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(54) Title: SOLUBILITY MODIFICATION OF CONDUCTIVE CONJUGATED BACKBONE POLYMERS VIA THE DOPANT MOIETIES

(57) Abstract

This invention relates to an electrically conductive solution comprised of a solvent conductive conjugated backbone homopolymer or copolymer dissolved therein.

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SOLUBILITY MODIFICATION OF CONDUCTIVE CONJUGATED BACKBONE POLYMERS VIA THE DOPANT MOIETIES

FIELD OF INVENTION

This invention relates to a process for forming an electrically conductive solution comprising a solvent or solvent mixture and a solution phase of one or more electrically conductive conjugated backbone polymers doped with one or more dopants. This invention also relates to the electrically conductive solution prepared by the process of this invention and to conductive blends or composite prepared from said conductive solution, such as parts, films, coatings, fibers, paints, and inks.

BACKGROUND OF INVENTION

There has recently been an increased interest in the electrochemistry and electrical phenomena of polymeric systems. Recently, work has intensified with backbone polymers having extended conjugation in at least one backbone chain. See for example, U.S. Patent Nos. 4,855,361; 4,798,685; 4,806,271; 4,822,638; 4,851,487; and 4,798,685; and PCT WO89/01694.

SUMMARY OF INVENTION

This invention relates to an electrically conductive solution comprising a solvent and an electrically conductive conjugated backbone polymer doped with a dopant, wherein said dopant is selected such that solubility parameter of said doped conjugated backbone polymer is such that the doped conjugated backbone polymer is soluble in said solvent.

This invention also relates to a process of forming an electrically conductive solution of

conductive conjugated backbone polymer doped with a dopant in a solvent or solvent mixture by modifying the solubility characteristics of the conjugated backbone polymer through the dopant such that the solubility parameter of said solvent and said doped polymer are such that said polymer dissolves in said solvent to form said electrically conductive solution, and to a method of using the solution to form an article of manufacture by removing to solvent from the solution solidifying said electrically conductive conjugated backbone polymer in the desired configuration.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The solution of this invention comprises two essential ingredients a solvent and an electrically conductive conjugated backbone polymer doped with a dopant so that the solubility parameters of the solvent and the doped electrically conductive conjugated are such that the desire amount of doped electrically conductive conjugated backbone polymer dissolves in the solvent to form the electrically conductive solution.

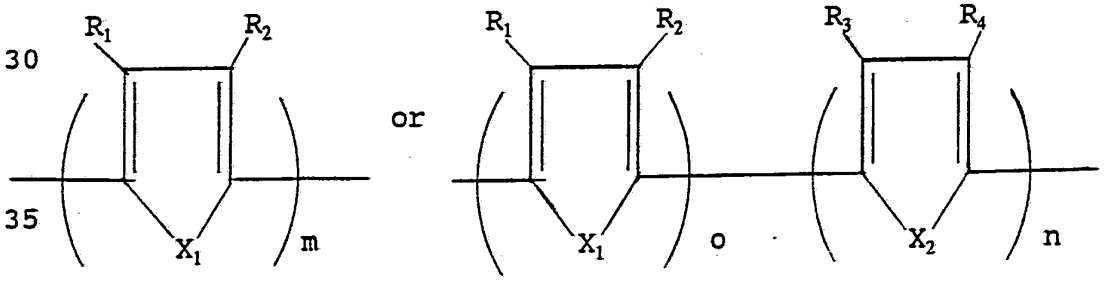
As used herein, a "solution" is a real solution or an ultrafine dispersion having an average particle size of less than about 100 nanometer. Solvents useful in the practice of this invention may vary widely. The only requirement is that the solvent is capable of dissolving the required quantity electrically conductive conjugated backbone polymer. Preferred solvents have dielectric constants measured at room temperature (i.e. 10-30°C) equal to or greater than 2.2. Illustrative of such useful solvents are water; dimethylsulfoxide; amides such as formamide, acetamide, N,N-dimethyl formamide, N,N-dimethyl acetamide, N-methyl pyrrolidinone, pyrrolidinone, and the like; alcohols and glycols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, glycol, glycerol, propanediol, benzyl alcohol, cresol, phenol,

cyclohexanol, 2-methoxy ethanol, and the like; acids, such as formic acid, acetic acid, propionic acid, butyric acid, sulfuric acid, trifluoroacetic acid, pentafluoropropionic acid, perfluorobutyric acid, phosphoric acid, phosphonic acid, sulfonic acid, and the like; ketones, such as acetone, 2-butanone, 3-pentanone, cyclohexanone, 2,4-pentadione, acetophenone, benzophenone, and the like; amines, such as methylamine, dimethylamine, dipropylamine, triethylamine, dibenzyl amine, picoline, and the like; nitro compounds of aliphatic and aromatic hydrocarbons such as nitromethane, nitroethane, nitrobenzene, nitrotoluene, nitroaniline, tetranitromethane, and the like; halogenated aliphatic and aromatic hydrocarbons such as methylene chloride, chloroform, chloromethane, dibromoethylene, trichloroethane, chlorobenzene, o-difluorobenzene, bromotoluene and the like; esters such as methyl formate, ethyl acetate, ethyl acetoacetate, methyl benzoate, benzyl acetate, ethyl oleate, butyl stearate, methyl salicylate, dimethyl phthalate, and the like; ethers such as methyl ether, ethyl ether, phenyl ether, tetrahydrofuran, 1,4-dioxane, and the like; phosphates, such as tricresyl phosphate, and the like; and silicates such as tetraethylsilicate, and the like; More preferred solvents are those having a relative dielectric constant equal to or greater than about 3.0 such as water, amides, acids dimethyl sulfoxide, amines, alcohols, ketones, and nitrohydrocarbons. Particularly preferred solvents are those having a relative dielectric constant equal to or greater than about 4.0, such as amides, acids, dimethyl sulfoxide, amines, and alcohols. The most preferred solvent is an amide, such as substituted or unsubstituted pyrrolidinone.

The other essential component of the solution of this invention is a doped electrically conductive conjugated backbone polymer. As used herein a

"conjugated backbone polymer" is a polyunsaturated polymer containing conjugated unsaturation bond systems along the polymer backbone. Illustrative of such polymers are poly(unsaturated) polymers such as substituted and unsubstituted polyacetylenes; substituted or unsubstituted poly(heteroaromatics), such as polythiophenes, poly(furans) polypyrroles, polyquinolines, polyisothianaphthenes, polycarbazoles, poly(alkyl thiophenes) and the like; substituted or unsubstituted poly(aromatics) such as polyphenylene sulfides, polyanilines, polyphenylenes, polynaphthalenes, and polyperinaphthalenes, poly(azulenes); and substituted or unsubstituted poly(aromatic vinylenes), such as poly(phenylene vinylene), poly(dimethoxy phenylene vinylene), poly(naphthalene vinylene) and the like; and substituted or unsubstituted poly(heteroaromatic vinylenes) such as poly(thienylene vinylene), poly(furylene vinylene), poly(carbazole vinylene), poly(pyrrole vinylene) and the like.

Preferred conjugated backbone homopolymer or copolymers are substituted or unsubstituted polyanilines, poly(heterocycles), and aromatic or heteroaromatic vinylenes. Illustrative of preferred homopolymers or copolymers of poly(heterocycles), and aromatic or heteraromatic vinylenes are those comprising moieties of the Formulas I to XIV:



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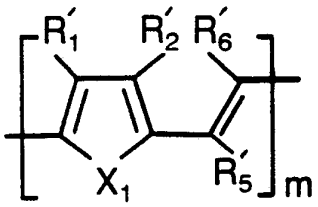

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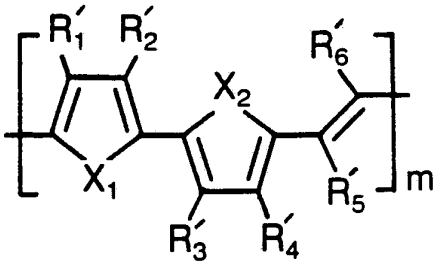

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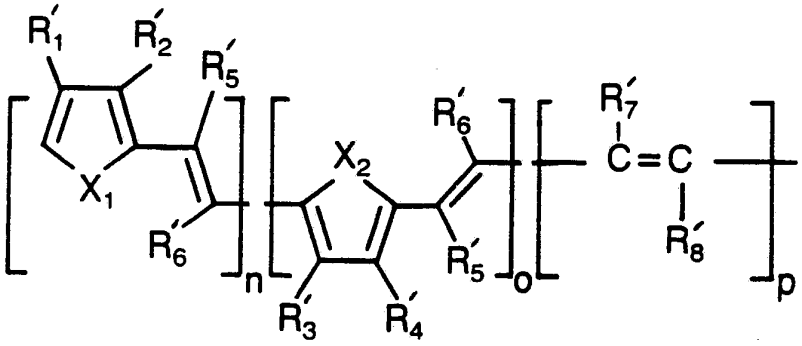

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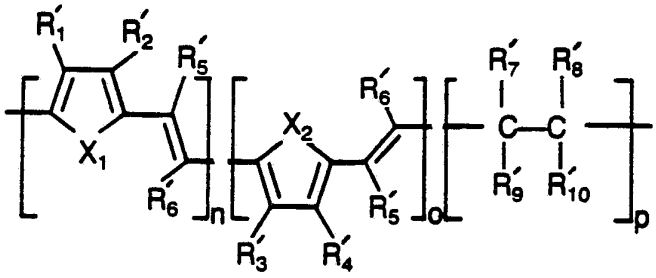

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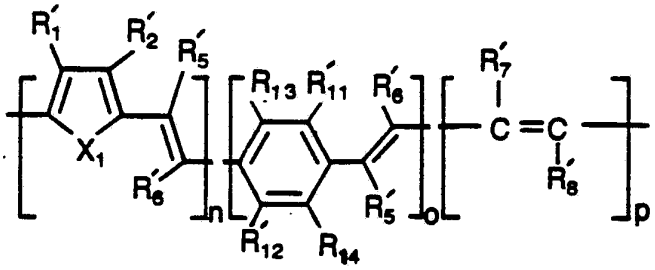

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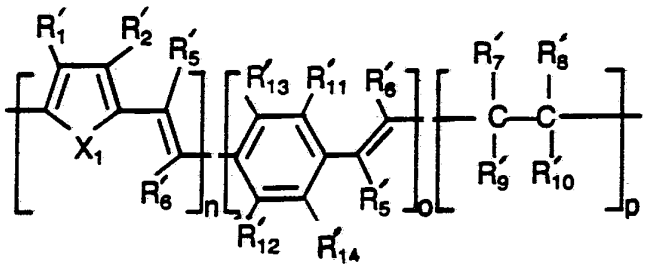

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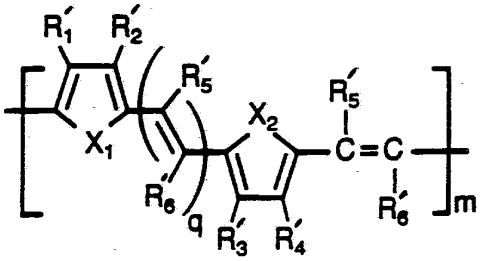

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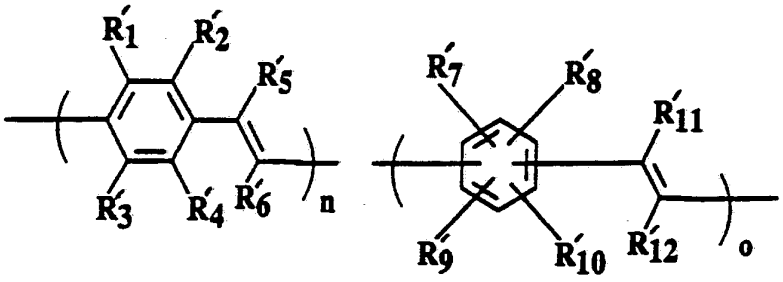

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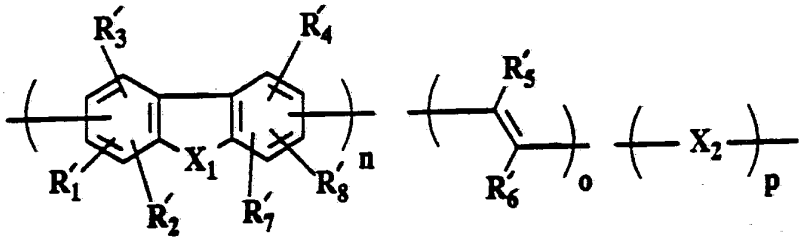

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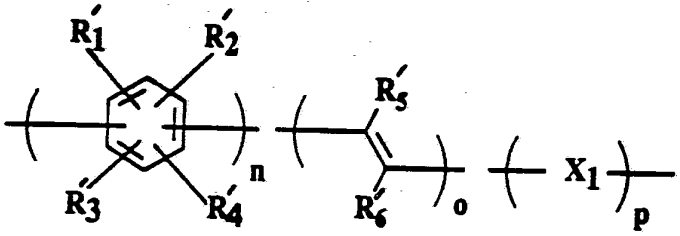

