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(54) Title: METHODS OF PURIFICATION OF 2-ARYL-3,3-BIS(4- HYDROXYARYL)PHTHALIMIDINES, AND POLYMERS DERIVED THEREFROM

(57) Abstract: A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine including heating a reaction mixture comprising a phenolphthalein compound and a primary arylamine in the presence of an acid catalyst to form a reaction mixture comprising a 2-aryl-3,3- bis(hydroxyaryl)phthalimidine; quenching the reaction mixture with an aqueous alkali solution to form a quenched reaction mixture; extracting the quenched reaction mixture with an aminoaryl compound to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine is provided. Methods for the manufacture of a polycarbonate, including manufacturing the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine, and polymerizing the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine in the presence of a carbonate source are provided.

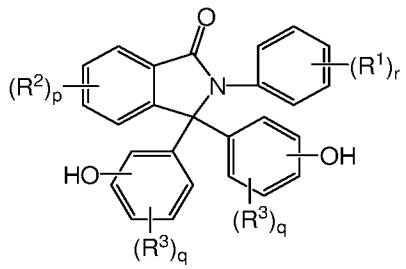
METHODS OF PURIFICATION OF 2-ARYL-3,3-BIS(4-HYDROXYARYL)PHTHALIMIDINES, AND POLYMERS DERIVED THEREFROM

BACKGROUND

[0001] There is a need for methods for the purification of 2-phenyl-3,3-bis(4-hydroxyphenyl)phthalimidine (also known as N-phenyl phenolphthalein bisphenol (PPPBP) or 3,3-bis(4-hydroxyphenyl)-2-phenylisoindolin-1-one)) wherein the product contains reduced amounts of an aminophenol (AP), or no aminophenol.

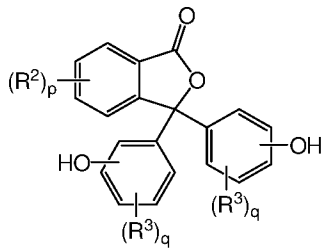
BRIEF SUMMARY

[0002] A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I)

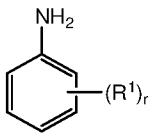


(I)

the method comprising heating a reaction mixture comprising a phenolphthalein compound of formula (II)



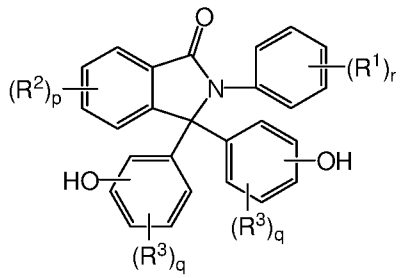
(II) and a primary arylamine of formula (III)



(III) in the presence of an acid catalyst to form a reaction mixture comprising a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I); quenching the reaction mixture with an aqueous alkali solution to form a quenched reaction mixture; extracting the quenched reaction mixture with an aminoaryl compound of formula (IV) $(R^4)(R^5)N\text{-}Ar(R^6)_s$ (IV) to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I), wherein in formulas (I), (II), (III), and (IV) each occurrence of R^1 is independently a phenyl or a $C_{1\text{-}25}$ hydrocarbyl, preferably a phenyl

or a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, each R^4 and R^5 is independently a hydrogen or C_{1-25} hydrocarbyl, preferably a hydrogen or C_{1-6} alkyl, more preferably a hydrogen, Ar is a C_{6-12} aromatic ring optionally comprising up to three heteroatoms in the ring, preferably a C_6 or a C_{12} aromatic ring, each R^6 is independently a halogen, nitro, cyano, or C_{1-25} hydrocarbyl, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, and r, p, q, and s are each independently 0 to 4, more preferably 0 or 1, preferably 0 is provided.

[0003] A 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising a phthalimidine of formula (I)



(I), wherein each occurrence of R^1 is independently a phenyl or C_{1-25} hydrocarbyl, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, and r, p, and q are each independently 0 to 4, more preferably 0 or 1, preferably 0; zero-1000 parts per million of an aminophenol, preferably zero-500 parts per million of an aminophenol, more preferably from zero-50 parts per million of an aminophenol is provided.

[0004] A method for the manufacture of a polycarbonate, comprising manufacturing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) by the described method; and polymerizing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in the presence of a carbonate source is provided.

[0005] The above described and other features are exemplified by the following detailed description.

DETAILED DESCRIPTION

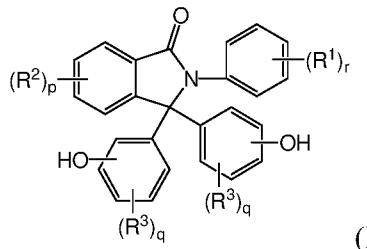
[0006] The present disclosure is generally directed to purifying phenolphthalein derivatives, in particular 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines, which are suitable for use as monomers or comonomers for preparing polycarbonates and other polymers. The

method generally includes forming a reaction mixture comprising a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine, quenching the reaction mixture with an aqueous alkali solution to form a quenched reaction mixture, and extracting the quenched reaction mixture with an aminoaryl compound to reduce the amount of aminophenol impurity. The method can include repeating the extraction steps, purification using activated carbon as an adsorbent, extraction with an organic solvent such as a chlorinated solvent for example 1,2-dichloroethane, dichloromethane, ortho dichlorobenzene (O-DCB), or chloroform, toluene, or xylene, for example, or a combination comprising at least one of the foregoing, to remove the aminoaryl compound. The heating, quenching, and extracting, or a combination thereof can be a continuous process.

[0007] This process can eliminate or reduce the existing downstream purification of PPPBP using activated carbon/acidic ion exchange resin as an adsorbent for removing the aminophenol impurity. The procedures in the method for purifying PPPBP are further described below.

[0008] The 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines produced in accordance with these methods can be used in the manufacture of polycarbonates and other polymers. The 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines purified in accordance with these methods can have improved properties, such as a lower level of aminophenol impurity. The methods described to purify 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines can simplify the process and allow for a continuous process, as well as reducing or eliminating the need for carbon adsorbents for impurity removal. The methods described can reduce or eliminate the need for solid isolations.

[0009] The 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines produced in accordance with this disclosure are of formula (I):

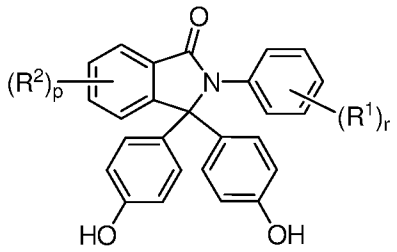


(I)

wherein each R^1 is independently a phenyl or a C_{1-25} hydrocarbyl, each R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, and r, p, and q are each independently 0 to 4. In some embodiments, R^1 is phenyl or a C_{1-6} alkyl group, and each R^2 and R^3 is independently a C_{1-6} alkyl group. In some embodiments, R^1 is a C_{1-3} alkyl group, and each R^2

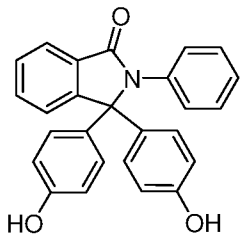
and R^3 are each independently a C_{1-3} alkyl group. In some embodiments, each R^1 is independently a C_{1-6} alkyl. In some embodiments, each R^1 is independently a C_{1-3} alkyl. In some embodiments, each R^2 and R^3 is independently a C_{1-6} alkyl. In some embodiments, each R^1 is a C_{1-3} alkyl. In some embodiments, r, p, and q are each independently 0 or 1. In some embodiments, r, p, and q are each independently 0.

[0010] In an embodiment, a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine is of formula (IA)



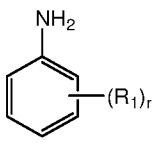
(IA),

wherein R^1 is a C_{1-3} alkyl, R^2 is a C_{1-3} alkyl or a halogen, p is 0 or 1, and r is 0 or 1. In an embodiment, each of p and r is zero. In an embodiment, a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine is 2-phenyl-3,3-bis(4-hydroxyphenyl)-2-phthalimidine. When each of p, q, and r is 0 in formulas (I) and (IA), the 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine is 2-phenyl-3,3-bis(4-hydroxyphenyl)-2-phthalimidine having formula (IB)



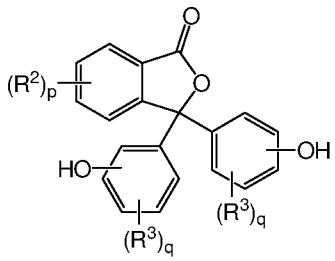
(IB).

