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(72) Inventor: HAN, Chien-Chung ; 164 Shunpike Road, Madison, NJ 07940 (US).

(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962 (US).

(54) Title: THERMALLY INDUCED CHAIN COUPLING IN SOLID STATE POLYANILINE

(57) Abstract

A process for increasing the intrinsic viscosity of polyaniline by heating the polyaniline in the solid state.

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THERMALLY INDUCED CHAIN COUPLING IN
SOLID STATE POLYANILINE

Background of the Invention

1. Field of the Invention

This invention relates to thermally induced chain coupling and/or crosslinking of one or more substituted or unsubstituted polyanilines to form homopolymers or block copolymers having a molecular weight which is higher than that of original polyanilines and having securing blocks derived from the original polyanilines.

2. Description of the Prior Art

There has recently been an increased interest in the electrochemistry and electrical phenomena of backbone polymers having extended conjugation in at least one backbone chain such as polyaniline. See for example, U.S. Patent Nos. 3,963,498; 4,025,463; 4,855,361; 4,798,685; 4,806,271; 4,822,638; 4,851,487; 4,798,685 and PCT WO89/01694.

Summary of the Invention

This invention is directed to a process for coupling and/or crosslinking neutral or electrically conductive polyaniline to form a polyaniline of higher molecular weight, said process comprises the step of heating said polyaniline or a composition comprising said polyaniline for a time and at a temperature sufficient to increase the molecular weight of the polyaniline to any extent.

The increase in molecular weight can be determined by conventional means such as formation of insoluble fractions and/or increases in intrinsic viscosity. When the process results in the formation of fractions which are insoluble in sulfuric acid (96 to 98 wt%) at 25°C, the molecular weight has increased. Also, when the process has resulted in the formation of material which soluble in sulfonic acid (96 to 98 wt%) at 25°C, the increase in molecular weight, if any, can be
determined by increase in the intrinsic viscosity.

As used herein, the "intrinsic viscosity" is the limiting viscosity number of said polyaniline, and is defined as the following:

\[ \lim_{c \to \infty} \frac{h-h_0}{c} \]

where \( c \) is the concentration of said polyaniline in a solution of a solvent; \( h \) is the viscosity of said polyaniline solution having a concentration equal to \( "C" \); and \( h_0 \) is the viscosity of the solvent used to dissolve the polyaniline for viscosity measurement. The intrinsic viscosity is measured by a Cannon – Ubbelohde viscometer using concentrate sulfuric acid (96–98wt%) as the solvent in a 25°C thermostat water bath.

**Description of the Preferred Embodiments**

The process of this invention comprises the step of heating neutral or electrically conductive polyaniline or a composition comprising said polyaniline for a time and at a temperature sufficient to increase the molecular weight of said polyaniline to the desired extent. The state of the polyaniline during the heating step is not critical. For example, the polyaniline may be neat and in the molten or solid state (below the melting point), or may be in a blend comprising the polyaniline and one or more other electrically conductive or neutral thermoplastic or thermosetting polymers such as polyester, nylons, phenolics, epoxies, polyolefins, alkyds, allylics and the like. The polyaniline or composition may be these various forms before it is fabricated in a form for heating or after such fabrication. The polyaniline may also be in solution either before the solution is configured in a form for heating or after such configuration.
The shape or configuration of the polyaniline is not critical and may vary widely. For example, the polyaniline may be in the shape of a coating, a fiber, a powder, a film, or a laminate or composite of two or more films formed by conventional coating, powder, molded part film, fiber, laminate or composite forming techniques, as for example those described in "Modern Plastics Encyclopedia", (McGraw Hill. 1991 edition). Such useful techniques include extrusion compounding, extrusion coating, extrusion laminating, solution spinning, compression molding, rational molding, steam-chest molding, transfer molding, compression and transfer molding, structural foam molding, multi-layer-blow molding, confection molding, blow molding, resin transfer molding, extrusion molding and injection molding, reaction injection molding and the like.

The polyaniline may be heated using any conventional heating means. Illustrative of such heating means are thermal ovens, infrared ovens, ultraviolet ovens, oil baths, solvent baths, oil, water, inorganic and organic liquids or melts or solutions or vapor, steam, heat-guns, hot-plates, heating rollers, cyclindrical band heater, flat strip heater, cartridge heater, tubular heaters, fluid bed dryer, and the like.

