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(54) **Title:** REVERSE ADDITION PROCESS FOR PREPARATION OF REGIOREGULAR CONDUCTING POLYMERS

(57) **Abstract:** The invention provides a method of preparing regioregular conducting polymers. The method includes adding a nickel (II) catalyst with the monomer-metal complex to provide the regioregular conducting polymer. Electronic devices can be made using the regioregular conducting polymers prepared as described herein.

REVERSE ADDITION PROCESS FOR PREPARATION OF REGIOREGULAR CONDUCTING POLYMERS

FIELD OF INVENTION

The invention relates to an improved process for making regioregular conducting polymers having high regioselectivity in a more efficient and less costly manner.

BACKGROUND OF THE INVENTION

Regioregular conducting polymers have received significant attention recently due to their nonlinear optical properties, electro-conductivity, and other valuable properties. They can be employed in electrical components such as transistors, diodes, triodes, and rectifiers in a variety of applications. The use of regioregular conducting polymers for these and other applications has often been hampered by irregular conductivity due a lack of purity.

There are several known synthetic methods for preparing regioregular conducting polymers. These known techniques, however, often provide substituted regioregular conducting polymers that have a less than optimal regioregularity. Highly regioregular conducting polymers are desired because monomer orientation has a great influence on the electro-conductivity of the polymer. A highly regioregular conducting polymer allows for improved packing and optimized microstructure, leading to improved charge carrier mobility.

Accordingly, there remains a need for improved synthetic methods for high purity and highly regioregular conducting polymers. Also needed are devices with high purity regioregular conducting polymers components for improved ease of manufacture and device operation.

SUMMARY OF INVENTION

The invention is directed to methods of preparing a regioregular conducting polymers as well as the regioregular conducting polymers prepared thereby. The methods of preparing regioregular conducting polymers disclosed herein utilize activated metals, which insert metal atoms directly into halo-aromatic or halo-heteroaromatic carbon bonds. Preferably, the activated metal is Rieke zinc (Zn*). Regioregular conducting polymers are provided if, for example, a nickel (II) catalyst or a platinum catalyst is used to accomplish the polymerization.

The regioregular conducting polymers may be, for example, unsubstituted or substituted homopolymers. For example, aromatic homopolymers may be prepared from one or more aromatic monomers, respectively. Heteroaromatic homopolymers may be prepared, for example, from heteroaromatic monomers. Preferably, the conducting polymers are, for example, unsubstituted or substituted polythiophene homopolymers, poly(3-substituted-thiophene) homopolymers, or poly(3,4-disubstituted-thiophene) homopolymers. Preferably, the regioregular conducting polymers are HT poly(3-substituted-thiophenes) or HT poly(3,4-disubstituted-thiophenes).

The present invention provides a method of preparing regioregular conducting polymer including adding a nickel (II) catalyst to a solution of a monomer-metal complex to provide the regioregular conducting polymer. This method (i.e., "reverse-addition") affords better results than the traditional (i.e., "normal-addition") method in which a solution of a monomer-metal complex is added to a solution of a nickel (II) catalyst. For example, the "reverse-addition" method affords regioregular conducting polymers with higher regioregularity than those obtained by the "normal-addition" method. This increase in regioregularity is very advantageous because it is very difficult to raise the ratio of the regioregular to regiorandom polymer. Further, higher regioregularity results in higher conductivity of the a regioregular conducting polymers.

The monomer-metal complex may be prepared by a method including contacting a dihalo-substituted monomer with an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I. Preferably the dihalo-substituted monomer is a 2,5-dihalothiophene and the activated

metal is an activated aluminum, manganese, copper, zinc, magnesium, calcium, titanium, iron, cobalt, nickel, indium, or a combination thereof. More preferably, the activated metal is Rieke zinc (Zn*).

The present invention is also directed to a regioregular conducting polymer composed of an improved regioregular conducting polymer having superior electroconducting properties. The improved regioregular conducting polymer is characterized by its monomeric composition, its degree of regioregularity, and its physical properties such as its molecular weight and number average molecular weight, its polydispersity, its conductivity, its purity obtained directly from its preparatory features, as well as other properties. The improved regioregular conducting polymer is characterized as well by the process for its preparation.

The present invention is as well directed to a thin film of a regioregular conducting polymer prepared by the methods described herein. The regioregular conducting polymer film can include a dopant.

The present invention also provides an electronic device including a circuit constructed with the regioregular conducting polymer prepared by any of the methods described herein. The electronic device may be a thin film transistor, a field effect transistor, a radio frequency identification tag, a flat panel display, a photovoltaic device, an electroluminescent display device, a sensor device, and electrophotographic device, or an organic light emitting diode.

The present invention provides a method of preparing a regioregular conducting polymer including adding a nickel (II) catalyst to a solution of a monomer-metal complex to provide the regioregular conducting polymer, wherein the monomer-metal complex is prepared by a method including combining a dihalo-monomer together with an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I; wherein the dihalo-monomer is an aromatic or heteroaromatic group substituted by two halogens wherein the halogens are the same or different.

In one embodiment, the dihalo-monomer comprises an aromatic group or a heteroaromatic group. Apart from the halogen substituents, the aromatic group or the

heteroaromatic group each can be unsubstituted or substituted by at least one substituent different from halogen.

In one embodiment, the aromatic or heteroaromatic group may be benzene, thiophene, pyrrole, furan, aniline, phenylene vinylene, thienylene vinylene, bis-thienylene vinylene, acetylene, fluorene, arylene, isothianaphthalene, p-phenylene sulfide, thieno[2,3-b]thiophene, thieno[2,3-c]thiophene, thieno[2,3-d]thiophene, naphthalene, benzo[2,3]thiophene, benzo[3,4]thiophene, biphenyl, or bithiophenyl, and wherein the aromatic or heteroaromatic group has from zero to about three substituents other than halogen. In another embodiment, the substituents of the foregoing aromatic or heteroaromatic group are each independently (C_1-C_{24})alkyl, (C_1-C_{24})alkylthio, (C_1-C_{24})alkylsilyl, or (C_1-C_{24})alkoxy that may be optionally substituted with about one to about five ester, ketone, nitrile, amino, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, or NH groups.

In yet another embodiment, the dihalo-monomer is selected from the group consisting of a 2,5-dihalo-thiophene, a 2,5-dihalo-pyrrole, a 2,5-dihalo-furan, a 1,3-dihalobenzene, a 2,5-dihalo-3-substituted-thiophene, a 2,5-dihalo-3-substituted-pyrrole, a 2,5-dihalo-3-substituted-furan, a 1,3-dihalo-2-substituted-benzene, a 1,3-dihalo-4-substituted-benzene, a 1,3-dihalo-5-substituted-benzene, a 1,3-dihalo-6-substituted-benzene, a 1,3-dihalo-2,4-disubstituted-benzene, a 1,3-dihalo-2,5-disubstituted-benzene, a 1,3-dihalo-2,6-disubstituted-benzene, a 1,3-dihalo-4,5-disubstituted-benzene, a 1,3-dihalo-4,6-disubstituted-benzene, a 1,3-dihalo-2,4,5-trisubstituted-benzene, a 1,3-dihalo-2,4,6-trisubstituted-benzene, a 1,3-dihalo-2,5,6-trisubstituted-benzene, a 1,4-dihalo-2-substituted-benzene, a 1,4-dihalo-3-substituted-benzene, a 1,4-dihalo-5-substituted-benzene, a 1,4-dihalo-6-substituted-benzene, a 1,4-dihalo-2,3-disubstituted-benzene, a 1,4-dihalo-2,5-disubstituted-benzene, a 1,4-dihalo-2,6-disubstituted-benzene, a 1,4-dihalo-3,5-disubstituted-benzene, a 1,4-dihalo-3,6-disubstituted-benzene, a 1,4-dihalo-3,5,6-trisubstituted-benzene, a 2,5-dihalo-3,4-disubstituted-thiophene, a 2,5-dihalo-3,4-disubstituted-pyrrole, or a 2,5-dihalo-3,4-disubstituted-furan.