[0011] The 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine of formula (I) can be prepared by a number of methods, including by the reaction of a primary arylamine, e.g., an aniline, of formula (III):



(III)

wherein R^1 and r are as defined above; with a phenolphthalein compound of formula (II):



(II)

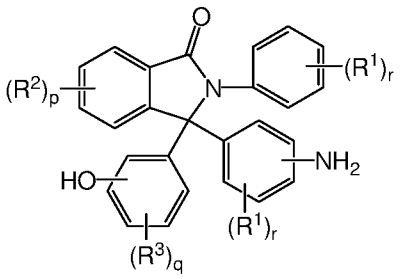
wherein R^2, R^3, p and q are as defined above, in the presence of an acid catalyst to form a reaction mixture comprising a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I).

[0012] The reaction mixture can be quenched by reaction with an aqueous alkali solution to form a quenched reaction mixture. The alkali can be sodium hydroxide, or another alkali metal hydroxide, or an alkaline earth metal hydroxide, for example. The quenched reaction mixture can be extracted with an aminoaryl compound of formula (IV) $(R^4)(R^5)N\text{-}Ar(R^6)_s$ where R^4, R^5, Ar, R^6, and s are as defined above, to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I). The aminoaryl compound of formula (IV) can be a primary aryl amine, such as aniline, or a substituted aniline, where the substitution is a halogen, or a nitro group, for example.

[0013] The extraction can be repeated until the desired level of the aminophenol impurity is reached in the aqueous layer. The aqueous layer can also be treated with a solvent, such as 1,2-dichloroethane (EDC) to remove aniline. The EDC treatment can be performed before, after, or in between the extraction with arylamine. The aqueous layer can also be treated with charcoal, to remove color, for example. The 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) can be precipitated from the extracted aqueous layer, using methods known in the art.

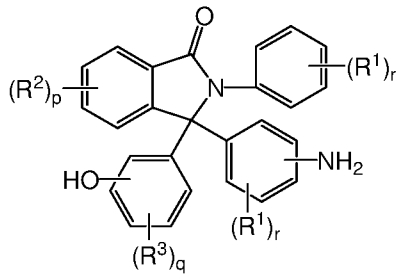
[0014] The purification or steps thereof can be performed continuously, as will be appreciated by one of ordinary skill in the art.

[0015] The precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 500-8000 parts per million of an aminophenol, for example an aminophenol of the formula



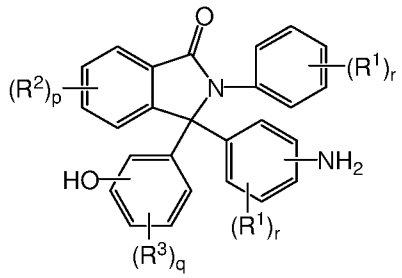
, where R^1, R^2, R^3, p, q, and r are as defined above.

[0016] In an embodiment, the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 800-6000 parts per million of an aminophenol, for example an aminophenol of the formula



, where R^1, R^2, R^3, p, q, and r are as defined above.

[0017] In an embodiment, the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 1000-6000 parts per million of an aminophenol, for example an aminophenol of the formula



, where R^1, R^2, R^3, p, q, and r are as defined above.

[0018] Exemplary primary arylamines include aniline. In some embodiments, the aminoaryl compound of formula (IV) has the same structure as the primary arylamine of formula (III). In an embodiment, the aminoaryl compound of formula (IV) and the primary arylamine of formula (III) is aniline.

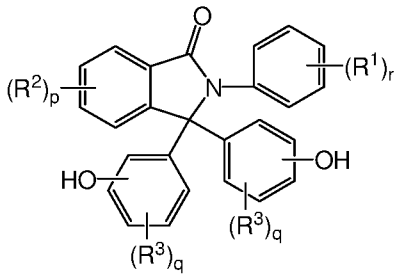
[0019] Exemplary acid catalysts include mineral acids, including hydrochloric acid. Amine salts of mineral acids can be formed from the reaction of mineral acids with amines. Examples of suitable amines for forming the acid catalysts include primary, secondary, and tertiary amines having any combination of aliphatic and aromatic groups bonded to the amine nitrogen. The mineral acids used for preparing the amine salts can be present in a fluid phase, for example, in a gaseous phase or in a liquid phase or in a combination of the gaseous

and liquid phases. Non-limiting examples of mineral acids include hydrogen chloride liquid, hydrogen chloride gas, sulfuric acid, nitric acid, and the like. The acid catalyst can be present at a concentration of 0.5-1.5 molar equivalents of the phenolphthalein compound of formula (II).

[0020] The heating can occur at a temperature of 135°C-180°C. In an embodiment, the heating can occur at a temperature of 155°C-175°C. The heating can be for 5-20 hours. In an embodiment, the heating can be for 8-15 hours.

[0021] The phthalimidine of formula (I) can be precipitated from the reaction mixture to provide a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I).

[0022] The methods described herein can be used to manufacture a 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising a phthalimidine of formula (I)



(I),

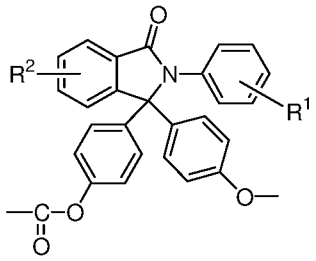
each occurrence of R^1 is independently a phenyl or C_{1-25} hydrocarbyl, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, and r, p, and q are each independently 0 to 4; zero-1000 parts per million of an aminophenol. In an embodiment, each occurrence of R^1 is independently a phenyl or a C_{1-6} alkyl. In an embodiment, each occurrence of R^1 is independently a C_{1-3} alkyl. In an embodiment, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen. In an embodiment, each occurrence of R^2 and R^3 is independently a C_{1-6} alkyl. In an embodiment, each occurrence of R^2 and R^3 is independently a C_{1-3} alkyl. In an embodiment, r, p, and q are each independently 0 to 4. In an embodiment, r, p, and q are each independently 0 or 1. In an embodiment, r, p, and q are each independently 0. In an embodiment, the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition includes zero-1000 parts per million of an aminophenol. In an embodiment, the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition includes zero-500 parts per million of an aminophenol. In an embodiment, the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition includes zero-50 parts per million of an aminophenol.

[0023] A polymer comprising structural units derived from the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine manufactured by the methods described herein is also provided.

The polymer can be a polycarbonate. In an embodiment, the polymer is a copolycarbonate comprising units derived from the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) and units derived from bisphenol A. A method for the manufacture of a polycarbonate, includes manufacturing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in accordance with a method described herein; and polymerizing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in the presence of a carbonate source

[0024] The 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines, including the exemplary 2-phenyl-3,3-bis(4-hydroxyphenyl)phthalimidine (PPPBP), are monomers or comonomers for producing a variety of polymers formed by reactions of the phenolic OH groups of the 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidines. Exemplary polymers that can be produced include homopolymers and copolymers of a polycarbonate, a polyestercarbonate, a polyester, a polyesteramide, a polyimide, a polyetherimide, a polyamideimide, a polyether, a polyethersulfone, a polycarbonate–polyorganosiloxane block copolymer, a copolymer comprising aromatic ester, ester carbonate, and carbonate repeat units, and a polyetherketone. An example of a copolymer comprising aromatic ester, estercarbonate, and carbonate repeat units is the copolymer produced by the reaction of a hydroxy-terminated polyester, such as the product of reaction of isophthaloyl chloride and terephthaloyl chloride with resorcinol, with phosgene and an aromatic dihydroxy compound, such as bisphenol A.

[0025] In some embodiments, polycarbonates having low color properties are synthesized, wherein the polycarbonates include structural units of formula (V):



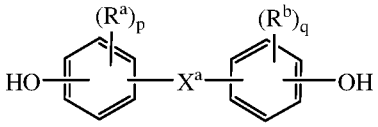
(V)

which are derived from a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine of formula (I), wherein R^1 and R^2 are as described previously; and the C=O structural units are derived from a C=O donor such as a carbonic acid diester in a melt transesterification process, or phosgene in an interfacial process.