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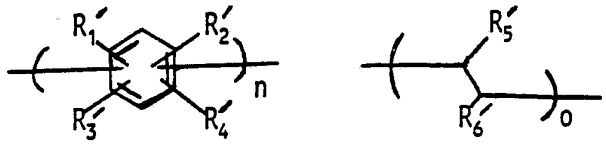

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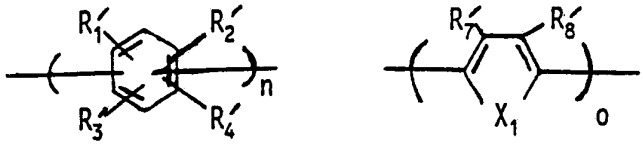


(XIV)

wherein:

m, and the sum of n, o and p are the same or different and are integers at least about 20, with the proviso that at least one of n or o is greater than zero;

q is an integer which can range from 0 to about 4;

R'_1, R'_2, R'_3, R'_4, R'_5, R'_6, R'_7, R'_8, R'_9, R'_{10}, R'_{11}, R'_{12}, R'_{13} and R'_{14} are the same or different at each occurrence and are hydrogen or isotopes thereof, hydroxyl, alkyl, alkenyl, aryl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkynyl, alkylaryl, arylalkyl, amido, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylamino, diarylamino, alkylamino, dialkylamino, alkylarylamino, arylthio, heteroaryl, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; halogen, nitro, cyano, or alkyl or phenyl substituted with one or more of acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; halo, amino, nitro, hydroxyl, cyano or epoxy moieties, or derivatives of a moiety of the formula:

$$-(OR'_{15})_r OR'_{16}$$

wherein:

R'_{15} is a divalent alkylene moiety having from 1 to about 7 carbon atoms;

R'_{16} is alkyl having from 1 to about 20 carbon atoms; and

r is a natural number from 1 to about 50; or

R'_1 and R'_2, or R'_3 and R'_4, or R'_5 and R'_6, or R'_7 and R'_8, or R'_9 and R'_{10}, or R'_{11} and R'_{12} or R'_{13} and R'_{14} substituents taken together may form an alkylene, alkenylene, or alkynylene group completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic or alicyclic carbon ring, which ring may optionally include one or more degrees of unsaturation or one or more heteroatoms of nitrogen, sulfur, phosphorus, selenium, sulfinyl, sulfonyl or oxygen; and

X_1 and X_2 are the same or different and are S, O, Se, NR'_{17}, or PR'_{17}, wherein R'_{17} is hydrogen, alkylaryl, arylalkyl, alkyl or R_1.

Illustrative of useful R'_1, R'_2, R'_3, R'_4, R'_5, R'_6, R'_7, R'_8, R'_9, R'_{10}, R'_{11}, R'_{12}, R'_{13} and R'_{14} groups are hydrogen; hydroxyl; cyano; nitro; halo; alkyl such as methyl, ethyl, butyl, pentyl, octyl, nonyl, tert-butyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like, alkenyl such as 1-propenyl, 4-butenyl, 1-pentenyl, 6-hexenyl, 1-heptenyl, 8-octenyl and the like; alkoxy such as propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonyloxy, ethoxy, octyloxy, and the like; alkanoyl such as butanoyl, pentanoyl, octanoyl, ethanoyl, propanoyl and the like; arylamino and diarylamino such as phenylamino, diphenylamino and the like; alkylsulfinyl, alkylsulfonyl, alkylthio, arylsulfonyl, arylthio, and the like, such as butylthio, neopentylthio, methylsulfinyl, benzylsulfinyl, phenylsulfinyl, propylthio, octylthio, nonylsulfonyl, octylsulfonyl, methylthio, isopropylthio, phenylsulfonyl, methylsulfonyl, nonylthio, phenylthio, ethylthio, bezylthio, phenethylthio, sec-butylthio, naphthylthio and the

like; alkoxycarbonyl such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl and the like; alkyl amino and dialkylamino such as dimethylamino, methylamino, diethylamino, ethylamino, dibutylamino, butylamino and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclooctyl, cycloheptanyl and the like; alkoxyalkyl such as methoxymethylene, ethoxymethylene, butoxymethylene, propoxyethylene, pentoxybutylene and the like; arylalkylamino such as methylphenylamino, ethylphenylamino and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenylene, phenoxymethylene and the like; and various substituted alkyl and aryl groups such as 1-hydroxybutyl, 1-aminobutyl, 1-hydroxylpropyl, 1-hydroxypentyl 1-hydroxyoctyl, 1-hydroxyethyl, 2-nitroethyl, trifluoromethyl, 3,4-epoxy-butyl, cyanomethyl, 3-chloropropyl, 4-nitrophenyl, 3-cyanophenyl, 1-hydroxymethyl, and the like; hydroxyl terminated alkyl and aryl groups such as, 2-hydroxy ethyl, 4-hydroxy butyl and 4-hydroxy phenyl; sulfonic acid, carboxylic acid and phosphoric acid terminated alkyl and aryl groups such as ethylsulfonic acid, propylsulfonic acid, butylsulfonic acid, phenylsulfonic acid, and the corresponding carboxylic and phosphoric acids and derivatives of said sulfonic, carboxylic and phosphoric acids as for example salts, esters and the like. Exemplary of other useful R'_1 to R'_{14} groups are moieties of the formula:

$$-(OR'_{15})_r OR'_{16}$$

where r, R'_{15} and R'_{16} are as described above. Useful R'_{15} groups include divalent moieties of the formulas $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$ and $-(CH_2CH(CH_3))-$, and useful R'_{16}, groups include $-CH_3$, $-CH_2CH_3$ and $-(CH_2)_8CH_3$. Illustrative of substituents having such R'_{15} and R'_{16} are ethyleneglycol monomethylether, diethylene glycol monomethylether, triethylene glycol monomethylether, tetraethylene glycol, monomethylether, and the like.

Illustrative of R'_{17} groups are hydrogen, methyl, ethyl, propyl, hexyl, octyl, nonyl, phenyl, benzyl, vinyl, allyl, dodecylphenyl, phenethyl, phenylpropyl, 2,4-dimethylphenyl, 4-methylphenyl and the like.

Polymers for use in the practice of this invention may vary widely, the only requirement is that they are comprised of conjugated backbone polymers. Polymers with oxidation potentials less than about 3.5V vs Li/Li^+ are more preferred for use in the practice of this invention. Of these more preferred polymers, preferred for use in the practice of this invention are homopolymers, and random or block copolymers of the above Formulas I to XIV in which:

m, and the sum of n, o and p are natural numbers at least about 40, preferably at least about 50, with the proviso that at least one of n or o is not zero;

q is an integer from 0 to about 4;

R'_1, R'_2, R'_3 and R'_4 are the same or different at each occurrence and are hydrogen or hydroxyl or alkyl having from 1 to about 20 carbon atoms, such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; phenyl; alkylphenyl such as 2,4-dimethylphenyl, 4-methylphenyl, 4-ethylphenyl, and 4-butylphenyl; phenylalkyl such as benzyl, phenethyl; alkxoy having from 1 to about 12 carbon atoms such as methoxy, ethoxy, and propoxy; alkanoyl having from 1 to 20 carbon atoms such as formyl, acetyl, and propionyl; alkylthio having from 1 to 20 carbon atoms such as methylthio, ethylthio, propylthio, dodecylthio and butylthio; alkoxyalkyl having from 1 to 20 carbon atoms such methoxymethyl, ethoxyethyl and heptoxypropyl; alkenyl having from 1 to about 20 carbon atoms such as allyl, vinyl and 3-butenyl; or phenyl and alkyl substituted with phosphonic acid and derivatives thereof, cyano, nitro, epoxy, hydroxyl, acid functional groups, such as

sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; or halo substituents such as trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 2-nitroethyl, 3-chloropropyl, 4-nitrophenyl, hydroxyethyl, $-CH_2CH_2CH_2SO_3H$; $-CH_2CH_2CH_2P(O)(OH)_2$; and $-CH_2CH_2CH_2CO_2H$: or moiety of the formula:

$$-(OR'_{15})_r OR'_{16}$$

wherein:

R'_{15} is divalent alkylene having from 1 to about 4 carbon atoms;

R'_{16} is alkyl having from 1 to about 10 carbon atoms; and

r is a natural number from 1 to about 25 such as ethylene glycol monomethylether and the like; or any of R'_1 and R'_2, or R'_3 and R'_4, substituents taken together may form an alkylene, alkenylene or alkynylene chain having from 2 to 20 carbon atoms completing a 4, 5, 6, 7, 8, 9 or 10 membered ring system(s) which may include one or more degrees of unsaturation or one or more heteroatoms of oxygen, nitrogen or sulfur such as 1,4-butandiyl, 1,2-ethanediyl, $-CH_2SCH_2-$, $-CH_2OCH_2-$, $-CH_2CH_2-NH-CH_2-$, or $-CH_2CH_2-NH-$;

R'_5 to R'_{14} are the same or different at each occurrence and are hydrogen, hydroxyl, alkyl having from 1 to about 12 carbon atoms, phenyl, alkylthio having from 1 to about 12 carbon atom or alkoxy having from 1 to about 12 carbon atoms; alkoxyalkyl having from 2 to about 12 carbon atoms; alkylamino having about 1 to about 12 carbon atoms alkyl; or phenyl substituted with hydroxyl, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts,

esters, and the like; cyano, nitro, epoxy, or halo substituents or any of R'_5 and R'_6, or R'_7 and R'_8, or R'_9 and R'_{10}, or R'_{11} and R'_{12} or R'_{13} and R'_{14} substituents together may form an alkenylene, alkynylene or alkylene chain having 2 to about 20 carbon atoms completing a 4, 5, 6, 7, 8, 9 or 10 membered ring system(s) which may include one or more degrees of unsaturation or one or more heteroatoms of oxygen, sulfur, or nitrogen such as 1,4-butandiyl, 1,2-ethanediyl, $-CH_2SCH_2-$ or $-CH_2OCH_2-$; and

X_1 and X_2 are the same or different and are oxygen, sulfur or NR_{17} wherein R'_{17} is hydrogen or alkyl or aryl.

Particularly preferred for use in the practice of this invention are homopolymers and random copolymers of the above-referenced Formula I to XIV wherein:

q is an integer from 0 to about 3;

m, and the sum of n, o and p are at least about 100 with the proviso that at least one of n or o is not zero;

R'_1, R'_2, R'_3 and R'_4 are the same or different at each occurrence and are hydrogen; hydroxyl; alkyl having from 1 to about 12 carbon atoms such as ethyl, methyl, propyl, n-butyl, sec-butyl, n-hexyl, n-octyl, and n-dodecyl; phenyl; alkoxy or alkylthio having from 1 to about 12 carbon atoms such as methylthio, ethylthio, propylthio, butylthio, methoxy, ethoxy and butoxy; alkoxyalkyl having from 1 to about 12 carbon atoms; or a moiety of the formula:

$$-(OR'_{15})_r OR'_{16}$$

wherein:

R_{15} is alkylene of about 2 to 3 carbon atoms;

R_{16} is alkyl of from 1 to about 10 carbon atoms; and

r is a natural number from 1 to about 10;

R'_5, R'_6, R'_7, R'_8, R'_9, R'_{10}, R'_{11}, R'_{12}, R'_{13} and

R'_{14} are the same or different at each occurrence and are hydrogen; hydroxyl; alkyl, such as methyl, ethyl or the like; substituted alkyl such as butylsulfonic acid, propylsulfonic acid, cyanomethyl, epoxybutyl, pentafluoroethyl, nitropropyl, and butylcarboxylic acid; alkoxy such as methoxy, ethoxy, butoxy, and the like; and alkylthio such as methylthio, ethylthio and the like; or any of R'_5 and R'_6, R'_7 and R'_8, R'_9 and R'_{10}, or R'_{11} and R'_{12}, or R'_{13} and R'_{14} together may be an alkenylene or alkylene chain forming an alicyclic, aromatic or heteroaromatic ring;

X_1 and X_2 are the same or different and are oxygen, sulfur or $-NR'_{17}$ where R'_{17} is hydrogen or alkyl having from 1 to about 10 carbon atoms.