In one embodiment, the regioregular conducting polymer is an unsubstituted or substituted poly(aromatic) homopolymer or a poly(heteroaromatic) homopolymer. In

another embodiment, the regioregular conducting polymer is an unsubstituted or substituted polythiophene homopolymer, a poly(3-substituted-thiophene) homopolymer, or a poly(3,4-disubstituted-thiophene) homopolymer. In yet another embodiment, the regioregular conducting polymer is a regioregular HT poly(3-substituted-thiophene) or a regioregular HT poly(3,4-disubstituted-thiophene).

In one embodiment, the monomer-metal complex is prepared by a method comprising combining a dihalo-monomer with a metal component selected from activated metal, a Grignard reagent, a RZnX reagent, a R_2ZX reagent, a R_3ZnM reagent and mixtures thereof, wherein R is a (C_2-C_{12}) alkyl group, M is magnesium, manganese, lithium, sodium or potassium and X is F, Cl, Br or I. In a preferred embodiment, the metal component is selected from activated metals. Suitable and preferred activated metals are defined in the following. Preferably, the activated metals are Rieke metals.

In one embodiment, the activated metal is Rieke zinc (Zn*).

In one embodiment, the method of preparing a regioregular conducting polymer includes adding a nickel (II) catalyst to a solution of a monomer-metal complex to provide the regioregular conducting polymer. In another embodiment, the regioregular conducting polymer is a regioregular HT poly(3-substituted-thiophene) or a regioregular HT poly(3,4-disubstituted-thiophene). In yet another embodiment, the monomer-metal complex is prepared by combining a dihalo-substituted monomer together with an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I.

In yet another embodiment, the nickel (II) catalyst is added to the monomer-metal complex at about 0°C to about 40°C.

In one embodiment, the regioregularity of the regioregular conducting polymer is greater than about 87%. In another embodiment, the regioregularity of the regioregular conducting polymer is greater than about 95%. In yet another embodiment, the regioregular conducting polymer is substituted with a straight-chain, branched-chain, or cyclic (C_1-C_{30})alkyl group.

In one embodiment, the regioregular conducting polymer is substituted with a hexyl group. In another embodiment, the average weight molecular weight of the

regioregular conducting polymer is about 5,000 to about 200,000. In yet another embodiment, the average weight molecular weight of the regioregular conducting polymer is about 40,000 to about 60,000.

In one embodiment, the regioregular conducting polymer prepared has a polydispersity index of about 1 to about 2.5. In another embodiment, the regioregular conducting polymer prepared has a polydispersity index of about 1.2 to about 2.2. In yet another embodiment, the 2,5-dihalo-thiophene is a 2,5-dichloro-3-substituted-thiophene, a 2,5-dibromo-3-substituted-thiophene, a 2,5-diiodo-3-substituted-thiophene, a 2,5-dichloro-3,4-disubstituted-thiophene, a 2,5-dibromo-3,4-disubstituted-thiophene, a 2,5-diiodo-3,4-disubstituted-thiophene, or a combination thereof.

In one embodiment, the nickel (II) catalyst is or is derived from Ni (dppe)Cl_2, Ni (dppp)Cl_2, Ni (PPh_3)$_2Br_2$, 1,5-cyclooctadienebis(triphenyl)nickel, dichoro(2,2'-dipyridine)nickel, tetrakis(triphenylphosophine)nickel, NiO, NiF_2, $NiCl_2$, $NiBr_2$, NiI_2, NiAs, Ni (dmph)$_2$, BaNiS, or a combination thereof.

In yet another embodiment, about 0.01 mol % to about 100 mol % of nickel (II) catalyst is employed, or preferably about 0.1 mol % to about 5 mol %, or more preferably about 0.1 mol % to about 3 mol %. In another embodiment, about 0.01 mol % to about 100 mol % of platinum catalyst is employed, or preferably about 0.1 mol % to about 5 mol %, or more preferably about 0.1 mol % to about 3 mol %.

In yet another embodiment, the method of preparing a regioregular HT poly(substituted-thiophene) includes adding a nickel (II) catalyst to a substituted-thiophene-zinc complex to provide the regioregular HT poly(substituted-thiophene), wherein the substituted-thiophene-zinc complex is prepared by a method including contacting a 2,5-dihalo-substituted-thiophene with Rieke zinc (Zn*), and wherein the regioregular HT poly(substituted-thiophene) is a regioregular HT poly(3-substituted-thiophene) or a HT poly(3,4-disubstituted-thiophene).

In one embodiment, the regioregular HT poly(substituted-thiophene) is substituted with a hexyl group.

In another embodiment, an electronic device including a circuit constructed with the regioregular conducting polymer or the regioregular HT poly(substituted-thiophene) is provided. In yet another embodiment, the device is a thin film transistor, a field

effect transistor, a radio frequency identification tag, a flat panel display, a photovoltaic device, an electroluminescent display device, a sensor device, and electrophotographic device, or an organic light emitting diode.

In one embodiment, a regioregular conducting polymer is provided. In another embodiment, a regioregular HT poly(substituted-thiophene) is provided.

In one embodiment, a crude regioregular conducting polymer having a regioregularity of at least about 87%, preferably greater than about 92%, more preferably greater than about 95% is provided. In another embodiment, a regioregular HT poly(substituted-thiophene) having a regioregularity of at least about 87%, preferably greater than about 92%, more preferably greater than about 95% is provided.

In one embodiment, a regioregular conducting polymer in the form of a thin film is provided. In another embodiment, a regioregular HT poly(substituted-thiophene) in the form of a thin film is provided.

In another embodiment, a regioregular conducting polymer having at least about 92% regioregularity; an average weight molecular weight of about 30,000 to about 70,000; and a conductance of about 10^{-5} to about 10^{-6} S/cm is provided.

DEFINITIONS

As used herein, certain terms have the following meanings. All other terms and phrases used in this specification have their ordinary meanings as one of skill in the art would understand. Such ordinary meanings may be obtained by reference to technical dictionaries, such as *Hawley's Condensed Chemical Dictionary* 11th Edition, by Sax and Lewis, Van Nostrand Reinhold, New York, N.Y., 1987, and *The Merck Index*, 11th Edition, Merck & Co., Rahway N.J. 1989.

As used herein, the term "and/or" means any one of the items, any combination of the items, or all of the items with which this term is associated.

As used herein, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to "a formulation" includes a plurality of such formulations, so that a formulation of compound X includes formulations of compound X.

As used herein, the term "about" means a variation of 10 percent of the value specified, for example, about 50 percent carries a variation from 45 to 55 percent. For integer ranges, the term about can include one or two integers greater than and less than a recited integer.

As used herein, the term "activated metal" refers to metal powder, metal dust, or metal granules, which have been activated chemically, thermally, electrochemically, or ultrasonically activated. Typically, the "activated metal" has a valence state of zero.