[0026] Specific polycarbonates are copolycarbonates having structural units derived from a phthalimidine compound of formula (I) and a dihydroxy compound of the formula HO-R^1-OH, in particular of formula (VI)

$$HO–A^1–Y^1–A^2–OH \qquad (VI)$$

wherein each of A^1 and A^2 is a monocyclic divalent aromatic group and Y^1 is a single bond or a bridging group having one or more atoms that separate A^1 from A^2. In an exemplary embodiment, one atom separates A^1 from A^2. Specifically, each R^1 can be derived from a dihydroxy aromatic compound of formula (VII):

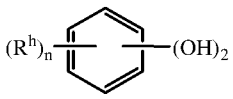


(VII)

wherein R^a and R^b each represent a halogen or C_{1-12} alkyl group and can be the same or different; and p and q are each independently integers of 0 to 4. X^a represents a single bond or a bridging group connecting the two hydroxy-substituted aromatic groups, where the single bond or the bridging group and the hydroxy substituent of each C_6 arylene group are disposed ortho, meta, or para (specifically para) to each other on the C_6 arylene group. In an embodiment, the bridging group X^a is -O-, -S-, -S(O)-, -$S(O)_2$-, -C(O)-, or a C_{1-18} organic group. The C_{1-18} organic group can be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The C_{1-18} organic group can be disposed such that the C_6 arylene groups connected thereto are each connected to a common alkylidene carbon or to different carbons of the C_{1-18} organic group. In some embodiments, p and q is each 1, and R^a and R^b are each a C_{1-3} alkyl group, specifically methyl, disposed meta to the hydroxy group on each arylene group.

[0027] In an embodiment, X^a is a substituted or unsubstituted C_{3-18} cycloalkylidene, a C_{1-25} alkylidene of formula –$C(R^c)(R^d)$ – wherein R^c and R^d are each independently hydrogen, C_{1-12} alkyl, C_{1-12} cycloalkyl, C_{7-12} arylalkyl, C_{1-12} heteroalkyl, or cyclic C_{7-12} heteroarylalkyl, or a group of the formula –$C(=R^e)$– wherein R^e is a divalent C_{1-12} hydrocarbon group. Exemplary groups of this type include methylene, cyclohexylmethylene, ethylidene, neopentylidene, and isopropylidene, as well as 2-[2.2.1]-bicycloheptylidene, cyclohexylidene, cyclopentylidene, cyclododecylidene, and adamantylidene. In another embodiment, X^a is a C_{1-18} alkylene group, a C_{3-18} cycloalkylene group, a fused C_{6-18} cycloalkylene group, or a group of the formula –B^1–W–B^2– wherein B^1 and B^2 are the same or different C_{1-6} alkylene group and W is a C_{3-12} cycloalkylidene group or a C_{6-16} arylene group.

[0028] Other useful aromatic dihydroxy compounds of the formula HO-R^1-OH include compounds of formula (VIII):



(VIII)

wherein each R^h is independently a halogen atom, a C_{1-10} hydrocarbyl such as a C_{1-10} alkyl group, a halogen-substituted C_{1-10} alkyl group, a C_{6-10} aryl group, or a halogen-substituted C_{6-10} aryl group, and n is 0 to 4. The halogen is usually bromine.

[0029] Some illustrative examples of specific aromatic dihydroxy compounds include the following: 4,4'-dihydroxybiphenyl, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)diphenylmethane, bis(4-hydroxyphenyl)-1-naphthylmethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2-(4-hydroxyphenyl)-2-(3-hydroxyphenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 1,1-bis (hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)isobutene, 1,1-bis(4-hydroxyphenyl)cyclododecane, trans-2,3-bis(4-hydroxyphenyl)-2-butene, 2,2-bis(4-hydroxyphenyl)adamantane, alpha, alpha'-bis(4-hydroxyphenyl)toluene, bis(4-hydroxyphenyl)acetonitrile, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-ethyl-4-hydroxyphenyl)propane, 2,2-bis(3-n-propyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(3-sec-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-t-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 2,2-bis(3-allyl-4-hydroxyphenyl)propane, 2,2-bis(3-methoxy-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dibromo-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dichloro-2,2-bis(5-phenoxy-4-hydroxyphenyl)ethylene, 4,4'-dihydroxybenzophenone, 3,3-bis(4-hydroxyphenyl)-2-butanone, 1,6-bis(4-hydroxyphenyl)-1,6-hexanedione, ethylene glycol bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfone, 9,9-bis(4-hydroxyphenyl)fluorine, 2,7-dihydroxypyrene, 6,6'-dihydroxy-3,3,3',3'- tetramethylspiro(bis)indane ("spirobiindane bisphenol"), 3,3-bis(4-hydroxyphenyl)phthalimide, 2,6-dihydroxydibenzo-p-dioxin, 2,6-dihydroxythianthrene, 2,7-dihydroxyphenoxathin, 2,7-dihydroxy-9,10-dimethylphenazine, 3,6-dihydroxydibenzofuran, 3,6-dihydroxydibenzothiophene, and 2,7-dihydroxycarbazole, resorcinol, substituted resorcinol compounds such as 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, 5-butyl resorcinol, 5-t-butyl resorcinol, 5-phenyl resorcinol, 5-cumyl

resorcinol, 2,4,5,6-tetrafluoro resorcinol, 2,4,5,6-tetrabromo resorcinol, or the like; catechol; hydroquinone; substituted hydroquinones such as 2-methyl hydroquinone, 2-ethyl hydroquinone, 2-propyl hydroquinone, 2-butyl hydroquinone, 2-t-butyl hydroquinone, 2-phenyl hydroquinone, 2-cumyl hydroquinone, 2,3,5,6-tetramethyl hydroquinone, 2,3,5,6-tetra-t-butyl hydroquinone, 2,3,5,6-tetrafluoro hydroquinone, 2,3,5,6-tetrabromo hydroquinone, or the like, or combinations comprising at least one of the foregoing dihydroxy compounds.

[0030] Specific examples of bisphenol compounds of formula (VII) include 1,1-bis(4-hydroxyphenyl) methane, 1,1-bis(4-hydroxyphenyl) ethane, 2,2-bis(4-hydroxyphenyl) propane (hereinafter "bisphenol A" or "BPA"), 2,2-bis(4-hydroxyphenyl) butane, 2,2-bis(4-hydroxyphenyl) octane, 1,1-bis(4-hydroxyphenyl) propane, 1,1-bis(4-hydroxyphenyl) n-butane, 2,2-bis(4-hydroxy-2-methylphenyl) propane, 1,1-bis(4-hydroxy-t-butylphenyl) propane, 3,3-bis(4-hydroxyphenyl) phthalimidine, and 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane (DMBPC). Combinations comprising at least one of the foregoing dihydroxy compounds can also be used. In one specific embodiment, the polycarbonate is a linear homopolymer derived from bisphenol A, in which each of A^1 and A^2 is p-phenylene and Y^1 is isopropylidene in formula (3).

[0031] Exemplary carbonic acid diesters useful in the formation of the polycarbonates in a melt transesterification process are of formula (IX):

$$(ZO)_2C=O \quad \text{(IX)}$$

wherein each Z is independently an unsubstituted or substituted C_{1-12} alkyl radical, or an unsubstituted or substituted C_{6-22} aryl radical. Examples of carbonic acid diesters include, but are not limited to, ditolyl carbonate, m-cresyl carbonate, dinaphthyl carbonate, diphenyl carbonate, diethyl carbonate, dimethyl carbonate, dibutyl carbonate, dicyclohexyl carbonate, and combinations thereof. Diphenyl carbonate is widely used as a carbonic acid diester due to its low cost and ready availability. Use of activated aromatic carbonates that are more reactive than diphenyl carbonate is also contemplated. Specific non-limiting examples of activated aromatic carbonates include bis(o-methoxycarbonylphenyl)carbonate, bis(o-chlorophenyl)carbonate, bis(o-nitrophenyl)carbonate, bis(o-acetylphenyl)carbonate, bis(o-phenylketonephenyl)carbonate, bis(o-formylphenyl)carbonate. Unsymmetrical combinations of these structures are also contemplated. Exemplary ester-substituted diaryl carbonates include, but are not limited to, bis(methylsalicyl)carbonate (CAS Registry No. 82091-12-1) (also known as BMSC or bis(o-methoxycarbonylphenyl)carbonate), bis(ethyl

salicyl)carbonate, bis(propyl salicyl) carbonate, bis(butylsalicyl) carbonate, bis(benzyl salicyl)carbonate, bis(methyl 4-chlorosalicyl)carbonate, and the like. In some embodiments, BMSC is used in the melt transesterification process.