Amongst these particularly preferred embodiments, most preferred are copolymers and homopolymers of Formula I to XIV in which:

q is an integer from 0 to about 2;

m, or the sum of n, o and p is at least about 125 with the proviso that at least one of n or o is not zero;

R'_1 to R'_4 are the same or different at each occurrence and are hydrogen, or alkyl, alkoxy or alkoxyalkyl having 1 to about 12 carbon atoms or a moiety of the formula:

$$-(OR'_{15})_r OR'_{16}$$

wherein:

R'_{15} is $-(CH_2)_2-$ or $-(CH_2CH(CH_3))-$;

R'16 is $-CH_3$ or $-CH_2CH_3$; and

r is a natural number 1 to about 6;

R'_5, R'_6, R'_7, R'_8, R'_9, R'10, R'_{11}, R'_{12}, R'13 and R'_{14} are the same or different at each occurrence and are hydrogen, hydroxyl, alkyl, or any of R'_5 and R'_6, R'_7 and R'_8, R'_9 and R'10, or R'_{11} and R'_{12}, or R'13 and R'14 together may form a divalent alkylene or

alkenylene chain forming an alicyclic, aromatic and/or heteroaromatic ring; and

X_1 and X_2 are sulfur or NR'17 where R'17 is hydrogen or alkyl having from 1 to about 7 carbon atoms.

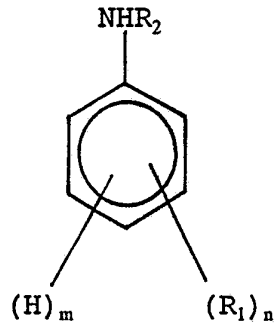
Still other preferred electrically conductive polymers are polyanilines. As used herein, "polyanilines" are homopolymers or copolymers in which at least 50 mole % of the recurring backbone monomeric units in vary ratio are selected from the group consisting of substituted or unsubstituted phenyl rings and amine linkages (-NH- or -NR- where R is substituent other than hydrogen) with varying amounts of substituted or unsubstituted quinoid rings and imine (-N=) linkages. As used herein, "neutral or undoped polyaniline" is characterized by an uncharged backbone, "polyaniline base" is a particular form of undoped polyaniline which contains at least one quinoid diimine linkage in the backbone and "electrically conductive or doped polyaniline" is characterized by a charged backbone which may be formed by a partial or complete protonation of the amine and/or imine nitrogen atoms.

Any form of such polyanilines can be conveniently used in the practice of this invention. Illustrative of useful forms are those described in Green, A.G. and Woodhead, A.E., CXVII-Aniline-black and Allied Compounds, Part II", J. Chem. Soc., 101 pp. 1117 (1912) and Kobayashi, et al., "Electrochemical Reactions... of Polyaniline Film-Coated Electrodes", J. Electroanal. Chem., 177, pp. 281-91 (1984) and in Shacklette, L.W., et al. "Structure and Properties of Polyaniline as Modeled by Single-Crystal Oligomers", J. Chem. Phys. 88 P 3955 (1988), which are hereby incorporated by references.

In the preferred embodiments of the invention, polyanilines for use in the invention are homopolymers and copolymers of the type derived from the polymerization of unsubstituted and substituted

anilines of the Formula XV:

Formula XV



wherein:

n is an integer from 0 to 5;

m is an integer from 0 to 5, with the proviso that the sum of n and m is equal to 5 and with the further proviso that at least one position on the aniline ring, preferably at the para position, is substituted with a substituent which will allow coupling of the aniline units, such halogen, hydrogen or other leaving group;

R_1 is the same or different at each occurrence and is selected from the group consisting of alkyl, deuterium, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, aryl, alkylsulfinyl, aryloxyalkyl, alkylsulfinylalkyl, alkoxyalkyl, alkylsulfonyl, arylthio, alkylsulfonylalkyl, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, halo, hydroxy, cyano, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; nitro, alkylsilane, or any of the foregoing aryl, aliphatic or cycloaliphatic groups substituted with one or more acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid,

phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; halo, nitro, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, cyano or epoxy moieties; or any two R_1 groups together or any R_1 group together with any R_2 group may form a substituted or unsubstituted alkylene, alkenylene or alkynylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroaromatic, heteroalicyclic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur, sulfinyl, ester, carbonyl, sulfonyl, or oxygen atoms wherein permissible substituents are one or more acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; halo, nitro, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, cyano or epoxy moieties ; or R_1 is an aliphatic moiety having repeat units of the formula:

$-(OCH_2CH_2)_qO-CH_3$, $-(OCH_2CH(CH_3))_qO-CH_3$,
$-(CH_2)_qCF_3$, $-(CF_2)_q-CF_3$ or $-(CH_2)_qCH_3$

wherein q is a positive whole number; and

R_2 is selected from the group consisting of permissible R_1 substituents and hydrogen.

Illustrative of useful R_1 groups are hydrogen, alkyl, such as methyl, ethyl, octyl, nonyl, tert-butyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like, alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; alkoxy such as propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonoxy, ethyoxy, octoxy, and the like; cycloalkenyl such as cyclohexenyl, cyclopentenyl and the like; alkanoyl such as butanoyl, pentanoyl, octanoyl, ethanoyl, propanoyl and the like; amino; alkylamino,

such as methylamino, ethylamino, butylamino and the like; dialkylamino, such as dimethylamino, methylethylamino and the like; arylamino such as phenylamino, p-methylphenylamino and the like; diarylamino, such as diphenylamino, p-nitrophenyl-p'-methylphenylamino and the like; alkylarylamino, such as 2-phenyl-4-methylamino and the like; alkylsulfinyl, alkylsulfonyl, alkylthio, arylthio, arylsulfinyl, and arylsulfonyl such as butylthio, neopentylthio, methylsulfinyl, benzylsulfinyl, phenylsulfinyl, propylthio, octylthio, nonylsulfonyl, octylsulfonyl, methylthio, isopropylthio, phenylsulfonyl, methylsulfonyl, nonylthio, phenylthio, ethylthio, benzylthio, phenethylthio, sec-butylthio, naphthylthio and the like; alkoxycarbonyl such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclo-octyl, cycloheptyl and the like; alkoxyalkyl such as methoxy-methyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl, phenoxymethyl and the like; and various substituted alkyl and aryl groups such as 1-hydroxybutyl, 1-aminobutyl, 1-hydroxypropyl, 1-hydroxypentyl, 1-hydroxyoctyl, 1-hydroxyethyl, 2-nitroethyl, trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 3-chloropropyl, 4-nitrophenyl, 3-cyanophenyl, and the like; acid and acid salts such as sulfonic acid, carboxylic acid and derivatives such as esters, and the like, salts; aliphatic or aryl groups substituted with acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like: such as ethylsulfonic acid, propylsulfonic acid, 4-nitrobenzene sulfonic acid, butylsulfonic acid, phenylsulfonic acid,

and the like.

Also illustrative of useful R_1 groups are divalent moieties derived from any two R_1 groups or a R_1 group with a R_2 group such as moieties having from about 2 to about 7 repeat units of the formula:

$$-(CR_3=CR_3)_b-$$
$$-(C(R_3)_2)_a-$$

wherein R_3 is the same or different at each occurrence and is hydrogen or alkyl, as for example $-(CH_2)_4-$, $-(CH_2)_3-$, $-(CH=CH-CH=CH)-$, $-[CH_2-CH(CH_3)-CH_2]-$ and $-(CH_2)_5-$, and groups comprised of such moieties which include one or more heteroatoms of oxygen, nitrogen, ester, sulfonyl, carbonyl, sulfinyl, and/or sulfur, such as $-CH_2SCH_2-$ $-CH_2NHCH_2-$, $-SCH_2NHCH_2-$, $-O-CH_2-CH_2O-$ $-O-CH_2-S-CH_2-$, $-CH_2S(O_2)CH_2-$, $-CH_2S(O)CH_2-$, $-OC(O)CH_2CH_2-$, $-CH_2C(O)CH_2-$ and $-CH_2-O-CH_2-$ to form heterocyclic amino compounds such as tetrahydronaphthylamine, dihydrobenzopyrroleamine, benzofuranamine, dihydrobenzopyranamine, dihydrobenzofuranamine, dihydrobenzoparaoxazineamine, dihydrobenzoparadiazineamine, dihydrobenzotriazoleamine, dihydro-benzothiazineamine,benzothiopyranamine, dihydro-benzoxazoleamine and the like. Exemplary of useful R_3 groups are divalent alkenylene chains containing 1 to about 3 unsaturated bonds such as divalent 1,3-butadiene and like moieties which may also include one or more divalent oxygen, nitrogen, sulfinyl, sulfonyl, carbonyl, ester, and/or sulfur groups which form such compounds as benzodiazineamine, benzodiazoleamine, benzotriazepine-amine, benzimidazolylamine, benzisoxazoleamine, benzoxazolylamine, benzothiazineamine, benzoxazineamine, naphthaleneamine, benzopyranamine, benzothiazineamine, anthraceneamine,

aminobenzothio-pyran,aminobenzodiazine, benzthiopyrone amine, amino-coumarin, benzthiopheneamine, benzothiodiazoleamine, and the like.

Exemplary of useful R_2 groups are hydrogen and the above-referenced representative R_1 groups described above such as alkyl as for example, methyl, ethyl, isopropyl, butyl, isobutyl, hexyl, octyl and the like; alkylsulfonyl such as methylsulfonyl, ethylsufonyl, propylsulfonyl and the like; arylsulfonyl such as phenylsulfonyl, p-methyl phenylsulfonyl, naphthylsulfonyl and the like.

Preferred polyanilines for use in the practice of this invention are those of the type derived from aniline of the above Formulas XV or is a derivative of said polyaniline, wherein:

n is an integer from 0 to about 2;

m is an integer from 2 to 4, with the proviso that the sum of n and m is equal to 4;

R_1 is aryl, alkyl or alkoxy having from 1 to about 30 carbon atoms, cyano, halo, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like: amino, alkylamino, dialkylamino, arylamino, hydroxy, diarylamino, alkylarylamino, or alkyl, aryl or alkoxy substituted with one or more acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; dialkylamino, arylamino, diarylamino, alkylarylamino, hydroxy, alkoxy, alkyl, and R_2 is the same or different at each occurrence and is a R_1 substituent or hydrogen.

Particularly preferred polyanilines for use in the practice of this invention are those of the type derived from head to tail polymerization of anilines of

the above Formula XV or derivatives of said polyanilines in which:

n is an integer from 0 to 1;

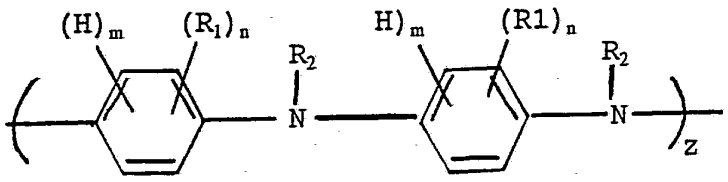
m is an integer from 4 to 5, with the proviso that the sum of n and m is equal to 5;

R_1 is aryl, alkyl or alkoxy having from 1 to about 20 carbon atoms, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like, halo, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, or alkyl or aryl substituted with acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, and halo substituents; and

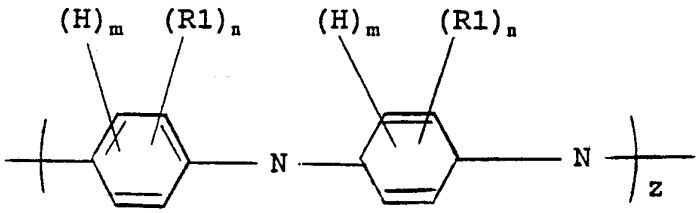
R_2 is the same or different at each occurrence and is a R_1 substituent or hydrogen.

In the preferred embodiments, the polymer is polyaniline. As used herein, "polyaniline" consists of repeat units of the Formulas XVI and/or XVII:

Formula XVI



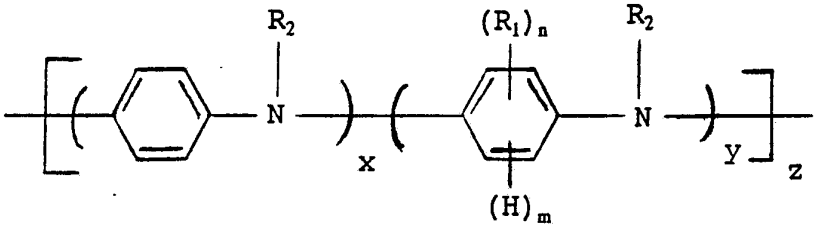
Formula XVII



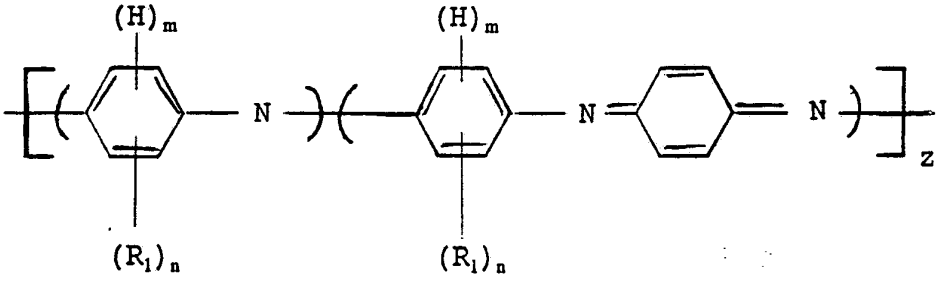
a combination thereof having various ratios of the above repeat units in the polyaniline backbone such as leucoemeraldine, protoemeraldine, emeraldine, nigraniline and pernigraniline.

