicals may be “substituted” or “unsubstituted”. A substituted aliphatic radical is defined as an aliphatic radical which comprises at least one substituent. A substituted aliphatic radical may comprise as many substituents as there are positions available on the aliphatic radical for substitution. Substituents which may be present on an aliphatic radical include but are not limited to halogen atoms such as fluorine, chlorine, bromine, and iodine. Substituted aliphatic radicals include trifluoromethyl, hexafluoroisopropylidene, chloromethyl; difluorovinylidene; trichloromethyl, bromoethyl, bromotrimethylene (e.g. $-\text{CH}_2\text{CHBrCH}_2-$), and the like. For convenience, the term “unsubstituted aliphatic radical” is defined herein to encompass, as part of

the “linear or branched array of atoms which is not cyclic” comprising the unsubstituted aliphatic radical, a wide range of functional groups. Examples of unsubstituted aliphatic radicals include allyl, carbonyl, dicyanoisopropylidene (i.e. $-\text{CH}_2\text{C}(\text{CN})_2\text{CH}_2-$), methyl (i.e. $-\text{CH}_3$), methylene (i.e. $-\text{CH}_2-$), ethyl, ethylene, formyl, hexyl, hexamethylene, hydroxymethyl (i.e. $-\text{CH}_2\text{OH}$), mercaptomethyl (i.e. $-\text{CH}_2\text{SH}$), methylthio (i.e. $-\text{SCH}_3$), methylthiomethyl (i.e. $-\text{CH}_2\text{SCH}_3$), methoxy, methoxycarbonyl (CH_3OCO), nitromethyl (i.e. $-\text{CH}_2\text{NO}_2$), thiocarbonyl, trimethylsilyl, t-butyl dimethylsilyl, trimethoxysilylpropyl, vinyl, vinylidene, and the like. Aliphatic radicals are defined to comprise at least one carbon atom. A $\text{C}_1 - \text{C}_{10}$ aliphatic radical includes substituted aliphatic radicals and unsubstituted aliphatic radicals containing at least one but no more than 10 carbon atoms.

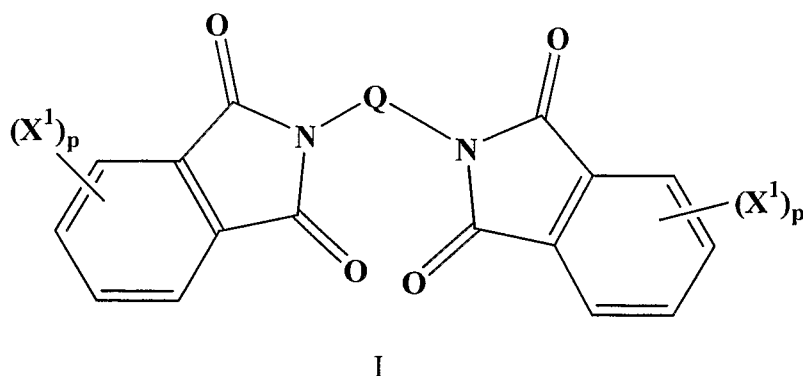
As used herein, the term “aromatic radical” refers to an array of atoms having a valence of at least one comprising at least one aromatic group. The array of atoms having a valence of at least one comprising at least one aromatic group may include heteroatoms such as nitrogen, sulfur, selenium, silicon 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, thienyl, 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 ($n = 1$), thienyl groups ($n = 1$), furanyl groups ($n = 1$), naphthyl groups ($n = 2$), azulenyl groups ($n = 2$), anthracenyl 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 tetrahydronaphthyl radical is an aromatic radical comprising an aromatic group (C_6H_3) fused to a nonaromatic component $-(\text{CH}_2)_4-$. Aromatic radicals may be “substituted” or “unsubstituted”. A substituted aromatic radical is defined as an aromatic radical which comprises at least one substituent. A substituted aromatic radical may comprise as many substituents as there are positions available on the aromatic radical for substitution. Substituents which may be present on an aromatic radical include, but are not limited to halogen

atoms such as fluorine, chlorine, bromine, and iodine. Substituted aromatic radicals include trifluoromethylphenyl, hexafluoroisopropylidenebis(4-phenyloxy) (i.e. $-\text{OPhC}(\text{CF}_3)_2\text{PhO}-$), chloromethylphenyl; 3-trifluorovinyl-2-thienyl; 3-trichloromethylphenyl (i.e. 3- $\text{CCl}_3\text{Ph}-$), bromopropylphenyl (i.e. $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Ph}-$), and the like. For convenience, the term “unsubstituted aromatic radical” is defined herein to encompass, as part of the “array of atoms having a valence of at least one comprising at least one aromatic group”, a wide range of functional groups. Examples of unsubstituted aromatic radicals include 4-allyloxyphenoxy, 4-benzoylphenyl, dicyanoisopropylidenebis(4-phenyloxy) (i.e. $-\text{OPhC}(\text{CN})_2\text{PhO}-$), 3-methylphenyl, methylenebis(4-phenyloxy) (i.e. $-\text{OPhCH}_2\text{PhO}-$), ethylphenyl, phenylethenyl, 3-formyl-2-thienyl, 2-hexyl-5-furanyl; hexamethylene-1,6-bis(4-phenyloxy) (i.e. $-\text{OPh}(\text{CH}_2)_6\text{PhO}-$); 4-hydroxymethylphenyl (i.e. 4- $\text{HOCH}_2\text{Ph}-$), 4-mercaptomethylphenyl (i.e. 4- $\text{HSCH}_2\text{Ph}-$), 4-methylthiophenyl (i.e. 4- $\text{CH}_3\text{SPh}-$), methoxyphenyl, methoxycarbonylphenyloxy (e.g. methyl salicyl), nitromethylphenyl (i.e. $-\text{PhCH}_2\text{NO}_2$), trimethylsilylphenyl, t-butyldimethylsilylphenyl, vinylphenyl, vinylidenebis(phenyl), and the like. The term “a $\text{C}_3 - \text{C}_{10}$ aromatic radical” includes substituted aromatic radicals and unsubstituted aromatic radicals containing at least three but no more than 10 carbon atoms. The aromatic radical 1-imidazolyl ($\text{C}_3\text{H}_2\text{N}_2-$) represents a C_3 aromatic radical. The benzyl radical (C_7H_8-) represents a C_7 aromatic radical.