As used herein, the term "activated zinc" refers to zinc powder, zinc dust, or zinc granules, which have been activated chemically, thermally, electrochemically, or ultrasonically activated. For example, zinc can be chemically activated by adding a small amount of I_2, a halogenated carbon compound, a halogenated silicon compound, or $HgCl_2$. Electrochemical activation of zinc can be carried out by applying a cathode voltage. Thermal activation can be effected by heating zinc granules or powder *in vacuo*. Activation can also be effected by ultrasound. Typically, the "activated zinc" has a valence state of zero.

As used herein, the term "alkyl" refers to a branched, unbranched, or cyclic hydrocarbon having, for example, from 1 to 30 carbon atoms, and often 1 to 12 carbon atoms. Examples include, but are not limited to, methyl, ethyl, 1-propyl (*n*-propyl), 2-propyl *i*-propyl), 1-butyl (*n*-butyl), 2-methyl-1-propyl (*i*-butyl), 2-butyl (*sec*-butyl), 2-methyl-2-propyl (*t*-butyl), 1-pentyl (*n*-pentyl), 2-pentyl, 3-pentyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 3-methyl-1-butyl, 2-methyl-1-butyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 3-methyl-3-pentyl, 2-methyl-3-pentyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, hexyl, octyl, decyl, dodecyl, and the like. The alkyl may be unsubstituted or substituted. The alkyl can also be optionally partially or fully unsaturated. As such, the recitation of an alkyl group includes both alkenyl and alkynyl groups. The alkyl may be a monovalent hydrocarbon radical, as described and exemplified above, or it may be a divalent hydrocarbon radical (i.e., alkylene).

As used herein, the term "alkylthio" refers to the group alkyl-S-, where alkyl is as defined herein. In one embodiment, alkylthio groups include, for example, methylthio, ethylthio, *n*-propylthio, *iso*-propylthio, *n*-butylthio, *tert*-butylthio, *sec*-

butylthio, *n*-pentylthio, *n*-hexylthio, 1,2-dimethylbutylthio, and the like. The alkyl group of the alkylthio may be unsubstituted or substituted.

As used herein, the term "alkylsilyl" refers to the group alkyl-SiH_2- or alkyl-SiR_2-, where alkyl is as defined herein, and each R is independently H or alkyl. Thiophenes may be substituted by alkylsilyl groups by any of the many techniques known to those of skill in the art, typically by coupling the thiophene with an alkylsilyl halide, many of which are disclosed in the Aldrich Handbook of Fine Chemicals, 2007-2008, Milwaukee, WI.

As used herein, the term "alkoxy" refers to the group alkyl-O-, where alkyl is as defined herein. In one embodiment, alkoxy groups include, for example, methoxy, ethoxy, *n*-propoxy, *iso*-propoxy, *n*-butoxy, *tert*-butoxy, *sec*-butoxy, *n*-pentoxy, *n*-hexoxy, 1,2-dimethylbutoxy, and the like. The alkyl group of the alkoxy may be unsubstituted or substituted.

As used herein, the term "aryl" refers to an aromatic hydrocarbon group derived from the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system. The radical may be at a saturated or unsaturated carbon atom of the parent ring system. The aryl group can have from 6 to 18 carbon atoms. The aryl group can have a single ring (e.g., phenyl) or multiple condensed (fused) rings, wherein at least one ring is aromatic (e.g., naphthyl, dihydrophenanthrenyl, fluorenyl, or anthryl). Typical aryl groups include, but are not limited to, radicals derived from benzene, naphthalene, anthracene, biphenyl, and the like. The aryl may be unsubstituted or optionally substituted, as described above for alkyl groups.

As used herein, the term "block copolymer" refers to any polymer prepared by coupling functional polyvalent polymers such as an AB block copolymer. The block copolymers of this invention may be an AB block copolymer, wherein the A block is a regioregular HT polythiophene, and the B block is also a regioregular HT polythiophene. The block copolymers of this invention may also be an ABA block copolymer, wherein the A block is a regioregular HT polythiophene and the B block is also a regioregular HT polythiophene. The block copolymers of this invention may further be an ABC block copolymer, wherein the A block is a regioregular HT

polythiophene, wherein the B block is also a regioregular HT polythiophene, and wherein the C block is also a regioregular HT polythiophene.

As used herein, the term "conducting polymer" refers to polymer that conducts electricity. Typically, conducting polymers are polymers, which contain in the main chain principally sp^2-hybridized carbon atoms, which may also be replaced by corresponding heteroatoms. In the simplest case, this means the alternating presence of double and single bonds in the main chain. Principally means that naturally occurring defects, which result in conjugation interruptions, do not devalue the term "conducting polymer." Furthermore, the term conducting is likewise used in this application text if, for example, arylamine units and/or certain heterocycles (i.e., conjugation via N, O or S atoms) and/or organometallic complexes (i.e., conjugation via the metal atom) are present in the main chain. By contrast, units such as, for example, simple alkyl bridges, (thio)ether, ester, amide, or imide links are defined as non-conducting segments. A partially conducting polymer is intended to mean a polymer in which relatively long conducting sections in the main chain are interrupted by non-conducting sections, or which contains relatively long conducting sections in the side chains of a polymer, which is non-conducting in the main chain. Also as used herein, the term "conducting polymer" is used generically to refer to a homopolymer, a random copolymer, a branched polymer, a block copolymer, and the like.

As used herein, the terms "film" or "thin film" refers to a self-supporting or free-standing film that shows mechanical stability and flexibility, as well as a coating or layer on a supporting substrate or between two substrates.

As used herein, the term "Grignard reagent" refers to composition formed via the action of an alkyl or aryl halide on magnesium metal.

As used herein, the term "halo" refers to a fluoro, chloro, bromo, or iodo group, substituent, or radical.

As used herein, the term "heteroaryl" is defined herein as a monocyclic, bicyclic, or tricyclic ring system containing one, two, or three aromatic rings and containing at least one nitrogen, oxygen, or sulfur atom in an aromatic ring, and which may be unsubstituted or substituted, for example, with one or more, and in particular one to three, substituents, as described above in the definition of "substituted." Examples of

heteroaryl groups include, but are not limited to, 2H-pyrrolyl, 3H-indolyl, 4H-quinolizinyl, acridinyl, benzo[b]thienyl, benzothiazolyl, β-carbolinyl, carbazolyl, chromenyl, cinnolinyl, dibenzo[b,d]furanyl, furazanyl, furyl, imidazolyl, imidizolyl, indazolyl, indolisinyl, indolyl, isobenzofuranyl, isoindolyl, isoquinolyl, isothiazolyl, isoxazolyl, naphthyridinyl, oxazolyl, perimidinyl, phenanthridinyl, phenanthrolinyl, phenarsazinyl, phenazinyl, phenothiazinyl, phenoxathiinyl, phenoxazinyl, phthalazinyl, pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolyl, pyridazinyl, pyridyl, pyrimidinyl, pyrimidinyl, pyrrolyl, quinazolinyl, quinolyl, quinoxalinyl, thiadiazolyl, thianthrenyl, thiazolyl, thienyl, triazolyl, tetrazolyl, and xanthenyl. In one embodiment the term "heteroaryl" denotes a monocyclic aromatic ring containing five or six ring atoms containing carbon and 1, 2, 3, or 4 heteroatoms independently selected from non-peroxide oxygen, sulfur, and N(Z) wherein Z is absent or is H, O, alkyl, aryl, or (C_1-C_6)alkylaryl. In another embodiment heteroaryl denotes an ortho-fused bicyclic heterocycle of about eight to ten ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, or tetramethylene diradical thereto.