Illustrative of these preferred polyanilines useful in the practice of this invention are those of the Formulas XVIII to XXI:

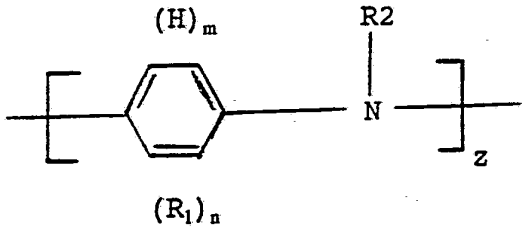
XVIII



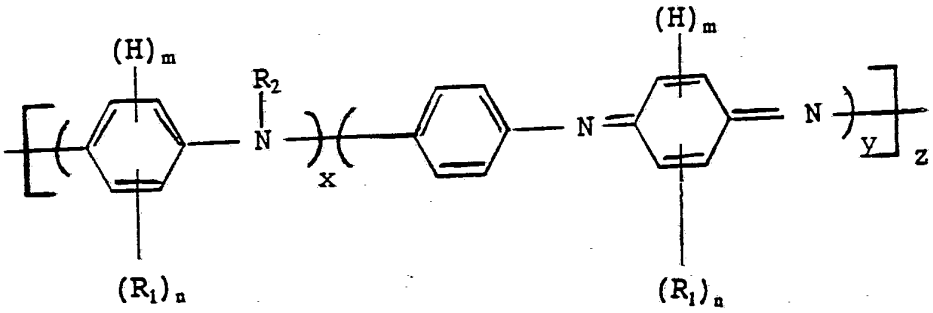
XIX



XX



XXI



wherein:

n, m, R_1 and R_2 are as described above;

x and y are the same or different at each occurrence and are integers equal to or greater than 0, with the proviso that the sum of x and y is greater than 0, preferably were x is an integer equal to or greater than 0 and/or that the ratio of x to y is greater than or equal to about 0, more preferably said ratio is equal to or greater than 0.5 and most preferably said ratio is equal to or greater than about 1; and

Preferred for use in the practice of this invention are polyanilines of the above Formulas XVIII to XXI in which:

n is an integer from 0 to about 3;

m is an integer from 1 to 4, with the proviso that the sum of n and m is equal to 4;

R_1 is alkyl, aryl or alkoxy having from 1 to about 30 carbon atoms, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like, amino, alkylamino, dialkylamino, arylamino, diarylamino, hydroxyamino, hydroxy, phosphinate alkylsulfonyl, arylsulfonyl, cyano, halo, or alkyl, aryl or alkoxy substituted with one or more acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like;

R_2 is the same or different at each occurrence and are hydrogen, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like;

x is an integer equal to or greater than 1;

y is equal to or greater than 0,

with the proviso that the ratio of x to y is equal to or greater than 0.5;

z is an integer equal to or greater than about 5;

Particularly preferred for use in the practice of this invention are polyanilines of the above Formulas XVIII to XXI in which:

n is an integer from 0 to 2;

m is an integer from 2 to 4, with the proviso that the sum of n and m is equal to 4;

R_1 is alkyl, alkoxy, amino, alkylamino, dialkylamino, arylamino, diarylamino, hydroxyamino, hydroxy, alkylsulfonyl, arylsulfonyl, acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like, or alkyl substituted with acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; wherein the aliphatic components of R_1 substituents include from 1 to about 30 carbon atoms and the aryl components of any R_1 substituent include from 6 to about 30 carbon atoms;

R_2 is the same or different at each occurrence and are hydrogen, alkyl, carboxylic acid, amino, alkylamino, dialkylamino, arylamino, diarylamino, hydroxyamino, hydroxy, alkylsulfonyl, arylsulfonyl, or alkyl substituted with one or more acid functional groups, such as sulfonic acid, carboxylic acid, phosphonic acid, phosphoric acid, phosphinic acid, boric acid, sulfinic acid and the derivatives thereof, such as salts, esters, and the like; wherein the aliphatic components of any R_2 substituent include from 1 to about 30 carbon atoms and the aryl components of any R_2 substituent include from 6 to 30 carbon atoms;

x is an integer equal to or greater than 2;

y is equal to or greater than 0, with the proviso that the ratio of x to y is greater than about 1; and

z is an integer equal to or greater than about 10.

Amongst the particularly preferred embodiments, most preferred for use in the practice of this invention are polyanilines of the above Formulas XIX or XXI in which:

n is an integer from 0 to 1;

m is an integer from 3 to 4, with the proviso that

the sum of n and m is equal to 4;

R_1 is alkyl of from 1 to about 20 carbon atoms, carboxylic acid, carboxylate, sulfonic acid, sulfonate, sulfinic acid, sulfinic acid salt, phosphinic acid, phosphinic acid salt, or alkyl of from 1 to about 20 carbon atoms substituted with one or more halo, carboxylic acid, carboxylate, sulfonic acid, sulfonate, sulfinic acid, sulfinic acid salt, phosphinic acid or phosphinic acid salt, phosphonic acid, phosphonic acid salt, substituents;

R_2 is carboxylic acid, methyl, ethyl, carboxylate, carboxylic acid, sulfonic acid, sulfonate, sulfinic acid, phosphinic acid, phosphinic acid salt, sulfinate, phosphonic acid, phosphonic acid salt, salt or hydrogen;

x is an integer equal to or greater than 2; and

y is an integer equal to or greater than 1, with the proviso that the ratio of x to y is greater than 1; and

z is an integer equal to or greater than about 10.

In the most preferred embodiment of the invention

n is 0;

m is 4;

x is an integer equal to or greater than 2;

y is an integer equal to or greater than 1 with the proviso that the ratio of x to y is greater than 1; and

z is an integer equal to or greater than about 10.

In the most preferred embodiments of this invention, the polyaniline is derived from aniline or N-alkylaniline either unsubstituted or substituted with at least one sulfonate, sulfonic acid, alkyl or alkoxy. Polyaniline derived from unsubstituted aniline is the polyaniline of choice.

In general, the number of repeat units in the conjugated backbone homopolymer or copolymer is not critical and may vary widely. The greater the number

of the greater the viscosity and molecular weight of the conjugated backbone homopolymer or copolymer. In those applications where a conjugated backbone homopolymer or copolymers of relatively low molecular weight and viscosity is required, such materials may be used, and in those applications where a conjugated backbone homopolymer or copolymer of relatively high molecular weight and viscosity is required, then such materials can be used. The number of repeat units is at least about 10. The upper limit can vary widely depending on the desired molecular weight and viscosity and the required degree of processibility, such as melt processibility, solution processibility and the like. In the preferred embodiments of the invention, the number of repeat units is at least about 20, and in the particularly preferred embodiments, the number of repeat units is at least about 30. Amongst the particularly preferred embodiments, most preferred are those embodiments in which the number of repeat units is at least about 40.

Conjugated backbone homopolymer and copolymers can be conveniently prepared through conventional procedures. Such procedures are well known in the art and will not be described herein in great detail. See for example U.S. Patent Nos. 4,940,640; 4,711,742; 4,521,589; 4,808,681; 4,983,322; 5,006,278 and 4,900,782 and "The Handbood of Conducting Polymers", edited by Terje A. Skotheim, Marcell Dikker, Inc. New York and Basel and references cited therein, all of which is hereby incorporated by reference. For example, preferred polyanilines can be prepared through use of chemical and electrochemical synthetic procedures. For example, one form of polyaniline can be prepared by treating aniline with ammonium persulfate $(NH_4)_2S_2O_8$ in excess 1M HCl. This powdered form of polyaniline is blue green in color. After methanol washing and air drying this material exhibits

a conductivity of about 5 S/cm. This conductive form of polyaniline can be treated with ammonium hydroxide in ethanol to form a non-conductive form of polyaniline which is purple in color and which has a conductivity of less than 10^{-10} S/cm. Other chemical procedures for preparation of various chemical forms of polyaniline are described in detail in Green et al and U.S. Patent Nos. 4,855,361, 4,798,685, 4,806,271, 4,822,638, 4,851,487 and 4,940,517 described above.

Useful forms of polyaniline can also be prepared electrochemically. For example, useful forms of polyaniline can be prepared by the electrochemical oxidation of aniline in aqueous fluoroboric acid electrolyte on a platinum foil anode.

Other chemical and electrochemical syntheses and transformations of the conductive form of polyaniline may be discovered and are presently contemplated as being useful. Moreover, additional forms or types of polyaniline may be elucidated in the future. Accordingly, no limitation to the syntheses, transformation, or structures herein described or postulated is intended beyond the limitations of the appended claims.

The conjugated backbone homopolymer or copolymer is doped with a suitable dopant to render the polymer electrically conductive, i.e. an electrical conductivity of at least about 10^{-9} ohm $^{-1}$ cm^{-1} by the four-in-line probe method. Any doping procedure may be used. Such methods are conventional and will not be described herein in any great detail. For example, the conjugated backbone homopolymer or copolymer is best doped by contacting the dopant with the polymer for a time sufficient to doped in the desired extent. The polymer can be contacted with the dopant in the gaseous state, in the liquid state, neat, or diluted by some suitable diluent such as a gas as for example air, or liquid such as water, or an organic liquid. The dopant

can be contacted with the conjugated backbone homopolymer or copolymer either during polymerization or after polymerization. In a preferred embodiment of the invention, the conjugated backbone homopolymer or copolymer may be doped in either by carrying out the polymerization in the presence of an acid having a pKa in the solution equal to or less than that of the homopolymer or copolymer. In general, the higher the pKa of the conjugated backbone homopolymer or copolymer, the higher the acid pKa can be used to provide a conductive polymer; and conversely, the lower the pKa of the conjugated backbone polymer the lower the pKa of the acid can be used to provide a desired degree of electrical conductivity. The pKa of the acid is preferably equal to or less than about 5, more preferably equal to or less than about 4, and the most preferably equal to or less than about 3.

In another preferred embodiment of the invention, the conjugated backbone copolymer or homopolymer can be doped after polymerization. For example, the conjugated backbone homopolymer or copolymer layer is doped by contact with a solution of the dopant in a suitable solvent such as water.

Dopants for use in the practice of this invention can vary widely.As used herein a dopant is a compound or compound mixture which is capable of doping said conjugated backbone polymer to render said polymer electrically conductive. Useful dopants may vary widely. Useful dopants may vary widely, in general, such dopant solute is derived from a compound, which upon addition to the conjugated backbone polymer, creates charge carriers (holes or free electrons) on the conjugated backbone polymer and renders the polymer conductive. Useful dopants include "oxidizing dopants" and "reducing dopants". As used herein an "oxidizing dopant" is a dopant which renders the conjugated backbone polymer with desired conductivity via an

oxidation step. As used herein an "reducing dopant" is a dopant which renders the conjugated backbone polymer with desired conductivity via a reduction step. Oxidizing dopants and reducing dopants are well known in the conductive polymer art, and any of such known oxidizing dopants and reducing dopants can be used. Dopants for use in the practice of this invention can vary widely and can be such materials which are known in the art for use in doping conjugated backbone polymers to form conductive or semi-conductive polymers, as for example, those described in detail in U.S. Patent Nos. 4,442,187 and 4,321,114 which are hereby incorporated by reference.

Useful reducing dopants are alkali metals, such as Li, Na, K, Rb, Cs, Fr, and the mixture thereof; alkaline-earth metals, such as Be, Mg, Ca, Sr, Ba, Ra, and the mixture thereof; the complexes formed between such alkali or alkaline-earth metals and some highly conjugated compounds, such as benzene, naphthalene, phenanthrene, anthracene, and other polynuclear aromatics, and the like; and ammonium solution of such alkali and alkaline metals and the like. Preferred reducing dopant for use in the practice of this invention are the complexes formed between alkali or alkaline metals and some highly conjugated compounds, such as naththalene.

Illustrative of useful dopant species are oxidizing dopants. Oxidizing dopants are well known in the conductive polymer art, and any of such known oxidizing dopants can be used.