As used herein the term “cycloaliphatic 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 “cycloaliphatic radical” does not contain an aromatic group. A “cycloaliphatic radical” may comprise one or more noncyclic components. For example, a cyclohexylmethyl group ($\text{C}_6\text{H}_{11}\text{CH}_2-$) is a cycloaliphatic 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 cycloaliphatic radical may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen; or may be composed exclusively of carbon and hydrogen. Cycloaliphatic radicals may be “substituted” or “unsubstituted”. A substituted cycloaliphatic radical is defined as a cycloaliphatic radical which comprises at least one substituent. A

substituted cycloaliphatic radical may comprise as many substituents as there are positions available on the cycloaliphatic radical for substitution. Substituents which may be present on a cycloaliphatic radical include but are not limited to halogen atoms such as fluorine, chlorine, bromine, and iodine. Substituted cycloaliphatic radicals include trifluoromethylcyclohexyl, hexafluoroisopropylidenebis(4-cyclohexyloxy) (i.e. $-\text{O C}_6\text{H}_{10}\text{C}(\text{CF}_3)_2 \text{C}_6\text{H}_{10}\text{O}-$), chloromethylcyclohexyl; 3-trifluorovinyl-2-cyclopropyl; 3-trichloromethylcyclohexyl (i.e. $3\text{-CCl}_3\text{C}_6\text{H}_{10}-$), bromopropylcyclohexyl (i.e. $\text{BrCH}_2\text{CH}_2\text{CH}_2 \text{C}_6\text{H}_{10}-$), and the like. For convenience, the term “unsubstituted cycloaliphatic radical” is defined herein to encompass a wide range of functional groups. Examples of unsubstituted cycloaliphatic radicals include 4-allyloxycyclohexyl, 4-acetyloxycyclohexyl, dicyanoisopropylidenebis(4-cyclohexyloxy) (i.e. $-\text{O C}_6\text{H}_{10}\text{C}(\text{CN})_2 \text{C}_6\text{H}_{10}\text{O}-$), 3-methylcyclohexyl, methylenebis(4-cyclohexyloxy) (i.e. $-\text{O C}_6\text{H}_{10}\text{CH}_2 \text{C}_6\text{H}_{10}\text{O}-$), ethylcyclobutyl, cyclopropylethenyl, 3-formyl-2-tetrahydrofuranyl, 2-hexyl-5-tetrahydrofuranyl; hexamethylene-1,6-bis(4-cyclohexyloxy) (i.e. $-\text{O C}_6\text{H}_{10} (\text{CH}_2)_6 \text{C}_6\text{H}_{10}\text{O}-$); 4-hydroxymethylcyclohexyl (i.e. $4\text{-HOCH}_2 \text{C}_6\text{H}_{10}-$), 4-mercaptomethylcyclohexyl (i.e. $4\text{-HSCH}_2 \text{C}_6\text{H}_{10}-$), 4-methylthiocyclohexyl (i.e. $4\text{-CH}_3\text{S } \text{C}_6\text{H}_{10}-$), 4-methoxycyclohexyl, 2-methoxycarbonylcyclohexyloxy ($2\text{-CH}_3\text{OCO } \text{C}_6\text{H}_{10}\text{O}-$), nitromethylcyclohexyl (i.e. $\text{NO}_2\text{CH}_2\text{C}_6\text{H}_{10}-$), trimethylsilylcyclohexyl, t-butyl dimethylsilylcyclopentyl, 4-trimethoxysilylethylcyclohexyl (e.g. $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_{10}-$), vinylcyclohexenyl, vinylidenebis(cyclohexyl), and the like. The term “a $\text{C}_3 - \text{C}_{10}$ cycloaliphatic radical” includes substituted cycloaliphatic radicals and unsubstituted cycloaliphatic radicals containing at least three but no more than 10 carbon atoms. The cycloaliphatic radical 2-tetrahydrofuranyl ($\text{C}_4\text{H}_7\text{O}-$) represents a C_4 cycloaliphatic radical. The cyclohexylmethyl radical ($\text{C}_6\text{H}_{11}\text{CH}_2-$) represents a C_7 cycloaliphatic radical.

As noted the present invention relates to a method for the efficient preparation of bis(halophthalimides). In one embodiment the present invention relates to a method for the preparation of bis(halophthalimides) having structure I



wherein X^1 is independently in each instance, a fluorine, chlorine, bromine or iodine group; and Q is a C_2 - C_{20} divalent aliphatic radical, a C_2 - C_{40} divalent aromatic radical, or a C_4 - C_{20} divalent cycloaliphatic radical; p is independently at each occurrence an integer in a range from 1 to 4 inclusive.

Bis(halophthalimides) having structure I are illustrated by 1,3-bis[N-(4-chlorophthalimido)]benzene (hereinafter sometimes "CIPAMI"). 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 "CIPAMI".

