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Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

- (54) **Title: IRON-CATALYZED OXIDATIVE POLYMERIZATION OF PHENOLS**

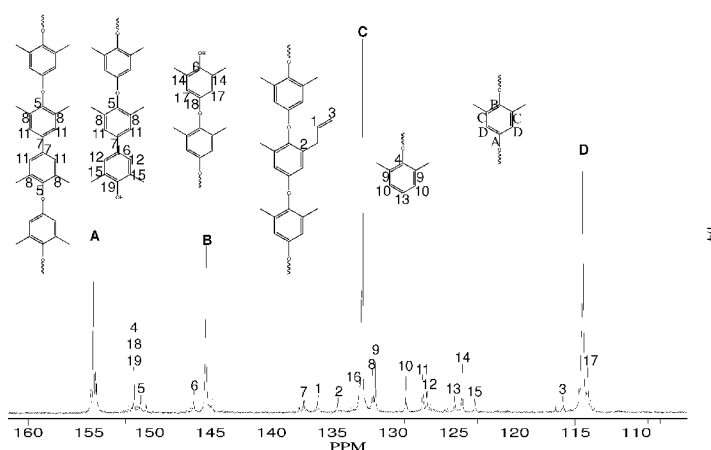


Fig. 1

- (57) **Abstract:** An improved method for making a poly(phenylene ether) polymer comprises oxidative polymerization of at least one phenol of the general structure described herein, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst. The method is applicable to phenols that include 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof. The iron complex can be Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof, and the liquid oxidant can be aqueous hydrogen peroxide. A poly(phenylene ether) made by the method is also disclosed.

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IRON-CATALYZED OXIDATIVE POLYMERIZATION OF PHENOLS

BACKGROUND OF THE INVENTION

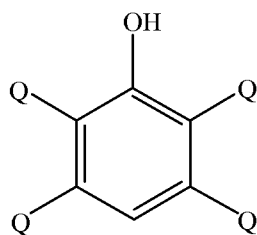
[0001] Poly(phenylene ether)s are a class of plastics known for excellent water resistance, dimensional stability, and inherent flame retardancy, as well as high oxygen permeability and oxygen/nitrogen selectivity. Properties such as strength, stiffness, chemical resistance, and heat resistance can be tailored by blending poly(phenylene ether)s with various other plastics in order to meet the requirements of a wide variety of consumer products, for example, plumbing fixtures, electrical boxes, automotive parts, and insulation for wire and cable. Improved properties useful for certain applications can be obtained with poly(phenylene ether) copolymers.

[0002] Poly(phenylene ether)s can be produced by oxidative polymerization of certain phenols in the presence of a metal catalyst. A catalyst comprising copper(I) and one or more aliphatic amine ligands, and molecular oxygen can be used. However, a liquid oxidant, which has the potential to provide enhanced contact between the phenolic monomers and liquid oxidant compared to molecular oxygen, can potentially increase polymerization rates and increase selectivity for the polymer. Liquid oxidants can be used with other metal catalysts as well. For example, a combination of iron complex, amine, and liquid oxidant can be used for the oxidative polymerization of 2,6-dimethylphenol (DMP) to form poly(2,6-dimethyl-1,4-phenylene ether).

[0003] If the phenol monomer(s) is liquid at the polymerization temperature, the polymerization can be conducted in the absence of added solvent. However, the poly(phenylene ether) will precipitate from the monomer and form a viscous slurry that is difficult to agitate and exhibits poor heat transfer. The polymerization can also be conducted in a polar solvent comprising oxygen and/or nitrogen atoms, for example 1,4-dioxane or acetonitrile. Depending on the oxidant used, a polar solvent can provide a single-phase polymerization mixture of phenol, catalyst, and oxidant. However, the poly(phenylene ether) can still precipitate as it is formed. Moreover, since many polar solvents are at least partially water-miscible, it can be problematic to do aqueous extractions of these polymerization mixtures to remove catalyst residues. Thus, from the standpoint of polymerization rate, heat transfer, and mass transfer, what is needed is a metal-catalyzed oxidative polymerization method that utilizes both a liquid oxidant and a non-polar solvent for the poly(phenylene ether) formed.

BRIEF DESCRIPTION OF THE INVENTION

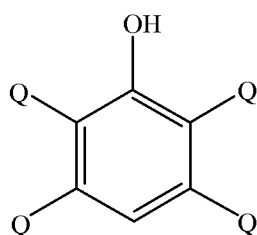
[0004] An improved method for making a poly(phenylene ether) polymer comprises oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst.

[0005] In some embodiments, a method of making a poly(phenylene ether) comprises oxidative polymerization of at least one phenol comprising 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof, in the presence of aqueous hydrogen peroxide, an iron complex comprising Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof, pyridine, a quaternary ammonium salt, and toluene, in the absence of added water other than any water present in the liquid oxidant or phase transfer catalyst.

[0006] Another embodiment is a poly(phenylene ether) made by a method comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid

oxidant and phase transfer catalyst; wherein the poly(phenylene ether) comprises 0.1 to 1,000 parts per million of iron.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Referring now to the drawings:

[0008] Fig. 1 depicts the 100 Mhz ^{13}C -NMR spectrum of the 90/10 wt/wt DMP/AMP copolymer of Example 1a, described in Example 17. Peaks are assigned to specific carbon atoms in monomer repeat units and end groups.

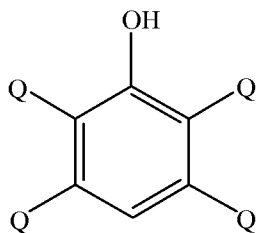
[0009] Fig. 2 depicts the 100 Mhz ^{13}C -NMR spectrum of the 80/10/10 wt/wt DMP/AMP/DPP copolymer of Example 3, described in Example 18. Peaks are assigned to specific carbon atoms in monomer repeat units and end groups.

[0010] Fig. 3 depicts the 100 Mhz ^{13}C -NMR spectrum of the 80/20 wt/wt DMP/MPP copolymer of Example 4, described in Example 19. Peaks are assigned to specific carbon atoms in monomer repeat units and end groups.

[0011] Fig. 4 depicts the 100 Mhz ^{13}C -NMR spectrum of the TMP homopolymer of Example 6, described in Example 20. Peaks are assigned to specific carbon atoms in monomer repeat units and end groups.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present inventors have determined a metal-catalyzed oxidative polymerization method for preparing a poly(phenylene ether) that utilizes both a liquid oxidant and a good solvent for the poly(phenylene ether) formed. The method provides good polymerization rate, heat transfer, and mass transfer. The method of making a poly(phenylene ether) comprises oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted $\text{C}_1\text{-C}_{12}$ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, $\text{C}_1\text{-C}_{12}$ hydrocarbylthio, $\text{C}_1\text{-C}_{12}$ hydrocarbyloxy, or $\text{C}_2\text{-C}_{12}$ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid

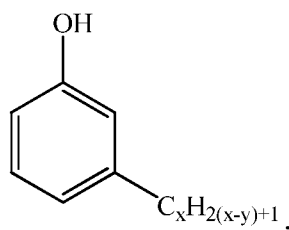
oxidant and phase transfer catalyst.

[0013] As used herein, the term “hydrocarbyl”, whether used by itself, or as a prefix, suffix, or fragment of another term, refers to a residue that contains only carbon and hydrogen. The residue can be aliphatic or aromatic, straight-chain, cyclic, bicyclic, branched, saturated, or unsaturated. It can also be a combination of aliphatic, aromatic, straight chain, cyclic, bicyclic, branched, saturated, and unsaturated hydrocarbon moieties. However, when the hydrocarbyl residue is specifically described as substituted, it can contain heteroatoms other than the carbon and hydrogen members of the substituent residue. Thus, when described as substituted, the hydrocarbyl residue contains one or more heteroatoms such as a halogen, oxygen, nitrogen, sulfur, phosphorus, or silicon. For example, when described as substituted, the hydrocarbyl residue can also contain one or more carbonyl groups, amino groups, alkoxy groups, or the like, or it can contain heteroatoms within the backbone of the hydrocarbyl residue.

[0014] Phenols wherein Q is hydrogen, methyl, allyl, or phenyl can be used. For example, the 2,6-disubstituted phenol can comprise, 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof. In some embodiments, the 2,6-disubstituted phenol comprises 2,6-dimethylphenol.

[0015] The poly(phenylene ether) can be a homopolymer or copolymer. For example, the poly(phenylene ether) can comprise poly(2,6-dimethyl-1,4-phenylene ether), poly(2,4,6-trimethyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2-allyl-6-methyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-methyl-6-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*o*-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*o*-phenyl-1,4-phenylene ether), or poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene-*co*-*m*-phenyl-1,4-phenylene ether). In some embodiments, the poly(phenylene ether) comprises poly(2,6-dimethyl-1,4-phenylene ether).