Illustrative of useful oxidizing dopants are AsF_5, $MoOCl_4$, $MoCl_5$, PCl_5, $POCl_3$, PCl_3, $AlCl_3$, NO^+ and NO_2^+ salts (such as $NOBF_4$, $NOPF_6$, $NOSbF_6$, $NOAsF_6$, $NOCH_3CO_2$, NO_2BF_4, NO_2PF_6, NO_2AsF_6, NO_2SbF_6, and $NO_2CF_3SO_2$), $HClO_4$, HNO_3, H_2SO_4, benzoylperoxide, SO_3, Br_2, $(FSO_3)_2$, $ZnCl_2$, FSO_3H, and Fe(III) salts (such as $Fe(BF_4)_3$, $FeBr_3$, $Fe(CH_3SO_3)_3$, $Fe(ClO_4)_3$, $FeCl_3$, $Fe(OTs)_3$, and $Fe(CF_3SO_3)_3$

which give rise to doped polymers containing dopant ions such as NO_3^-, $CH_3SO_3^-$, $AlCl_4^-$, BF_4^-, $ZnCl_4^-$, PCl_4^-, PF_6^-, AsF_6^-, SbF_6^-, $CF_3SO_3^-$, ClO_4^-, OTs^-, SO_3^{-2}, $C_6H_5CO_2^-$, $CH_3SO_3^-$, FSO_3^-, and $FeCl_4^-$. Other useful oxidizing dopants include electrolyte salts such as $LiClO_4$, $LiBF_4$, $LiAsF_6$, $NaPF_6$, Bu_4NClO_4, Bu_4NOTs, $Bu_4NCF_3SO_3$, $LiCF_3SO_3$, AgOTs, and the like. Preferred oxidizing dopants for use in the practice of this invention are oxidizing dopants selected from the group consisting of $MoOCl_4$, $MoCl_5$, PCl_5, $POCl_3$, and Fe (III) salts such as $Fe(ClO_4)_3$, $FeCl_3$, $FeBr_3$, and $Fe(CF_3SO_3)_3$, and particularly preferred oxidizing dopants for use in the practice of this invention are dopants selected from the group consisting of $MoOCl_4$, $MoCl_5$, PCl_5, $POCl_3$, $FeBr_3$ and $FeCl_3$. Amongst these particularly preferred embodiments, most preferred oxidizing dopants are those embodiments in which the oxidizing dopant is $FeCl_3$.

Illustrative of other dopants are oxidizing protonic acid dopants. Such dopants include inorganic acid, hydrofluoric acid, hydroiodic acid, phosphoric acid, nitric acid, iodic acid, sulfuric acid and the like.

Illustrative of still other useful dopants are non-oxidizing protonic acids such as those of containing anionic moieties of the formula:

$$R_4(PO_3^{=})_r(PO_2(R_6)^-)_r(BO_2^{=})_r(SO_3^-)_r(CO_2^-)_r(PO_2^{=})_r$$
$$(PO(R_6)^-)_r(SO_2^-)_r$$

and having one or more cationic moieties selected from the group consisting of:

$$M^{+s}$$

wherein:

R_4 and R_6 are the same or different at each occurrence and are organic radical or amino;

M is a species having a positive charge equal to s, provided that at least one of M^{+s} is a proton or a moiety which can be transformed by radiation, heat, chemicals and the like into a proton under use conditions such as NH_4^+, $^+N(CH_3)_2H_2$, $^+N(C_2H_5)H_3$, Ph_3S^+ and the like;

s is the same or different at each occurrence and is an integer equal to 1 to 8;

r is the same or different at each occurrence and is 0 or a positive integer equal to or greater than 1, with the proviso that at least one of r is other than 0.

The R_4 and R_6 group may vary widely and can be a substituted or unsubstituted aliphatic radical such as alkyl, nitroalkyl, haloalkyl and the like, or a substituted or unsubstituted aromatic radical such as phenyl, halophenyl, nitrophenyl, anthracyl, naphthyl, phenanthryl and the like. R_4 and R_6 groups may also be a polymeric radical such as a polymer having recurring pendant phenyl groups in the polymeric backbone substituted with sulfonic acid and derivatives thereof such as salts and esters, phosphoric acid and derivatives thereof such as salts and esters, phosphonic acid and derivatives thereof such as salts and esters, sulfinic acid and derivatives thereof such as salts and esters, carboxylic acid and derivatives thereof such as salts and esters, boric acid and derivatives thereof such as salts and esters, or phosphonic acid and derivatives thereof such as salts and esters; moieties such as sulfonated or phosphonated polystyrene, poly(2-methylstyrene), poly(4-phenylstyrene), poly(2-vinyl naphthalene), poly(vinyl benzoate), poly(benzyl methacrylate) and the like. In the particularly preferred embodiments of the invention, R_4 and R_6 are aromatic radical and in the most preferred embodiments R_4 and R_6 are substituted or unsubstituted phenyl or naphthyl. The nature of the M^{+s}

group may vary widely. For example, M^{+s} may be be a non-metal cation such as Bu_4N^+, H^+, NO^+, NO_2^+, NH_4^+, $^+N(CH_3)_2H_2$, $^+N(C_2H_5)H_3$, Ph_3S^+ and the like, or may be a metal cation such as Na^+, Li^+, Ag^+, Ba^{+2}, Co^{+3}, Al^{+3}, Fe^{+3} and the like.

Preferred for use in the practice of this invention are organic acid dopants, more preferably those having anionic moieties of the formulas:

$$R_4(PO_3^=)_r(PO_2^=)_r(SO_2^-)_r(PO_2(R_6)^-)_r(SO_3^-)_r(CO_2^-)_r$$
$$(PO(R_6)^-)(BO_2^=)_r$$

and having a cationic moiety of the Formula:

$$M^{+s}$$

wherein at least one of the cationic moieties of the formula M^{+s} is a proton or is a moiety which can be transformed into a proton under use conditions;

M^{+s} is a cationic species having a positive charge s;

s is an integer equal to or greater than 1, preferably from 1 to about 8;

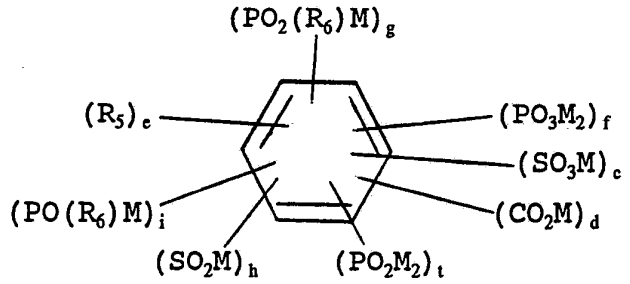
R_4 and R_6 are organic radicals or amino, and

r is an integer equal to or greater than 1, preferably from 1 to about 8;

More preferred for use in the practice of this invention as dopants are acids or acid derivatives of the formula:

$$R_4(PO_2(R_6)M)_g(PO_3M_2)_f(SO_3M)_c(CO_2M)_d(PO_2M_2)_t(SO_2M)_h$$
$$(PO(R_6)M)_i$$

or



wherein:

M is H^+, or other metal or non-metal cation with the proviso that at least one of M is H^+ or a moiety which can be thermally or chemically transformed into a proton under use conditions, such as $^+NH_4$, $^+N(CH_3)_2H_2$, $^+N(C_2H_5)H_3$, Ph_3S^+ and the like

t is 0, 1, 2, 3 or 4;

h is 0, 1, 2, 3 or 4;

i is 0, 1, 2, 3 or 4;

c is 0, 1, 2, 3 or 4;

d is 0, 1, 2, 3 or 4;

f is 0, 1, 2, 3 or 4;

g is 0, 1, 2, 3 or 4, with the proviso that at least one of c, d, f, g, h, i or t is other than 0;

e is 0, 1 or 2; and

R_4 and R_5 are the same or different at each occurrence and are nitro, cyano, hydroxy, halo, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, alkoxy, or substituted or unsubstituted alkoxy, aryl or alkyl having from 1 to about 30 carbon atoms wherein permissible substituents include sulfonate salt, perhaloalkyl, phenyl, alkoxy, halo, cyano, amino, haloalkyl, hydroxy, sulfonic acid, phosphoric acid, phosphate salt, boric acid, sulfinate salt, phosphinate salt, sulfinic acid, borate salt,

phosphinic acid, phosphonate salt, phosphonic acid, carboxylic acid, nitro, carboxylate salt and the like, or any two R_6, or any two R_5, or R_4 and any R_6 substituents together may form an alkenylene chain completing a fused-ring system which chain may be unsubstituted or substituted with one or more halo, phosphoric acid, hydroxy, boric acid, nitro, cyano, amino, sulfinate salt, phosphinic acid, alkylamino, dialkylamino, phosphinate salt, arylamino, diarylamino, alkylarylamino, sulfinic acid, phosphate salt, carboxylate salt, phosphonic acid, phosphonate salt, sulfonate salt, borate salt, sulfonic acid or carboxylic acid groups, or R_4 or R_5 is a moiety of the formula:

$$-(CH_2)_qCF_3,\ -(CF_2)_qCF_3,\ -(CH_2)_qCH_3$$
$$-(OCH_2CH_2)_qOCH_3 \text{ or } -(OCH_2CH(CH_3))_qOCH_3$$

wherein:

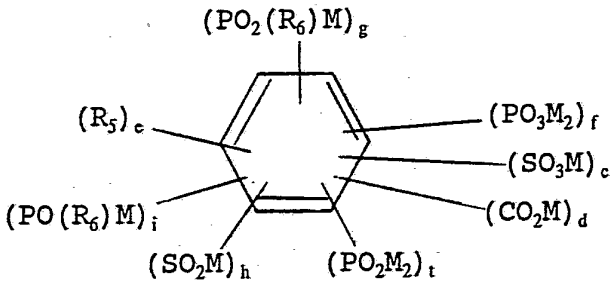
q is a positive whole number from 1 to about 10; and

R_6 is alkyl, aryl, aryloxy or alkoxy.

In the particularly preferred embodiment of this invention, useful dopants are acids and/or acid derivatives of the above formula:

$$R_4(PO_2(R_6)M)_g(PO_3M_2)_f(SO_3M)_c(CO_2M)_d(PO_2M_2)_t(SO_2M)_h(PO(R_6)M)_i$$

or



wherein:

c is 0, 1, 2 or 3;

d, t, f, g, h and i are the same or different at each occurrence and are with the proviso that at least one of c, d, t, f or g, i or h is other than 0;

e is 0, 1 or 2;

R_4 and R_5 are the same or different are hydroxy, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkyl aryl amino, substituted or unsubstituted phenyl or alkyl wherein permissible substituents are selected from the group consisting of alkyl, hydroxy, amino, alkylamino, dialkylamine, arylamine, diarylamino, alkylarylamino, hydroxy, phenyl, haloalkyl, perhaloalkyl, cyano, amino, nitro, alkoxy, boric acid, borate salts, phosphonate, phosphonic acid, carboxylate salts, sulfonate salts, phosphate salts, phosphinic acid, phosphinate salt, sulfonic acid, carboxylic acid, phosphoric acid, sulfinic acid or sulfinate salts or any two R_6, or any two R_5 or R_4 and any R_6 substituents together may form an unsubstituted or substituted or alkenylene chain completing a naphthalene, anthracene or phenanthrene fused ring system wherein permissible substituents are as described above or R_4 or R_5 is a moiety of the formula:

$$-(CH_2)_qCF_3, -(CF_2)_qCR_3, -(CH_2)_qCH_3,$$
$$-(OCH_2CH_2)_qOCH_3 \text{ or } -(OCH_2CH(CH_3))_q\ OCH_3$$

wherein:

q is a positive whole number from 1 to about 10;

R_6 is alkyl, alkoxy, aryloxy or aryl; and

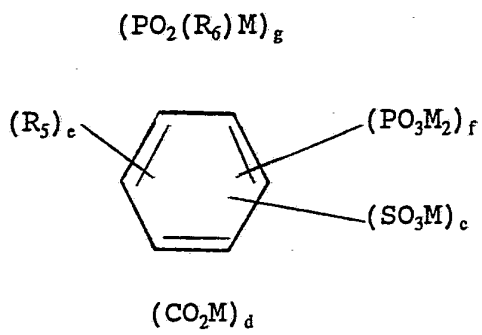
M is H^+, or other metal or non-metal cation, with the proviso that at least one of M is H^+ or a moiety which can be thermally or chemically transformed into a proton under use conditions.

In the most preferred embodiments of this invention, useful dopants are acids and/or acid

derivatives of the formula:

$$R_4(PO_2(R_6)M)_g(PO_3M_2)_f(SO_3M)_c(CO_2M)_d$$

or



wherein:

c, d, e, f and g are the same or different and are 0, 1 or 2, with the proviso that at least one of c, d, f and g is not 0;

R_4 and R_5 are the same or different at each occurrence and are alkyl, phenyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, or alkyl substituted with one or more fluoro, sulfonic acid, sulfonate salt, alkoxy, carboxylate salt, hydroxy, nitro, cyano, phosphinic acid, phosphonic acid, phosphinate salt, phosphonate salt, amino or carboxylic acid groups, or phenyl substituted with one or more alkyl, alkoxy, fluoroalkyl, sulfonic acid, phosphinic acid, phosphonic acid, phosphinate salt, phosphonate salt, sulfonate salt, carboxylate, hydroxy, nitro, cyano, or carboxylic acid groups or any two R_6, or R_4 and any R_6, or any two R_5, substituents together may form an alkylene or alkenylene chain completing a naphthalene, anthracene or phenanthrene fused system which may be substituted with one or more alkyl,

alkoxy, fluoro, phosphinic acid, phosphinate salt, phosphonic acid, phosphonate salt, fluoroalkyl, sulfonic acid, sulfonate salt, carboxylic acid, carboxylate salt, hydroxy, nitro, amino or cyano groups;

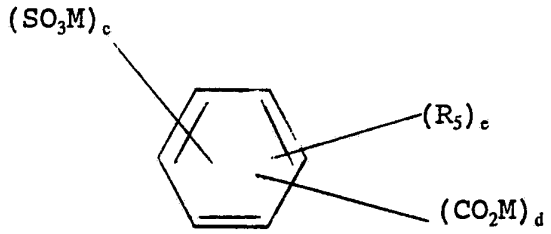
R_6 is aryl, aryloxy, alkyl or alkoxy; and

M is H^+ or other metal or non-metal cation, with the proviso that at least one of M is H^+ or is a moiety which can be thermally transformed into a proton under use conditions.