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:



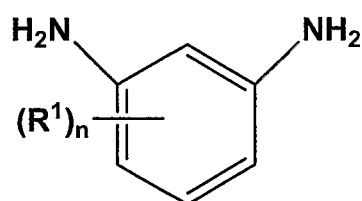
II

wherein A^1 is a C_2 - C_{20} divalent aliphatic radical, a C_2 - C_{40} divalent aromatic radical, or a C_4 - C_{20} divalent cycloaliphatic radical. Suitable aliphatic diamine compounds represented by structure II (A^1 is a C_2 - C_{20} 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 (A^1 is a C_2 - C_{40} divalent aromatic radical) include 1, 4-dimainonaphthalene, 2, 6-dimainonaphthalene, 4, 4'-diaminobiphenyl, and the like. Suitable cycloaliphatic diamine compounds represented by structure II (A^1 is a C_4 - C_{20} divalent

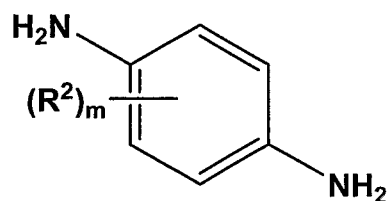
cycloaliphatic radical) include trans-1,2-diaminocyclopentane, trans-1,4-(bisaminomethyl)cyclohexane, and the like.

In one embodiment, the diamine compound is selected from the group consisting of oxydianiline, bis(4-aminophenyl)sulfone, meta-phenylenediamine and para-phenylenediamine and mixtures thereof.

In a preferred embodiment of the invention, the diamine compound is selected from the group represented by structures III and IV



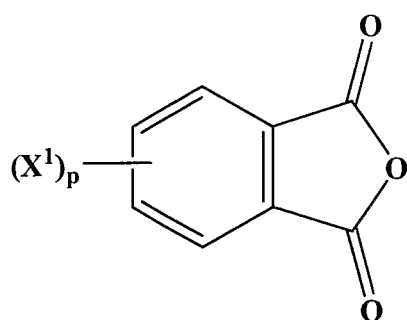
III



IV

wherein R^1 and R^2 are independently at each occurrence a halogen atom, a nitro group, a cyano group, a C_2 - C_{20} aliphatic radical, a C_2 - C_{40} aromatic radical, or a C_4 - C_{20} divalent aliphatic radical; and “n” and “m” are independently integers ranging from about 0 to about 4. Examples of suitable compounds are meta-phenylenediamine, 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, and combinations thereof.

The halophthalic anhydrides employed according to the method of the present invention are typically cyclic anhydrides represented by structure V



V

wherein X^1 is chloro, bromo, or fluoro, and p is an integer in a range from 1 to 4 inclusive. 4-chlorophthalic anhydride (CAS # 118-45-6) is a preferred anhydride.

As noted, the method of the present invention employs a solvent. Thus, in step (A) of the method of the present invention a mixture comprising at least one halophthalic anhydride and at least one solvent is prepared. Preferably the solvent is an inert solvent. Suitable solvents include dichlorobenzenes, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dichlorotoluene, 1,2,4-trichlorobenzene, diphenyl sulfone, monoalkoxybenzenes such as anisole, and the like, and mixtures thereof. In a preferred embodiment, the inert solvent is chosen such that the boiling point of the solvent system is at least about 20°C higher than the boiling point of water under the prevailing reaction conditions. The prevailing reaction conditions include the temperature and pressure at which the imidization reaction is carried out. In one embodiment, the imidization reaction is carried out under superatmospheric pressure (i.e. the pressure is greater than 1 atmosphere). Ortho-dichlorobenzene (o-DCB) is frequently a the solvent of choice for the reaction.

In one embodiment, the halophthalic anhydride is added to the solvent of choice with vigorous stirring while keeping the mixture hot. Temperatures greater than 150°C are preferred. The solvent, the diamine and the halophthalic anhydride are typically combined in amounts such that the total solids content during the reaction to form the bis(halophthalimide) does not exceed about 25 percent by weight, more preferably the total solids content during the reaction to form the bis(halophthalimide) does not exceed about 17 percent by weight. "Total solids content" expresses the proportion

of the reactants as a percentage of the total weight including liquids present in the reaction at any given time. In one embodiment, as solvent and water are distilled from the reaction mixture, additional solvent is added to maintain the total solids content within the preferred range. The terms total solids content and “% solids” are used interchangeable herein. This is effected by the addition of solvent to compensate for any increase in solids content.

In a second step, step (B), at least one diamine is added to the mixture comprising the halophthalic anhydride and the solvent prepared in step (A) to form a reaction mixture. The diamine compound is metered into the mixture formed in step (A). The diamine compound may be added either as a solid, a melt, or in solution in an inert solvent. In a preferred embodiment, the diamine compound is added as a hot melt at an addition rate which is sufficiently slow to ensure sufficient mixing of the reactants and to avoid undue caking of solids in the reaction medium. The addition of the diamine compound is also carried out in such a fashion so that the solids content of the reaction mixture is maintained at less than about 25% by weight, more preferably less than about 17% by weight. The reaction mixture formed in step (B) is said to be characterized by an “initial molar ratio of halophthalic anhydride to diamine”. The “initial molar ratio of halophthalic anhydride to diamine” is the “actual” or “true” ratio of halophthalic anhydride moieties to diamine moieties present in the reaction mixture in step (B). As a result of the uncertainty in the weights of reactants used the “initial molar ratio of halophthalic anhydride to diamine” typically has a value which is different than the ratio calculated based upon the weights of halophthalic anhydride and diamine added in steps (A) and (B). Uncertainty in the weights of halophthalic anhydride and diamine used can be pronounced when large-scale reactions are being carried out. Moreover, a stoichiometric imbalance can lead to undesired consequences such as “clumping” of the product bis(halophthalimide). The “actual” molar ratio can be determined by performing an high performance liquid chromatography (HPLC) analysis on the reaction mixture after most of the reactants have been converted to the bis(halophthalimide) product.