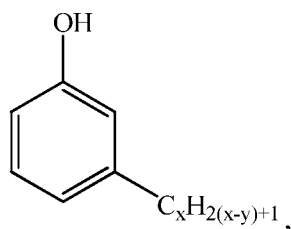
[0016] The method can be used to polymerize phenolic vegetable oils. For example, the method can be used when the first phenol comprises a phenol having the structure:



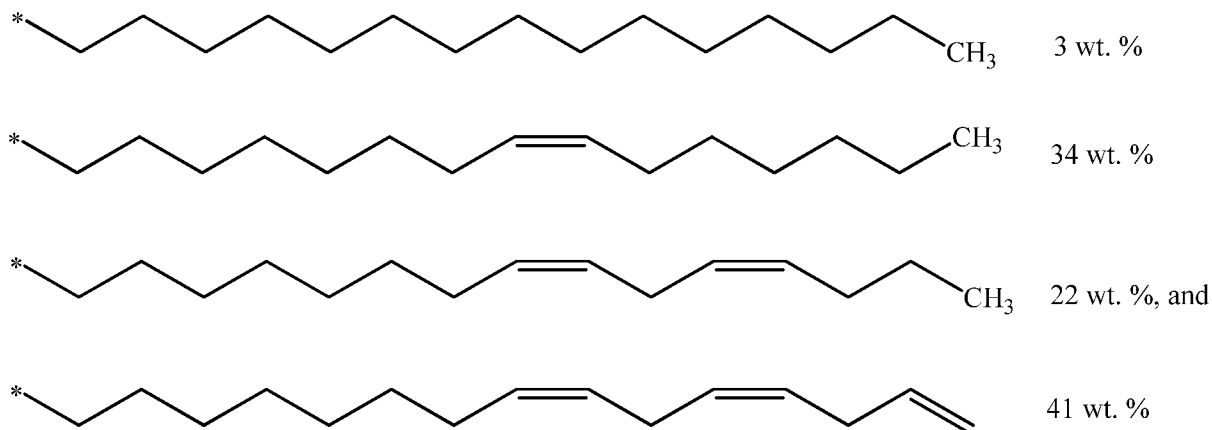
wherein x is an integer from 12 to 24 and y is an integer from 0 to 7. The variable x can be an integer greater than or equal to 13 or 14, and less than or equal to 24, 22, 20, 18, or 16. In some embodiments, x is an integer from 12 to 18, specifically 14 to 16. The variable y can be an integer greater than or equal to 0, and less than or equal to 7, 6, 5, or 4, wherein y represents the number of double bonds in the alkyl chain. In some embodiments, x is an integer from 14 to 16, and y is an integer from 0 to 4, specifically 0 to 3, and more specifically 1 to 3.

[0017] The phenolic vegetable oil can comprise unsaturated or polyunsaturated alkyl chains. For example, in the foregoing structure, y represents the number of double bonds in the alkyl chain. In some embodiments, y is an integer greater than or equal to 1, specifically 1 to 7, and more specifically 1 to 3, wherein the alkyl chains are unsaturated. A saturated phenolic vegetable oil can be obtained by selective catalytic hydrogenation of the corresponding unsaturated or polyunsaturated phenolic vegetable oil in which the unsaturated or polyunsaturated alkyl chain is reduced to a saturated alkyl chain, but the aromatic group is not affected.

[0018] The at least one phenol can be cardanol. Cardanol is the main component obtained by thermal treatment of cashew nutshell liquid (CNSL). Cardanol is a mixture of phenols having the structure:



wherein x is 15 and y is 0, 1, 2, and 3. In particular, cardanol is a mixture of phenols wherein the $-C_xH_{2(x-y)+1}$ radical has the following structures. The amounts of each phenol, based on the total weight of cardanol, are provided next to each structure:



[0019] The method is not limited to phenolic vegetable oils. In some embodiments, the at least one phenol is not a phenolic vegetable oil, and in particular, not an ethylenically unsaturated phenolic vegetable oil.

[0020] The polymerization can be catalyzed by an iron complex, which is a coordination compound comprising an iron atom and a ligand bonded to the iron atom by a coordinate bond. The atom participating directly in the coordinate bond to the iron is an electron-pair donor. The electron-pair donor can be, for example, nitrogen, oxygen, phosphorus, or combination thereof. The ligand can be a monodentate ligand, a bidentate ligand, a tridentate ligand, a quadridentate ligand, or a quinquedentate ligand, in which the number of electron-donor atoms that can form coordinate bonds to iron is 1, 2, 3, 4, or 5, respectively.

[0021] When the metal complex comprising iron and a ligand carries a positive charge, for example when the iron is in the (III) oxidation state, the iron complex can also comprise a negatively charged counterion to provide a net charge of zero. A conjugated base of a Brønsted acid can be used, for example fluoride, chloride, bromide, iodide, sulfate, nitrate, carbonate, perchlorate, tetrafluoroborate, hexafluorophosphate, methanesulfonate, trifluoromethanesulfonate, toluenesulfonate, acetate, trifluoroacetate, propionate, benzoate, hydroxide, methoxide, ethoxide, oxide, or combination thereof. The iron complex can also be coordinated with a solvent that is an electron-pair donor, for example water, an amine, or an ether. The solvent-coordinated iron complex can be formed in the process of making the iron complex, or it can form in situ during the polymerization.

[0022] In some embodiments, the ligand coordinated to the iron atom in the iron complex comprises a quadridentate ligand. Examples of quadridentate ligands include tris(2-pyridyl methyl)amine, tris(2-imidazolyl methyl)amine, tris(1-methyl-2-imidazolyl methyl)amine, tris(2-benzimidazolyl methyl)amine, tris(2-benzoxazolyl methyl)amine, tris(2-benzthiazolyl methyl)amine, tris(1-pyrazolyl methyl)amine, tris(3,5-dimethyl-1-pyrazolyl methyl)amine, tris(3,5-dipropyl-1-pyrazolyl methyl)amine, tris(3,5-diphenyl-1-pyrazolyl methyl)amine, nitrilotriacetic acid, nitrilotriethanol, nitrilotri-1-propanol, tris(2-pyridyl-2-ethyl)amine, tris(1-pyrazolyl-2-ethyl)amine, N-(2-mercaptoethyl)-N,N-diethanol amine, N-(diphenyl phosphinoethyl)-N,N-diethanol amine, triethylene glycol, tripropylene glycol, triethylene tetramine, N,N''-dimethyl triethylene tetramine, N,N,N''',N'''-tetramethyl triethylene tetramine, N,N'-bis(2-hydroxyethyl)ethylene diamine, N,N'-bis(3-hydroxypropyl)ethylene diamine, N,N'-ethylene diamine diacetic acid, N,N'-bis(2-pyridyl methyl)ethylene diamine, N,N'-bis(2-imidazolyl methyl)ethylene diamine, N,N'-bis(2-benzimidazolyl methyl)ethylene diamine, N,N'-bis(2-mercaptoethyl)ethylene diamine, N,N'-bis(diphenyl phosphinoethyl)ethylene diamine,

N,N'-disalicylidene ethylene diamine, N,N'-bis(1-methyl-3-oxobutylidene) ethylene diamine, N-2-hydroxyethyl-N'-salicylidene ethylene diamine, N-2-hydroxyethyl-N'-salicylidene-1,3-propylene diamine, N-3-hydroxypropyl-N'-salicylidene-1,3-propylene diamine, N-3-hydroxypropyl-N'-salicylidene ethylene diamine, N-2-dimethyl aminoethyl-N'-salicylidene ethylene diamine, N-2-pyridyl methyl-N'-salicylidene ethylene diamine, N,N'-bis(2-amino-3-benzylidene)ethylene diamine, 1-(diacetylmonoxime imino)-3-(diacetyl monoxymatoimino)propane, 12-crown-4,1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetraazacyclotetradecane-5,7-dione, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, 1,4,7,10-tetrathiacyclododecane, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene, porphyrin, phthalocyanine, anions obtained by removing one or more protons from the aforementioned compounds, or combination thereof.

[0023] The tetradentate ligand can comprise N,N'-di(salicydene)ethylene diamine, and the iron complex can comprise N,N'-di(salicydene)ethylene diamine coordinated to the iron atom. For example, the iron complex can comprise the N,N'-di(salicydene)ethylene diaminato iron(III) cation, or Fe(III)(salen)^+ , in combination with an anion. In some embodiments, the iron complex comprises N,N'-di(salicydene)ethylene diaminato iron(II) (Fe(II)(salen)), N,N'-di(salicydene)ethylene diaminato iron(III) chloride (Fe(III)(salen)Cl); μ -oxo-N,N'-bis(salicydene)ethylene diaminato iron(III) ($[\text{Fe(III)(salen)}]_2\text{O}$); or combination thereof.

[0024] The at least one phenol and iron in the iron complex can be used in a molar ratio of 2:1 to 10,000:1, specifically 10:1 to 5,000:1, or more specifically 100:1 to 1000:1. In some embodiments, the at least one phenol and iron in the iron complex are used in a 2:1 to 10,000:1 molar ratio.

[0025] A co-catalyst can be used to enhance the activity of the iron complex. The co-catalyst can be an amine ligand, a diketone ligand, a metal halide, or combination thereof. In some embodiments, the co-catalyst is an amine ligand. The amine ligand can be soluble in the first phenol, the non-polar solvent, or combination thereof. In some embodiments, the amine ligand comprises pyridine, 2,6-lutidine, 2-picoline, 3-choropyridine, 4-methoxypyridine, di-*n*-butylamine, di-*n*-methylbutylamine, triethylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, or combination thereof. The molar ration of amine ligand to iron can be 0.001:1 to 1000:1, specifically 0.1:1 to 500:1, and more specifically 1:1 to 100:1.

[0026] Advantageously, a liquid oxidant can be used. A liquid oxidant has advantages over a gaseous oxidant, for example oxygen or air. Depending upon their relative amounts in the gas phase, a gaseous oxidant can form an explosive mixture with flammable solvent vapor, while

a liquid oxidant will reside primarily in the liquid phase. Moreover, since gaseous oxidants like oxygen have limited solubility in non-polar solvents, contact of the oxygen with the at least one phenol is limited to the non-polar solvent/oxygen interface, which can limit the polymerization rate. However liquid oxidants can be in intimate contact with the first phenol, either by being co-dissolved in the non-polar solvent, or by forming a stable emulsion, thereby increasing polymerization rates.

[0027] The liquid oxidant can comprise a peroxide (containing a –O–O– group) or hydroperoxide (containing a –O–OH group). In some embodiments, the liquid oxidant comprises hydrogen peroxide, an alkyl peroxide, an alkyl hydroperoxide, a ketone peroxide, a diacyl peroxide, a diperoxy ketal, a peroxyester, a peroxydicarbonate, a peroxy acid, a perbenzoic acid, or combination thereof. Examples of specific liquid oxidants include hydrogen peroxide, 2-butanone peroxide, cyclohexanone peroxide, benzyl peroxide, benzoyl peroxide, lauryl peroxide, di-*tert*-butyl peroxide, *tert*-butyl cumyl peroxide, dicumyl peroxide, *tert*-butyl hydroperoxide, cumene hydroperoxide, *tert*-butyl peroxybenzoate, *tert*-amyl peroxybenzoate, *tert*-butyl peroxyoctoate, 2,2-bis(*tert*-butylperoxy)butane, 2,2-bis(*tert*-butylperoxy)octane, 2,5-dimethylhexane-2,5-dihydroperoxide, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hex-3-yne, α,α' -bis(*tert*-butylperoxy-meta-isopropenyl)benzene, di(*tert*-butylperoxy) isophthalate, performic acid, peracetic acid, perbenzoic acid, di(trimethylsilyl) peroxide, trimethylsilyl triphenylsilyl peroxide, and combination thereof. The specific liquid oxidant can depend upon the specific phenol(s), solvent, catalyst, amine ligand, polymerization temperature and time, and other factors. In some embodiments, the oxidant comprises hydrogen peroxide, cumene hydroperoxide, or combination thereof. In some embodiments, the liquid oxidant comprises hydrogen peroxide.