As used herein, the terms "heterocycle" or "heterocyclyl" refer to a saturated or partially unsaturated ring system, containing at least one heteroatom selected from the group oxygen, nitrogen, and sulfur, and optionally substituted with one or more groups as defined herein under the term "substituted." A heterocycle may be a monocyclic, bicyclic, or tricyclic group containing one or more heteroatoms. A heterocycle group also can contain an oxo group (=O) attached to the ring. Non-limiting examples of heterocycle groups include 1,3-dihydrobenzofuran, 1,3-dioxolane, 1,4-dioxane, 1,4-dithiane, 2*H*-pyran, 2-pyrazoline, 4*H*-pyran, chromanyl, imidazolidinyl, imidazolinyl, indolinyl, isochromanyl, isoindolinyl, morpholine, piperazinyl, piperidine, piperidyl, pyrazolidine, pyrazolidinyl, pyrazolinyl, pyrrolidine, pyrroline, quinuclidine, and thiomorpholine. The term "heterocycle" also includes, by way of example and not limitation, a monoradical of the heterocycles described in Paquette, Leo A., Principles of Modern Heterocyclic Chemistry (W.A. Benjamin, New York, 1968), particularly Chapters 1, 3, 4, 6, 7, and 9, The Chemistry of Heterocyclic Compounds, A Series of Monographs" (John Wiley & Sons, New York, 1950 to present), in particular Volumes

13, 14, 16, 19, and 28, and *J. Am. Chem. Soc.* 1960, *82*, 5566. In one embodiment of the invention "heterocycle" includes a "carbocycle" as defined herein, wherein one or more (e.g., 1, 2, 3, or 4) carbon atoms have been replaced with a heteroatom (e.g., O, N, or S).

As used herein, the term "high regioregularity" refers to a compound or polymer that is at least about 85% regioregular, preferably at least about 87% regioregular, more preferably at least about 90% regioregular, even more preferably at least about 92% regioregular, yet more preferably at least about 95% regioregular, further preferably at least about 97% regioregular, or most preferably at least about 99% regioregular.

As used herein, the terms "HT polythiophene" or "HT" refers to the head-to-tail orientation of monomers in a polythiophene. The HT polythiophene may be an unsubstituted HT polythiophene, a HT poly(3-substituted-thiophene), or a HT poly(3,4-disubstituted-thiophene). The percent regioregularity present in an HT polythiophene may be determined by standard ^{1}H NMR techniques. The percent regioregularity may be increased by various techniques, including Soxhlet extraction, precipitation, and recrystallization.

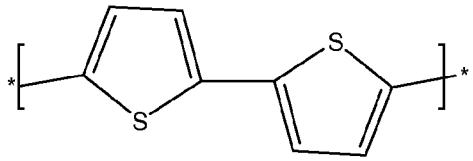
As used herein, the term "metal catalyst" refers to a polymerization catalyst for the monomer-metal complex.

As used herein, the term "monomer-metal complex" refers to a monomer moiety (e.g., thiophene) that is associated with a metal atom (e.g., zinc). The monomer-metal complex is typically a monomer-metal halide complex (e.g., thiophene-zinc halide complex). The "halide" or "halo" group may be fluoro, chloro, bromo, or iodo.

As used herein, the terms "preferred" and "preferably" refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

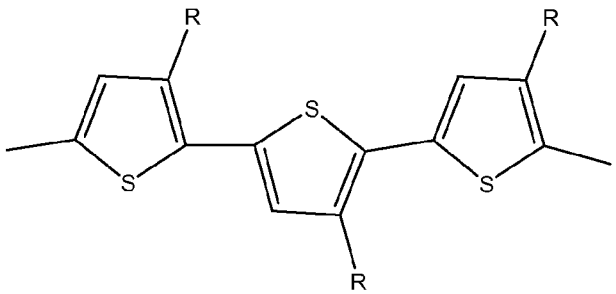
As used herein, the term "regioregular" refers to a polymer where the monomers are arranged in a substantially head-to-tail orientation. For example, although many

conventional polymers have all α-α couplings, they have a mixture of head-head, head-tail, and tail-tail orientations.

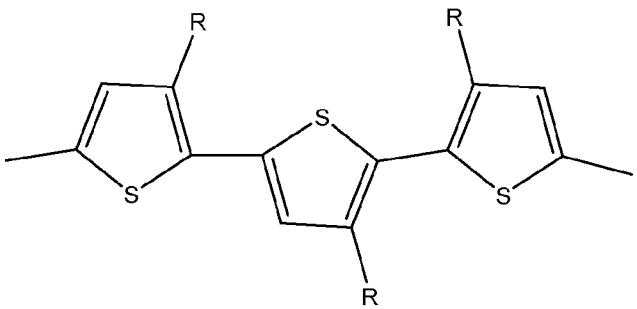


α-α Linkage

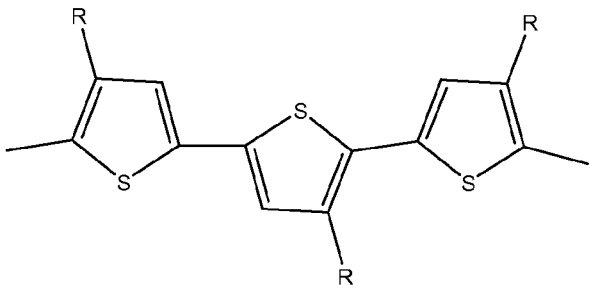
Thus, conventional polymers are not completely regioregular (formerly referred to as regiospecific and stereospecific), i.e., with all head-head, head-tail, or tail-tail orientations. Nor are conventional polymers completely regiorandom, i.e., with an equal amount of each orientation (25% head-tail & head-tail, 25% head-tail & head-head, 25% tail-tail & head-tail, 25% tail-tail & head-head).



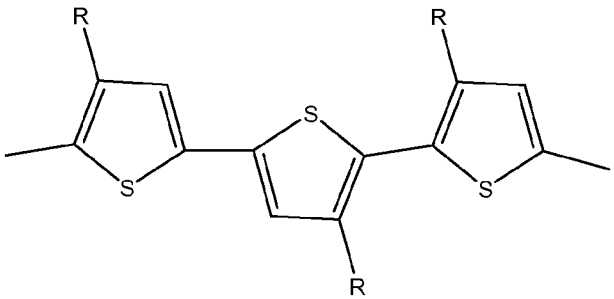
Head-Tail and Head-Tail Linkage



Head-Tail and Head-Head Linkage



Tail-Tail and Head-Head Linkage



Tail-Tail and Head-Head Linkage

For further description and discussion of the terms regiorandom and regioregular (or regioselective), *see* U.S. Patent No. 5,756, 653, which is hereby incorporated by reference.

As used herein, the term "room temperature" refers to about 23°C.

As used herein, the term "Rieke zinc (Zn*)" refers to an activated form of zinc prepared by the method described in U.S. Patent No. 5,756,653, which is hereby incorporated by reference.