With respect to the amounts of halophthalic anhydride and diamine employed, it is preferable to have an excess of the halophthalic anhydride in the reaction mixture.

Preferably, 2.01 to 3.0 molar equivalents of the halophthalic anhydride with respect to the diamine compounds are employed, more preferably 2.01 to 2.5 molar equivalents of the halophthalic anhydride with respect to the diamine compound are employed.

Typically, the bis(halophthalimide) product is produced in a slurry form that is largely free from by-products and unreacted reactants, and isolation and purification of the bis(halophthalimide) product from the slurry is not required prior to polymerization to form polyetherimide.

In some embodiments an imidization catalyst may be added to the reaction mixture. Suitable imidization catalysts are known in the art. They include salts of organophosphorus acids, particularly phosphinates such as sodium phenylphosphinate (SPP) 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 generally preferred. The catalyst, when opted for, may be added before the diamine compound has been added, after the diamine compound has been added, or together with the diamine compound. In a preferred embodiment of the present invention, the catalyst, when used in the reaction mixture, is added after the addition of the diamine compound.

Step (C) of the method of the present invention comprises heating the reaction mixture formed in step (B) to a temperature of at least 100°C, optionally in the presence of the imidization catalyst described. Typically the reaction mixture is heated to a temperature of at least 150°C, preferably in a range from about 150°C to about 250°C, and more preferably in a range from about 175°C to about 225°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 starting materials product bis(halophthalimide). Typically, step (C) also provides for the removal of at least some of the water of imidization resulting from reaction of the halophthalic anhydride with the diamine. In one embodiment, about 95 % of the water of imidization is removed in step (C).

In step (D) the reaction mixture formed by the combination of steps (A)-(C) is analyzed to determine the “initial molar ratio of halophthalic anhydride to diamine”. As note, in conventional methods for the production of bis(halophthalimides), the amount of halophthalic anhydride present in the reaction mixture can only be roughly estimated based on the initial added amount. In one aspect of the invention, a suitable analytical tool may be employed to determine accurately the amount of each the reactants initially employed. This information may then be used to determine if any of the reactants need to be added to compensate for the deficiency of the same. In one embodiment of the invention, the analytical tool used to determine the initial molar ratio of halophthalic anhydride to diamine is a chromatographic method. In a typical embodiment of the present invention, a high performance liquid chromatography (HPLC) technique is used. Other analytical methods such as, but not limited to, gas chromatography, infra-red spectroscopy, ultraviolet spectroscopy, and the like may be used to monitor the reaction.

In step (E) any stoichiometric deficiency revealed by determining the initial molar ratio halophthalic anhydride to diamine is corrected by the addition of halophthalic anhydride or diamine to achieve a “corrected molar ratio” of halophthalic anhydride to diamine. Typically, because the quantity of halophthalic anhydride or diamine needed to correct the stoichiometry is small, weighing errors can be minimized using small more reliable mass measuring equipment. The corrected molar ratio is generally much closer to the molar ratio of reactants intended initially than is the initial molar ratio. In a further embodiment of the invention, the analytical tool used to monitor the reaction mixture is also coupled to a controlling unit that is capable of automatically monitoring and maintaining the stoichiometry between the reactants.

A further feature of the present invention is the solids content of the reaction mixture which at any given time during the course of the reaction should be typically less than 25% by weight, preferably in the range from about 10% to about 17% by weight. By “solids content” is meant the proportion of the reactants as a percentage of the total weight including liquids. This is effected by the addition of solvent to compensate for any increase in solids content.

Another embodiment of the present invention involves the removal of water from the reaction mixture. The water may be present in the system from a variety of sources; the reactor, or as a component of one or more of the reactants or solvents employed. Moreover, water is also produced as the by-product of the imidization reaction. Regardless of its origin, the presence of residual water in the product bis(halophthalimide) is detrimental to the polymerization reaction for which the bis(halophthalimide) is typically intended. Thus, in one aspect, the present invention provides a bis(halophthalimide) product which is suitable for use in a polymerization reaction to form polyetherimide. Typically, at least 95% of the water present during step (C) of the reaction is removed from the reaction mixture during step (C) and the remaining water is removed during step (D). Water removal may be accomplished using means well-known in the art such as a distillation process. In one embodiment of the invention, the reactor is designed such that water is removed efficiently using flush mounted valves, wherein the valves are properly designed with low volume configuration and the reaction vessel is devoid of any water retention zones.

In one embodiment, the reaction vessel comprises spray nozzles from which hot solvent (e.g. hot o-DCB) is directed at the reactor walls outlets in order to "chase" water from the reactor directing a spray of hot solvent on the interior surfaces of the reactor (typically surfaces which are above the level of the contents of the reaction vessel) serves to drive water adhering to the walls of the reactor from the reactor, and has the added benefit of washing solid reactants and product off of the reactor walls and back into the reaction mixture. In one embodiment, the solvent is o-DCB that is maintained at a temperature of at least about 180°C.