[0028] Advantageously, the polymerization is conducted in a non-polar solvent. Non-polar solvents have several advantages over polar solvents. A polar solvent can provide a single-phase polymerization mixture of the at least one phenol and oxidant. However, the poly(phenylene ether) can precipitate from the polar solvent as it is formed. For example, poly(2,6-dimethyl-1,4-phenylene ether) is insoluble in methanol and 2-propanol. Precipitation of the poly(phenylene ether) can cause heat transfer and mass transfer problems, for example difficulty in stirring the polymerization mixture. Advantageously, poly(phenylene ether) is soluble in the non-polar solvents disclosed herein. Moreover, since many polar solvents are at least partially water-miscible, aqueous extraction of these polymerization mixtures to remove catalyst residues can be problematic due to the absence of two layers, or if two layers are present, difficulty in separating the two layers. Moreover, the water used in aqueous extraction can be

contaminated with polar solvent, and therefore must be treated as hazardous waste.

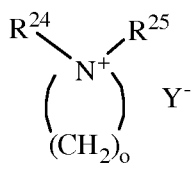
Advantageously, non-polar solvents have much lower solubility in water, so contamination of water used in aqueous extraction can be minimized with a non-polar solvent. The non-polar solvent can comprise an aromatic solvent or a chlorinated solvent. For example, the non-polar solvent can comprise benzene, toluene, ethylbenzene, cumene, xylenes, mesitylene, tetralin, chlorobenzene, dichlorobenzenes, chloroform, and combination thereof. In some embodiments, the non-polar solvent comprises toluene, xylenes, mesitylene, chlorobenzene, dichlorobenzenes, chloroform, or combination thereof.

[0029] When certain liquid oxidants, for example aqueous hydrogen peroxide, are used, the liquid oxidant can be immiscible with the non-polar solvent and dissolved phenol. This is an advantage when isolating the poly(phenylene ether) from the reaction mixture. Moreover, contact between the liquid oxidant and the immiscible non-polar solvent phases can be improved by use of a phase transfer catalyst, and polymerization rates can be thereby increased. The phase transfer catalyst can comprise a nonionic surfactant, a non-ionic surfactant, or a cationic surfactant. In some embodiments, the phase transfer catalyst comprises a cationic surfactant. In some embodiments, the phase transfer catalyst comprises a quaternary ammonium salt, a quaternary phosphonium salt, or combination thereof. The foregoing salts include an anionic counterion. Examples of anionic counterions include chloride, bromide, iodide, sulfate, phosphate, carboxylate, acetate, mesylate, tosylate, nitrate, nitrite, or a boron-containing anion. A combination of different counterions can be used. The quaternary ammonium or phosphonium salts have the chemical formula $G_4N^+Y^-$ or $G_4P^+Y^-$, where each Y^- is independently an anionic counterion, and each G is independently C_{1-32} acyl, C_{2-32} alkenyl or alkynyl, C_{3-8} cycloalkyl, C_{6-24} aryl, C_{7-24} arylalkylene (*e.g.*, benzyl), di(C_{1-32} alkyl)amino, or C_{3-9} heteroaryl containing 1 to 3 heteroatoms (N, P, O, S, or combination thereof). Each of the foregoing groups can optionally be substituted with 1 to 4 substituents such as C_{1-6} alkyl, C_{1-6} alkoxy, nitro, cyano, halogen, di(C_{1-32} alkyl)amino, C_{1-6} alkylcarbonyloxy (*e.g.*, $H_3CC(O)O^-$), C_{2-32} alkenyl or alkynyl, C_{3-8} cycloalkyl, C_{6-24} aryl, C_{7-24} arylalkylene, or C_{3-9} heteroaryl.

[0030] Examples of quaternary ammonium salts include tetra(C_{1-16} alkyl)ammonium salts, tetra(C_{6-24} aryl)ammonium salts, and tetra(C_{7-24} arylalkylene)ammonium salts. Examples of specific tetra(C_{1-16} alkyl)ammonium salts include tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium iodide, tetrabutylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium fluoride, tetrabutylammonium acetate, tetrahexylammonium chloride, tetraheptylammonium chloride, benzyltriethylammonium bromide, MAQUAT™ (a C_{12} - C_{15} alkyldimethylbenzylammonium chloride),

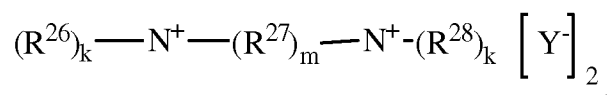
hexadecyltrimethylammonium bromide, ALIQUAT™ 336 (methyltrioctylammonium chloride), ADOGEN™ 464 (methyltri(C₈-C₁₀ alkyl)ammonium chloride), and 1,6-bis(tributylammonium)hexane dibromide. Examples of tetra(C₆₋₂₄)arylammonium salts include tetraphenylammonium bromide.

[0031] Dialkyl heterocycloaliphatic salts having the following structure can be used:



wherein R²⁴ and R²⁵ are each independently an alkyl groups having 1 to 4 carbons and n equals 4 to 6, o is an integer from 1 to 12, and Y⁻ is defined as above.

[0032] Bis-alkyl quaternary ammonium salts having the following structure can be used:



wherein R²⁶ and R²⁸ are each independently an alkyl having 1 to 12 carbons, each R²⁷ is a hydrocarbyl group having 1 to 12 carbons provided that all R²⁷ groups, taken together, have 4 to 12 carbons, k is an integer from 1 to 3, and m is 4-k provided that at least three of the R²⁶, R²⁷ and R²⁸ are aliphatic or alicyclic, and Y⁻ is defined as above.

[0033] Quaternary phosphonium salts include tetra(C₁₋₁₆)alkyl, tetra(C₆₋₂₄)aryl, mixed (C₇₋₂₄arylalkylene)(C₁₋₁₆alkyl), and mixed (C₆₋₂₄aryl)(C₁₋₁₆alkyl) phosphonium salts, and phosphazanium salts. Specific examples of quaternary phosphonium salts include tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, methylbenzyltriphenylphosphonium bromide, tetraphenylphosphonium bromide, and trihexyl-tetradecylphosphonium chloride.

[0034] The amount of phase transfer catalyst can be 0.001 to 10 weight percent, specifically 0.01 to 2 weight percent, or more specifically 0.05 to 1 weight percent, based on the weight of the at least one phenol.

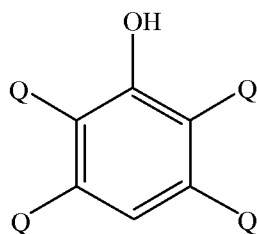
[0035] The inventors have determined that poly(phenylene ether)s having a weight average molecular weight of at least 1,000 atomic mass units, specifically 1,000 to 50,000 atomic mass units, and more specifically, 1,000 to 30,000 atomic mass units, can be made using aqueous hydrogen peroxide as the liquid oxidant, Fe(II)(salen), Fe(III)(salen)Cl, [Fe(salen)]₂O, or combination thereof as the iron complex, pyridine as the amine ligand, and a quaternary ammonium salt as the phase transfer catalyst. Thus, in some embodiments, a method of preparing a poly(phenylene ether) comprises oxidative polymerization of at least one phenol comprising 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-

diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof, in the presence of aqueous hydrogen peroxide, an iron complex comprising Fe(II)(salen), Fe(III)(salen)Cl, [Fe(II)(salen)]₂O, or combination thereof, pyridine, a quaternary ammonium salt, and toluene, in the absence of added water other than any water present in the liquid oxidant or phase transfer catalyst.

[0036] The polymerization can be conducted under a wide range of temperatures and times, which depend in part on the specific liquid oxidant, iron complex, and phase transfer catalyst used. The polymerization temperature is a balance between polymerization time and liquid oxidant decomposition rates. If the temperature is too low, the polymerization can take too long, or not occur at all. If the polymerization temperature is too high, the liquid oxidant can decompose before it has a chance to initiate polymerization. In order to achieve an economically feasible polymerization time, the minimum polymerization temperature can be 0, 20, or 30 °C. Factors that determine the maximum temperature include the decomposition temperature of the liquid oxidant, the reactivity of the phenol, and the boiling point of the non-polar solvent. For some liquid oxidants, the polymerization can be conducted at a polymerization temperature of 0 to 120 °C, specifically 10 to 100 °C, and more specifically 20 to 90 °C.

[0037] The polymerization time is determined in part by the polymerization temperature, the reactivity of the phenol, and the activity of the catalyst. For practical reasons, the polymerization time should be less than or equal to 12 hours. The oxidative polymerization can be conducted for a polymerization time of 10 minutes to 12 hours, specifically 30 minutes to 10 hours, and more specifically 1 to 8 hours. In some embodiments, the oxidative polymerization is conducted at 0 to 120 °C for 10 minutes to 12 hours. The liquid oxidant can be added all at once to a mixture of the at least one phenol, iron complex, amine ligand, phase transfer catalyst, and non-polar solvent, or it can be added continuously to the mixture. In some embodiments, the liquid oxidant is added over a period of 1 minute to 12 hours, specifically, 30 minutes to 8 hours, and more specifically, 1 to 4 hours.