In the especially preferred embodiments of this invention, useful dopants are acids or acid derivatives of the formula:

$$R_4(SO_3M)_c\ (CO_2M)_d$$

or



wherein:

c is 1, 2 or 3;

d is 1, 2 or 2 with the proviso that at least one of c, d is not 0

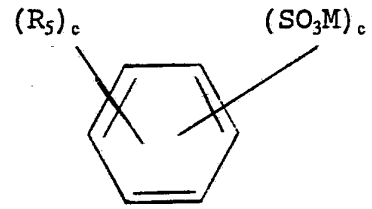
e is 0, 1 or 2;

R_4 and R_5 are th same or different at each occurrence and are hydroxy, dialkylamino, diarylamino, alkylarylamino, amino, alkylamino, arylamino, alkyl,

phenyl, alkyl substituted with one or more fluoro, sulfonic acid, sulfonate salt, alkoxy, dialkylamino, diarylamino, alkylarylamino, carboxylate salt, hydroxy, alkylamino, arylamino, phosphonic acid, nitro, cyano, phosphinic acid, phosphinate salt, phosphonate, amino or carboxylic acid groups, or phenyl substituted with one or more alkyl, alkoxy, fluoroalkyl, dialkylamino, diarylamino, alkylarylamino, sulfonic acid, alkylamino, arylamino, sulfonate salt, carboxylate salt, hydroxy, phosphinate acid, phosphinate salt, nitro, cyano, amino or carboxylic groups; or any two R_6, or any two R_5, or R_4 and any R_6 substituents together may form an alkylene or alkenylene chain completing a naphthalene, anthracene or phenanthrene fused system which may be substituted with one or more alkyl, alkoxy, fluoro, fluoroalkyl, sulfonic acid, sulfonate salt, carboxylic acid, phosphinic acid, phosphinate salts, carboxylate salt, hydroxy, nitro, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, or cyano groups;

M is H^+ or other metal or non-metal cation or a moiety which can be thermally tranformed into a proton under conditions.

In the process of the embodiment of this invention of choice, the dopant is a sulfonic acid or sulfonic acid derivative of the formula:



wherein;

c is 1, 2 or 3;

e is 0, 1 or 2;

R_5 is alkyl or alkyl substituted with one or more fluoro groups, or any two R_5 groups together may form

an alkenylene chain completing a naphthalene fused ring system which may be substituted with one or more sulfonic acid, sulfonic salt group or a combination thereof; and

M is a proton, or other metal or non-metal cation, with the proviso that at least one of M is proton.

The other important requirement for the dopant to be used in the preferred embodiments of this invention is that the dopant or dopant mixture should have a desired set of averaged solubility parameters which will modify, after coupling to said polymer via doping interaction, the solubility parameters of said doped conducting polymer to establish a relationship to the solubility parameters of said solvent or solvent mixture to render said conductive polymer soluble in said solvent or solvent mixture to the desired extent.

The resultant solubility parameter of the doped conjugated backbone is equal to the volume fractional sum of the solubility parameters of the individual components(i.e. the neutral conjugated backbone polymer and the dopant or dopants), as expressed in the following equation:

$$\delta = \Sigma \Phi\iota \, \delta\iota = \Sigma\left(\frac{\chi\iota \, \nu\iota}{\Sigma\chi\iota\nu\iota}\right)\delta\iota$$

wherein:

Φ_i is the volume fraction of the i-th component;

δ_i is the solubility parameter of the i-th component;

χ_i is the molar fraction of the i-th component; and

V_i is the molar volume of i-th component.

The molar volume of the i-th component is equal to

the ratio of the molecular weight of the i-th component to the density of the i-th component.

The value for solubility parameters of the i-th component (δ_i) can be found in the Handbook of Chemistry and Physics CRC Press, 67th ed. 1986 and "Handbook of Solubility Parameters and Other Cohesion Parameters" (by A.F.M. Barton; CRC Press, 1983) and "Polymer Handbook" (edited by J. Brandrup and E.H. Immergut; John Wiley & Sons, 1989). The solubilty parameters of the i-th component (δ_i) can also be calculated from the heat of vaporization of component i according to following equation:

$$\delta_i = \left[\frac{D_i(\Delta H_i^v - RT)}{M_i} \right]^{1/2}$$

wherein:

D_i is the density of the i-th component M_i is the molecular weight of the i-th component;

ΔH_i^v is the heat of vaporization of the i-th component which may be found in "Handbook of Physics and Chemistry";

T is the temperature (in Kelvin) at which the measurement was conducted; and

R is ideal gas constant.

Other useful methods to estimate the solubility parameter of the i-th component is the group contribution methods as disclosed in the previously mentioned three handbooks. In these methods the energy of vaporization of the i-th component is measured by linearly adding up energy of vaporization of the individual consisting sub-groups (or functional groups)

according to the following equation:

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i} \right)^{1/2} = \left(\sum \frac{N_j \Delta e_j}{V_i} \right)^{1/2}$$

wherein:

ΔE^v_i is the energy of vaporization of the i-th component;

V_i is the molar volume of the i-th component;

Δe_j is the energy of evaporation contributed from the sub-group type j of the i-th component which can be found in the "Handbook of Solubility Parameters and Other Cohesion Parameters" (A.F.M. Barton, CRC Press, 1983);

N_j is the number group of the sub-group type j of the i-th component.

The solubility parameter of useful solvents can be determined by any suitable means. For example, solubility parameters can be obtained from suitable handbooks as for example the three handbooks mentioned hereinabove. The solubility parameter can also be determined through use of conventional methods as for example group contribution methods.

The amount of dopant used in the practice of this invention can vary widely. Any amount of dopant can be used as long as the used amount renders a desired amount of conjugated backbone polymers soluble in the desired solvent or solvent mixture for conveniently performing the desired process. In the preferred embodiments of this invention, an amount of dopant is used to render from about 0.001 wt% to about 100 wt% of said conjugated backbone polymer soluble in said solvent or solvent mixture; more preferred from about 0.1 wt% to about 100 wt% of said conjugated polymer;

particularly preferred from about 1 wt% to about 100 wt%; most preferred from about 10 wt% to about 100 wt %.

The concentration of the dissolved electrically conductive conjugated polymer in the desired solvent or solvent mixture is not critical. Any concentration can be used which is suitable for any processing techniques either known in the art or will developed in the future. In the preferred embodiments of this invention, the concentration of said conjugated polymer in the solution is at least about 0.001 wt % based on the weight of said solution; more preferred is at least 0.01 wt%; particularly preferred is at least 0.1 wt %, and most preferred is at least 1 wt%.

The solution of this invention can be formed through use of any suitable procedure, as for example by direct dissolution of the doped electrically conductive polymer in a suitable solvent; or, alternatively by dissolving the dopant and the neutral polymer individually in any appropriate solvent. For example, the neutral conjugated backbone polymer can be dissolved (if soluble) or dispersed (if insoluble) in the desired solvent and then mix with the desired dopants or dopant solution of the same or different solvent or solvent mixture. The conjugated polymer can also be dissolved in a solvent other than the desired solvent and then mix with a solution of said desired dopant in the desired solvent. For another example, the conjugated polymer and the desired dopant can be first dissolved separately in a slovent different from the desired solvent and then mix to each other in the desired solvent. For another example the conjugated polymer and the desired dopant can be dispersed sequentially or simultaneously in the desired solvent and then followed by the addition of a compoud or solvent which will initiate the formation of a solution phase of doped conducting polymer by enhancing the

dissolution characteristics of at least one of said dispersed components in the desired solvent.

Another aspect of this invention relates to a method of using the conductive solution for making conductive articles, such as films, fibers, foams, parts, paints, and inks. Methods for forming such conductive articles can vary widely. Any method known in the art may be used. For example, solution spinning and gel spinning techniques can be used for forming conductive fibers from the conductive solution of this invention. Spin coating, cast coating, doctor blades, transfer coating, graphic printing can be used for forming conductive films either free standing or on a substrate and coatings from the conductive solution of this invention. Conductive composites or blends can be prepared from the conductive solution of this invention by adding desired organic or inorganic fillers or binders into said conductive solution. This formed conductive blends or composite can then be processed further, using any processing method known in the art, into various conductive articles, such as conductive films, fibers, foams, parts, paints and inks. Illustrative of such techniques are compression molding, cold molding, blow molding, injection molding, transfer molding, sluch or rotational molding, extrusion molding, calendering, sintering, compaction, extrusion, agitation, fusion, and the like. Useful fillers, binders or substrates may be formed of organic materials, inorganic materials, or a combination of such materials. Illustrative of useful inorganic fillers, binders or substrates are materials such as carbon black, graphite, mica, clay, glass, ceramics, SiO_2, and the like. Useful organic fillers, binders and substrates include polymeric materials such as thermoset and thermoplastic polymers. Thermoset polymers for use in the practice of this invention may vary widely. Illustrative of such useful thermoset

polymers are alkyds derived from the esterification of a polybasic acid such as phthalic acid and a polyhydric alcohol such as glycol; allylics such as those produced by polymerization of dialkyl phthalate, dialkyl isophthalate, dialkyl maleate, and dialkyl chlorendate; amino resins such as those produced by addition reaction between formaldehyde and such compounds as melamine, urea, aniline, ethylene urea, sulfonamide and dicyandiamide; epoxies such as epoxy phenol novolak resins, diglycidyl ethers of bisphenol A and cycloaliphatic epoxies; phenolics such as resins derived from reaction of substituted and unsubstituted phenols such as cresol and phenol with an aldehyde such as formaldehyde and acetaldehyde; polyesters; silicones; and urethanes formed by reaction of a polyisocyanate such as 2,6-tolylene diisocyanate, 4,4-diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate and 4,4'-dicyclohexylmethane diisocyanate with a polyol such as polyether polyol (trimethylol propane, 1,2,6-hexanetriol, 2-methyl glycoside, pentaerythitol, poly(1,4-tetramethylene ether) glycol, sorbitol and sucrose), polyester polyols such as those prepared by esterification of adipic acid, phthalic acid and like carboxylic acids with an excess of difunctional alcohols such as ethylene glycol, diethylene glycol, propanediols and butanediols.

Thermoplastic polymers for use in the formulation of the composition of this invention may vary widely. Illustrative of such polymers are polyesters such as poly(pivaloyl lactone), poly(para-hydroxybenzoate), poly(ethylene oxybenzoate), poly(ethylene isophthalate), poly(ethylene terephthalate), poly(1,4-cyclohexane dimethylene terephthalate), poly(ethylene-1,5-naphthalate), poly(ethylene-2,6-naphathalate) and the like; polyamides such as poly(4-aminobutyric acid) (nylon 4), poly(6-aminohexanoic acid) (nylon 6),

poly(11-aminoundecanoic acid) (nylon 11), poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide), (nylon 6,10), poly[bis(4-aminocyclohexyl)-methane-1,10-decanedicarboxamide] (Quiana)(trans), poly(metaphenylene isophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), and the like; polycarbonates such as poly[methane bis(4-phenyl)carbonate], poly[1,1-ethane bis(4-phenyl)carbonate], poly[4,4-heptane bis(4-phenyl)carbonate], poly [1,1-(1-phenyl-ethane)bis(4-phenyl)carbonate], poly[diphenylmethane bis(4-phenyl)carbonate], poly[1,1-cyclohexane bis(4-phenyl) carbonate], poly[thio bis(4-phenyl)carbonate], poly [2,2-propane bis-[4-(2-methyl phenyl)]carbonate], poly [2,2-propane bis-[4-(2-chlorophenyl)]carbonate], and the like; polymers derived from the polymerization of α,β-unsaturated monomers such as polyethylene, acrylonitrile/butadiene/styrene terpolymer, polypropylene, poly(4-methyl-1-pentene), polyisobutylene, poly(isoprene), 1,2-poly(1,3-butadiene) , polystyrene, poly(vinyl chloride), poly(vinylidene fluoride), poly(vinylidene chloride), poly(tetrafluoroethylene) (Teflon), poly(chlorotrifluoroethylene), poly(vinyl alcohol), poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), polyacrylonitrile,polyacrylamide and the like; polydienes such as poly(1,3-butadiene) and the like; polyoxides such as poly [2,2-bis(chloromethyl)-trimethylene-3-oxide] (penton), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(2,6-diphenyl-1,4-phenylene oxide) (Texax, P30) and the like; polysulphides such as poly(phenylene sulphide) and the like; polysulfones such as poly[4,4'-isopropylidene diphenoxy di(4-phenylene)

sulphone]; noryl, and mixtures thereof.