In another embodiment of the invention, the water removal is also effected by a "partial condensation" process. Partial condensation is a technique in which a multi-component vapor stream is subjected to a selective partial condensation by passage through a condenser maintained at a temperature greater than the boiling point of one or more of the lower boiling components but less than the boiling point of at least one higher boiling component. As the multi-component vapor stream encounters the condenser, the higher boiling components condense back to the liquid phase and may be returned to the source, whereas the components which boil at a temperature less

than the temperature at which the condenser is maintained pass through the condenser, largely without condensing. It should be noted that this is extremely useful when trying to dry reaction mixtures comprising water and orthodichlorobenzene (o-DCB). Typically to dry such a reaction mixture by a simple distillation technique, roughly 10 volumes of o-DCB must be distilled per unit volume water distilled in order to dry the reaction mixture. The use of the partial condensation technique significantly lowers the amount of o-DCB which must be taken overhead with the water and thereafter separated from the water. It will be understood by those skilled in the art that the boiling points referred to are the boiling points of water and solvent under the conditions in the system. Water may be boiling at a temperature greater than or less than 100°C.

Those skilled in the art will understand that as a mixture of water and solvent are removed from the reaction vessel by distillation, at least a portion of the reactants and product may be entrained out of the reaction vessel with the water and solvent. Thus, in a further embodiment of this invention, the monomers and solvent that may have been entrained from the reaction vessel during the reaction are separated from a water phase and/or otherwise dried to remove water. The monomers and solvent are then recycled to the same reaction mixture or to a subsequent reaction mixture.

The bis(halophthalimide) produced from the reaction between the halophthalic anhydride and the diamine compound in an inert solvent may optionally be isolated through conventional techniques such as filtration, centrifugation and the like; or the slurry may be used as such for the next step *viz.* polymerization. It is within the scope of the present invention to use the slurry as such for making polymers.

In a further embodiment of the present invention, a phase transfer catalyst is added as a solution in the same inert solvent or in a different inert solvent or mixtures thereof, to the mixture comprising the product and an inert solvent and the resulting mixture is dried until it contains less than 20ppm water. The phase transfer catalyst is necessary to effect polymerization. The drying is done under superatmospheric pressures at high temperatures, preferably at about 220°C and 20 psig.

In one aspect of the invention, the bishalophthalimide is prepared using a stainless steel hot oil jacketed reaction vessel comprising the following features:

- (A) a 4-blade turbine agitator
- (B) reactor baffles
- (C) re-pad nozzles on the top of the reactor to reduce space where water can get trapped
- (D) zero volume agitator housing to reduce space where water can get trapped
- (E) spray nozzles in the top of the tank that deliver a spray of hot (180°C) o-DCB
- (F) electro-polished sides to reduce the tendency of solids to adhere to the side of the vessel
- (G) a zero-volume sample tap
- (H) sufficient insulation to insure that the top of the vessel remains hot
- (I) a second oil jacket that can be employed to heat the top of the reactor if necessary
- (J) tempered oil loops that can control the temperature of the upper and lower jacket.

The agitator and the baffles were designed as described to ensure there is efficient mixing of the reaction mixture. This also ensures that there is sufficient contact between the reactants and that no local hot spots will be created. In one embodiment the baffles are approximately one inch in width and are separated from the reactor wall by a gap of about 7.6 cm (3 inches). In a further embodiment, the baffles have a height that does not exceed the operating liquid level in the tank.

In one embodiment the reactor is equipped with re-pad nozzles and zero volume agitator housing thereby further limiting undesired retention of water within the interior spaces of the reactor. In certain embodiments of the present invention the reactor is equipped with a "sample tap", which is used to draw samples out for analysis, said sample tap being "zero volume" to ensure no moisture can get trapped

in the spaces (e.g. piping) associated with the sample tap. The zero volume sample tap is also provides that there is no wastage during the withdrawal of samples.

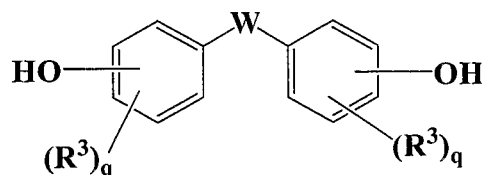
In one embodiment, the reactor comprises at least one hot-oil jacket. In certain embodiments, the top of the reactor is provided with a dedicated oil jacket to ensure greater control of the temperature. Typically, The reactor is provided with tempered oil loops that are capable of controlling the temperature of all sides of the reactor. Extra insulation is advantageously provided to ensure accurate control of the temperature. In one embodiment, the oil jacket is capable of maintaining the internal temperature of the reactor at least about 220°C (425°F).

In one embodiment, the internal surfaces of of the reactor are made of stainless steel and are optionally electropolished. Electropolishing is a process that is used to smooth, polish, deburr and clean stainless steel by selectively removing irregular features on the metal surface. When electropolishing stainless steel, elemental iron is removed, and a layer of chromium-rich oxide forms on the surface. This oxide film is thickest over depressions and thinnest over projections. At the projections the electrical resistance is least and current density greatest; therefore, the effects of electropolishing are also the greatest in these locations. The oxide layer also provides for minimal moisture absorption, surface cleanliness and high corrosion resistance. Thus, in reactors which have been subjected to electropolishing the reactor walls are typically free of cracks and pits. In addition, solids typically do not adhere to the walls, thereby reducing caking of solids within the reactor.

Each of the reactor features discussed provide a greater measure of control over the reaction to form bis(halophthalimides). Thus, the reactor features disclosed help to endure that (a) the reaction goes to completion; (b) by-products formation is minimized ; (c) caking of solids or solids adhering to the walls of the reactor is minimized ; and (d) the product bis(halophthalimide) comprises less than 20ppm water.