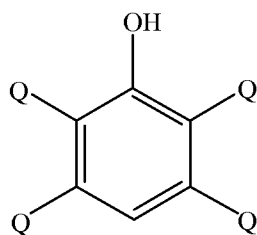
[0038] The method can be used to make a wide variety of poly(phenylene ether) homopolymers and copolymers. Depending on the particular isolation and purification methods used, the poly(phenylene ether) can comprise all, or a fraction of, the iron from the iron complex used in the method. Thus in some embodiments, the poly(phenylene ether) solution comprises 0.1 to 10,000 parts per million, specifically 0.1 to 1,000 parts per million, and more specifically, 0.1 to 100 parts per million of iron. In some limitations, iron cannot be detected in the poly(phenylene ether). Thus, a poly(phenylene ether) can be made by a method comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst, wherein the poly(phenylene ether) comprises 0.1 to 10,000 parts per million of iron.

[0039] This invention includes at least the following embodiments.

[0040] Embodiment 1: A method of making a poly(phenylene ether), comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst.

[0041] Embodiment 2: The method of embodiment 1, wherein the at least one phenol comprises 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof.

[0042] Embodiment 3: The method of embodiment 1 or 2, wherein the poly(phenylene ether) is selected from poly(2,6-dimethyl-1,4-phenylene ether), poly(2,4,6-trimethylphenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene ether), poly(2,6-

dimethyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2-allyl-6-methyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-methyl-6-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*m*-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*o*-phenyl-1,4-phenylene ether), and poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene-*co*-*m*-phenyl-1,4-phenylene ether).

[0043] Embodiment 4: The method of any of embodiments 1-3, wherein the at least one phenol is not a phenolic vegetable oil.

[0044] Embodiment 5: The method of any of embodiments 1-4, wherein the iron complex comprises Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof.

[0045] Embodiment 6: The method of any of embodiments 1-5, wherein the amine ligand comprises pyridine, 2,6-lutidine, 2-picoline, 3-choropyridine, 4-methoxypyridine, di-*n*-butylamine, di-*n*-methylbutylamine, triethylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, or combination thereof.

[0046] Embodiment 7: The method of any of embodiments 1-6, wherein the liquid oxidant comprises hydrogen peroxide, an alkyl peroxide, an alkyl hydroperoxide, a ketone peroxide, a diacyl peroxide, a diperoxy ketal, a peroxyester, a peroxydicarbonate, a peroxy acid, a perbenzoic acid, or combination thereof.

[0047] Embodiment 8: The method of any of embodiments 1-7, wherein the liquid oxidant comprises hydrogen peroxide, cumene hydroperoxide, or combination thereof.

[0048] Embodiment 9: The method of any of embodiments 1-8, wherein the phase transfer catalyst comprises a quaternary ammonium salt, a quaternary phosphonium salt, or combination thereof.

[0049] Embodiment 10: The method of any of embodiments 1-9, wherein the non-polar solvent comprises toluene, xylenes, mesitylene, chlorobenzene, dichlorobenzenes, chloroform, or combination thereof.

[0050] Embodiment 11: The method of any of embodiments 1-10, wherein the at least one phenol and iron in the iron complex are used in a 2:1 to 10,000:1 molar ratio.

[0051] Embodiment 12: The method of any of embodiments 1-11, wherein the oxidative polymerization is conducted at 0 to 120 °C for 10 minutes to 12 hours.

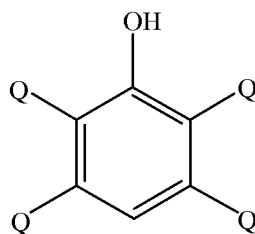
[0052] Embodiment 13: The method of any of embodiments 1-12, wherein the liquid oxidant is added over a period of 1 minute to 12 hours.

[0053] Embodiment 14: The method of any of embodiments 1-13, wherein the at least one phenol comprises 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination

thereof; wherein the liquid oxidant comprises aqueous hydrogen peroxide; wherein the iron complex comprises Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof; wherein the amine ligand comprises pyridine; wherein the phase transfer catalyst comprises a quaternary ammonium salt; and wherein the non-polar solvent comprises toluene.

[0054] Embodiment 14a: A method of preparing a poly(phenylene ether), the method comprising oxidative polymerization of at least one phenol comprising 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof, in the presence of aqueous hydrogen peroxide, an iron complex comprising Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof, pyridine, a quaternary ammonium salt, and toluene, in the absence of added water other than any water present in the liquid oxidant or phase transfer catalyst.

[0055] Embodiment 15: A poly(phenylene ether) made by a method comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen, in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst; wherein the poly(phenylene ether) comprises 0.1 to 10,000 parts per million of iron.

EXAMPLES

[0056] The materials utilized in the examples are described below in Table 1.

Table 1. Materials

CAS Number	Chemical Name	Purity (wt%)	Abbrev.
25134-01-4	Poly(2,6-dimethyl-1,4-phenylene ether)	varies	PPE
7722-84-1	Aqueous H ₂ O ₂ /H ₂ O	50%	-
108-88-3	Toluene	99%	-
67-56-1	Methanol	99%	-
110-86-1	Pyridine	99%	-
68424-85-1	C ₁₂ -C ₁₅ Alkyldimethylbenzylammonium chloride	80-82%	MAQUAT™
4906-22-3	3,3',5,5'-Tetramethyldiphenoquinone	varies	TMDQ
576-26-1	2,6-Dimethylphenol	50%	DMP
2432-11-3	2,6-Diphenylphenol	99%	DPP
17755-10-1	2-Methyl-6-phenylphenol	99%	MPP
580-51-8	3-Phenylphenol (<i>m</i> -Phenylphenol)	85%	<i>m</i> -PP
3354-58-3	2-Allyl-6-methylphenol	98%	AMP
2416-94-6	2,3,6-Trimethylphenol	97%	TMP
90-43-7	2-Phenylphenol (<i>o</i> -phenylphenol)	99%	<i>o</i> -PP
95-48-7	2-Methylphenol (<i>o</i> -cresol)	99%	-
111-92-2	Di- <i>n</i> -butylamine	99.5%	DBA
927-62-8	N,N-Dimethylbutylamine	98%	DMBA
4062-60-6	Di- <i>tert</i> -butylethylenediamine	98%	DBEDA
626-60-8	3-Chloropyridine	99%	-
109-06-8	2-Picoline	98%	-
620-0806	4-Methoxypyridine	97%	-
103-83-8	Dimethylbutylamine	99.5%	DMBA
11-92-2	Dibutylamine	99.5%	DBA
694-59-7	Pyridine N-oxide	95%	-
94-93-9	N,N'-Di(salicydene)ethylene diamine; or 2,2'-Ethylenebis(nitriliomethylidene)diphenol		salen
65966-75-8	N,N'-Di(salicydene)ethylene diaminato iron(II) chloride; or 2,2'-Ethylenebis(nitriliomethylidene)diphenol iron(III) chloride	100%	Fe(III)salen chloride
139-13-9	2,2',2''-Nitrilotriacetic acid	40%	NTA

[0057] Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (M_w/M_n , or D) were determined by gel permeation chromatography (GPC) in chloroform using polystyrene standards. The T_g of the polymers were measured by differential scanning calorimeter (DSC) and taken from the second heating scans. Char mass was measured using thermal gravimetric analysis (TGA). The char mass was measured at 600 °C, 700 °C and 800 °C, respectively.

COMPARATIVE EXAMPLE 1 AND EXAMPLES 1-8

[0058] The solids concentration in the polymerization mixtures was 20 wt%. Fe(III)(salen) chloride was employed as the catalyst in the all the polymerizations. The monomer

: Fe molar ratio in the polymerization mixtures was about 550 : 1. Target and measured monomer composition, number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (M_w/M_n), glass transition temperature (T_g), and char mass data for the polymers are provided in Table 2.

COMPARATIVE EXAMPLE 1. SYNTHESIS OF 2,6-DIMETHYLPHENOL HOMOPOLYMER

[0059] 21.61 Grams DMP, 66.9 grams toluene, 1.85 grams DBA, 1.03 grams DMBA, 1.18 grams diamine mix of 30 wt% DBEDA and 16 wt% MAQUAT™ in toluene, 0.12 grams Cu_2O , and 1.496 grams HBr were charged to a polymerization vessel and stirred with an agitator. Molecular oxygen was bubbled through the polymerization mixture to initiate polymerization. The reactor temperature was maintained at 30 °C throughout the polymerization (for the residence time). The resulting polymer was equilibrated at 90 °C for 2 hours in the absence of oxygen. During “equilibration”, TMDQ, a dimer of DMP which formed as a by-product of the polymerization, was incorporated into the polymer backbone.

[0060] Cu catalyst present in the polymerization mixture was extracted by chelation with aqueous NTA at 60 °C. The aqueous layer containing NTA and Cu was separated from the polymerization mixture by centrifugation. The catalyst-free polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The polymer was obtained as a dry powder after drying in a ventilated hood overnight and in vacuum oven at 130 °C for 2 hours.