[0032] The melt transesterification process is carried out by combining a catalyst, the carbonic acid diester of formula (IX), the phthalimidine compound of formula (I), and optionally a dihydroxy comonomer; and mixing the reaction mixture under reactive conditions for a time period effective to produce the polycarbonate product. Exemplary melt transesterification catalysts include alkali metal compounds, alkaline earth metal compounds, tetraorganoammonium compounds, tetraorganophosphonium compounds, and combinations comprising at least one of the foregoing catalysts. Specific examples of alkali metal compounds or alkaline earth metal compounds include, but are not limited to, sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate, potassium bicarbonate, sodium carbonate, potassium carbonate, lithium carbonate, sodium acetate, potassium acetate, sodium stearate, potassium stearate, sodium hydroxyborate, sodium phenoxyborate, sodium benzoate, potassium benzoate, lithium benzoate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, dilithium hydrogen phosphate, disodium salts, dipotassium salts, and dilithium salts of bisphenol A, and sodium salts, potassium salts, lithium salts of phenol, and the like. Specific examples of tetraorganoammonium compounds and tetraorganophosphonium compounds include, but are not limited to tetramethylammonium hydroxide, tetrabutylammonium hydroxide, tetraethylphosphonium hydroxide, tetrabutylphosphonium acetate, tetrabutylphosphonium hydroxide, and the like.

[0033] In some embodiments, the catalyst is tetrabutylphosphonium acetate. In an alternative embodiment, the catalyst comprises a mixture of an alkali metal salt or alkaline earth metal salt with at least one quaternary ammonium compound, at least one quaternary phosphonium compound, or a mixture thereof. For example, the catalyst can be a mixture of sodium hydroxide and tetrabutylphosphonium acetate. In another embodiment, the catalyst is a mixture of sodium hydroxide and tetramethylammonium hydroxide. In yet another embodiment, the catalyst comprises the salt of a non-volatile inorganic acid, for example alkali metal salts of phosphites; alkaline earth metal salts of phosphites; alkali metal salts of phosphates; and alkaline earth metal salts of phosphates, including but not limited to NaH_2PO_3, NaH_2PO_4, $Na_2H_2PO_3$, KH_2PO_4, CsH_2PO_4, $Cs_2H_2PO_4$, or a mixture thereof. In some embodiments, the transesterification catalyst comprises both the salt of a non-volatile

acid and a basic co-catalyst such as an alkali metal hydroxide. This concept is exemplified by the use of a combination of NaH_2PO_4 and sodium hydroxide as the transesterification catalyst.

[0034] Any of the catalysts disclosed above can be used as combinations of two or more substances. Moreover, the catalyst can be added in a variety of forms. For example, the catalyst can be added as a solid as a powder, or it can be dissolved in a solvent, for example, in water or alcohol. The total catalyst composition can be about 1 X 10^{-7}-about 2 X 10^{-3} moles, and in other embodiments, about 1 X 10^{-6}-about 4 X 10^{-4} moles, for each mole of the combination of, for example, the purified PPPBP and the aromatic dihydroxy comonomer.

[0035] The progress of the polymerization reaction can be monitored by measuring the melt viscosity or the weight average molecular weight of the reaction mixture using techniques known in the art such as gel permeation chromatography. These properties can be measured by taking discreet samples or can be measured on-line. After the desired melt viscosity or molecular weight is reached, the final polycarbonate product can be isolated from the reactor in a solid or molten form. The method of making polycarbonates as described in the preceding sections can be made in a batch or a continuous process.

[0036] In some embodiments, the melt-polymerized polycarbonate is prepared in an extruder in the presence of one or more catalysts. The reactants for the polymerization reaction can be fed to the extruder in powder or molten form. In some embodiments, the reactants are dry blended prior to addition to the extruder. The extruder can be equipped with pressure reducing devices (e.g., vents) that serve to remove the activated phenol byproduct and thus drive the polymerization reaction toward completion. The molecular weight of the polycarbonate product can be manipulated by controlling, among other factors, the feed rate of the reactants, the type of extruder, the extruder screw design, and configuration, the residence time in the extruder, the reaction temperature, and the pressure reducing techniques present on the extruder. The molecular weight of the polycarbonate product can also depend upon the structures of the reactants and the catalyst employed.

[0037] Alternatively, the polycarbonates can be prepared by an interfacial polymerization process. Although the reaction conditions for interfacial polymerization can vary, an exemplary process involves dissolving or dispersing a dihydric phenol reactant in aqueous caustic soda or potash, adding the resulting mixture to a water-immiscible solvent medium, and contacting the reactants with a carbonate precursor in the presence of a catalyst

such as triethylamine or a phase transfer catalyst, under controlled pH conditions, e.g., about 8-about 12. Exemplary water immiscible solvents include methylene chloride, 1,2-dichloroethane, chlorobenzene, toluene, and the like.

[0038] Exemplary carbonate precursors for interfacial polymerization include a carbonyl halide such as carbonyl bromide or carbonyl chloride, or a haloformate such as a bishaloformates of a dihydric phenol (e.g., the bischloroformates of bisphenol A, hydroquinone, or the like) or a glycol (e.g., the bishaloformate of ethylene glycol, neopentyl glycol, polyethylene glycol, or the like). Combinations comprising at least one of the foregoing types of carbonate precursors can also be used. In an exemplary embodiment, an interfacial polymerization reaction to form carbonate linkages uses phosgene as a carbonate precursor, and is referred to as a phosgenation reaction.

[0039] Among the phase transfer catalysts that can be used for interfacial polymerization are tetraorganoammonium compounds and tetraorganophosphonium compounds of the formula $(R_3)_4Q^+X$, wherein each R_3 is the same or different, and is a C_{1-10} alkyl group; Q is a nitrogen or phosphorus atom; and X is a halogen atom or a C_{1-8} alkoxy group or C_{6-18} aryloxy group. Exemplary phase transfer catalysts include, for example, $[CH_3(CH_2)_3]_4NX$, $[CH_3(CH_2)_3]_4PX$, $[CH_3(CH_2)_5]_4NX$, $[CH_3(CH_2)_6]_4NX$, $[CH_3(CH_2)_4]_4NX$, $CH_3[CH_3(CH_2)_3]_3NX$, and $CH_3[CH_3(CH_2)_2]_3NX$, wherein X is Cl^-, Br^-, a C_{1-8} alkoxy group or a C_{6-18} aryloxy group. An effective amount of a phase transfer catalyst can be about 0.1-about 10 wt% based on the weight of bisphenol in the phosgenation mixture. In another embodiment an effective amount of phase transfer catalyst can be about 0.5-about 2 wt% based on the weight of bisphenol in the phosgenation mixture.

[0040] All types of polycarbonate end groups are contemplated as being useful in the polycarbonate composition, provided that such end groups do not significantly adversely affect desired properties of the compositions. Branched polycarbonate blocks can be prepared by adding a branching agent during polymerization. A chain stopper (also referred to as a capping agent) can be included during polymerization. The chain stopper limits molecular weight growth rate, and so controls molecular weight in the polycarbonate. Exemplary chain stoppers include certain mono-phenolic compounds, mono-carboxylic acid chlorides, or mono-chloroformates.

[0041] The interfacial method described above can be suitably adapted to produce polycarbonates through the intermediate formation of 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine bischloroformate. This method is sometimes called the

bischloroformate polymerization method. In some embodiments, the method comprises reacting a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine with phosgene in an organic solvent, and then reacting the bischloroformate either with a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine, or an aromatic dihydroxy compound in the presence of an acid acceptor and an aqueous base to form the polycarbonate. The interfacial polymerization method and the bischloroformate polymerization method can be carried in a batch or a continuous mode using one or more reactor systems. To carry out the process in a continuous mode, one or more continuous reactors, such as for example, a tubular reactor can be used. In some embodiments, the continuous method comprises introducing into a tubular reactor system phosgene, at least one solvent (example, methylene chloride), at least one bisphenol, aqueous base, and optionally one or more catalysts (example, a trialkylamine) to form a flowing reaction mixture. The flowing mixture is then passed through the tubular reactor system until substantially all of the phosgene has been consumed. The resulting mixture is next treated with a mixture comprising an aqueous base, at least one endcapping agent, optionally one or more solvents, and at least one catalyst. The endcapped polycarbonate thus formed is continuously removed from the tubular reactor system.

[0042] The processes disclosed herein can advantageously be used to prepare, for example, PPPBP homopolycarbonate and copolycarbonates having a weight average molecular weight (Mw) of about 3,000- about 150,000 Daltons and a glass transition temperature (Tg) of about 80oC- about 300°C. The number average molecular weights (Mn) of the homopolycarbonate and copolycarbonates can be from about 1,500-about 75,000 Daltons.