It is also within the scope of the invention to produce polyetherimides from a mixture of solvent and bis(halophthalimide) produced according to the method of the present invention. In one embodiment, at least one comonomer as a slurry or a solution is

added to the mixture of solvent and bis(halophthalimide). The at least one comonomer typically comprises a metal salt (e.g. the disodium salt of bisphenol A) of at least one bisphenol having structure VI



VI

wherein R^3 is a halogen atom, a nitro group, a cyano group, a C_1 - C_{12} aliphatic radical, C_3 - C_{12} cycloaliphatic radical, or a C_3 - C_{12} aromatic radical; q is independently at each occurrence an integer from 0 to 4 inclusive; W is a bond, an oxygen atom, a sulfur atom or a selenium atom, an SO_2 group, an SO group, a CO group, a C_1 - C_{20} aliphatic radical, C_3 - C_{20} cycloaliphatic radical, or a C_3 - C_{20} aromatic radical. The reaction of the metal salt of biphenol VI with the bis(halophthalimide) prepared according to the method of the present invention affords polyetherimide compositions. Typically, the metal salt of the bisphenol is an alkali metal salt or an alkaline earth metal salt of the bisphenol. In an alternate embodiment, the at least one comonomer comprises a metal salt (e.g. the disodium salt of resorcinol) of a dihydroxy benzene. Dihydroxy benzenes are illustrated by resorcinol, hydroquinone, methylhydroquinone and the like.

EXAMPLES

The following examples are set forth to provide those of ordinary skill in the art with a detailed description of how the methods claimed herein are evaluated, and are not intended to limit the scope of what the inventors regard as their invention. Unless indicated otherwise, parts are by weight, temperature is in ° C.

A 500-gallon stainless steel hot oil jacketed reactor with the configuration as described in the specifications was used for the reaction. The vessel was charged with chlorophthalic anhydride (ClPA)/o-dichlorobenzene (o-DCB) at about 12% solids content, 355.9 pounds of dry weight ClPA. The material was heated to reflux before analysis by High Performance Liquid Chromatography (HPLC) to determine the

molar ratio of diacids to anhydrides. The solution was also analyzed for 3- and 4-CIPA and phthalic anhydride. Phthalic anhydride was added at this stage as chain stopper.

Molten meta-phenylene diamine (mPD) (103.5 pounds) was then slowly metered, over a 2 to 4 hour period to the reaction mixture that was maintained at a temperature in the range of about 175°C to about 180°C (350°F to 356°F), with agitation. The temperature of the oil on the jacket of the reactor was set at 204°C (400°F). The water of imidization and o-DCB was taken overhead and condensed. The % solids of CIPAMI in the reactor was not allowed to surpass 17% solids. Hot o-DCB was added to the reactor to keep the solids at the desired level (15 to 17%). The initial mPD charge was 1.5 pounds deficient relative to the required amount of mPD so that the CIPAMI product was anhydride rich. This was done to prevent sticking of the material to the sides of the vessel. At this level of solids content, the non-Newtonian mixture stirred with sufficient efficiency where the material was mixing well in the reactor and there were no stagnant areas in the tank.

Upon the completion of the mPD addition and after the bulk of the water had been removed from the tank, a sample of the reaction mixture was taken, and the stoichiometry of the reaction mixture was determined using HPLC. Additional CIPA solution was added until the stoichiometry of the CIPAMI was 0.05 to 0.3 mole% rich in CIPA with respect to the amount of mPD charged to the reactor. The analytical method worked very well when the bulk of the water had been removed. Running the reaction near reflux facilitated this. This resulted in a clean HPLC trace, and generally, there was no chlorophthalic acids present to complicate the determination of the stoichiometry. Additionally, most of the bis-amide-acids were ring closed, and most of the monoamine had reacted with CIPA. The CIPA and monoimides were clearly delineated in the HPLC trace resulting from running the reaction as described above.

Once the CIPAMI had been adjusted to the desired stoichiometry, Sodium Phenylphosphinate (SPP) imidization catalyst was added to the reaction mixture and the CIPAMI was dried in the level control mode at atmospheric pressure in the

presence of the imidization catalyst. In this manner, o-DCB was removed from the tank while hot dry o-DCB was sprayed into the headspace of the reactor, while maintaining a constant level (weight) in the reactor. Any water lingering in the head of the reactor was thus forced up and out of the reactor. After the overheads of the reactor are dry (<20 ppm o-DCB), then enough o-DCB was removed from the tank to afford CIPAMI at 20 to 25% solids. This procedure resulted in insignificant amounts of CIPAMI adhered to the walls of the vessel. Any CIPAMI that did adhere to the wall were removed with a spray nozzle or was dissolved during the subsequent polymerization reaction (i.e., it is not strongly adhered to the walls). This led to polymer with very low and acceptable levels of residual CIPAMI.

Example 2

The general procedure as described in Example 1 was followed. In the final step, SPP imidization catalyst was left out of the reaction, and the CIPAMI was dried under pressure (18 to 25 psig), at a temperature in a range of from about 218°C to about 250°C (425°F to 480°F), at a solids contents of from about 15% to 17%. Hot o-DCB spray was used to chase water from the vessel in the level control mode. Once the overhead o-DCB was found to contain less than 20 ppm water, the pressure was relieved from the vessel and the amount of solid CIPAMI in the slurry was adjusted to a range of from about 20% to about 25% solids just prior to the polymerization reaction.