Table 2. Summary of Polymer Compositions and Characterization Results

Ex.	Target Comp. (wt%)	Actual Comp. (wt%)	M _n (amu)	M _w (amu)	D	T _g (°C)	Char Mass in N ₂ (wt%)			Hydroxyl (wt%)
							600 °C	700 °C	800 °C	
Comp. 1	DMP (100)	DMP (100)	15093	27101	1.8	205				
1a	DMP (90) + AMP (10)	DMP (90.1) + AMP (9.9)	1207	2208	1.82	119.3	27.09	22.20	20.87	1.36
1b	DMP (80) + AMP (20)	DMP (83.0) + AMP (17.0)	1900	3700	1.94	142.2	32.97	29.80	28.01	1.1
2a	DMP (90) + DPP (10)	DMP (89.4) + DPP (10.6)	1600	2461	3.37	136	28.92	26.89	24.68	1.34
2b	DMP (70) + DPP (30)	DMP (72) + DPP (28)	1800	3000	1.7	153.4	28.95	26.07	24.09	1.13
3	DMP (80) + AMP (10) + DPP (10)	DMP (82.6) + AMP (8.8) + DPP (8.6)	1212	1893	2.58	125.7	27.51	25.5	22.95	2.31
4	DMP (80) + MPP (20)	DMP (82.2) + MPP (17.8)	1323	2136	3.02	149.7	28.07	25.59	22.41	1.90
5	DMP (80) + AMP (10) + <i>m</i> -PP (10)	DMP (89.7) + AMP (8.2) + <i>m</i> -PP (2.1)	1051	2079	4.96	132.3	26.23	24.0	22.52	1.02
6	TMP (100)	TMP (100)	1261	2025	3.07	172.9	21.13	19.58	18.39	1.79
7a	DMP (75) + <i>o</i> -PP (25)	DMP (78.8) + <i>o</i> -PP (21.2)	1801	3704	2.05	149.1	32.36	29.07	26.81	-
7b	DMP (50) + <i>o</i> -PP (50)	DMP (60.8) + <i>o</i> -PP (39.2)	5200	20400	3.9	153.4	39.96	36.63	33.83	-
8	DMP (100)	DMP (100)	1493	2908	4.36	148.1	22.49	19.33	16.93	1.90

EXAMPLE 1A: SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL COPOLYMER

[0061] 25.84 Grams DMP, 117.7 grams toluene, 2.87 grams AMP, 0.15 grams of Fe(III)(salen) chloride, 5.55 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™ was charged to the polymerization vessel. 15.70 Grams of 50 wt% H₂O₂/H₂O was added all at once, and the resulting mixture stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours with an agitator, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 1B. SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL COPOLYMER

[0062] Example 1a was repeated, except the weight ratio of DMP to AMP was increased from 80:20 to 90:20, and the 50 wt% H₂O₂/H₂O was added continuously over 2 hours. As can be seen from Table 2, this resulted in a copolymer having a higher molecular weight than the copolymer of Example 1a.

EXAMPLE 2A. SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2,6-DIPHENYLPHENOL COPOLYMER

[0063] 22.97 Grams DMP, 120.57 grams toluene, 2.87 grams DPP, 0.132 grams of Fe(III)(salen) chloride, 3.99 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 13.58 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 2B. SYNTHESIS OF 2,6-DIMETHYL PHENOL / 2,6-DIPHENYL PHENOL COPOLYMER

[0064] Example 2a was repeated, except the weight ratio of DMP to DPP was reduced from 90:10 to 70:20, and the 50 wt% H₂O₂/H₂O was added over 3 hours. As can be seen from Table 2, this resulted in a copolymer having a higher molecular weight than the copolymer of Example 2b.

EXAMPLE 3. SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL / 2,6-DIPHENYLPHENOL COPOLYMER

[0065] 22.97 Grams DMP, 120.57 grams toluene, 2.87 grams DPP, 2.87 grams of AMP, 0.137 grams of Fe(III)(salen) chloride, 4.99 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 14.90 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 4. SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2-METHYL-6-PHENYL PHENOL COPOLYMER

[0066] 22.97 Grams DMP, 120.57 grams toluene, 5.74 grams MPP, 0.137 grams of Fe(III)(salen chloride), 3.76 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 14.90 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 5. SYNTHESIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL / *m*-PHENYLPHENOL COPOLYMER

[0067] 22.97 Grams DMP, 120.57 grams toluene, 2.87 grams *m*-PP, 2.87 grams of AMP, 0.137 grams of Fe(III)(salen) chloride, 4.99 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 14.10 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 6. SYNTHESIS OF 2,3,6 TRIMETHYLPHENOL HOMOPOLYMER

[0068] 13.92 Grams DMP, 73.12 grams toluene, 0.075 grams of Fe(III)(salen) chloride, 2.28 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 7.75 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 7A. SYNTHESIS OF 2,6-DIMETHYLPHENOL / *o*-PHENYLPHENOL COPOLYMER

[0069] 16.5 Grams DMP, 5.5 grams *o*-PP, 115.12 grams toluene, 0.153 grams of Fe(III)salen chloride, 4.646. grams pyridine, and 0.014 grams of 50 wt% of MAQUAT™ were charged to a polymerization vessel and stirred with an agitator. 15.78 grams 50 wt% H₂O₂/H₂O was introduced continuously over a period of 1 hour. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 7B. SYNTHESIS OF 2,6-DIMETHYLPHENOL / *o*-PHENYLPHENOL COPOLYMER

[0070] Example 7a was repeated, except the weight ratio of DMP to *o*-PP was reduced from 75:25 to 50:50, and the 50 wt% H₂O₂/H₂O was added continuously over 3 hours. As can be seen from Table 2, this resulted in a copolymer having a higher molecular weight than the copolymer of Example 7a.

EXAMPLE 8. SYNTHESIS OF 2,6-DIMETHYLPHENOL HOMOPOLYMER

[0071] 13.92 grams DMP, 73.12 grams toluene, 0.075 grams of Fe(III)(salen) chloride, 2.28 grams pyridine, 0.014 grams of 50 wt% of MAQUAT™, and 7.75 grams 50 wt% H₂O₂/H₂O were charged to a polymerization vessel and stirred with an agitator. The temperature was maintained at 30 °C. The resulting mixture was stirred at 30 °C for 3 hours, and then equilibrated at 90 °C for 3 hours. The polymerization mixture was precipitated in methanol,

filtered, reslurried in methanol, and filtered again. The polymer was obtained as a dry powder after drying in a hood overnight and in a vacuum oven at 130 °C for 2 hours.

EXAMPLE 9-15. EFFECT OF AMINE LIGAND

[0072] The impact of type of amine ligand for the iron complex on PPE molecular weight and yield was evaluated by conducting oxidative polymerization of DMP in the absence of amine ligand (Comparative Example 2), and in the presence of amine ligands such as di-*n*-butylamine, di-*n*-methylbutylamine, pyridine N-oxide, 4-methoxypyridine, 3-chloropyridine and 2-picoline (Examples 9-15). The general procedure of Example 8 was used. Table 3 compares the effect of amine ligand on the weight average molecular weight, number average molecular weight, and polydispersity of PPE made using H₂O₂ in the presence of Fe(III)(salen) chloride. The H₂O₂ : monomer molar ratio was unity. In Example 12, the PPE was isolated by air drying the polymerization mixtures to remove the solvent followed by vacuum drying in an oven. In Examples 9-11 and 13-15, the PPE was isolated by precipitation in methanol.

Table 3. Effect of Amine Ligand on PPE

Ex.	Amine Ligand	Conj. Acid pKa	Gel Phase Chromatography			NMR M _n	T _g	% Char Mass 850 °C	
			M _n	M _w	D			Air	N ₂
C.2	None	-	1366	2408	1.76	1044	132.9	0.12	19.57
9	Pyridine	5.14	1296	2370	1.82	1396	142	0.28	18.14
10	DMBA	10.28	1701	2643	1.55	1658	-	-	-
11	DBA	10.78	2519	3670	1.41	1597	149.7	0.25	19.2
12	Pyridine N-Oxide	0.79	226	326	1.44	391	83.5	0.17	10.30
13	3-Chloropyridine	2.84	1230	3039	2.46	1159	135.4	1.6	23.01
14	2-Picoline	5.97	1304	2378	1.82	1310	140.2	2.35	21.24
15	4-Methoxy-pyridine	6.67	2564	3482	1.35	1514	152.3	0.35	18.0

[0073] Lower selectivity towards the desired product (PPE) and lower average molecular weight were obtained in the oxidative polymerization in the absence of amine ligand. Selectivity for TMDQ by-product was higher. The presence of pyridine (Example 9) resulted in higher selectivity towards PPE and higher molecular weight by NMR analysis. This effect may be due to pyridine modifying the activity of the iron complex by formation of a coordinate bond to the iron atom. The impact of using an aliphatic amine ligand was evaluated by conducting the oxidative coupling polymerization in the presence of DMBA (Example 10) and DBA (Example 11). The basicity of pyridine and DMBA are of the same order of magnitude. The PPE yield was lower with DMBA than with pyridine, pointing toward greater catalytic activity of the

Fe(III)(salen) chloride + pyridine combination compared to the Fe(III)(salen) chloride + DMBA combination. Similar results were observed with the Fe(III)(salen) chloride + DBA combination.

[0074] The influence of electron-withdrawing and electron-donating groups on the pyridine ring and on the ring nitrogen of pyridine on PPE properties was evaluated. The average molecular weight of PPE synthesized in the presence of pyridine N-oxide was lower than that obtained in the presence of pyridine and the substituted pyridines. PPE synthesized using 3-chloropyridine, which has an electron-withdrawing chloro group (Example 13), was found to have greater polydispersity than the polymer produced with 2-picoline (Example 14), which has an electron-donating methyl group, and the polymer produced with pyridine.

EXAMPLE 16. EVALUATION OF OXIDANTS

[0075] The effect of oxidant on polymer yield and molecular weight was investigated by polymerizing DMP with the following oxidants: gaseous O₂, *meta*-chloroperbenzoic acid (MCPBA, a solid having a melting point of 92-94 °C), *tert*-butyl hydroperoxide (TBHP), benzoyl peroxide, and cumene hydroperoxide (CHP). No polymerization was observed with O₂ or MCPBA. In contrast, oxidative polymerization with benzoyl peroxide resulted in nearly complete conversion of DMP to TMDQ. A low yield of PPE was obtained with cumyl hydroperoxide.

EXAMPLES 17-20. NMR ANALYSIS

[0076] Comonomer repeat unit compositions were determined using ¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectroscopy (after derivatization). NMR peak assignments for copolymers were made based on known chemical shifts of the corresponding homopolymers, and on the relative intensities of the peaks associated with the comonomers in the copolymers. ChemOffice NMR shift prediction software was also used to make peak assignments.

[0077] All ¹H-NMR spectra were acquired on a Varian Mercury Plus 400 instrument operating at an observe frequency of 400.14 MHz. Spectra for all samples were collected under quantitative conditions. Approximately 60 mg sample were added to 1 mL CDCl₃. Spectral parameters included an 8000 Hz spectral width, 2.7 second acquisition time (21.1 K data points), 4.85 microsecond pulse width (45° flip angle), and 5 second pulse delay. The “s2pul” pulse sequence was employed. Generally, 128 acquisitions were adequate to achieve good signal-to-noise. Data processing was carried out using “NetNMR” software with 0.5 Hz line broadening and a polynomial baseline correction routine.