[0043] Polymers comprising structural units derived from the phthalimidines, in particular PPPBP can be used to manufacture polymer blends comprising the polymer and at least one other thermoplastic polymer. The at least one other thermoplastic polymer includes vinyl polymers, acrylic polymers, polyacrylonitrile, polystyrenes, polyolefins, polyesters, polyurethanes, polyamides, polysulfones, polyimides, polyetherimides, polyphenylene ethers, polyphenylene sulfides, polyether ketones, polyether ether ketones, ABS polymers, polyethersulfones, poly(alkenylaromatic) polymers, polybutadiene, polyacetals, polycarbonates, polyphenylene ethers, ethylene-vinyl acetate copolymers, polyvinyl acetate, liquid crystal polymers, ethylene-tetrafluoroethylene copolymer, aromatic polyesters, polyvinyl fluoride, polyvinylidene fluoride, polyvinylidene chloride, tetrafluoroethylene, polycarbonate-polyorganosiloxane block copolymers, copolymers comprising aromatic ester,

estercarbonate, and carbonate repeat units, and combinations comprising at least one of the foregoing polymers.

[0044] The polymers and polymer blends described hereinabove are valuable for producing articles. In some embodiments, an article comprises a polymer comprising structural units derived from a 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine of formula (I) prepared by following the process described above.

[0045] Polymers, particularly polycarbonate homopolymers and copolymers comprising structural units derived from the high purity 2-aryl-3,3-bis(4-hydroxyaryl)phthalimidine in general, and PPPBP in particular exhibit lower visual coloration. As such, these polycarbonate polymers are useful for producing articles having a number of useful properties, including lower visual color, among others. The polycarbonate homopolymers and copolymers have high glass transition temperatures of higher than or equal to about 180°C. One of the unique properties of these polycarbonates, especially those that have glass transition temperatures of greater than or equal to about 180°C is that during melt processing they exhibit a shear-thinning behavior. That is, the polymers have the ability to flow under an applied shear. Therefore, standard melt processing equipment used for BPA polycarbonates can advantageously be used for producing articles. The polycarbonates also have high transparency, as measured by percent light transmission, of greater than or equal to about 85 percent.

[0046] In addition to the polymer, the thermoplastic compositions comprising the polymers can include various additives ordinarily incorporated into polymer compositions of this type, with the proviso that the additive(s) are selected so as to not significantly adversely affect the desired properties of the thermoplastic composition, in particular low color. Such additives can be mixed at a suitable time during the mixing of the components for forming the composition. The additive can be soluble or non-soluble in polycarbonate. The additive composition can include an impact modifier, flow modifier, filler (e.g., a particulate polytetrafluoroethylene (PTFE), glass, carbon, mineral, or metal), reinforcing agent (e.g., glass fibers), antioxidant, heat stabilizer, light stabilizer, ultraviolet (UV) light stabilizer, UV absorbing additive, plasticizer, lubricant, release agent (such as a mold release agent), antistatic agent, anti-fog agent, antimicrobial agent, colorant (e.g., a dye or pigment), surface effect additive, radiation stabilizer, flame retardant, anti-drip agent (e.g., a PTFE-encapsulated styrene-acrylonitrile copolymer (TSAN)), or a combination comprising at least one or more of the foregoing. For example, a combination of a heat stabilizer, mold release

agent, and ultraviolet light stabilizer can be used. In general, the additives are used in the amounts generally known to be effective. For example, the total amount of the additive composition (other than any impact modifier, filler, or reinforcing agent) can be 0.001-10.0 wt%, or 0.01-5 wt%, each based on the total weight of the polymer in the composition.

[0047] The methods described herein are further illustrated by the following non-limiting examples.

EXAMPLES

Example 1 (Comparative)

[0048] A reaction mixture containing PPPBP was obtained via reaction of aniline and phenolphthalein in the presence of hydrochloric acid, as described, for example, in US Patent 8,809,486. After the reaction mixture was cooled to 100°C, it was quenched with aqueous hydrochloric acid (150 milliliters (ml)) and water (300 ml). During quenching, PPPBP precipitated out of the reaction mixture. The reaction mixture was kept at 100°C for 1 hour (hr) and the resulting slurry was filtered and the solid was washed with 250 ml water. The resultant solid PPPBP (crude PPPBP) was dried at 100°C for 5 hrs and analyzed by high pressure liquid chromatography (HPLC) to obtain the amount of aminophenol impurity (AP), phenolphthalein (PP), and PPPBP in weight percent (wt%). Results are provided in Table 1. Dry wt. of crude PPPBP was 118.2 grams.

Table 1.

Analysis of Crude PPPBP	wt% by HPLC
Total Impurities	3.25
AP	0.51
PP	0.83
Purity of PPPBP	96.75

Example 2

[0049] The reaction procedure was similar to Example 1 to produce the PPPBP. The reaction mixture was cooled to 100°C and quenching was carried out with alkali solution (45 g of sodium hydroxide dissolved in 600 ml of water) instead of hydrochloric acid solution. Once the reaction mixture was clear, 100 ml of aniline was added and stirred for 30 minutes, and the mixture was allowed to settle. Two layers, an organic layer, and an aqueous (alkali) layer containing PPPBP separated out. The aqueous layer (designated as PPP-ANILINE-I)

was analyzed by HPLC to determine the wt% of AP, phenolphthalein (PP) and PPPBP. Results are provided in Table 2.

Table 2.

PPP-ANILINE-I	wt% by HPLC
Total Impurities	2.63
AP	0.42
PP	1.56
Purity of PPPBP	97.37

[0050] The same procedure of aniline extraction and separation was carried out four more times (designated as PPP-ANILINE-treatment II to V in Table 3). The composition of PPPBP after each aniline treatment and organic phase separation is provided in Table 3.

Table 3.

	wt% by HPLC			
Sample Name	AP	PP	PPPBP	Total impurity
PPP-ANILINE-treatment II	0.2364	1.50	97.84	2.16
PPP-ANILINE-treatment III	0.1729	2.65	96.62	3.38
PPP-ANILINE-treatment IV	0.0678	1.02	98.43	1.57
PPP-ANILINE-treatment V	0.0264	0.97	98.31	1.69

[0051] As can be seen from the results in Tables 2 and 3, a five stage extraction of a reaction mixture containing 0.51 wt% of AP (with respect to the amount of PPPBP) results in an AP concentration of 264 ppm by weight of AP in PPPBP.

[0052] To remove traces of aniline from the aqueous alkali layer after the above described extractions with aniline, the alkali solution was mixed with 100 ml of 1,2-dichloroethane (EDC). The aqueous alkali solution was then separated by decantation. The alkali solution was then treated with 10 wt% (by weight of PPPBP) charcoal to decolorize the solution for 1 hr. After that, the resulting solution was filtered to remove the charcoal. The alkaline mother liquor was neutralized with aqueous hydrochloric acid. During neutralization, PPPBP precipitated and was filtered to provide 120 grams of wet product. Product analysis at two stages is shown in Table 4.

Table 4.

	wt% by HPLC			
Sample Name	AP	PP	PPPBP	Total impurity
After EDC treatment	0.0186	0.85	98.74	1.26
After charcoal treatment	0.0012	1.20	98.56	1.44

[0053] As can be seen from Table 4, the AP concentration in PPPBP fell to 12 ppm by weight of PPPBP after only a single charcoal treatment step.

[0054] The PPPBP was further purified to remove the residual phenolphthalein from the solid crystals by trituration. Accordingly, 120 grams of wet cake and 300 ml of (90:10) methanol:water were charged to a round bottom of flask and heated to 60°C and maintained at that temperature for 1 hr. After that, the slurry was cooled to 10°C and maintained at that temperature for 1 hr. The slurry was filtered and washed with 200 ml of hot water. A white colored product was obtained and dried at 100°C for 9 hrs. An amount of 96.0 g of white dry product was obtained and analyzed by HPLC, to determine the amount of AP, PP, and PPPBP. Results are shown in Table 5.

Table 5.

	wt% by HPLC			
Sample Name	AP	PP	PPPBP	Total impurity
PPP-After trituration	0.0018	0.01	99.95	0.05

Example 3

[0055] In this example the order of extraction was reversed. First, the alkali mixture was treated 3 times with EDC as described above, followed by two treatments with aniline, as described above. Results are provided in Table 6.

Table 6.

Stage	Process monitoring by HPLC (wt%)			
	AP	PP	PPPBP	Total impurities
Alkali solution of reaction mixture	0.5861	0.6747	97.06	2.94
After 1st EDC treatment	0.5062	0.7066	97.55	2.45
After 2nd EDC treatment	0.4110	0.6281	97.68	2.32
After 3rd EDC treatment	0.2903	0.4910	97.88	2.12
After 1st Aniline extraction	0.1908	0.4007	98.44	1.56

After 2nd Aniline extraction	0.0941	0.2700	99.11	0.89

[0056] These results show that performing the aniline extraction first is more effective than performing the EDC treatment first for AP removal.