Once the polymerization reaction was completed in the imidization/polymerization vessel, the reaction mixture was transferred to the quench vessel. The polymerization vessel was then washed with hot o-DCB to clean the tank. This rinse was found to contain undetectable amounts of CIPAMI and was then sent forward to the quench tank as long as there was no residual CIPAMI adhered to the wall. The polymer made from this process contained less than 100 ppm CIPAMI. Batches where these conditions were not followed (high solids, higher oil temperature, no stoic control during mPD addition) contained 1000 to 3000 ppm CIPAMI.

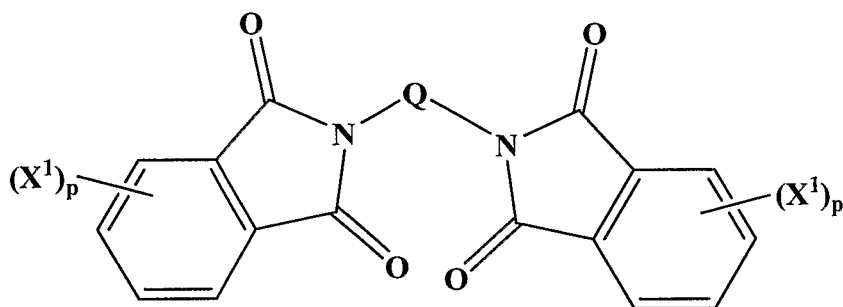
The o-DCB/water collected off the condenser of the reactor contained a 'precipitate thought to comprise CIPA and mPD adducts. o-DCB comprising this precipitate was subsequently used in the preparation of an additional batch of CIPAMI.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood by those skilled in the art that variations and modifications can be effected within the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A method for preparing a bis(halophthalimide), said method comprising:
 - (A) preparing a mixture comprising at least one halophthalic anhydride and at least one solvent,
 - (B) adding to the mixture formed in step (A) at least one diamine to form a reaction mixture, said reaction mixture being characterized by “an initial molar ratio of halophthalic anhydride to diamine”;
 - (C) heating the reaction mixture formed in step (B) to a temperature of at least 100°C, optionally in the presence of an imidization catalyst;
 - (D) analyzing the reaction mixture formed by the combination of steps (A)-(C) to determine the initial molar ratio of halophthalic anhydride to diamine; and
 - (E) performing one step selected from the group consisting of:
 - (i) adding anhydride or diamine to the mixture formed by the combination of steps (A)-(C) to achieve a “corrected molar ratio” of halophthalic anhydride to diamine, said corrected molar ratio being in a range between about 2.01 and about 2.3, and heating to a temperature of at least 100°C to obtain a bis(halophthalimide) product mixture that is substantially free of water; and
 - (ii) heating to a temperature of at least 100°C the reaction mixture formed by the combination of steps (A)-(C) to obtain a bis(halophthalimide) product mixture that is substantially free of water.
2. The method according to claim 1 wherein said analyzing the reaction mixture formed by the combination of steps (A)-(C) to determine the initial molar ratio of halophthalic anhydride to diamine, comprises determining a concentration of halophthalic anhydride, a concentration of by-product halophthalic acid, and a concentration of intermediate monophthalimide monoamine in the reaction mixture formed by the combination of steps (A)-(C).

3. The method according to claim 1 wherein said bis(halophthalimide) has structure I



I

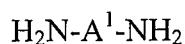
wherein X^1 and X^2 are independently fluorine, chlorine, bromine or iodine; and Q is a C_2 - C_{20} divalent aliphatic radical, a C_2 - C_{40} divalent aromatic radical, or a C_4 - C_{20} divalent cycloaliphatic radical; p is independently at each occurrence an integer ranging from 1 to 4.

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

5. The method according to claim 1 wherein the solvent is selected from the group consisting of chlorobenzene, o-dichlorobenzene, anisole, toluene, xylene, and mesitylene.

6. The method according to claim 1 wherein the solvent is o-dichlorobenzene.

7. The method according to claim 1 wherein the at least one diamine has structure II

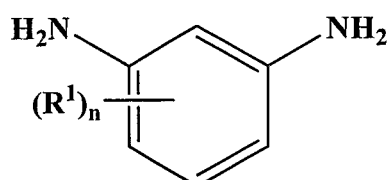


II

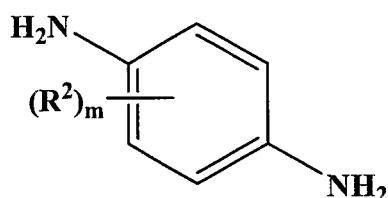
wherein A^1 is a C_2 - C_{20} divalent aliphatic radical, a C_2 - C_{40} divalent aromatic radical, or a C_4 - C_{20} divalent cycloaliphatic radical.

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

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



III



IV

wherein R^1 and R^2 are independently at each occurrence a halogen atom, a nitro group, a cyano group, a C_2 - C_{20} aliphatic radical, a C_2 - C_{40} aromatic radical, or a C_4 - C_{20} cycloaliphatic radical; and “n” and “m” are independently integers ranging from 0 to 4.

10. The method according to claim 9 wherein the aromatic diamine is selected from the group consisting of meta-phenylene diamine and para-phenylene diamine.