[0078] All ^{13}C -NMR spectra were acquired on a Varian Mercury Plus operating at 100 MHz. The instrument was equipped with a 10 millimeter broadband probe. Approximately 500 mg of sample were dissolved in 4.0 mL of CDCl_3 containing $\text{Cr}(\text{acac})_3$ (15 mg/mL). The decoupler was gated off during the pulse delay to eliminate NOE and to ensure complete relaxation of carbon nuclei between scans. Acquisition parameters included a pulse delay of 5 seconds and a 45° flip angle. Also, a 30.2 kHz spectral width and 30 K data points resulted in a 1.00 second acquisition time. Generally, 7500 scans were required for adequate signal-to-noise. Broadband proton decoupling was carried out using the “Waltz-16” pulse sequence. The CDCl_3 signal was used as a chemical shift reference ($\delta = 77.0$ ppm). Resulting spectra were processed using 2 Hz exponential apodization and were baseline corrected using a polynomial fit routine. All data processing was done using “NetNMR” software.

[0079] ^{31}P -NMR spectroscopy was used for the identification and quantification of phenolic functionality in the polymers. This technique involved the derivatization of phenolic residues of the polymers with 2-chloro-1,3,2-dioxaphospholane. This reaction produced a variety of structurally similar 2-aryloxy-1,3,2-dioxaphospholanes differing only in aromatic ring substitution. Because of the sensitivity of the ^{31}P -nucleus to its electronic environment, the various phenolic end groups were identified from ^{31}P -chemical shifts of their corresponding phosphite derivatives. In addition to quantification of phenolic end groups, this method can also quantify alcohol and acidic functionalities in the polymers. 2,4-dibromophenol was used as an chemical shift reference.

[0080] ^{31}P NMR spectra of derivatized polymers were acquired on a Varian Mercury Plus operating at 162 MHz. The instrument was equipped with a 10 millimeter broadband probe. Approximately 300 mg of sample were dissolved in 4.0 mL of CDCl_3 containing 0.75 mg/mL 2,4-dibromophenol (internal standard) and 15mg/ml $\text{Cr}(\text{acac})_3$ (T_1 relaxation enhancement reagent to reduce data acquisition times). The decoupler was gated off during the pulse delay to eliminate NOE and to ensure complete relaxation of phosphorus nuclei between scans. Acquisition parameters included a pulse delay of 3 second and a 45° flip angle. Also, a 16.2 kHz spectral width and 12.6 K data points resulted in a 800 millisecond acquisition time. Generally, 1000 scans were required for adequate signal-to-noise. Broadband proton decoupling was carried out using the “Waltz-16 pulse” sequence. The internal standard, 2,4-dibromophenol signal was used as a chemical shift reference ($\delta = 129.95$ ppm). Resulting spectra were processed using 1 Hz exponential apodization and were baseline corrected using a polynomial fit routine. All data processing was done using “NetNMR” software.

[0081] Assignments of the peaks in the polymers were made based on known chemical shifts of the homopolymers plus the relative intensities of the peaks with respect to the monomer composition. Additional assistance with structure elucidation and with peak assignments was accomplished with the aid of ChemOffice NMR shift prediction software.

[0082] The ^{13}C -NMR spectra of Examples 1a, 3, 4, and 6 are provided in Fig. 1-4, respectively. In Examples 21 and 22 below, numbers in parentheses indicate specific carbon atoms associated with the indicated repeat unit or end group, and correlate with specific NMR chemical shifts as shown in the figures.

EXAMPLE 17. NMR ANALYSIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL

[0083] The ^1H -NMR spectrum of the 80/20 wt/wt DMP/AMP copolymer of Example 1a exhibits peaks associated with DMP repeat units and end groups. Peaks corresponding to DMP head groups, tail groups, and repeat units were observed at 6.35, 7.1, and 6.46 ppm, respectively. In addition, several peaks generated from incorporation of TMDQ into the polymer backbone were observed (7.35 ppm). TMDQ formed as a by-product of DMP oxidation in the absence of oxygen was incorporated into the DMP chain as biphenol groups. The predominant structures from TMDQ were internal biphenol units. Also observed were biphenol head groups, and internal biphenol units with a DMP head group and a DMP repeat unit chain as tail. In addition to DMP, the ^1H -NMR spectrum showed peaks corresponding to AMP repeat units at 5 ppm and 5.85 ppm.

[0084] The ^{13}C -NMR spectrum confirmed incorporation of AMP into the copolymer that was observed with ^1H -NMR spectroscopy. Fig. 1 shows the proposed repeat unit and end group structures along with their corresponding carbon chemical shift assignments. For example, peaks corresponding to the allyl group were observed at 136 and 134.5 ppm.

[0085] Quantitative determination of the phenolic end groups present in the copolymer was done by derivatization and ^{31}P -NMR analysis. The spectrum shows the DMP head group at 131.26 ppm. The amount of this group, reported as -OH, was 0.97 wt%. Also present at 130.72 ppm was 0.11 wt% terminal biphenol -OH. The spectrum also shows 0.33 wt% of the AMP head group -OH at 131.7 ppm.

EXAMPLE 18. NMR ANALYSIS OF 2,6-DIMETHYLPHENOL / 2-ALLYL-6-METHYLPHENOL / 2,4-DIPHENYLPHENOL COPOLYMER

[0086] The ^{13}C -NMR spectrum of the 80/10/10 wt/wt DMP/AMP/DPP copolymer of Example 3 is depicted in Fig. 2 and shows peaks associated with DMP repeat units. These include the peaks corresponding to the DMP head group at 146.5 ppm (6) and the DMP tail group at 125 ppm (5). TMDQ formed as a by-product of DMP oxidation, and in the absence of oxygen incorporated into the DMP chain as biphenol groups. Peaks generated from the incorporation of TMDQ into the polymer backbone were observed at 150.5 ppm (5) and 137.1 ppm (7). Peaks corresponding to DPP repeat units were observed at 154.9 ppm (26), 115.1 ppm (24), 129.3 ppm (20), 128.7 (21), 129.4 ppm (22), and 129.3 ppm (23).

[0087] The ^1H -NMR spectrum of the 80/10/10 DMP/AMP/DPP copolymer confirmed the same repeat units that were observed in the ^{13}C -NMR spectrum. Quantitative determination of the phenolic end groups was done by derivatization and ^{31}P -NMR spectroscopy. The ^{31}P -NMR spectrum shows the DMP head group at 131.26 ppm. The amount of this group reported as OH was 1.62 wt%. Present at 130.72 ppm was 0.25 wt% of biphenyl head group -OH. The spectrum also shows 0.16 wt% of AMP head group -OH at 131.7 ppm, and 0.26 wt% of DPP head group -OH at 131.7 ppm.

EXAMPLE 19. NMR ANALYSIS OF 2,6-DIMETHYLPHENOL / 2-METHYL-6-PHENYLPHENOL COPOLYMER

[0088] The ^{13}C -NMR of the 80/20 wt/wt DMP/MPP copolymer of Example 4 is depicted in Fig. 3, and confirms formation of a DMP/MPP copolymer. While the composition of the monomer mixture was 80/20 wt/wt DMP/MPP, the actual repeat unit composition was estimated to be 82.2/17.8 wt/wt. Peaks corresponding to biphenol head groups were observed at 151.5 ppm (19), 123.1 ppm (15), and 127.1 ppm (12). Peaks corresponding to biphenol internal units were observed at 150.9 ppm (5), 131.7 ppm (8), and 127.2 ppm (11). Peaks corresponding to DMP head groups were observed at 146.1 ppm (6), 124.1 ppm (14), and 114 ppm (17). Also observed were peaks corresponding to DMP tail groups at 125 ppm (13), 131.2 ppm (9) and 128.9 ppm (10). Peaks observed at 154.5 ppm (15), 114.9 ppm (28), 129.3 ppm (35), and 128.7 ppm (34) were indicative of MPP repeat units. The total hydroxyl (-OH) content of the DMP/MPP copolymer was 1.9 wt%, as determined by integration of the appropriate peak in the ^{13}P -NMR spectrum.

EXAMPLE 20. NMR ANALYSIS OF 2,4,6-TRIMETHYLPHENOL HOMOPOLYMER

[0089] The ^1H -NMR and ^{13}C -NMR spectra of TMP homopolymer of Example 6 confirm the presence of head-to-tail TMP repeat units. The ^{13}C -NMR spectrum is depicted in Fig. 4.

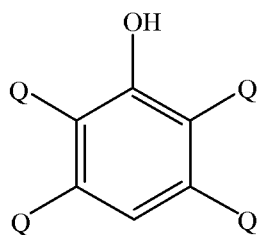
The hydroxyl (-OH) content of the homopolymer as determined by derivatization and ³¹P-NMR spectroscopy was 1.79 wt%.

[0090] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) is to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. “Or” means “and/or.” The endpoints of all ranges directed to the same component or property are inclusive and independently combinable. Disclosure of a narrower range or more specific group in addition to a broader range or larger group is not a disclaimer of the broader range or larger group. All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. Each range disclosed herein constitutes a disclosure of any point or sub-range lying within the disclosed range. The terms “first” and “second” and the like, as used herein do not denote any order, quantity, or importance, but are only used to distinguish one element from another. “Comprises” as used herein includes embodiments “consisting essentially of” or “consisting of” the listed elements. A “combination” is inclusive of blends, mixtures, reaction products, and the like. 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., it includes the degree of error associated with measurement of the quantity).

[0091] 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:

1. A method of making a poly(phenylene ether), comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen,

in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst.

2. The method of claim 1, wherein the at least one phenol comprises 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof.