As used herein, the term "substituted" is intended to indicate that one or more (e.g., 1, 2, 3, 4, or 5, in some embodiments 1, 2, or 3, and in other embodiments 1 or 2) hydrogen atoms on the group indicated in the expression using "substituted" is replaced with a selection from the indicated organic or inorganic group(s), or with a suitable organic or inorganic group known to those of skill in the art, provided that the indicated

atom's normal valency is not exceeded, and that the substitution results in a stable compound. Suitable indicated organic or inorganic groups include, for example, alkyl, alkenyl, alkynyl, alkoxy, halo, haloalkyl, hydroxy, hydroxyalkyl, aryl, heteroaryl, heterocyclyl, cycloalkyl, alkanoyl, alkoxycarbonyl, amino, alkylamino, dialkylamino, trifluoromethylthio, difluoromethyl, acylamino, nitro, trifluoromethyl, trifluoromethoxy, carboxy, carboxyalkyl, keto, thioxo, alkylthio, alkylsulfinyl, alkylsulfonyl, alkylsilyl, and cyano. Additionally, the suitable indicated groups can include, for example, -X, -R, $-O^-$, -OR, -SR, $-S^-$, $-NR_2$, $-NR_3$, =NR, $-CX_3$, -CN, -OCN, -SCN, -N=C=O, -NCS, -NO, $-NO_2$, $=N_2$, $-N_3$, NC(=O)R, -C(=O)R, -C(=O)NRR $-S(=O)_2O^-$, $-S(=O)_2OH$, $-S(=O)_2R$, $-OS(=O)_2OR$, $-S(=O)_2NR$, -S(=O)R, $-OP(=O)O_2RR$, $-P(=O)O_2RR$, $-P(=O)(O^-)_2$, $-P(=O)(OH)_2$, -C(=O)R, -C(=O)X, -C(S)R, -C(O)OR, $-C(O)O^-$, -C(S)OR, -C(O)SR, -C(S)SR, -C(O)NRR, -C(S)NRR, -C(NR)NRR, where each X is independently a halogen (or "halo" group): F, Cl, Br, or I, and each R is independently H, alkyl, aryl, heterocyclyl, protecting group or prodrug moiety. As would be readily understood by one skilled in the art, when a substituent is keto (i.e., =O), or thioxo (i.e., =S), or the like, then two hydrogen atoms on the substituted atom are replaced.

As used herein, the terms "stable compound" and "stable structure" are meant to indicate a compound or polymer that is sufficiently robust to survive isolation to a useful degree of purity from a reaction mixture. The compounds and polymers of the present invention are typically stable compounds. Intermediates and metal complexes may be somewhat instable or non-isolable components of the methods of the invention.

As used herein, the term "thiophene-zinc complex" refers to a thiophene moiety that is associated with a zinc atom. The thiophene-zinc complex is typically a thiophene-zinc halide complex. The "halide" or "halo" group may be fluoro, chloro, bromo, or iodo.

As to any of the above groups, which contain one or more substituents, it is understood, of course, that such groups do not contain any substitution or substitution patterns that are sterically impractical and/or synthetically non-feasible. In addition, the compounds of this invention include all stereochemical isomers arising from the substitution of these compounds.

DETAILED DESCRIPTION OF THE INVENTION

The invention is directed to methods of preparing a regioregular conducting polymers as well as the regioregular conducting polymers prepared thereby. The methods of preparing regioregular conducting polymers disclosed herein utilize activated metals, which insert metal atoms directly into halo-aromatic or halo-heteroaromatic carbon bonds. Preferably, the activated metal is Rieke zinc (Zn*). Regioregular conducting polymers are provided if, for example, a nickel (II) catalyst or a platinum catalyst is used to accomplish the polymerization.

The regioregular conducting polymers may be, for example, unsubstituted or substituted homopolymers. For example, aromatic homopolymers may be prepared from one or more aromatic monomers, respectively. Heteroaromatic homopolymers may be prepared, for example, from heteroaromatic monomers. Preferably, the conducting polymers are, for example, unsubstituted or substituted polythiophene homopolymers, poly(3-substituted-thiophene) homopolymers, or poly(3,4-disubstituted-thiophene) homopolymers. Preferably, the regioregular conducting polymers are HT poly(3-substituted-thiophenes) or HT poly(3,4-disubstituted-thiophenes).

The present invention provides a method of preparing regioregular conducting polymer including adding a nickel (II) catalyst to a solution of a monomer-metal complex to provide the regioregular conducting polymer. This method (i.e., "reverse-addition") affords better results than the traditional (i.e., "normal-addition") method in which a solution of a monomer-metal complex is added to a solution of a nickel (II) catalyst. For example, the "reverse-addition" method affords regioregular conducting polymers with higher regioregularity than those obtained by the "normal-addition" method. This increase in regioregularity is very advantageous because it is very difficult to raise the ratio of the regioregular to regiorandom polymer. Further, higher regioregularity results in higher conductivity of the a regioregular conducting polymers.

The monomer-metal complex may be prepared by a method including contacting a dihalo-substituted monomer with an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I. Preferably the dihalo-substituted monomer is a 2,5-dihalothiophene and the activated

metal is an activated aluminum, manganese, copper, zinc, magnesium, calcium, titanium, iron, cobalt, nickel, indium, or a combination thereof. More preferably, the activated metal is Rieke zinc (Zn*).

The present invention is also directed to a regioregular conducting polymer composed of an improved regioregular conducting polymer having superior electroconducting properties. The improved regioregular conducting polymer is characterized by its monomeric composition, its degree of regioregularity, and its physical properties such as its molecular weight and number average molecular weight, its polydispersity, its conductivity, its purity obtained directly from its preparatory features, as well as other properties. The improved regioregular conducting polymer is characterized as well by the process for its preparation.

The present invention is as well directed to a thin film of a regioregular conducting polymer prepared by the methods described herein. The regioregular conducting polymer film can include a dopant.

The present invention also provides an electronic device including a circuit constructed with the regioregular conducting polymer prepared by any of the methods described herein. The electronic device may be a thin film transistor, a field effect transistor, a radio frequency identification tag, a flat panel display, a photovoltaic device, an electroluminescent display device, a sensor device, and electrophotographic device, or an organic light emitting diode.

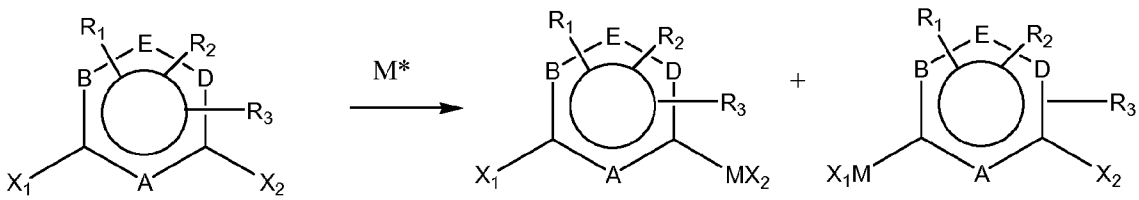
General Preparatory Methods

A number of exemplary methods for the preparation of polymers of the invention are provided herein. These methods are intended to illustrate the nature of such preparations and are not intended to limit the scope of applicable methods. Certain compounds can be used as intermediates for the preparation of other compounds or polymers of the invention.

Regioregular Conducting Polymers

Scheme 1 illustrates the method of preparing the monomer-metal complex using the method described herein.

Scheme 1.



wherein

A, B, and D are each independently sulfur, nitrogen, oxygen, phosphorous, silicon, or carbon;

E may be absent, sulfur, nitrogen, oxygen, phosphorus, silicon, or carbon, and when absent, B forms a bond with D;

X_1 and X_2 are each independently halogen;

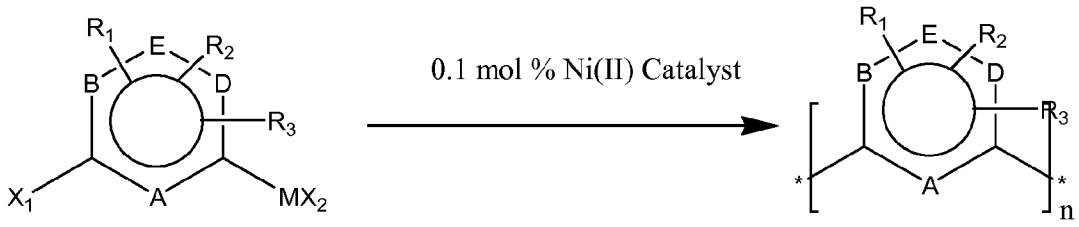
R_1, R_2, and R_3 are each independently absent, an alkyl, alkylthio, alkylsilyl, or alkoxy group that is optionally substituted with about one to about five ester, ketone, nitrile, amino, halo, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, and/or NP groups wherein P is a substituent as described above or a nitrogen protecting group, and M* is an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I, wherein the circle indicates an aromatic structure in which the A, B, D, and E groups have additional hydrogen atoms needed to maintain a neutral ring structure.