Example 4

[0057] A set of experiments was carried out using a series of EDC extractions without an aniline extraction. The starting AP composition was higher in the reaction mixture used for this example as compared to the previous examples. Results are provided in Table 7.

Table 7.

Stage	Process monitoring by HPLC (wt%)			
	AP	PP	PPPBP	Total impurities
Crude reaction mixture	0.6547	0.7147	95.96	4.04
After 1st EDC treatment	0.5873	0.6677	97.48	2.52
After 2nd EDC treatment	0.6153	0.5354	97.50	2.50
After 3rd EDC treatment	0.5153	0.6534	97.67	2.33
After 4th EDC treatment	0.5066	0.5839	97.82	2.18

[0058] The data indicates that extraction with EDC alone is not as effective for AP removal.

Example 5

[0059] The reaction procedure was similar to Example 1 to produce the PPPBP. The extraction of AP was conducted in a continuous manner using a liquid-liquid extraction column with 4 inch diameter. The column was packed with structured Shear Metal V-shaped Packing (SMVP) packing and had 5 stages. The SMVP packing was provided by Koch-Glitsch. In the operation the aqueous phase was continuous and aniline was used as a dispersed phase. The aqueous phase flow rate was 73 kilograms per hour (kg/hr). The column was run with 4 different aniline phase flow rates, 62 kg/hr, 47 kg/hr, 37.5 kg/hr and 25.5 kg/hr, varying the oil to aqueous ratio (O/A ratio) from 0.85 to 0.35. The column operating temperature was approximately 35-40°C.

[0060] The samples of aqueous phase were collected at each stage and analyzed for AP composition, after precipitating the crude product using acid. Table 8 shows the AP concentration at different stages of an extraction column at two O/A ratios. It was found that

under the operating conditions used, three stages were sufficient to remove the AP to a level of < 400 ppm (solid basis). Table 9 shows the effect of O/A ratio on amount of AP present in the aqueous phase outlet.

Table 8.

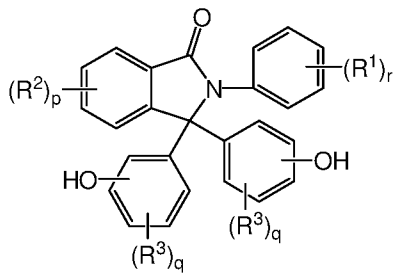
Section No. from Bottom	AP composition, ppm	
	O/A ratio 0.35	O/A ratio 0.5
1	319	255
2	356	212
3	395	332
4	1066	527
5	1870	1034

Table 9.

O/A ratio	AP composition, ppm
0.35	164
0.52	169
0.65	218
0.83	245

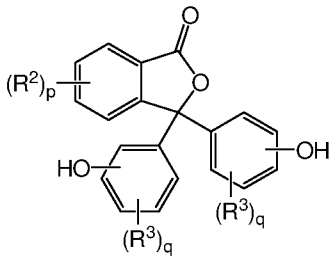
[0061] The methods and polymers are further illustrated by the following embodiments, which are non-limiting.

[0062] Embodiment 1: A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I)



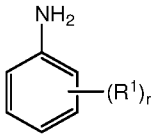
(I)

the method comprising heating a reaction mixture comprising a phenolphthalein compound of formula (II)



(II)

and a primary arylamine of formula (III)



(III) in the presence of an acid catalyst to form a reaction mixture comprising a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I); quenching the reaction mixture with an aqueous alkali solution to form a quenched reaction mixture; extracting the quenched reaction mixture with an aminoaryl compound of formula (IV) $(R^4)(R^5)N\text{-}Ar(R^6)_s$ (IV) to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I), wherein in formulas (I), (II), (III), and (IV) each occurrence of R^1 is independently a phenyl or a C_{1-25} hydrocarbyl, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, each R^4 and R^5 is independently a hydrogen or C_{1-25} hydrocarbyl, Ar is a C_{6-12} aromatic ring optionally comprising up to three heteroatoms in the ring, each R^6 is independently a halogen, nitro, cyano, or C_{1-25} hydrocarbyl, and r, p, q, and s are each independently 0 to 4.

[0063] Embodiment 2: The method of Embodiment 1, wherein in formulas (I), (II), (III), and (IV) each occurrence of R^1 is independently a phenyl or a C_{1-6} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-6} alkyl, each R^4 and R^5 is independently a hydrogen or C_{1-6} alkyl, Ar is a C_6 or a C_{12} aromatic ring, each R^6 is independently a C_{1-6} alkyl, and r, p, q, and s are each independently 0 or 1.

[0064] Embodiment 3: The method of Embodiment 1 or 2, wherein in formulas (I), (II), (III), and (IV) each occurrence of R^1 is independently a C_{1-3} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-3} alkyl, each R^4 and R^5 is independently a hydrogen or C_{1-6} alkyl, Ar is a C_6 or a C_{12} aromatic ring, each R^6 is independently a C_{1-6} alkyl, r, p, q, and s are each independently 0 or 1.

[0065] Embodiment 4: The method of any one or more of Embodiments 1 to 3, wherein in formulas (I), (II), (III), and (IV) each occurrence of R^2 and R^3 is independently a C_{1-3} alkyl, each R^4 and R^5 is independently a hydrogen, each R^6 is independently a C_{1-3} alkyl, r, p, q, and s are each independently 0.

[0066] Embodiment 5: The method of any one or more of Embodiments 1 to 4, further comprising repeating the extracting with the aminoaryl compound.

[0067] Embodiment 6: The method of any one or more of Embodiments 1 to 5, wherein the heating, quenching, and extracting is a continuous process.

[0068] Embodiment 7: The method of any one or more of Embodiments 1 to 6, further comprising treating the extracted aqueous layer with charcoal.

[0069] Embodiment 8: The method of any one or more of Embodiments 1 to 7, further comprising extracting the extracted aqueous layer with 1,2-dichloroethane to remove aniline.

[0070] Embodiment 9: The method of any one or more of Embodiments 1 to 8, further comprising precipitating the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) from the extracted aqueous layer.

[0071] Embodiment 10: The method of any one or more of Embodiments 1 to 9, wherein the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 500-8000 parts per million of an aminophenol.

[0072] Embodiment 11: The method of any one or more of Embodiments 1 to 10, wherein the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 800-6000 parts per million of an aminophenol.

[0073] Embodiment 12: The method of any one or more of Embodiments 1 to 11, wherein the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 1000-6000 parts per million of an aminophenol.

[0074] Embodiment 13: The method of any one or more of Embodiments 1 to 12, wherein the primary arylamine is aniline.

[0075] Embodiment 14: The method of any one or more of Embodiments 1 to 13, wherein the acid catalyst is a mineral acid.

[0076] Embodiment 15: The method of any one or more of Embodiments 1 to 14, wherein the acid catalyst is hydrochloric acid.

[0077] Embodiment 16: The method of any one or more of Embodiments 1 to 15, wherein the acid catalyst is present at a concentration of 0.5-1.5 molar equivalents of the phenolphthalein compound of formula (II).

[0078] Embodiment 17: The method of any one or more of Embodiments 1 to 16, wherein the aqueous alkali solution is present at a concentration of 1.5-3.0 molar equivalents of the phenolphthalein compound of formula (II).

[0079] Embodiment 18: The method of any one or more of Embodiments 1 to 17, wherein the aminoaryl compound of formula (IV) has the same structure as the primary arylamine of formula (III).

[0080] Embodiment 19: The method of any one or more of Embodiments 1 to 18, wherein the aminoaryl compound of formula (IV) is aniline and the primary arylamine of formula (III) is aniline.

[0081] Embodiment 20: The method of any one or more of Embodiments 1 to 19, wherein the heating is from 135-180°C.

[0082] Embodiment 21: The method of any one or more of Embodiments 1 to 20, wherein the heating is from 155-175°C.

[0083] Embodiment 22: The method of any one or more of Embodiments 1 to 21, wherein the heating is for 5-20 hours.

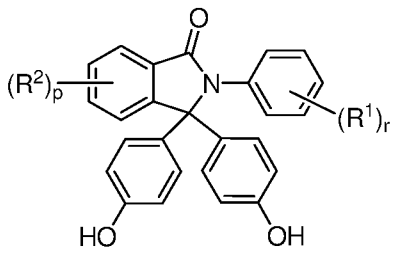
[0084] Embodiment 23: The method of any one or more of Embodiments 1 to 22, wherein the heating is for 8-15 hours.

[0085] Embodiment 24: The method of any one or more of Embodiments 1 to 23, wherein the aqueous alkali solution comprises an aqueous solution of an alkali metal hydroxide or an alkaline earth metal hydroxide.