The polyaniline is heated for a time and at a temperature sufficient to increase the molecular weight to the desired extent. In general, the longer the heating time and the higher the heating temperature the greater the increase in the molecular. Conversely, the shorter the heating times and the lower the heating temperatures, the smaller the increase in the molecular weight. In general, the effective heating times will vary widely depending on the amount of polyaniline, the
desired increase in molecular weight, heating temperature, the form of polyaniline and the like, and can range from a fraction of a minute to days or more. Preferably, heating times are at least about a fraction of a minute and heating temperatures are at least about 30°C and are selected such that the incremental change in intrinsic viscosity is at least about 0.05 dL/g. The upper limit to heating temperatures and times are usually not critical provided that thermally induced polymer degradation does not significantly impair the desired properties of the articles and the upper level in intrinsic viscosity is not critical provided that the final viscosity is not so high as to impair the desired properties. Preferred heating temperatures are at least about 40°C, and heating temperatures and heating times are selected such that the incremental change in the intrinsic viscosity is equal to or greater than about 0.1 dL/g; more preferred heating temperatures are at least about 80°C and heating times and heating temperatures are selected such that the incremental change in the intrinsic viscosity is equal to or greater than about 0.15 dL/g; and most preferred heating temperatures are at least about 100°C and heating temperatures and heating times are selected such that the incremental change in intrinsic viscosity is equal to or greater than about 0.20 dL/g.

It has been discovered that shorter heating times can be employed if the polyaniline includes a "plasticizing agent" or if the heating step is carried out in the presence of such a "plasticizing agent". This effect is most notable when the polyaniline or compositions is in the solid state and is heated at a temperature below its melting point. As used herein a "plasticizing agent" is an agent which will soften and increase the flexibility of all or part of the
polyaniline, enhancing the degree of motion freedom of the polyaniline chains. This is believed to allow the polyaniline segments or end groups to approach each other more easily at the right angles and distances for effective chain coupling reactions to occur. The extent to which the flexibility and softness of the polyaniline is enhanced can be conveniently measured by the change in glass transition temperature ($T_g$) as measured by differential scanning calorimetry (DSC) analysis of the $T_g$ of the initial polyaniline and the $T_g$ of the polyaniline containing plasticizer at same heating rate. In general, in these preferred embodiments sufficient plasticizer(s) is added such that the $T_g$ of the polyaniline is reduced by at least about 0.01°C. Preferred reductions in $T_g$ is at least about 0.1°C, more preferred reductions in $T_g$ is at least about 0.5°C and most preferred reductions in $T_g$ is at least about 1°C.

Illustrative of useful plasticizing agents are water; alcohols, such as methanol, and the like; ethers, such as diethyl ether, and the like; ketones, such as acetone, and the like; ureas such as diethylurea, and the like; phenols such as t-butyl phenol, and the like; aromatics as for example diphenyls, halogenated diphenyls, benzene, and the like; amides and phosphoramides such as N,N-dimethyl formamide, hexamethyl phosphoramidate, and the like; sulfur containing compounds such as dimethyl sulfoxide, and the like; amines such as triethylamine, morpholine, pyridine, and the like; esters such as ethyl acetate, and the like; aromatic acids, and esters thereof such as phthalic acid, dimethyl phthalate, and the like; aliphatic acids and esters of aliphatic acids such as esters of adipic acid and sebacic acid, and the like, glycol and glycol derivatives, such as glycerol,
glycerolmonoacetate, and the like; phosphates, silicates and borates such as triethyl phosphate, ethyl silicate, amyl borate, and the like; aromatic and aliphatic sulfonic acids and their derivatives such as toluene sulphonamide, nonyl sulfonic acid, benzene sulfonic acid, and the like; fluorinated hydrocarbons, fluorinated carboxylic acid and fluorinated sulfonic acids, such as prefluoro propanoic acid, pentafluoro ethane sulfonic acid, and the like; and synthetic waxes, thermo plastic resins, and the like;

Preferred plasticizing agents are water, alcohols, ketones, phenols, amines, esters, glycol derivatives, fluorinated carboxylic and sulfonic acids, dimethyl sulfoxide, amides and phosphoramides. More preferred plasticizing agents are water, alcohols, ketones, amines, esters, fluorinated carboxylic and sulfonic acids, dimethyl sulfoxide, amides and phosphoramides. Most preferred plasticizing agents are water, alcohols, especially, methanol, ethanol, isopropanol, and n-propanol; ketones, especially acetone, methyl ethyl ketone and methyl t-butyl ketone; amines, especially triethyl amine, tributyl amine, morpholine, piperidine and pyrrolidine; fluorinated carboxylic and sulfonic acids, especially perfluoroaliphatic acids, such as perfluorobutyric acid, perfluorooctanoic acid, trifluoromethane sulfonic acid, and pentafluoro ethane sulfonic acid; dimethyl sulfoxide; amides, especially N,N-dimethyl formamide, N,N-dimethyl acetamide, N-methyl pyrrolidinone and pyrrolidinone, and phosphoroamides especially hexamethyl phosphoramidate.