The dihalo-substituted monomer may be dissolved in a suitable solvent, such as an ethereal solvent, for example, tetrahydrofuran. The reaction flask may be cooled before introduction of the activated metal reagent. The activated metal reagent may be added into the reaction flask and stirred for a sufficient period of time to form the monomer-metal complex by exchanging a halometallo (MX) group with one of the X (halo) groups of the dihalo-substituted monomer.

After formation of the monomer-metal complex, the nickel (II) catalyst may be added to the reaction vessel containing the monomer-metal complex, for example, as

shown below in Scheme 2. The resulting mixture may be stirred for a sufficient amount of time to effect the formation of the regioregular conducting polymer, which typically precipitates from the reaction mixture. The regioregular conducting polymer may be isolated by transferring the reaction mixture into a volume of solvent in which the regioregular conducting polymer is substantially insoluble. Further work-up can include filtering, washing with methanol, and drying under high vacuum. Additional purification may be carried out by Soxhlet extraction with, for example, a hydrocarbon solvent, such as hexanes.

Scheme 2



wherein

A, B, and D are each independently sulfur, nitrogen, oxygen, phosphorous, silicon, or carbon;

E may be absent, sulfur, nitrogen, oxygen, phosphorus, silicon, or carbon, and when absent, B forms a bond with D;

X_1 and X_2 are each independently halogen;

n indicates the number of monomeric units present to provide the desired molecular weight of the polymer;

R_1, R_2, and R_3 are each independently absent, an alkyl, alkylthio, alkylsilyl, or alkoxy group that is optionally substituted with about one to about five ester, ketone, nitrile, amino, halo, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, and/or NP groups wherein P is a substituent as described above or a nitrogen protecting group, and M* is an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I, wherein the circle indicates an aromatic structure in which the A, B, D, and E groups have additional hydrogen atoms needed to maintain a neutral ring structure.

A variety of activated metals can be used to form the monomer-metal complex. Suitable activated metals may include, for example, zinc, aluminum, manganese, copper, and the like.

Typically, the temperature of the formation of the monomer-metal complex is at least about -78°C, preferably at least about 0°C, and more preferably at least about 23°C. Typically, the temperature of the formation of the monomer-metal complex is no

greater than about 100°C, preferably no greater than about 60°C, and more preferably no greater than about 40°C.

Typically, the formation of the monomer-metal complex is sufficiently complete within at least about 5 minutes, and preferably at least about 30 minutes. Typically, the reaction time is no more than about 24 hours, more preferably no more than about 8 hours, and even more preferably no more than about 1 hour.

The preferred conditions for the polymerization of the monomer-metal complex to form regioregular conducting polymers may include, for example, the use of an inert atmosphere (e.g., nitrogen, helium, or argon), and suitable temperatures and times.

Typically, the temperature of the polymerization is at least -78°C, preferably at least 0 °C, and more preferably at least 23°C. Typically, the temperature of the polymerization is no greater than the boiling point of the solvent used, preferably no greater than 60°C, and more preferably no greater than 40°C.

Typically, the polymerization is sufficiently complete within at least 2 hours, and preferably at least 24 hours. Typically, the polymerization is no more than 72 hours, more preferably no more than 48 hours, and even more preferably no more than 30 hours.

The polymerization can be carried out in the same solvent as was the preparation of the monomer-metal complex. The entire reaction sequence can be carried out without any isolation of intermediates.

Suitable dihalo-monomers may include, for example, any dihalo-substituted or unsubstituted (C_6-C_{30})aryl monomer or dihalo-substituted or unsubstituted (C_3-C_{30})heteroaryl monomer. The aromatic or heteroaromatic monomer may be, for example, benzene, thiophene, pyrrole, furan, aniline, phenylene vinylene, thienylene vinylene, bis-thienylene vinylene, acetylene, fluorene, arylene, isothianaphthalene, p-phenylene sulfide, thieno[2,3-b]thiophene, thieno[2,3-c]thiophene, thieno[2,3-d]thiophene, naphthalene, benzo[2,3]thiophene, benzo[3,4]thiophene, biphenyl, or bithiophenyl, and the like. The aromatic or heteroaromatic monomer may have from zero to about three substituents other than halogen. The substituents are each independently (C_1-C_{24})alkyl, (C_1-C_{24})alkylthio, (C_1-C_{24})alkylsilyl, or (C_1-C_{24})alkoxy that may be optionally substituted with about one to about five ester, ketone, nitrile,

amino, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, or NH groups.

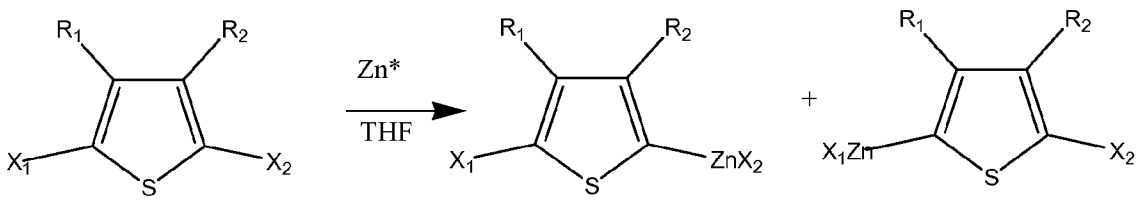
Suitable dihalo-monomers include, for example, a 2,5-dihalo-thiophene, a 2,5-dihalo-pyrrole, a 2,5-dihalo-furan, a 1,3-dihalobenzene, a 2,5-dihalo-3-substituted-thiophene, a 2,5-dihalo-3-substituted-pyrrole, a 2,5-dihalo-3-substituted-furan, a 1,3-dihalo-2-substituted-benzene, a 1,3-dihalo-4-substituted-benzene, a 1,3-dihalo-5-substituted-benzene, a 1,3-dihalo-6-substituted-benzene, a 1,3-dihalo-2,4-disubstituted-benzene, a 1,3-dihalo-2,5-disubstituted-benzene, a 1,3-dihalo-2,6-disubstituted-benzene, a 1,3-dihalo-4,5-disubstituted-benzene, a 1,3-dihalo-4,6-disubstituted-benzene, a 1,3-dihalo-2,4,5-trisubstituted-benzene, a 1,3-dihalo-2,4,6-trisubstituted-benzene, a 1,3-dihalo-2,5,6-trisubstituted-benzene, a 1,4-dihalo-2-substituted-benzene, a 1,4-dihalo-3-substituted-benzene, a 1,4-dihalo-5-substituted-benzene, a 1,4-dihalo-6-substituted-benzene, a 1,4-dihalo-2,3-disubstituted-benzene, a 1,4-dihalo-2,5-disubstituted-benzene, a 1,4-dihalo-2,6-disubstituted-benzene, a 1,4-dihalo-3,5-disubstituted-benzene, a 1,4-dihalo-3,6-disubstituted-benzene, a 1,4-dihalo-3,5,6-trisubstituted-benzene, a 2,5-dihalo-3,4-disubstituted-thiophene, a 2,5-dihalo-3,4-disubstituted-pyrrole, a 2,5-dihalo-3,4-disubstituted-furan, or a combination thereof.