In the preferred embodiments of the invention, the non-conductive homopolymer or copolymer is a thermoplastic homopolymer or copolymer. Preferred thermoplastic polymers are polyamides, polyesters, poly(carbonates), poly(α-olefins), poly(vinyl halides), polysulfones and acrylonitrile/butadiene/styrene terpolymer. More preferred thermoplastic homopolymer or copolymers are polyamides, polycarbonates, polyesters and poly(α-olefins), and most preferred thermoplastic polymers are poly(ethylene terephthalate), nylon-6, nylon-6,6, nylon-12, polyethylene, polypropylene and polystyrene.

The electrically conductive solution of the invention, and the article of this invention formed from the solution can be used for any purpose for which conductive solutions and articles are useful. Examples of articles include conductive polymer housings for EMI Shielding of sensitive electronic equipment such as microprocessors; infrared, radio frequency and microwave absorbing shields; flexible electrical conducting connectors; conductive bearings and brushes; semiconducting photoconductor junctions; electrodes; capacitors; optically transparent or non-transparent corrosion-preventing coatings for corrodible materials such as steel; antistatic materials and optically transparent or non-transparent coatings for packaging electronic components; carpet fibers; waxes for floors in computer rooms; antistatic finishes for CRT screens, aircraft, and auto windows; and the like.

Various other applications are anticipated for the conducting coatings produced by the present process and solution such as in conducting plastic gas tanks; solar window coatings; transparent electrical elements for heated windows and heated liquid crystal displays; electrochromic displays, electrical contacts for electroluminescent displays and electroluminescent

lights, and electrical contacts for piezoelectric films for transparent loud speakers; transparent conducting coatings for windows in burglar alarm systems; membrane coatings for chemical separations (such as O_2 and N_2, for example); and conducting coatings for membrane switches; and a discharge layer or photoresist layer for lithographic process.

Specially useful coating of conducting polymers are those which are transparent in the visible spectral region. By transparent in the visible region, it is meant that at least 30% of the solar energy spectrum in the visible region is transmitted by the coating. Since transparency is inversely related to conducting polymer thickness, a desired degree of transparency can be obtained by limiting the thickness of this layer, such as by limiting contact time with the initiating agent or with monomer and oxidizing agent. Dual pane windows for the control of solar heating are a particularly useful application area for use of the present process for depositing transparent conjugated polymer coatings.

EXAMPLE I

Into a solution containing 1770 mL H_2O, 50g aniline (0.54 mole) and 172g tosylic acid (0.90 mole) was added dropwise at 15°C a solution of ammonium persulfate (153.4g in 336.5 mL H_2O) over a period of 40 minutes. The reaction was then allowed to continue at 15°C for 0.5 hour.

The resulting solid precipitates was collected and washed by 6 L tosylic acid aqueous solution (10 wt%) and then with 3 L of methanol. A blue solid was obtained which dried in air for 25 h, and dried at 130°C for 3 h under dynamic vacuum to give a green powder. The conductivity of the dried and pressed pellet was 1 Scm^{-1} as measured by the four in line probe method. The conductivity of the moisture-saturated pellet was 20 Scm^{-1} by the

four-in-line probe method.

The yield was 78g. The intrinsic viscosity (in H_2SO_4 at 25°C was 0.66 dL/g. The elemental analysis were:

C: 64.37%(wt%) H: 4.86% N: 8.59%
S: 8.40% O: 13.51%
Moisture: less than 0.8 wt%

EXAMPLE II

Poly(anilinium tosylate) (50g) obtained in Example I was suspended in 500 mL H_2O and stirred with 30g of sodium carbonate at ambient temperature for 20 hrs. The resulting solid was collected by filtration and rinsed with 2 L of deionized water. The filter cake was dispersed in 1.5 L of deionized water and stirred for 4 h to remove sodium carbonate residue. The solid was then re-collected by filtration and rinsed with 2 L of deionized water. The resulting filter cake was air-dried at 25°C for 20 h and then vacuum-dried at 80°C for 3 h.

The elemental analysis results showed that the sample was free of dopant (S < 0.03 wt%) and sodium carbonate (Na, non-detactable).

EXAMPLE III

The modified effect of the dopant species on the solubility of a conjugated backbone polymer was examined by mixing a selected dopant, such as a protonic acid dopant, with a undoped conjugated backbone polymer, such as polyaniline, in the presence of a solvent, such as N-methyl pyrrolidinone. A typical experiment is as follows:

Into a 2 dram vial was placed 0.1 g of the neutral polyaniline obtained in Example II. To the vial 2 mL of N-methyl pyrrolidinone was added. The neutral polyaniline dissolved to form a blue solution. Into this blue solution about 0.2 g of a selected acid

dopant was added to doped the polyaniline in the solution. The doped polyaniline either remained dissolved in the solvent to form an electrically conductive solution, or precipitated out of the solvent, depending the acid dopant used. The results are summarized in the following Table I.

TABLE I

DOPANT	RESULT
Trifluoroacetic Acid	Green Solution
Pentafluoropropionic Acid	Green Solution
Perfluorooctanoic Acid	Green Precipitation
Perfluorodecanoic Acid	Green Precipitation
Trifluoromethane Sulfonic Acid	Green Solution
Methane Sulfonic Acid	Green Precipitation
Ethane Sulfonic Acid	Green Solution

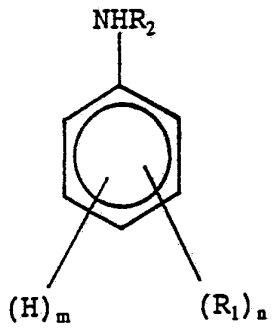
WHAT IS CLAIMED IS

1. An electrically conductive solution comprising:

a solvent having dissolved therein an electrically conductive conjugated backbone copolymer or homopolymer doped with a dopant, wherein said dopant is selected such that the solubility parameter of said doped conjugated backbone polymer is such that said doped conjugated backbone polymer is soluble in said solvent to any extent.

2. A solution according to claim 1 wherein said conjugated backbone copolymer or homopolymer is a polaniline of the type derived from a aniline of the Formula XV:

Formula XV



wherein:

n is an integer from 0 to 5;

m is an integer from 0 to 5, with the proviso that the sum of n and m is 5 and with the further proviso that at least one position of the aniline ring, preferably at the para position, is substituted with a substituent which will allow coupling of the aniline units such halo, hydrogen or other leaving group;

R_1 is phosphinic acid, phosphonic acid, sulfonic acid, boric acid, phosphoric acid, alkylamino,

dialkylamino, arylamino, diarylamino, alkylarylamino, amino, sulfonate salt, borate salt, hydroxy, phosphonate salt, phosphinate salt, phosphate salt, sulfinic acid, nitro, sulfinate salt, carboxylic acid, halo, carboxylate salt, cyano, deuterium, or substituted or unsubstituted alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkynyl, dialkylamino, arylamino, diarylamino, alkylarylamino, aryloxy, hydroxy, alkylthioalkyl, alkylaryl, arylalkyl, aryloxy, amino, alkylthioalkyl, alkylaryl, arylalkyl, alkylsufinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, arylsulfinyl, alkoxycarbonyl, alkylsilane, or arylsulfonyl, wherein permissible substituents are one or more amino, phosphinate salt, alkylamino, dialkylamino, arylamino, diarylamino,phosphinic acid, alkylarylamino, phosphonic acid, sulfonic acid, boric acid, sulfinic acid, sulfinate salt, phosphoric acid, sulfonate salt, borate salt, carboxylate salt, phosphonate salt, phosphate salt, carboxylic acid, halo, nitro, hydroxy, cyano or epoxy moieties; or any two R_1 substituents or any one R_1 substituent and R_2 substituent taken together may form substituted or unsubstitued alkylene, alkynylene or alkenylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroalicyclic, heteroaromatic or alicyclic carbon ring, which ring may optionally include one or more divalent ester, carbonyl, nitrogen, sulfur, sulfinyl, sulfonyl or oxygen, wherein permissible substituents are one or more amino, alkylamino, phosphinic acid, phosphinate salt, dialkylamino, arylamino, diarylamino, alkylarylamino, phosphonic acid, sulfonic acid, boric acid, sulfinic acid, sulfinate salt, phosphoric acid, sulfonate salt, borate salt, carboxylate salt, phosphonate salt, phosphate salt, carboxylic acid, halo, nitro, hydroxy, cyano or epoxy moieties, or R_1 is an aliphatic moiety having repeat units of the formula:

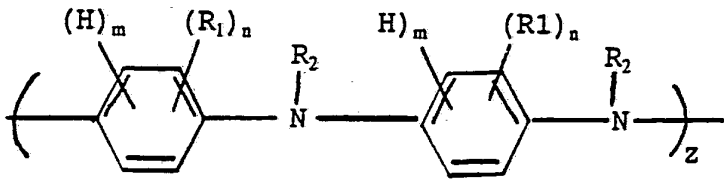
$(OCH_2CH_2)_q$ O-CH_3, $(OCH_2CH(CH_3))_q$O-CH_3,
$(CH_2)_qCF_3$, $(CF_2)_qCF_3$ or $(CH_2)_q$ CH_3

wherein q is a positive whole number; and

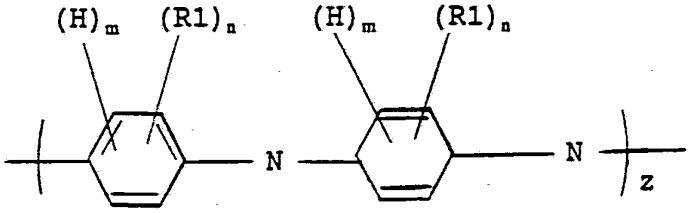
R_2 is the same or different at each occurrence and is R_1 substituents or hydrogen.

3. A solution according to claim 2 wherein the polyaniline comprises repeat units of the Formulas XVI or XVII:

Formula XVI



Formula XVII



or any combinations thereof;

wherein:

n is an integer from 0 to 5;

m is an integer from 0 to 5, with the proviso that the sum of n and m is 5 and with the further proviso that at least one position of the aniline ring, preferably at the para position, is substituted with a substituent which will allow coupling of the aniline units such halo, hydrogen or other leaving group;

R_1 is phosphinic acid, phosphonic acid, sulfonic acid, boric acid, phosphoric acid, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, amino, sulfonate salt, borate salt, hydroxy, phosphonate salt, phosphinate salt, phosphate salt, sulfinic acid, nitro, sulfinate salt, carboxylic acid, halo, carboxylate salt, cyano, deuterium, or substituted or unsubstituted alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkynyl, dialkylamino, arylamino, diarylamino, alkylarylamino, aryloxy, hydroxy, alkylthioalkyl, alkylaryl, arylalkyl, aryloxy, amino, alkylthioalkyl, alkylaryl, arylalkyl, alkylsufinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, arylsulfinyl, alkoxycarbonyl, alkylsilane, or arylsulfonyl, wherein permissible substituents are one or more amino, phosphinate salt, alkylamino, dialkylamino, arylamino, diarylamino,phosphinic acid, alkylarylamino, phosphonic acid, sulfonic acid, boric acid, sulfinic acid, sulfinate salt, phosphoric acid, sulfonate salt, borate salt, carboxylate salt, phosphonate salt, phosphate salt, carboxylic acid, halo, nitro, hydroxy, cyano or epoxy moieties; or any two R_1 substituents or any one R_1 substituent and R_2 substituent taken together may form substituted or unsubstitued alkylene, alkynylene or alkenylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroalicyclic, heteroaromatic or alicyclic carbon ring, which ring may optionally include one or more divalent ester, carbonyl, nitrogen, sulfur, sulfinyl, sulfonyl or oxygen, wherein permissible substituents are one or more amino, alkylamino, phosphinic acid, phosphinate salt, dialkylamino, arylamino, diarylamino, alkylarylamino, phosphonic acid, sulfonic acid, boric acid, sulfinic acid, sulfinate salt, phosphoric acid, sulfonate salt, borate salt, carboxylate salt, phosphonate salt, phosphate salt, carboxylic acid, halo, nitro, hydroxy, cyano or

epoxy moieties, or R_1 is an aliphatic moiety having repeat units of the formula:

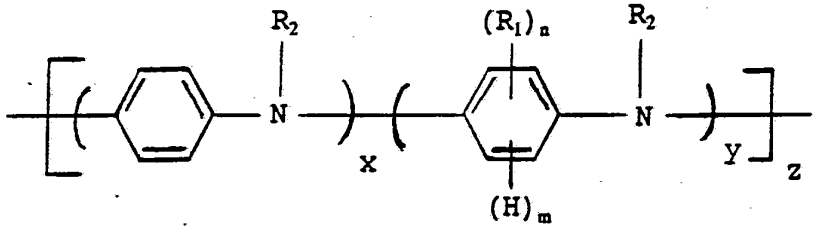
$$(OCH_2CH_2)_q\ O\text{-}CH_3,\ (OCH_2CH(CH_3))_qO\text{-}CH_3,$$
$$(CH_2)_qCF_3,\ (CF_2)_qCF_3 \text{ or } (CH_2)_q\ CH_3$$

wherein q is a positive whole number; and

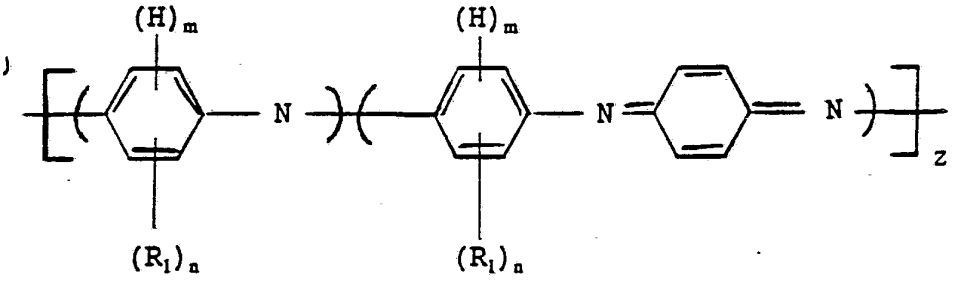
R_2 is the same or different at each occurrence and is R_1 substituents or hydrogen.