The number average molecular weight of the polyaniline (as measured by gel permeation chromatography) is believed to be increased by a coupling reaction as for example by linear coupling (i.e. at the ends of the polymer chain) such as head to
tail, or head to head, or tail to tail, by branching (i.e. along the polymeric backbone at any site other than the end recurring monomeric units), by cross-linking of two or more polyaniline chains forming a two or three dimension polymeric network or by a combination thereof. In the preferred embodiments of the invention, the increased number average molecular weight results primarily from linear coupling and branching and in the more preferred embodiments the number average molecular weight is increased primarily by linear coupling. It has been discovered that the heating temperature affects the ratio of linear coupling to branching. In general, at higher temperatures i.e. equal to or greater than about 150°C molecular weight is increased to a greater extent by branching, and such branching increases thereafter with increasing temperature. At lower temperatures i.e. less than about 150°C, molecular weight is increased to a greater extent by linear coupling and such linear coupling increases thereafter with decreasing temperature until the temperature at which no further increases in intrinsic viscosity occur is reached.

The temperature ranges and heating times at which linear coupling predominates and at which branching predominates will vary depending on the particular polyaniline. Such can be readily determined through use of simple heating experiments coupled with NMR analysis with the particular substituted or unsubstituted polyaniline. As representative, example unsubstituted polyaniline when heated at a temperature of up to about 160°C will increase its molecular weight predominantly by linear coupling. However, at a temperature of greater than about 130°C the polyaniline will begin to increase its molecular weight also by branching and the degree of branching will increase
with increasing temperature. Similarly, other substituted polyanilines can be evaluated to determine the range at which branching or linear coupling occurs. Preferred heating temperatures for linear coupling with unsubstituted polyaniline are from about 30°C to about 150°C, more preferred heating temperatures for linear coupling are from about 50°C to about 130°C and most preferred heating temperatures for linear coupling are from about 80°C to about 130°C. Preferred heating temperatures for branching with unsubstituted polyanilines are greater than about 100°C, more preferred heating temperatures for branching are greater than about 130°C and most preferred heating temperatures for branching are greater than about 150°C.

Polyanilines for use in the process of this invention may vary widely and will preferably have an intrinsic viscosity of less than about 1.6dL/g, and more preferably from about 1.5dL/g to about 0.05dL/g. Any form of substituted and unsubstituted polyaniline can be conveniently used in the practice of this invention. Examples of unsubstituted and substituted polyaniline useful in this invention are characterized by different ratios of phenylene amine and quinone imine backbone segments and include leucoemeraldine, protoemeraldine, emeraldine, nigraniline and pernigraniline.

In the preferred embodiments, polyaniline homopolymers and copolymers are of the type derived from the polymerization of one or more unsubstituted
and substituted anilines of the Formula I:

\[
\text{NH}R_2
\]

\[
\text{H}_m
\]

\[
R_1
\]

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 halo, 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, alkylsulfanyl, arylsulfanyl, alkylsulfanyalkyl, alkoxyalkyl, phosphonic acid, alkylsulfonyle, arylthio, alkylsulfonylealkyl, boric acid, phosphoric acid, sulfinate salts, arylationinyl, alkoxy carbonyl, aryloxybenzyl, carboxylic acid, phosphonic acid, halo, hydroxy, cyano, sulfinic acid, carboxylate salts, borate salts, phosphate salts, sulfone salts, phosphinate salts, phosphonate salts, phosphonic acid, sulfonic acid, nitro, alkylsilane, or any of the foregoing aryl, aliphatic or cycloaliphatic groups substituted with one or more phosphonic acid, sulfonic acid, phosphoric acid, boric acid, carboxylate salt, borate salt, sulfonate salt, phosphinate salt,
phosphonate salt, phosphate salt, phosphinic acid, carboxylic acid, halo, nitro, amino, alkylamino, dialkylamino, arylamine, diarylamino, alkylarylamino, cyano or epoxy moieties; or any two $R_1$ groups together or any $R_2$ group together with any $R_3$ 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, sulfanyl, or oxygen atoms wherein permissible substituents are one or more phosphonic acid, sulfonic acid, phosphoric acid, boric acid, carboxylate salt, borate salt, sulfonate salt, phosphinate salts, phosphonate salt, phosphate salt, phosphinic acid, carboxylic acid, halo, nitro, amino, alkylamino, dialkylamino, arylamine, diarylamino, alkylarylamino, cyano or epoxy moieties; or $R_1$ is an aliphatic moiety having repeat units of the formula:

$$-(OCH_2CH_2)_qO-CH_3, \quad -(OCH_2CH(CH_3))_qO-CH_3,$$

$$-(CH_2)_q CF_3, \quad -(CF_2)_q CF_3 \text{ or } -(CH_2)_q CH_3$$

wherein $q$ is a positive whole number; and $R_2$ is selected from the group consisting of permissible $R_1$ substituents hydrogen.