3. The method of claim 1, wherein the poly(phenylene ether) is selected from poly(2,6-dimethyl-1,4-phenylene ether), poly(2,4,6-trimethyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2-allyl-6-methyl-1,4-phenylene-*co*-2,6-diphenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-2-methyl-6-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*m*-phenyl-1,4-phenylene ether), poly(2,6-dimethyl-1,4-phenylene-*co*-*o*-phenyl-1,4-phenylene ether), and poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene-*co*-*m*-phenyl-1,4-phenylene ether).

4. The method of claim 1, wherein the at least one phenol is not a phenolic vegetable oil.

5. The method of claim 1, wherein the iron complex comprises Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof.

6. The method of any of claims 1-5, wherein the amine ligand comprises pyridine, 2,6-lutidine, 2-picoline, 3-choropyridine, 4-methoxypyridine, di-*n*-butylamine, di-*n*-methylbutylamine, triethylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, or combination thereof.

7. The method of any of claims 1-5, wherein the liquid oxidant comprises hydrogen peroxide, an alkyl peroxide, an alkyl hydroperoxide, a ketone peroxide, a diacyl peroxide, a diperoxy ketal, a peroxyester, a peroxydicarbonate, a peroxy acid, a perbenzoic acid, or combination thereof.

8. The method of any of claims 1-5, wherein the liquid oxidant comprises hydrogen peroxide, cumene hydroperoxide, or combination thereof.

9. The method of any of claims 1-5, wherein the phase transfer catalyst comprises a quaternary ammonium salt, a quaternary phosphonium salt, or combination thereof.

10. The method of any of claims 1-5, wherein the non-polar solvent comprises toluene, xylenes, mesitylene, chlorobenzene, dichlorobenzenes, chloroform, or combination thereof.

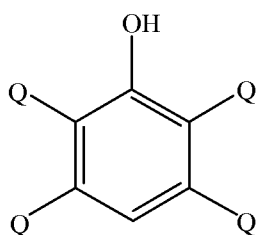
11. The method of any of claims 1-5, wherein the at least one phenol and iron in the iron complex are used in a 2:1 to 10,000:1 molar ratio.

12. The method of any of claims 1-5, wherein the oxidative polymerization is conducted at 0 to 120 °C for 10 minutes to 12 hours.

13. The method of any of claims 1-5, wherein the liquid oxidant is added over a period of 1 minute to 12 hours.

14. The method of any of claims 1-5, wherein the at least one phenol comprises 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2-allyl-6-methylphenol, *o*-phenylphenol, *m*-phenylphenol, or combination thereof; wherein the liquid oxidant comprises aqueous hydrogen peroxide; wherein the iron complex comprises Fe(II)(salen), Fe(III)(salen)Cl, [Fe(III)(salen)]₂O, or combination thereof; wherein the amine ligand comprises pyridine; wherein the phase transfer catalyst comprises a quaternary ammonium salt; and wherein the non-polar solvent comprises toluene.

15. A poly(phenylene ether) made by a method comprising oxidative polymerization of at least one phenol of the structure:



wherein each Q is independently hydrogen, halogen, unsubstituted or substituted C₁-C₁₂ hydrocarbyl wherein the hydrocarbyl group is not tertiary hydrocarbyl, C₁-C₁₂ hydrocarbylthio, C₁-C₁₂ hydrocarbyloxy, or C₂-C₁₂ halohydrocarbyloxy wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein at least one of Q is not hydrogen,

in the presence of a non-polar solvent, a liquid oxidant, an iron complex, an amine ligand, and a phase transfer catalyst, and in the absence of added water other than any water present in the liquid oxidant and phase transfer catalyst;

wherein the poly(phenylene ether) comprises 0.1 to 10,000 parts per million of iron.