Regioregular Substituted Polythiophenes

The preparation of a preferred embodiment, regioregular substituted polythiophene, is described in Schemes 3 and 4.

Scheme 3 illustrates the method of preparing thienylzinc bromide using the method described in U.S. Patent No. 5,756,653 (*see*, e.g., column 54, lines 15-40),

Scheme 3.



I II

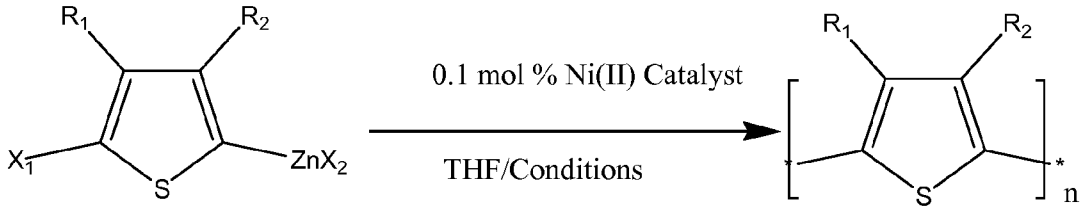
wherein X_1 and X_2 are each independently halogen, R_1 and R_2 are each independently absent, an alkyl, alkylthio, alkylsilyl, or alkoxy group that is optionally substituted with about one to about five ester, ketone, nitrile, amino, halo, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, and/or NP groups wherein P is a substituent as described above or a nitrogen protecting group, and Zn* is Rieke zinc.

The 2,5-dihalo-3-substituted-thiophene may be dissolved in a suitable solvent, such as an ethereal solvent, for example, tetrahydrofuran. The reaction flask may be cooled before introduction of the Rieke zinc (Zn*) reagent. The Rieke zinc (Zn*) may be added into the reaction flask and stirred for a sufficient period of time to form the thiophene-zinc complex by exchanging a halozinc (ZnX) group with one of the X (halo) groups of the thiophene.

After formation of the thiophene-zinc complex, the nickel (II) catalyst may be added to the reaction vessel containing the thiophene-zinc complex, for example, as shown below in Scheme 4. The resulting mixture may be stirred for a sufficient amount of time to effect the formation of the HT polythiophene, which typically precipitates from the reaction mixture. The HT polythiophene may be isolated by transferring the reaction mixture into a volume of solvent in which the HT polythiophene is

substantially insoluble. Further work-up can include filtering, washing with methanol, and drying under high vacuum. Additional purification may be carried out by Soxhlet extraction with, for example, a hydrocarbon solvent, such as hexanes.

Scheme 4



I

wherein X_1 and X_2 are each independently halogen, R_1 and R_2 are each independently absent, an alkyl, alkylthio, alkylsilyl, or alkoxy group that is optionally substituted with about one to about five ester, ketone, nitrile, amino, halo, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, and/or NP groups wherein P is a substituent as described above or a nitrogen protecting group, n indicates the number of monomeric units present to provide the desired molecular weight of the polymer; and the Ni (II) catalyst is any nickel (II) catalyst that effectuates polymerization of the thiophene zinc complex.

The formation of the HT polythiophene can be carried out at suitable and effective temperature. In one embodiment, the polymerization is carried out at temperatures of about -100°C to about 80°C. In another embodiment, the polymerization is conducted at temperatures of about -20°C to about 40°C. The polymerization can be carried out in the same solvent as was the preparation of the thiophene metal complex. The polymerization reaction step with the Ni (II) catalyst can be carried out at about 0°C to about the boiling point of the solvent used in this step of the reaction. Typically, the polymerization reaction step with the Ni (II) catalyst is carried out at about 0°C to about 25°C. The entire reaction sequence can be carried out without any isolation of intermediates.

One advantage of the methods described herein for preparing HT polythiophenes is that transmetallation of the thiophene-metal complex with zinc allows for polymerization at a lower temperature. Polymerization of the thiophene-zinc complex proceeds smoothly at ambient temperatures (e.g., about 18°C to about 25°C) without the need for a heat source or for refluxing conditions. A more significant advantage is that the method described herein produces a polymer of greater regioregularity (higher percentage of head-to tail thiophene linkages). Additionally, lower catalyst loading is used, thus providing a less expensive procedure.

Activated Metals

An activated metal is highly reactive metal, which has a high surface area and lacks a passivating surface oxide. The activated metal may be, for example, a metal powder, a metal dust, or metal granules. The activated metal may be activated by, for example, chemical, thermal, electrochemical, or ultrasonic methods. Typically, the activated metal has a valence state of zero. Preferably, the activated metals are Rieke metals, which are prepared by the methods developed by one of the present inventors, Dr. Reuben D. Rieke. The Rieke method typically involves the reduction of a tetrahydrofuran suspension of an anhydrous metal chloride (e.g., F, Cl, Br, or I) with an alkali metals. Typical alkali metals used in the Rieke method include, for example, potassium, sodium, and lithium. For example, the preparation of Rieke magnesium employs potassium as the reductant as follows:

$$MgCl_2 + 2\,K \rightarrow Mg + 2\,KCl$$

Many activated metals are prepared by this method, including, for example, aluminum, manganese, copper, zinc, magnesium, calcium, titanium, iron, cobalt, nickel, and indium. In some cases, the reaction is carried out with a catalytic amount of an electron carrier such, for example, biphenyl or naphthalene. The activated metal is typically used *in situ*.

Suitable activated metals include, for example, aluminum, manganese, copper, zinc, magnesium, calcium, titanium, iron, cobalt, nickel, indium, or a combination thereof. Preferably, the activated metal is Rieke zinc.

2,5-Dihalo-Thiophenes

In a preferred embodiment, the dihalo-monomers are dihalo-thiophenes. The 2,5-dihalo-thiophene may be a 2,5-dihalo-3-substituted-thiophene, an unsubstituted 2,5-dihalo-thiophene, or a 2,5-dihalo-3,4-disubstituted-thiophene. The dihalo-thiophenes are typically difluoro-, dichloro-, dibromo-, or diiodo-thiophenes, which may be unsubstituted or substituted in the 3 and/or 4 positions. Combinations of 2,5-dihalothiophenes, 2,5-dihalo-3-substituted-thiophenes, and 2,5-dihalo-3,4-disubstituted-thiophenes may also be employed.

Suitable unsubstituted dihalo-thiophenes may include, for example, 2,5-difluorothiophene, 2,5-dichlorothiophene, 2,5-dibromothiophene, 2,5-diiodothiophene, 2-fluoro-5-chlorothiophene, 2-fluoro-5-bromothiophene, 2-fluoro-5-iodothiophene, 2-chloro-5-fluorothiophene, 2-chloro-5-bromothiophene, 2-chloro-5-iodothiophene, 2-bromo-5-fluorothiophene, 2-bromo-5-chlorothiophene, 2-bromo-5-iodothiophene, 2-iodo-5-fluorothiophene, 2-iodo-5-chlorothiophene, and 2-iodo-5-bromothiophene. These 2,5-dihalothiophenes, which are not substituted in the 3- and/or 4-positions, may be useful to prepare a block copolymer that includes, for example, an unsubstituted polythiophene block and one or more substituted polythiophene blocks. For example, an unsubstituted polythiophene may be combined with a block of either 3-substutituted polythiophene and/or a block of 3,4-disubstituted polythiophene. Alternatively, a 3-substutituted polythiophene can be combined with a block of 3,4-disubstituted polythiophene.