Illustrative of the polyanilines useful in the practice of this invention are those of the Formulas II to V:
wherein:

n, m, R₁ and R₂ 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 x is an integer equal to or greater than about 1 and/or the ratio of x to y is greater than or equal to about 0; and
z is the same or different and is an integer equal to or greater than 1.
Preferred for use in the practice of this invention are polyanilines of the above Formulas II to V in which:

- \( n \) 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, sulfonic acid, carboxylic acid, boric acid, borate salt, phosphoric acid, phosphate salt, phosphonic acid, phosphonate salt, phosphinic acid, phosphinate salt, sulfinic acid, sulfinate salt, carboxylate salt, sulfonate salt, amino, alkylamino, dialkylamino, arylamino, hydroxy, diarylamino, alkylarylamino, or alkyl, aryl or alkoxy substituted with phosphonic acid, phosphate salt, phosphoric acid, borate salt, sulfonate salt, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, carboxylate salt, hydroxy, alkoxy, phosphonic acid, boric acid, alkyl, phosphinic acid, phosphonate salt, phosphinate salts, carboxylic acid or sulfonic acid substituents;
- \( R_2 \) is the same or different at each occurrence and is a \( R_1 \) substituent or hydrogen;
- \( x \) 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 greater than about 0.5; and

- \( z \) 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 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 aryl, alkyl or alkoxy having from 1 to about
20 carbon atoms, sulfonic acid, halo, carboxylic acid, amino, carboxylate salt, alkylamino, phosphonate salt, dialkylamino, arylamino, phosphonic acid, boric acid, phosphate salt, phosphoric acid, borate salt, diarylamino, alkylarylamino, or alkyl or aryl substituted with carboxylic acid, phosphoric acid, boric acid, phosphate salt, phosphonic acid, borate salt, sulfonate salt, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, carboxylate salt, halo, phosphonate salt, or sulfonic acid substituents;

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

$x$ 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 5. Amongst the particularly preferred embodiments, most preferred for use in the practice of this invention are polyanilines of the above Formulas III or V 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 aryl, alkyl, alkoxy, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, halo, sulfonic acid, sulfonate salt, carboxylic acid or carboxylate salt, or alkyl or aryl substituted with one or more sulfonic acid, carboxylate salt, amino, alkylamino, dialkylamino, arylamino, diarylamino, halo, alkylarylamino, sulfate salt, sulfonate salt, or carboxylic acid substituents, wherein the aromatic moieties include from 6 to about 21 carbon atoms and the aliphatic moieties include from 1 to about 15 carbon atoms;
R₃ is hydrogen;
x is an integer equal to or greater than 2;
y is equal to or greater than 1, with the proviso
that the ratio of x to y is equal to or greater than
about 2; and
z is an integer equal to or greater than about 5.

In the most preferred embodiments of this
invention, the polyaniline is derived from
unsubstituted aniline, alkoxy, alkyl or sulfonic acid
substituted aniline or copolymers thereof with
unsubstituted polyaniline being the polyaniline of
choice.

In general, the number of aniline repeat units is
not critical and may vary widely and is preferably at
least about 10. The upper limit can vary widely
depending on the desired viscosity and molecular
weight. The number of aniline repeat units is
preferably at least about 20, more preferably at least
about 30, and most preferably at least about 40.

Useful polyanilines can be prepared through use of
conventional chemical and electrochemical synthetic
procedures. See for example, Green, A.G. and Woodhead,
A.E., J. Chem. Soc., 101 pp. 1117 (1912) and Kobayashi,
et al., "Electroanal. Chem., 177. pp. 281-91 (1984) and
89/01694.

The polyaniline may be electrically neutral or
electrically conductive polyaniline may be used.
Polyaniline is rendered electrically conductive by
doping with a dopant solute.

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 to form conductive
or semi-conductive polyaniline.

Illustrative of useful dopants are AsF₅, MoOCl₄,
MoCl₅, PCl₅, POCl₃, PCl₃, AlCl₃, NO⁺ and NO₂⁺ salts (such as NOBF₄, NOPF₆, NOSbF₆, NOAsF₆, NOCH₃CO₂, NO₂BF₄, NO₂PF₆, NO₂AsF₆, NO₂SbF₆, and NO₂CF₃SO₂), HClO₄, HNO₃, H₂SO₄, benzoyl peroxide, SO₃, Br₂, (FSO₃)₂, ZnCl₂, FSO₃H, and Fe(III) salts (such as Fe(BF₄)₃, FeBr₃, Fe(CH₃SO₃)₃, Fe(ClO₄)₃, FeCl₃, Fe(OTs)₃, and Fe(CF₃SO₃)₃, which give rise to doped polymers containing dopant solutes such as NO₃⁻, CH₃SO₃⁻, AlCl₄⁻, BF₄⁻, ZnCl₄⁻, PCl₆⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, CF₃SO₃⁻, ClO₄⁻, OTs⁻, SO₃⁻², C₆H₅CO₂⁻, CH₃SO₃⁻, FSO₃⁻, and FeCl₄⁻. Other useful oxidizing dopants include electrolyte salts such as LiClO₄, LiBF₄, LiAsF₆, NaPF₆, Bu₄NClO₄, Bu₄NOTs, Bu₄NCF₃SO₃, LiCF₃SO₃, AgOTs, hydrofluoric acid, hydroiodic acid, phosphoric acid, nitric acid, boric acid, sulfuric acid, and the like.