11. The method according to claim 1 wherein the temperature of the reaction mixture in step (C) is at least 150°C .

12. The method according to claim 1 wherein the temperature of the reaction mixture in step (C) is at least 200°C .

13. The method according to claim 1 wherein the imidization catalyst is sodium phenylphosphinate.

14. The method according to claim 1 further comprising at least one step selected from the group consisting of; adding the imidization catalyst prior to step (B), and adding the imidization catalyst following step (B).
15. The method according to 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.
16. The method according to claim 1 wherein said analyzing comprises analysis by liquid chromatography, gas chromatography, or a combination thereof.
17. The method according to claim 1 wherein at least one of steps (A)-(C) and (E) is performed in a reactor free of water retention zones.
18. The method according to claim 1 wherein at least one of steps (A)-(C) and (E) is performed in a reactor equipped with at least one flush-mounted valve.
19. The method according to claim 1 wherein step (E) comprises distilling a mixture of water and organic components, to produce a product mixture that is substantially free of water and a distillate comprising water, solvent, unreacted halophthalic anhydride, and diamine.
20. The method according to claim 19 wherein said distillate is subjected to water removal and recycling.
21. The method according to claim 20 wherein said recycling comprises at least one process step selected from the group consisting of (a) preparing a mixture comprising at least one halophthalic anhydride and at least one solvent, (b) adding at least one diamine to the mixture comprising at least one halophthalic anhydride and at least one solvent, to form a reaction mixture, wherein a portion of the at least one of said halophthalic anhydride, said solvent, and said diamine is provided by said distillate.
22. The method according to claim 19 wherein said distilling is carried out at superatmospheric pressure.

23. The method according to claim 1 further comprising adding at least one phase transfer catalyst prior to or during step (E) to afford a product mixture comprising a phase transfer catalyst, said product mixture being substantially free of water.
24. The method according to claim 1 wherein each of steps (A)-(C) and (E) is characterized by a percent solids content, said percent solids content being less than about 17% solids.
25. The method according to claim 1 wherein in step (B), said diamine is added at a rate such that the concentration of unreacted diamine in the reaction mixture at any given time is minimized.
26. The method according to claim 1 wherein said adding at least one diamine in step (B) comprises the addition of said diamine in molten form.
27. The method according to claim 1 wherein said adding at least one diamine in step (B) comprises the addition of said diamine together with a solvent.
28. The method according to claim 1 wherein step (C) and optionally step (E) further comprises distilling water from the reaction mixture through a condenser maintained at a temperature greater than the boiling point of water and less than the boiling point of the solvent, wherein the boiling point of the solvent is greater than the boiling point of water .
29. The method according to claim 28 wherein said distilling is carried out at a pressure of at least 1 atmosphere.
30. The method according to claim 28 wherein a difference between the boiling point of water and solvent is at least 20°C.
31. The method according to claim 1 wherein step (E) and optionally step (C) further comprises distilling water from the reaction mixture through a condenser maintained at a temperature greater than the boiling point of water and less than the boiling point of the solvent, wherein the boiling point of the solvent is greater than the boiling point of water.

32. The method according to claim 31 wherein said distilling is carried out at a pressure of at least 1 atmosphere.

33. The method according to claim 32 wherein a difference between the boiling point of water and solvent is at least 20°C.

34. A method for preparing a bis(chlorophthalimide); said method comprising:

(A) preparing a mixture comprising 3-chlorophthalic anhydride, 4-chlorophthalic anhydride and at least one solvent;

(B) adding to the mixture formed in step (A) at least one aromatic diamine, to form a reaction mixture, said reaction mixture being characterized by an initial molar ratio of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride to aromatic diamine;

(C) heating the reaction mixture formed in step (B) optionally in the presence of an imidization catalyst, to a temperature of at least 100°C;

(D) analyzing the reaction mixture formed by the combination of steps (A)-(C) to determine the initial molar ratio of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride to aromatic diamine; and

(E) performing one step selected from the group consisting of:

(i) adding a mixture of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride, or aromatic diamine to the reaction mixture formed by the combination of steps (A)-(C) to achieve a corrected molar ratio of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride to aromatic diamine, said corrected molar ratio being in a range between about 2.01 and about 2.3, and heating to a temperature of at least 100°C to obtain a bis(chlorophthalimide) product mixture that is substantially free of water; and

(ii) heating to a temperature of at least 100°C the reaction mixture formed by the combination of steps (A)-(C) to obtain a bis(chlorophthalimide) product mixture that is substantially free of water.

35. A method for preparing a bis(4-chlorophthalimide); said method comprising:

(A) preparing a mixture comprising 4-chlorophthalic anhydride and orthodichlorobenzene;

(B) adding to the mixture formed in step (A) a mixture of meta-phenylene diamine and para-phenylene diamine, to form a reaction mixture, said reaction mixture being characterized by an initial molar ratio of 4-chlorophthalic anhydride to meta-phenylene diamine and para-phenylene diamine;

(C) heating the reaction mixture formed in step (B) in the presence of a catalyst, to a temperature of at least 100°C;

(D) analyzing the reaction mixture formed by the combination of steps (A)-(C) to determine the initial molar ratio of 4-chlorophthalic anhydride to meta-phenylene diamine and para-phenylene diamine; and

(E) performing one step selected from the group consisting of:

(i) adding 4-chlorophthalic anhydride, or a mixture of meta-phenylene diamine and para-phenylene diamine to the reaction mixture formed by the combination of steps (A)-(C) to achieve a corrected molar ratio of 4-chlorophthalic anhydride to meta-phenylene diamine and para-phenylene diamine, said corrected molar ratio being in a range between about 2.01 and about 2.3, and heating to a temperature of at least 100°C to obtain a bis(4-chlorophthalimide) product mixture that is substantially free of water; and

(ii) heating to a temperature of at least 100°C the reaction mixture formed by the combination of steps (A)-(C) to obtain a bis(4-chlorophthalimide) product mixture that is substantially free of water.