[0086] Embodiment 25: The method of any one or more of Embodiments 1 to 24, wherein the aqueous alkali solution comprises sodium hydroxide.

[0087] Embodiment 26: The method of any one or more of Embodiments 1 to 25, comprising combining the acid catalyst and the primary arylamine in an optional solvent to form an initial composition; removing water from the initial composition to provide a reduced water composition; and adding the phenolphthalein compound of formula (II) to the reduced water composition to provide the reaction mixture.

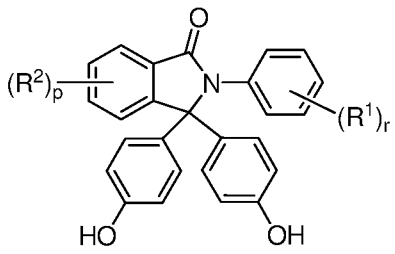
[0088] Embodiment 27: The method of any one or more of Embodiments 1 to 26, wherein the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) is of formula (IA)



(IA)

wherein R^1 is a C_{1-3} alkyl, R^2 is a C_{1-3} alkyl or a halogen, p is 0 or 1, and r is 0 or 1.

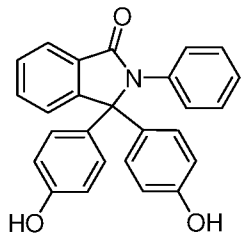
[0089] Embodiment 28: The method of any one or more of Embodiments 1 to 27, wherein the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) is of formula (IA)



(IA)

wherein each of p and r is zero, and the phthalimidine of formula (I) is 2-phenyl-3,3-bis(4-hydroxyphenyl)-2-phthalimidine.

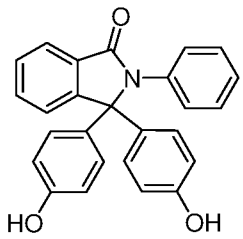
[0090] Embodiment 29: The method of any one or more of Embodiments 1 to 28, wherein each of q, p and r is zero, and the phthalimidine of formula (I) is 2-phenyl-3,3-bis(4-hydroxyphenyl)-2-phthalimidine of formula (IB)



(IB).

[0091] Embodiment 30: The method of any one or more of Embodiments 1 to 29, wherein the acid catalyst is hydrochloric acid, the primary arylamine is aniline, the phenolphthalein compound is phenolphthalein, and the aminoaryl compound is aniline.

[0092] Embodiment 31: A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (IB)



(IB), the method comprising heating a reaction mixture comprising phenolphthalein and aniline in the presence of hydrochloric acid from 135-180°C for 5-20 hours to form a reaction mixture comprising a 2-aryl-3,3 bis(hydroxyaryl)phthalimidine of formula (IB); quenching the reaction mixture with an aqueous sodium hydroxide solution to form a quenched reaction mixture; extracting the

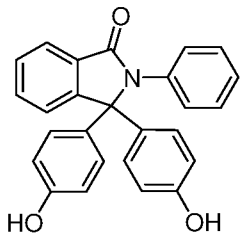
quenched reaction mixture with aniline to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (IB).

[0093] Embodiment 32: The method of Embodiment 31, further comprising repeating the extracting with aniline.

[0094] Embodiment 33: The method of Embodiments 31 or 32, wherein the heating, quenching, and extracting is a continuous process.

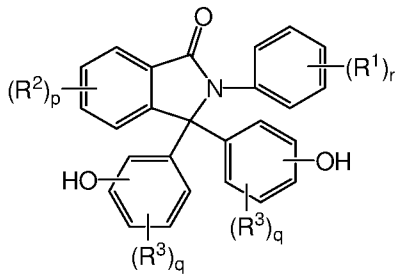
[0095] Embodiment 34: The method of any one or more of Embodiments 31 to 33, further comprising treating the extracted aqueous layer with charcoal, extracting the extracted aqueous layer with 1,2-dichloroethane to remove aniline, precipitating the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (IB) from the extracted aqueous layer, or a combination comprising one or more of the foregoing.

[0096] Embodiment 35: A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (IB)



(IB), the method comprising combining hydrochloric acid and aniline in an optional solvent to form an initial composition; removing water from the initial composition to provide a reduced water composition; and adding phenolphthalein to the reduced water composition to provide a reaction mixture, heating the reaction mixture comprising phenolphthalein and aniline in the presence of hydrochloric acid from 135-180°C for 5-20 hours to form a reaction mixture comprising a 2-aryl-3,3 bis(hydroxyaryl)phthalimidine of formula (IB). quenching the reaction mixture with an aqueous sodium hydroxide solution to form a quenched reaction mixture, extracting the quenched reaction mixture with aniline to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (IB).

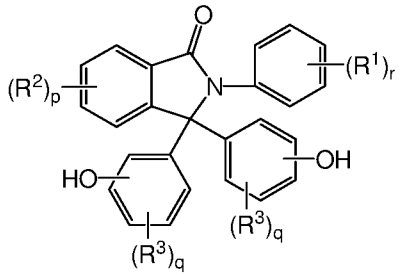
[0097] Embodiment 36: A 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising a phthalimidine of formula (I)



(I),

wherein each occurrence of R^1 is independently a phenyl or C_{1-25} hydrocarbyl, each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, and r, p, and q are each independently 0 to 4; zero-1000 parts per million of an aminophenol.

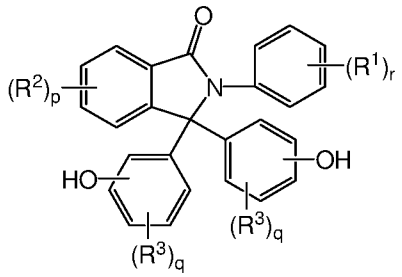
[0098] Embodiment 37: A 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising a phthalimidine of formula (I)



(I),

wherein each occurrence of R^1 is independently a C_{1-6} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-6} alkyl, and r, p, and q are each independently 0 or 1; zero-500 parts per million of an aminophenol.

[0099] Embodiment 38: A 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising a phthalimidine of formula (I)



(I),

wherein each occurrence of R^1 is independently a C_{1-3} alkyl, each occurrence of R^2 and R^3 is independently a C_{1-3} alkyl, and r, p, and q are each independently 0; zero-50 parts per million of an aminophenol.

[00100] Embodiment 39: A method for the manufacture of a polycarbonate, comprising manufacturing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in

accordance with any one or more of Embodiments 1 to 37; and polymerizing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in the presence of a carbonate source.

[00101] The term "hydrocarbyl" is defined herein as a monovalent moiety formed by removing a hydrogen atom from a hydrocarbon. Representative hydrocarbyls are alkyl groups having 1 to 25 carbon atoms, such as, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, undecyl, decyl, dodecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, and the isomeric forms thereof; aryl groups having 6 to 25 carbon atoms, such as ring-substituted and ring-unsubstituted forms of phenyl, tolyl, xylyl, naphthyl, biphenyl, tetraphenyl, and the like; arylalkyl groups having 7 to 25 carbon atoms, such as ring-substituted and ring-unsubstituted forms of benzyl, phenethyl, phenpropyl, phenbutyl, naphthoctyl, and the like; and cycloalkyl groups, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and the like. The term "aryl" as used herein refers to various forms of aryl groups that have been described hereinabove for the "hydrocarbyl" group. "Alkyl" refers to a straight or branched chain, saturated monovalent hydrocarbon group. Unless otherwise indicated, each of the foregoing groups can be unsubstituted or substituted, provided that the substitution does not significantly adversely affect synthesis, stability, or use of the compound. The term "substituted" as used herein means that at least one hydrogen on the designated atom or group is replaced with another group, provided that the designated atom's normal valence is not exceeded. When the substituent is oxo (i.e., =O), then two hydrogens on the atom are replaced. Combinations of substituents and/or variables are permissible provided that the substitutions do not significantly adversely affect synthesis or use of the compound. Exemplary groups that can be present on a "substituted" position include, but are not limited to, cyano; hydroxyl; nitro; azido; alkanoyl (such as a C_{2-6} alkanoyl group such as acyl); carboxamido; C_{1-6} or C_{1-3} alkyl, cycloalkyl, alkenyl, and alkynyl (including groups having at least one unsaturated linkages and from 2 to 8, or 2 to 6 carbon atoms); C_{1-6} or C_{1-3} alkoxys; C_{6-10} aryloxy such as phenoxy; C_{1-6} alkylthio; C_{1-6} or C_{1-3} alkylsulfinyl; C_{1-6} or C_{1-3} alkylsulfonyl; aminodi(C_{1-6} or C_{1-3})alkyl; C_{6-12} aryl having at least one aromatic rings (e.g., phenyl, biphenyl, naphthyl, or the like, each ring either substituted or unsubstituted aromatic); C_{7-19} arylalkyl having 1 to 3 separate or fused rings and from 6 to 18 ring carbon atoms; or arylalkoxy having 1 to 3 separate or fused rings and from 6 to 18 ring carbon atoms, with benzyloxy being an exemplary arylalkoxy.