Preferred dopants are non-oxidizing protonic acids such as those described in PCT WO 89/01694 as for example those containing anionic moieties of the formula:
\[ R₄(PO₃⁻)₉(PO₂(R₆)⁻)₉(BO₂⁻)₉(SO₃⁻)₉(CO₂⁻)₉(PO₂⁻)₉ \]

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

\[ M^{+S} \]

wherein:

R₄ and R₆ are the same or different at each occurrence and are organic radical or amino such as alkyl aryl, (i.e. benzene or naphthalene, etc.) polystyrene, and the like;

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 NH₄⁺⁺, N(CH₃)₂H₂, N(C₂H₅)₃H₃ 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.

Illustrative of these preferred dopants are 1-anthracene sulfonic acid, 9-anthracene sulfonic acid, 2-phenanthrene sulfonic acid, 3-phenanthrene sulfonic acid, 9-phenanthrene sulfonic acid, perfluoro octyl sulfonic acid, perfluoro octyl carboxylic acid, octylsulfonic acid, dodecylsulfonic acid, cetyl sulfonic acid, toluenesulfonic acid (TsOH), dodecylbenzene sulfonic acid, naphthalene sulfonic acid, benzene disulfonic acid, 1,3-benzene disulfonic acid, 2,5-dihydroxy-1,4-benzene disulfonic acid, camphor sulfonic acid naphthalene trisulfonic acid dodecylbenzene sulfonic acid, ethane sulfonic acid 1,5-naphthalene disulfonic acid, nickel phthalocyanine tetrathionic acid, phenyl phosphonic acid, diphenyl phosphinic acid, phenyl phosphinic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, sulfamic acid, 5-sulfosalicylic acid, trion (4,5-dihydroxy-1,3-benzene disulfonic acid), vinyl sulfonic acid, sulfanilic acid, 4-sulfophthalic acid, sulfoacetic acid, methyl phosphinic acid, phenylphosphonic acid, methyl phosphonic acid, methyl orange, sulfonated polystyrene, sulfonated poly(2-vinyl naphthalene), naphthol yellow, naphthol blue black, 1,2-naphthoquinone-4-sulfonic acid, naphthylazoxine S, 1-octane sulfonic acid, t-butyl phosphonic acid, ethyl phosphonic acid, butyl phosphonic acid, 1,2-benzene disulfonic acid, 4-octylbenzene sulfonic acid, 2-mesitylene sulfonic acid, 2,6-naphthalene disulfonic acid, 2-naphthalene
sulfonic acid, 1,3,6-naphthalene trisulfonic acid,
1,3,7-naphthalene trisulfonic acid, sulfonazo III acid,
biphenyl disulfonic acid, biphenyl sulfonic acid,
1,8-dihydroxynaphthalene-3,6-disulfonic acid,
3,6-dihydroxynaphthalene-2,7-disulfonic acid,
4,5-dihydroxynaphthalene-2,7-disulfonic acid,
6,7-dihydroxy-2-naphthalene sulfonic acid,
1-naphthalene phosphoric acid, 1-naphthalene sulfonic acid, 1-naphthalene-5,7-dinitro-8-hydroxy,
1-naphthalene-4-hydroxy sulfonic acid, 4-bromo benzene sulfonic acid, 4-hydroxy-5-isopropyl-2-methyl benzene sulfonic acid, 3,4-diamino benzene sulfonic acid benzene phosphoric acid, 1,3,5-benzene trisulfonic acid, 2-methyl-5-isopropyl benzene sulfonic acid, 3,4-dinitro benzene sulfonic acid, 2-methoxy benzene sulfonic acid, 1-naphthalene-5-hydroxy sulfonic acid, 1-naphthalene-7-hydroxy sulfonic acid, 1-naphthalene-3-hydroxy sulfonic acid, 2-naphthalene-1-hydroxy sulfonic acid, 4-phenylamino benzene sulfonic acid, 1,6-naphthalene disulfonic acid, 1,5-naphthalene disulfonic acid, 1,3-naphthalene-7-hydroxy disulfonic acid, and Me₃SiOSO₂CF₃.