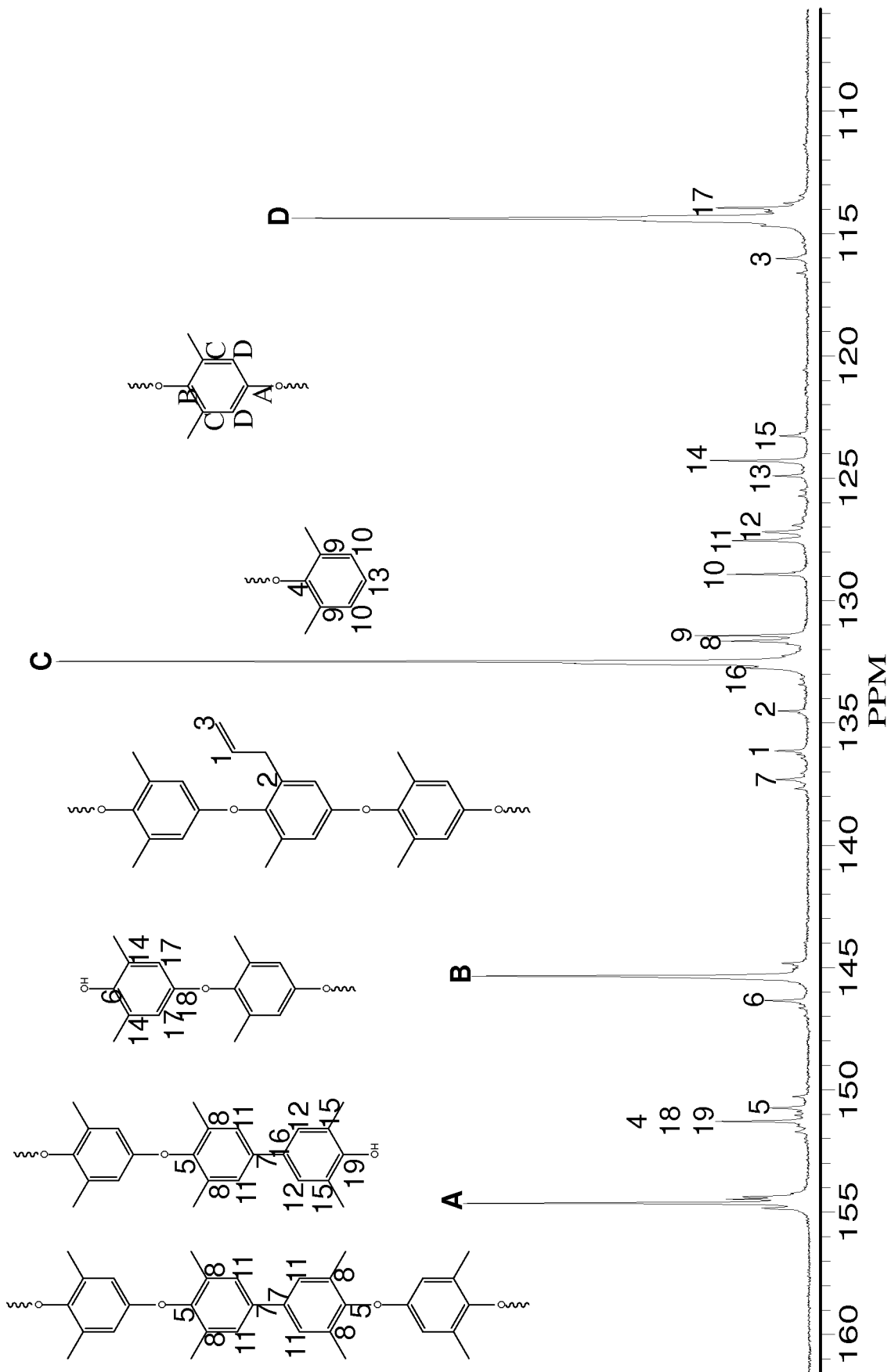


Fig. 1

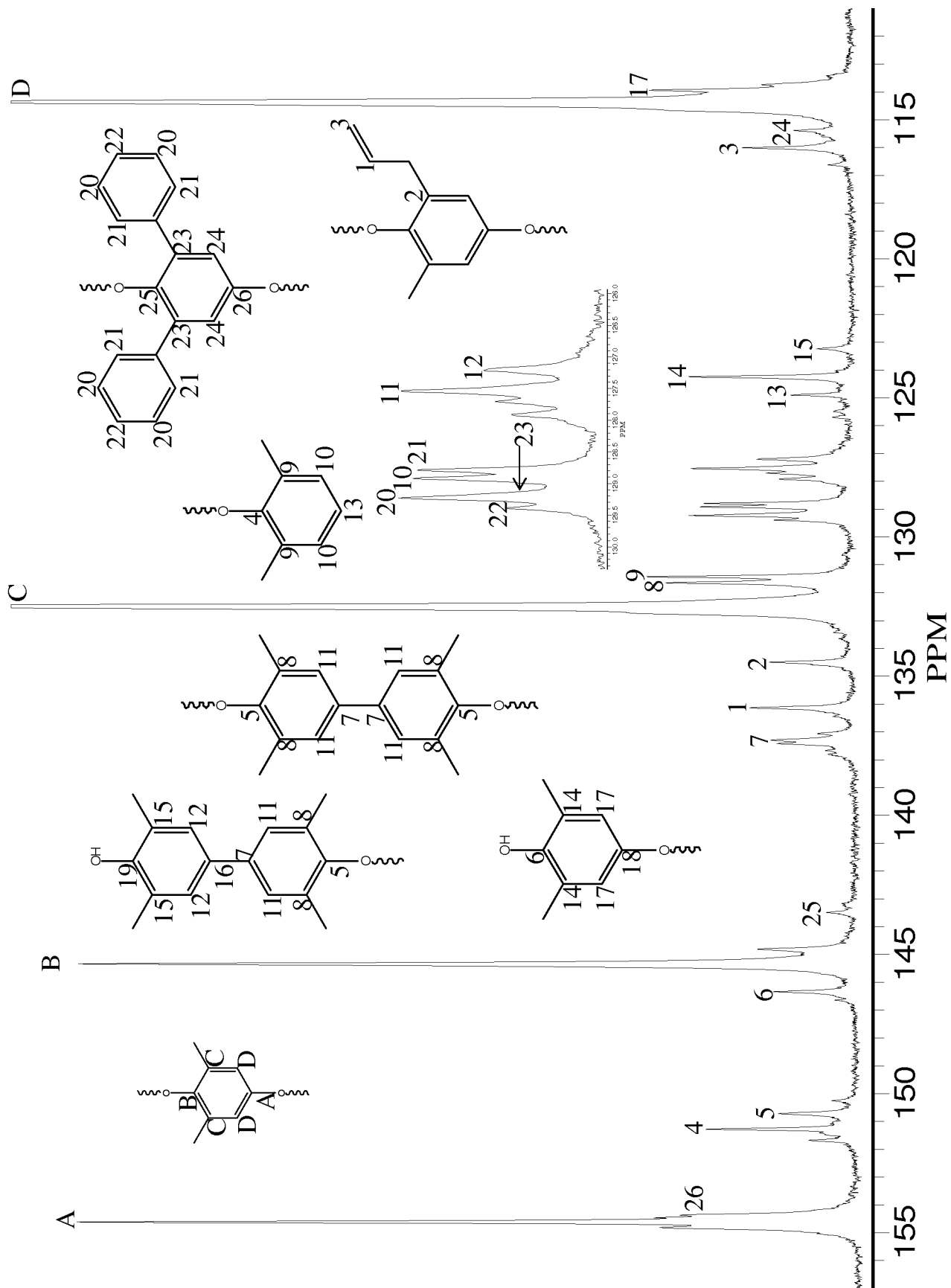


Fig. 2

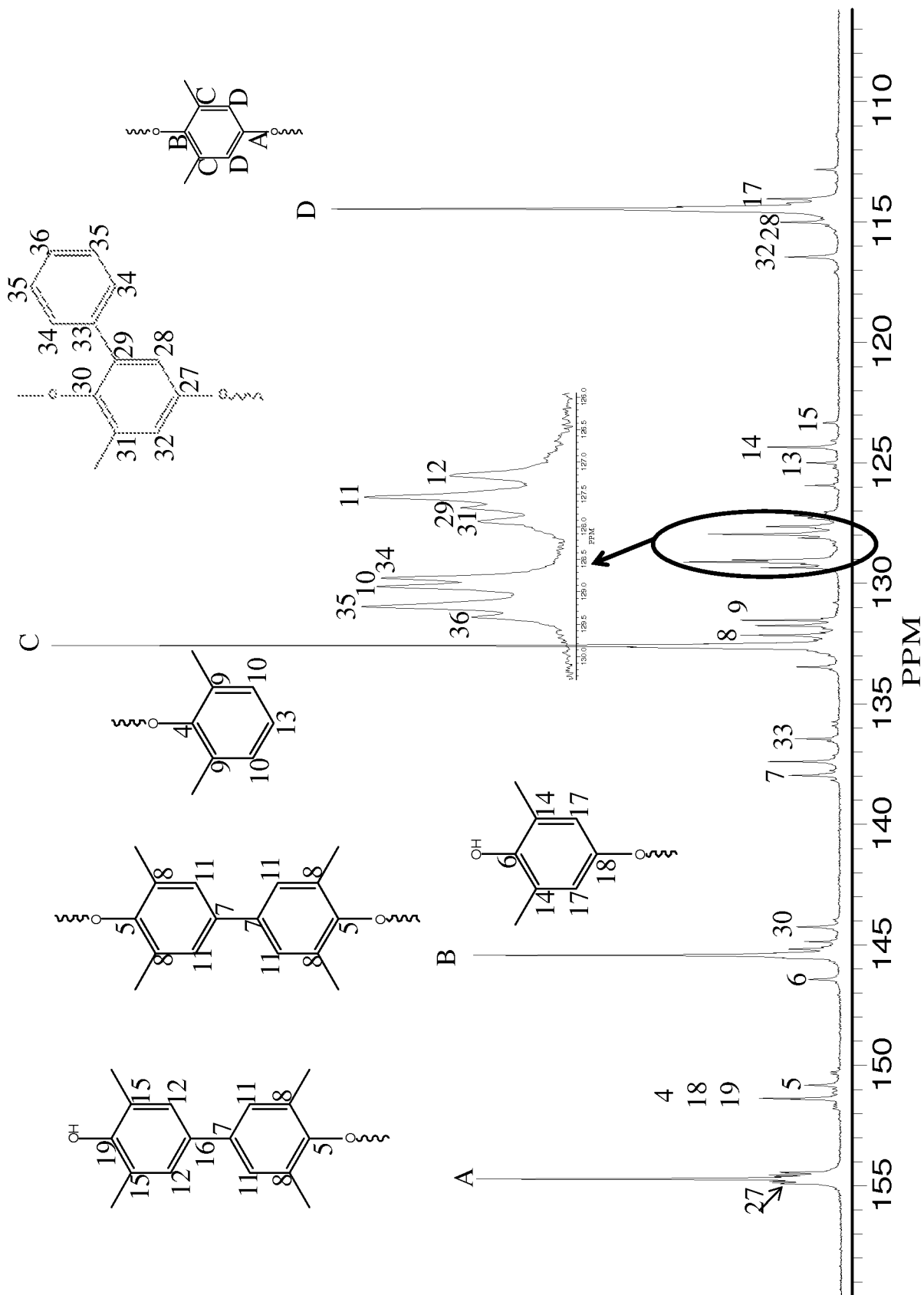


Fig. 3

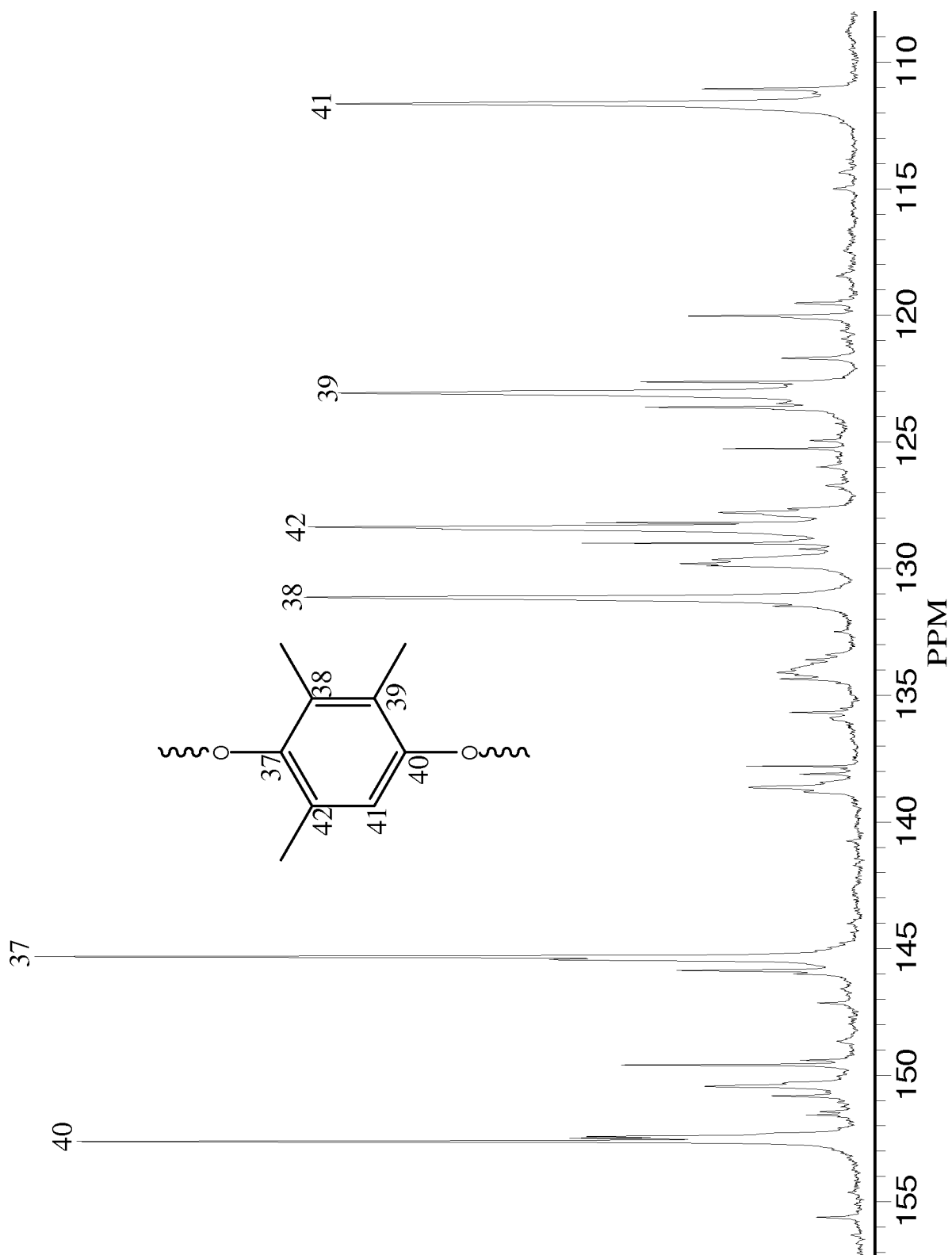


Fig. 4

A. CLASSIFICATION OF SUBJECT MATTER**C08G 65/38(2006.01)i, C08G 65/40(2006.01)i, C08L 71/12(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
C08G 65/38; B01D 69/04; C08G 61/02; C08G 65/46; C08G 65/44; C08G 65/40; C08L 71/12Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: poly(phenylene ether), phenol, oxidative polymerization, non-polar solvent, iron complex, hydrogen peroxide**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103709398 A (JINAN DEV ZONE XINGHUO SCIENCE & TECHNOLOGY RES INST) 09 April 2014 See abstract; claims 1-8.	15
A		1-14
X	CN 100422237 C (ASAHI KASEI K. K.) 01 October 2008 See abstract; claims 1-3.	15
X	US 2008-0071059 A1 (NISHIDE, H. et al.) 20 March 2008 See abstract and claims 1-5.	15
X	US 2009-0211967 A1 (DELSMAN, E. R. et al.) 27 August 2009 See claims 1-5.	15
X	WO 96-37535 A1 (THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL) 28 November 1996 See claims 1-21.	15

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 November 2015 (27.11.2015)

Date of mailing of the international search report

30 November 2015 (30.11.2015)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/046894

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