4. A solution according to claim 3 wherein said homopolymer or copolymer is composed of the Formulas XVIII to XXI:

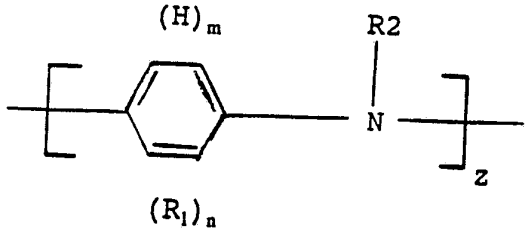
XVIII



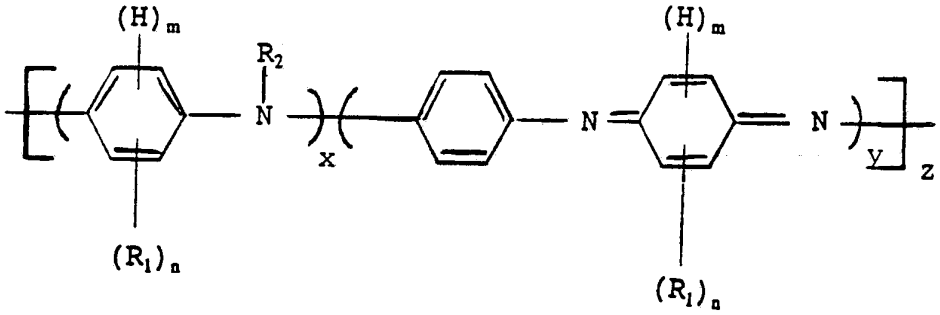
XIX



XX



XXI



wherein:

x and y are the same or different at each occurrence and are integers equal to or greater than 0, with the proviso that the sum or x and y are greater than 0;

z is an integer equal to or greater than about 1;

n is an integer from 0 to 3;

m is an integer from 1 to 4, with the proviso that the sum of n and m is 4;

R_1 is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, alkylthio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, aryl, arythio, arylsulfinyl, alkoxycarbonyl, phosphinic acid, phosphonic acid, alkylsilyl, boric acid, arylsulfonyl,

carboxylic acid, halo, hydroxy, phosphate salt, sulfonate salt, phosphonate salt, borate salt, phosphinate salt, carboxylate salt, nitro, cyano, sulfonic acid, phosphoric acid or aryl, alkyl or alkoxy substituted with one or more sulfonic acid, carboxylic acid, sulfinate salt, phosphoric acid, boric acid, sulfinic acid, halogen, nitro, cyano, epoxy, hydroxy, sulfonate salt, phosphate salt, phosphonate salt, phosphinic acid, phosphinate salt, carboxylate salt, phosphonic acid or borate salt substituents; or any two R_1 groups or any one R_1 group and R_2 group together may form a substituted or unsubstituted alkylene or alkenylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered heteroaromatic, heteroalicyclic, aromatic or alicyclic carbon ring, which chain may optionally include one or more divalent nitrogen, ester, carbonyl, sulfur, sulfinyl, sulfonyl or oxygen group, wherein permissible substituents are one or more sulfonic acid, carboxylic acid, sulfinate salt, phosphoric acid, boric acid, sulfinic acid, halogen, nitro, cyano, epoxy, hydroxy, sulfonate salt, phosphate salt, phosphonate salts, phosphinic acid, phosphinate salt, carboxylate salts, phosphonic acid or borate salt substituents.

R_2 is the same of different at each occurrence and is R_1 substituents or hydrogen.

5. A solution according to claim 4 wherein m is 3; n is 1; R_1 is the same or different at each occurrence and is alkyl having from 1 to about 10 carbon atoms or alkoxy having from 1 to about 10 carbon atoms; R_2 is hydrogen or alkyl having from 1 to about 10 carbon atoms; x is an integer equal to or greater than 1; y is equal to or greater than 0; and z is an integer equal to or greater than about 5.

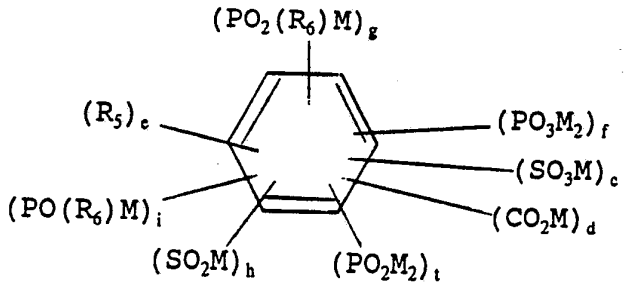
6. A solution according to claim 5 wherein R_2 is hydrogen.

7. A solution according to claim 6 wherein m is 4 and n is 0.

8. A solution according to claim 6 wherein said dopants are acids or acid derivatives of the formula:

$$R_4(PO_2(R_6)M)_g(PO_3M_2)_f(SO_3M)_c(CO_2M)_d(PO_2M_2)_t(SO_2M)_h$$
$$(PO(R_6)M)_i$$

or



wherein:

M is H^+, or other metal or non-metal cation with the proviso that at least one of M is H^+ or a moiety which can be thermally or chemically transformed into a proton under use conditions, such as

t is 0, 1, 2, 3 or 4;

i is 0, 1, 2, 3 or 4;

h is 0, 1, 2, 3 or 4;

c is 0, 1, 2, 3 or 4;

d is 0, 1, 2, 3 or 4;

f is 0, 1, 2, 3 or 4;

g is 0, 1, 2, 3 or 4 with the proviso that at least one of t, i, h, c, d, f or g is other than 0;

e is 0, 1 or 2; and

R_4, R_5 and R_6 are the same or different at each occurrence and are nitro, cyano, hydroxy, halo, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, alkoxy, or substituted or unsubstituted

alkoxy, aryl or alkyl having from 1 to about 30 carbon atoms wherein permissible substituents include sulfonate salt, perhaloalkyl, phenyl, alkoxy, halo, cyano, amino, haloalkyl, hydroxy, sulfonic acid, phosphoric acid, phosphate salt, boric acid, sulfinate salt, phosphinate salt, sulfinic acid, borate salt, phosphinic acid, phosphonate salt, phosphonic acid, carboxylic acid, nitro, carboxylate salt and the like, or any two R_6 or any two R_5 or any R_4 and R_6 substituents together may form an alkenylene chain completing a fused-ring system which chain may be unsubstituted or substituted with one or more halo, phosphoric acid, hydroxy, boric acid, nitro, cyano, amino, sulfinate salt, phosphinic acid, alkylamino, dialkylamino, phosphinate salt, arylamino, diarylamino, alkylarylamino, sulfinic acid, phosphate salt, carboxylate salt, phosphonic acid, phosphonate salt, sulfonate salt, borate salt, sulfonic acid or carboxylic acid groups, or R_4 or R_5 is a moiety of the formula:

$$-(CH_2)_qCF_3,\ -(CF_2)_qCF_3,\ -(CH_2)_qCH_3$$
$$-(OCH_2CH_2)_qOCH_3 \text{ or } -(OCH_2CH(CH_3))_qOCH_3$$

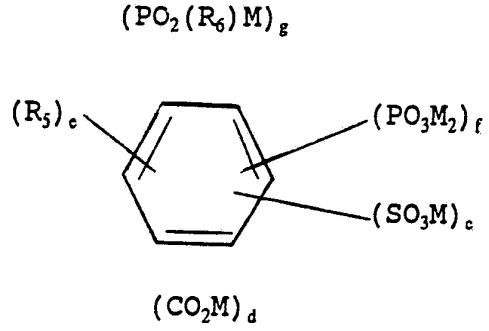
wherein:

q is a positive whole number from 1 to about 10.

9. A solution according to claim 8 wherein said dopants are acids and/or acid derivatives of the formula:

$$R_4(PO_2(R_6)M)_g(SO_3M)_c(CO_2M)_d(PO_3M_2)_f$$

or



wherein:

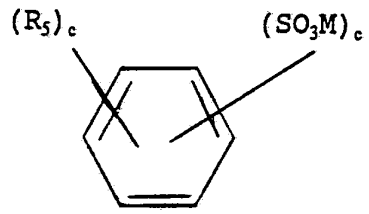
c, d, e, f and g are the same or different and are 0, 1 or 2 with the proviso that at least one of c, d, and g is not 0;

R_6 is aryl, aryloxy, alkyl or alkoxy;

R_4 and R_5 are the same or different at each occurrence and are alkyl, phenyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, or alkyl substituted with one or more fluoro, sulfonic acid, sulfonate salt, alkoxy, carboxylate salt, hydroxy, nitro, cyano, phosphinic acid, phosphinate salt, amino or carboxylic acid groups, or phenyl substituted with one or more alkyl, alkoxy, fluoroalkyl, sulfonic acid, phosphinic acid, phosphinic salt, sulfonate salt, carboxylate, hydroxy, nitro, cyano, or carboxylic acid groups or any two R_6 or any two R_5 or any R_4 and R_6 substituents together may form an alkenylene chain completing a naphthalene anthracene or phenanthrene fused system which may be substituted with one or more alkyl, alkoxy, fluoro, phosphinic acid, phosphinate salt, fluoroalkyl, sulfonic acid, sulfonate salt, carboxylic acid, carboxylate salt, hydroxy, nitro, amino or cyano groups; and

M is H^+ or other metal or non-metal cation, with the proviso that at least one of M is H^+ or is a moiety which can be thermally transformed into a proton under solution conditions.

10. A solution according to claim 9 wherein said dopant is a sulfonic acid, a sulfonic acid derivative, or a combination thereof of the formula:



wherein;

c is 1, 2 or 3;

e is 0, 1 or 2;

R_5 is alkyl or alkyl substituted with one or more fluoro, or any two R_5 groups together may form an alkenylene chain completing a naphthalene fused system which may be substituted with one or more sulfonic acid or sulfonic acid salt group; and

M is a proton, or other metal or non-metal cation, with the proviso that at least one of M is a proton.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/07309

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H01B1/12; C08G73/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	H01B ; C08G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	WO,A,9 106 887 (THE OHIO STATE UNIVERSITY SEARCH FOUNDATION) 16 May 1991 see claims 1-12	1-4,8-10
X	EP,A,0 432 929 (MILLIKEN RESEARCH) 19 June 1991 see the whole document	1-4,8-10
X	EP,A,0 361 429 (NITTO DENKO) 4 April 1990 see the whole document	1-4,8-10
A	WO,A,9 010 297 (ALLIED-SIGNAL) 7 September 1990 see claims 1-17	1-10

-/--

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
30 NOVEMBER 1992	- 4. 12. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	drouot

INTERNATIONAL SEARCH REPORT

International application No.

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	WO,A,9 001 775 (LOCKHEED) 22 February 1990 see claims 1-11 ---	1-4,8-10
	US,A,4 983 322 (R.L.ELSENBAUMER) 8 January 1991 cited in the application see the whole document ---	1-4,8-10
	WO,A,8 901 694 (ALLIED-SIGNAL) 23 February 1989 cited in the application see the whole document -----	1-4,8-10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9207309 SA 64253

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 30/11/92

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