The amount of dopant added to the polyaniline is not critical and may vary widely. In general, sufficient dopant is added to the polyaniline to at least form doped polymer which is a semi-conductor which has a conductivity of at least about 10⁻⁶ ohm⁻¹cm⁻¹. The upper level of conductivity is not critical and will usually depend on the type of aniline polymer employed. The amount of dopant employed is preferably sufficient to provide a conductivity of at least about 10⁻⁴ ohm⁻¹cm⁻¹, more preferably is sufficient to provide a conductivity of from about 10⁻² ohm⁻¹cm⁻¹ to about 10⁻¹ ohm⁻¹cm⁻¹, and most preferably is sufficient to provide a conductivity from
about $10^0 \text{ohm}^{-1} \text{cm}^{-1}$ to about $10^2 \text{ohm}^{-1} \text{cm}^{-1}$ usually being the amounts of choice.
5   The method of forming the doped electrically conductive polyaniline is not critical and may vary widely. Suitable techniques are those described in U.S. Patent Nos. 4,442,187 and 4,321,114.
10   The essential polyaniline can include other optional ingredients. The nature of such optional ingredients can vary widely, and include those materials which are known to those of skill in the art for inclusion in polymer articles. Examples of such materials include other polymers such as polycarbonate, polycrylonitrile, polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl alcohol, polyethylene oxide, polystyrene, nylon, polyesterimide, polyimide, polyetherimide, cellulose, poly(1,4-cyclohexyldiene dimethylene terephthalate), poly(phenylene sulfide), phenolic resins, poly(ethylene terephthalate), alkyl resins poly(4-aminobutyric acid), poly(hexamethylene adipamide), poly(p-phenylene terephthalamide), poly[methane bis(4-phenyl)carbonate], acetate butyrate, allylic resins, polypropylene, polyethylene, cellulose acetate, epoxy resins, polyphenylene oxide, polyvinyl acetate, polyacetylene graphite, metal carbon blacks, conductors, reinforcing fibers and inert fillers (such as clays and glass).
15   As will be appreciated by those skilled in polymer processing, the ability to form polymer articles through use of relatively low molecular weight polyaniline which are thereafter processed to form polyaniline having a higher molecular weight and strength enables one to prepare articles of a wide variety of shapes and sizes. Thus, for example, by spreading the relatively low molecular weight polyaniline on a surface and thereafter heating the
polyaniline for a time and at a temperature sufficient to increase the molecular the desired extent.

When the original polyaniline is electrically conductive then the product will be electrically conductive. If the original polyaniline is neutral, the article will be neutral but can be render electrically conductive by conventional means, as for example by contacting the article with an aqueous toluene sulfonic acid solution, films, or coatings of any desired thickness can be prepared. Through use of this invention, extremely thin films can be prepared which are substantially transparent. By extruding a melt or a heater solution of the polyaniline through a die, removing volatiles where present and cooling fibers, films or molded articles can be made. Similarly, by removing volatiles from the solution or cooling a melt of the polyaniline in a mold of the desired shape, shaped articles conforming in shape to the mold can be prepared.

It is contemplated that, if additional soluble components are introduced into the solution or melt, they will, unless also volatile, be present in the shaped article formed. If the additional components are very volatile, then foamed or expanded cellular forms of the polymer may be formed. If the non-soluble components are present (or suspended) in the solution or in the melt of the polyaniline or the polymer will form around, or be filled with, the insoluble material. Where the amount of non-soluble component greatly exceeds the doped or undoped polymer remaining, individual particles or shapes of non-soluble components coated or impregnated with doped or undoped polymer will be formed.

Examples of articles formed from non-soluble components and the present doped polymer solutions
include conductive polymer coated-housings for sensitive electronic equipment (microprocessors), infrared and microwave absorbing shields, flexible electrical conducting connectors, conductive bearings, brushes and semiconducting photoconductor junctions, antistatic materials for packaging electronic components, carpet fibers, waxes for floors in computer rooms and an antistatic spray finisher for plastics, and thin, optically transparent antistatic finishes for CRT screens, aircraft, auto windows and the like.

The following specific examples are present to illustrate the invention and are not to be construed as limitations thereon.