[00102] The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. "Or" means "and/or." The modifier "about" used in

connection with a quantity is inclusive 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).

[00103] The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of "less than or equal to 25 wt%, or 5 wt% to 20 wt%," is inclusive of the endpoints and all intermediate values of the ranges of "5 wt% to 25 wt%," etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. The suffix "(s)" is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). "Optional" or "optionally" means that the subsequently described event or circumstance can or can not occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

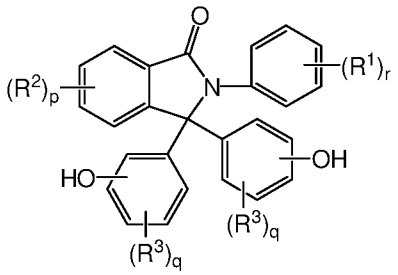
[00104] All publications, patents, and patent applications cited in this specification are herein incorporated by reference, and for any and all purposes, as if each individual publication, patent or patent application were specifically and individually indicated to be incorporated by reference. In the case of inconsistencies, the present disclosure will prevail

[00105] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

CLAIMS

What is claimed is:

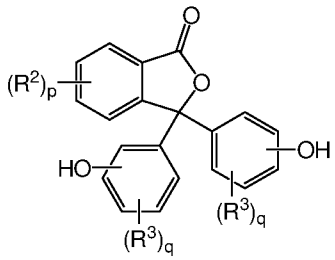
1. A method for the purification of a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I)



(I)

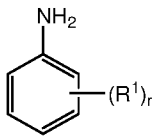
the method comprising

heating a reaction mixture comprising a phenolphthalein compound of formula (II)



(II)

and a primary arylamine of formula (III)



(III)

in the presence of an acid catalyst to form a reaction mixture comprising a 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I);

quenching the reaction mixture with an aqueous alkali solution to form a quenched reaction mixture;

extracting the quenched reaction mixture with an aminoaryl compound of formula (IV)

$$(R^4)(R^5)N\text{-}Ar(R^6)_s$$

to form an organic layer and an extracted aqueous layer comprising a crude 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I),

wherein in formulas (I), (II), (III), and (IV)

each occurrence of R^1 is independently a phenyl or a C_{1-25} hydrocarbyl, preferably a phenyl or a C_{1-6} alkyl, more preferably a C_{1-3} alkyl,

each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl,

each R^4 and R^5 is independently a hydrogen or C_{1-25} hydrocarbyl, preferably a hydrogen or C_{1-6} alkyl, more preferably a hydrogen,

Ar is a C_{6-12} aromatic ring optionally comprising up to three heteroatoms in the ring, preferably a C_6 or a C_{12} aromatic ring,

each R^6 is independently a halogen, nitro, cyano, or C_{1-25} hydrocarbyl, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, and

r, p, q, and s are each independently 0 to 4, more preferably 0 or 1, preferably 0.

2. The method of claim 1, further comprising repeating the extracting with the aminoaryl compound.

3. The method of claim 1 or 2, wherein the heating, quenching, and extracting is a continuous process.

4. The method of any one or more of the preceding claims, further comprising treating the extracted aqueous layer with charcoal.

5. The method of any one or more of the preceding claims, further comprising extracting the extracted aqueous layer with an organic solvent, preferably 1,2-dichloroethane to remove aniline.

6. The method of any one or more of the preceding claims, further comprising precipitating the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) from the extracted aqueous layer.

7. The method of claim 6, wherein the precipitated 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) comprises 500-8000 parts per million, preferably 800-6000 parts per million, more preferably 1000-6000 parts per million of an aminophenol.

8. The method of any one or more of the preceding claims, wherein the primary arylamine is aniline.

9. The method of any one or more of the preceding claims, wherein the acid catalyst is a mineral acid, preferably hydrochloric acid.

10. The method of any one or more of the preceding claims, wherein the acid catalyst is present at a concentration of 0.5-1.5 molar equivalents of the phenolphthalein compound of formula (II).

11. The method of any one or more of the preceding claims, wherein the aqueous alkali solution is present at a concentration of 1.5-3.0 molar equivalents of the phenolphthalein compound of formula (II).

12. The method of any one or more of the preceding claims, wherein the aminoaryl compound of formula (IV) has the same structure as the primary arylamine of formula (III), preferably wherein the aminoaryl compound of formula (IV) is aniline.

13. The method of any one or more of the preceding claims, wherein the heating is from 135-180°C, preferably from 155-175°C.

14. The method of any one or more of the preceding claims, wherein the heating is for 5-20 hours, preferably 8-15 hours.

15. The method of any one or more of the preceding claims, wherein the aqueous alkali solution comprises an aqueous solution of an alkali metal hydroxide or an alkaline earth metal hydroxide, preferably sodium hydroxide.

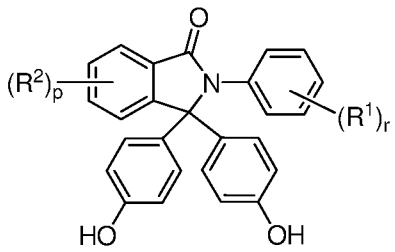
16. The method of one or more of the preceding claims, comprising

combining the acid catalyst and the primary arylamine in an optional solvent to form an initial composition;

removing water from the initial composition to provide a reduced water composition; and

adding the phenolphthalein compound of formula (II) to the reduced water composition to provide the reaction mixture.

17. The method of any one or more of the preceding claims, wherein the 2-aryl-3,3-bis(hydroxyaryl)phthalimidine of formula (I) is of formula (IA)



(IA)

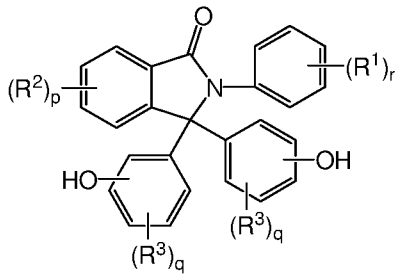
wherein R^1 is a C_{1-3} alkyl, R^2 is a C_{1-3} alkyl or a halogen, p is 0 or 1, and r is 0 or 1;

preferably wherein each of p and r is zero, and the phthalimidine of formula (I) is 2-phenyl-3,3-bis(4-hydroxyphenyl)-2-phthalimidine.

18. The method of any one or more of the preceding claims, wherein the acid catalyst is hydrochloric acid, the primary arylamine is aniline, the phenolphthalein compound is phenolphthalein, and the aminoaryl compound is aniline.

19. A 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine composition, comprising

a phthalimidine of formula (I)



(I),

wherein

each occurrence of R^1 is independently a phenyl or C_{1-25} hydrocarbyl, preferably a phenyl or a C_{1-6} alkyl, more preferably a C_{1-3} alkyl,

each occurrence of R^2 and R^3 is independently a C_{1-25} hydrocarbyl or halogen, preferably a C_{1-6} alkyl, more preferably a C_{1-3} alkyl, and

r, p, and q are each independently 0 to 4, more preferably 0 or 1, preferably 0;

zero-1000 parts per million of an aminophenol, preferably zero-500, more preferably from zero-50 parts per million of an aminophenol.

20. A method for the manufacture of a polycarbonate, comprising

manufacturing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in accordance with any one or more of claims 1 to 18; and

polymerizing the 2-aryl-3,3-bis(4-hydroxyaryl) phthalimidine of formula (I) in the presence of a carbonate source.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054156

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D209/46 C08G64/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/121150 A1 (GEN ELECTRIC [US]; BASALE RAJSHEKHAR [IN]; BASTIAN HYACINTH MARY [IN];) 9 October 2008 (2008-10-09) examples 3-4	1-20
X	WO 2015/162564 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 29 October 2015 (2015-10-29) pages 27-35	19
X	WO 2006/012162 A2 (GEN ELECTRIC [US]; RAI VINOD KUMAR [IN]; ARAKALI RADHAKRISHNA SRINIVAS) 2 February 2006 (2006-02-02)	19
Y	page 8, paragraph 2	1-20
X	US 2010/152416 A1 (BHOTLA VENKATA RAMA NARAYANAN GANAPATHY [IN] ET AL) 17 June 2010 (2010-06-17)	19
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☐ Further documents are listed in the continuation of Box C.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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