EXAMPLE 1

Aniline (50g, 0.54 mole) and 204.4g of p-toluene sulfonic acid monohydrate (1.08 mole, Aldrich Chemical) and 0.12g of iron (II) sulfate heptahydrate were dissolved in 1750 mL of H₂O in a three neck round bottom flask equipped with a mechanical stirrer and an addition funnel. After the reaction mixture was cooled to 15°C, an aqueous solution of ammonium persulfate (157g in 270 mL H₂O) was added dropwise through the addition funnel. The overall addition time was 2 hrs. and 50 min. After the addition was finished, the reaction mixture was stirred for another 30 minutes. The resultant solid was collected by filtration. The filtration cake was then dispersed and stirred for 30 min. in 1.5L of a 12 wt% aqueous solution of p-toluene sulfonic acid for four times. Each time, the solid was re-collected and then re-dispersed into a fresh p-toluene sulfonic acid solution. After the above treatment, the filter cake was then dispersed and stirred for 30 min. in 1.5L of 8 wt% methanol solution of p-toluene sulfonic acid for two times. Each time, a fresh p-toluene sulfonic acid was used. The final
filter cake was dried at 25°C in air for 15 hrs. and then at 130°C under dynamic vacuum for 3 hrs. Yield was 83g. Elemental Analysis (wt%) was C(63.77), H(4.99), N(8.30), S(8.88), O(13.87). Intrinsic Viscosity in concentrate sulfuric acid at 25°C was 0.58 dL/g. Percent of the insoluble in concentrated H₂SO₄ was 0%. Surface area was 12.3 m²/g.

EXAMPLE 2

Another batch of polyaniline was prepared using the procedure of Example 1, except the drying step. After drying in air at 25°C for 15 hrs., the polyaniline was dried at 130°C under dynamic vacuum for 27 hrs. Yield was 85g. Elemental Analysis (wt%) was C(63.68), H(4.83), N(8.15), S(8.79), O(14.67). Intrinsic Viscosity in concentrate sulfuric acid at 25°C was 0.88 dL/g. Percent of the insoluble in concentrated H₂SO₄ was 0%. Surface area was 13.0 m²/g.

EXAMPLE 3

Aniline (50ml 51.1g, 0.55 mole) and 340 mL of 65 wt% aqueous solution of p-toluene sulfonic acid (Sloss Chemical) were dissolved in 1570 mL of H₂O in a three neck round bottom flask equipped with a mechanical stirrer and an addition funnel. The reaction mixture was cooled to 20°C and 10mL of an aqueous solution of ammonium persulfate (137.8g in 530 mL H₂O) was added in one portion. The resultant mixture was stirred for 10 minutes and the remainder of the ammonium persulfate solution was added dropwise. The overall addition time was 30 min. After the addition was finished, the reaction mixture was stirred for another 30 minutes. The resultant solid was collected by filtration. The filter cake was then dispersed and stirred in 1.5 L of a 2 wt% aqueous solution of p-toluene sulfonic acid at
60°C for 60 min. The solid was collected and the same treatment was repeated 3 more times with a fresh p-toluene sulfonic acid solution each time. The last filter cake was then dispersed and stirred in 1.5L methanol at ambient temperature for 30 min. The solid was collected and the same treatment was repeated. The resultant filter cake was dried in air at 25°C for 30 min. and then under dynamic vacuum at 130°C for 3 hrs. Yield was 75g. Elemental Analysis (wt%) was C(65.66), H(5.06), N(8.85), S(7.89), O(12.24).

Intrinsic Viscosity in concentrate sulfuric acid at 25°C was 0.67 dL/g. Percent of the insoluble in concentrated H₂SO₄ was 0%. Surface area was 18.4 m²/g.

**EXAMPLE 4**

Another batch of polyaniline was prepared according to the procedure of Example 3, except the heat treatment conditions. This batch of polyaniline was heated at 130°C in a closed vacuum system in the presence of saturated hot water steam for 3 hrs.

Yield was 73g. Elemental Analysis (wt%) was C(65.04), H(4.81), N(8.73), S(8.09), O(12.74).

Intrinsic Viscosity in concentrate sulfuric acid at 25°C was 1.40 dL/g. Percent of the insoluble in concentrated H₂SO₄ was 29.6%. Surface area was 18.4 m²/g.

**EXAMPLE 5**

A piece of poly(ethylene terephlate) film (4 x 4 inch) was coated with 1.6 wt% solution of poly(anilinium tosylate) in pyrrolidine by a transfer coating technique. In this technique, polyaniline solution was homogeneously laid down on the plastic film by a metal screen roller which contained hundreds of regularly engraved cells per square inch. The coated film was heated for 3 minutes at 100°C by an infrared oven. The coating turned green and conductive
after the solvent evaporated away. The surface resistance measured by a 4-in-line probe method was $10^6$ Ohm/sq. The prepared coating had very good abrasive resistance. The coating stayed intact after rubbed against a paper towel. For comparison, another coating was prepared similarly, except without heating treatment. The coating also turned green and had a similar conductivity as the one prepared in the above. This coating however had poor abrasive resistance. The coating flaked off when rubbed against a paper towel.

**EXAMPLE 6**

Green conductive poly(anilinium tosylate) powders (5g) was prepared as in Example 3, and was suspended in 35 mL of N-methyl pyrrolidinone. After the addition of 3.3 g of tripropylamine, the suspended poly(anilinium tosylate) powder started to dissolve forming a blue solution of low viscosity (water-like viscosity). The resulting solution mixture was then heated at 83°C for 20 minutes to form a highly viscous homogeneous blue solution. This viscous solution was further transformed into a blue solid rubber-like gel by further heating at 105°C for 20 minutes. From this gel, blue conductive polymer fibers were spun. After air-drying and redoping with 10 wt% p-toluene sulfonic acid for 20 minutes, green conductive fibers were obtained. The conductivity was about 0.15 cm$^{-1}$ as measured by a four-in-line probe.
WHAT IS CLAIMED IS:

1. A process for increasing the molecular weight of polyaniline which comprises heating neutral or electrically conductive polyaniline or a combination thereof for a time and at a temperature sufficient to increase the

2. A process according to claim 1 wherein said polyaniline is a polyaniline homopolymer or copolymer of the type derived from polymerizing an aniline of the formula:

\[ \text{NH}_{R_2} \]

\[ (H)_m \]

\[ (R_4)_n \]

\[ \text{n is an integer from 0 to 5;} \]

\[ \text{m is an integer from 0 to 5, with the proviso that the sum of n and m is 5;} \]

\[ R_1 \text{ is phosphinic acid, phosphonic acid, sulфонic acid, boric acid, phosphoric acid, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, amino, sulfonate salt, borate salt, hydroxy, phosphonate salt, phosphinate salt, phosphate salt, sulfinic acid, nitro, sulfinate salt, carboxylic acid, halo, carboxylate salt, cyano, deuterium, or substituted or unsubstituted alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkynyl, dialkylamino, arylamino, diarylamino, alkylarylamino, aryloxy, hydroxy, alkylthioalkyl, alkylaryl, arylalkyl, aryloxy, amino, alkylthioalkyl, alkylaryl, arylalkyl, alkylsulfynyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, aroylsulfinyl, alkoxy carbonyl, alkylsilane, or} \]
aryl sulfonyl, wherein permissible substituents are one or more amino, phosphinate salt, alkylamino, dialkylamino, arylamino, diarylamino, phosphinic acid, alkyllarylamino, 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 $R_3$ substituents or any one $R_3$ substituent and $R_2$ substituent taken together may form substituted or unsubstituted 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, alkyllarylamino, 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 $R_3$ is an aliphatic moiety having repeat units of the formula:

\[(\text{OCH}_2\text{CH}_2)_q \text{O-CH}_3, \text{OCH}_3, (\text{OCH}_2\text{CH(CH}_3)_q)\text{O-CH}_3, \]

\[(\text{CH}_2)_q\text{CF}_3, (\text{CF}_2)_q\text{CF}_3 \text{ or } (\text{CH}_2)_q \text{ CH}_3\]

wherein $q$ is a positive whole number; and

$R_2$ is the same or different at each occurrence and $R_3$ is $R_1$ substituents or hydrogen.

3. A process according to claim 2 wherein $R_2$ is hydrogen.

4. A process according to claim 3 wherein said homopolymer or copolymer is of the formulas II to V:
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;

R₁ is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, alkyldialkylamino, alkylothio, alkyldialkylthio, alkylandaryl, arylalkyl, alkylsulfonyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio,

arylsulfonyl, alkoxy carbonyl, 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 R₃ groups or any one R₃ group and R₃ group together may form a substituted or unsubstituted alkylene or alkenylene chain completing a 3, 5, 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; and $R_2$ is hydrogen.

5. A process according to claim 4 wherein $m$ is from about 3 to about 4 and wherein $R_3$ is the same or different at each occurrence and is alkyl or alkoxy having from 1 to about 30 carbon atoms.

6. A process according to claim 4 wherein said polyaniline is derived from unsubstituted aniline.

7. The process of claim 1 wherein said polyaniline comprises a mixture of two or more different types of mixture and wherein after treatment in the process said polyaniline comprises a block copolymer formed of blocks of two or more of said polyanilines.

8. The process of claim 1 wherein said polyaniline is neutral.

9. The process of claim 1 wherein said polyaniline is electrically conductive.

10. The process of claim 1 wherein said polyaniline comprises a plasticizing agent.
INTERNATIONAL SEARCH REPORT

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

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

IPC5: C 08 G 73/02

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System | Classification Symbols
----------------------|------------------------
IPC5                  | C 08 G; C 08 L

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO, A1, 9010297 (ALLIED-SIGNAL INC.) 7 September 1990, see the whole document</td>
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<td>A</td>
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  *E* earlier document but published on or after the international filing date
  *L* document which may throw doubts on the 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
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  *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
  *S* document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 25th June 1992
Date of Mailing of this International Search Report: 10 JUL 1992
International Searching Authority: EUROPEAN PATENT OFFICE
Signature of Authorized Officer: Mme N. KUIPER
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 92/01824

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 EDF file on 29/05/92.
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For more details about this annex: see Official Journal of the European patent Office, No. 12/82