The dihalo-thiophenes listed above may be substituted in the 3 and/or 4-positions with an (C_1-C_{24})alkyl, a (C_1-C_{24})alkylthio, a (C_1-C_{24})alkylsilyl, or a (C_1-C_{24})alkoxy group that may be optionally substituted with about one to about five ester, ketone, nitrile, amino, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, or NH groups.

Suitable 2,5-dihalo-3-substituted-thiophenes may include, for example, 2,5-difluoro-3-hexylthiophene, 2,5-dichloro-3-hexylthiophene, 2,5-dibromo-3-hexylthiophene, 2,5-diiodo-3-hexylthiophene, 2-fluoro-3-hexyl-5-chlorothiophene, 2-fluoro-3-hexyl-5-bromothiophene, 2-fluoro-3-hexyl-5-iodothiophene, 2-chloro-3-hexyl-

5-fluorothiophene, 2-chloro-3-hexyl-5-bromothiophene, 2-chloro-3-hexyl-5-iodothiophene, 2-bromo-3-hexyl-5-fluorothiophene, 2-bromo-3-hexyl-5-chlorothiophene, 2-bromo-3-hexyl-5-iodothiophene, 2-iodo-3-hexyl-5-fluorothiophene, 2-iodo-3-hexyl-5-chlorothiophene, 2-iodo-3-hexyl-5-bromothiophene, ethyl-5-(2-5-difluorothiophen-3-yl)pentanoate, ethyl-5-(2-5-dichlorothiophen-3-yl)pentanoate, ethyl-5-(2-5-dibromothiophen-3-yl)pentanoate, ethyl-5-(2-5-diiodothiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-5-chlorothiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-5-bromothiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-chloro-5-bromothiophen-3-yl)pentanoate, ethyl-5-(2-chloro-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-bromo-5-chlorothiophen-3-yl)pentanoate, ethyl-5-(2-bromo-5-chlorothiophen-3-yl)pentanoate, ethyl-5-(2-bromo-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-iodo-5-chlorothiophen-3-yl)pentanoate, ethyl-5-(2-iodo-5-bromothiophen-3-yl)pentanoate, and ethyl-5-(2-iodo-5-fluorothiophen-3-yl)pentanoate. Preferably, the 2,5-dihalo-3-substituted-thiophene is 2-bromo-3-hexyl-5-iodothiophene or ethyl-5-(2-bromo-5-iodothiophen-3-yl)pentanoate.

Suitable 2,5-dihalo-3,4-disubstituted thiophenes may include, for example, ethyl-5-(2-5-difluoro-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-5-dichloro-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-5-dibromo-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-5-diiodo-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-5-chloro-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-5-bromo-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-fluoro-3-hexyl-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-chloro-3-hexyl-5-fluorothiophen-3-yl)pentanoate, ethyl-5-(2-chloro-3-hexyl-5-bromothiophen-3-yl)pentanoate, ethyl-5-(2-chloro-3-hexyl-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-bromo-5-chloro-3-hexylthiophen-3-yl)pentanoate, ethyl-5-(2-bromo-3-hexyl-5-iodothiophen-3-yl)pentanoate, ethyl-5-(2-iodo-3-hexyl-5-chlorothiophen-3-yl)pentanoate, ethyl-5-(2-iodo-3-hexyl-5-bromothiophen-3-yl)pentanoate, and ethyl-5-(2-iodo-5-fluoro-3-hexylthiophen-3-yl)pentanoate.

Solvents

The solvent employed in these methods can be aprotic organic solvents. One or multiple solvent compounds, or mixtures, can be used. Suitable solvents include

ethereal or polyethereal solvents. Examples of such solvents include ethyl ether, methyl-*t*-butyl ether, tetrahydrofuran (THF), dioxane, diglyme, triglyme, 1,2-dimethoxyethane (DME or glyme), and the like. A typical solvent is tetrahydrofuran.

Catalysts

Many metal catalysts can be used in the polymerizations in these methods. The metal catalyst can comprise an organometallic compound or a transition metal complex. For example, the metal catalyst can be a nickel, platinum, or palladium compound. Preferably, the metal catalysts are nickel (II) catalysts, which afford regioselective polythiophene block copolymers.

An effective amount of the Ni (II) catalyst is employed, such that a sufficient amount of catalyst is employed to effect the reaction in less than about 5 days. Typically, this is an amount of about 0.01-10 mole percent (mol %), however, any amount of the Nickel (II) catalyst can be employed, such as 50 mol %, 100 mol %, or more. Typically, about 0.1 mol% Nickel (II) catalyst to about 5 mol% Nickel (II) catalyst is employed, or preferably, about 0.1 mol% Nickel (II) catalyst to about 3 mol% Nickel (II) catalyst is employed, based on the amount of monomer present.

Examples of suitable nickel (II) catalysts include, for example, Ni $(PR_3)_2X_2$ wherein R is $(C_1\text{-}C_{20})$alkyl, $(C_6\text{-}C_{20})$aryl, and X is halo, $NiLX_2$ wherein L is a suitable nickel (II) ligand and X is halo. Suitable nickel (II) ligands include 1,2-bis(diphenylphosphino)ethane, 1,3-diphenylphosphinopropane, [2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)] diphenylphosphine, bis(triphenylphosphine), and (2,2'-dipyridine) ligands. Other suitable Ni (II) catalysts include Ni $(CN)_4^{-2}$, NiO, Ni $(CN)_5^{-3}$, $Ni_2Cl_8^{-4}$, NiF_2, $NiCl_2$, $NiBr_2$, NiI_2, NiAs, Ni $(dmph)_2$ wherein dmph is dimethylglyoximate, BaNiS, $[NiX(QAS)]^+$ wherein X is halo and QAS is As(*o*-$C_6H_4AsPh_2)_3$, $[NiP(CH_2CH_2CH_2AsMe_2)_3CN]^+$, [Ni $(NCS)_6]^{-4}$, $KNiX_3$ wherein X is halo, [Ni $(NH_3)_6]^{+2}$, and [Ni $(bipy)_3]^{+2}$ wherein bipy is bipyridine.

Typical nickel catalysts also include 1,2-bis(diphenylphosphino)ethane nickel (II) chloride (Ni $(dppe)Cl_2$), 1,3-diphenylphosphinopropane nickel (II) chloride (Ni

(dppp)Cl_2), 1,5-cyclooctadiene bis(triphenyl) nickel, dibromo bis(triphenylphosphine) nickel, dichoro(2,2'-dipyridine) nickel, and tetrakis(triphenylphosophine) nickel (0).

General techniques and methods known by those of ordinary skill in the art can be used in methods of the invention, such as the various standard procedures for carrying out the polymerization, and for isolating and purifying the products.

Polymer Structure and Properties of Conducting Polymers

Typically, conducting polymers are organic polymers that, due to their conjugated backbone structure, show high electrical conductivities under some conditions (relative to those of traditional polymeric materials). Performance of these materials as a conductor of holes or electrons is increased, when they are doped, oxidized, or reduced. Upon low oxidation (or reduction) of conducting polymers, in a process, which is frequently referred to as doping, an electron is removed from the top of the valence band (or added to the bottom of the conduction band) creating a radical cation (or polaron). Formation of a polaron creates a partial delocalization over several monomeric units. Upon further oxidation, another electron can be removed from a separate polymer segment, thus yielding two independent polarons. Alternatively, the unpaired electron can be removed to create a dication (or bipolaron). In an applied electric field, both polarons and bipolarons are mobile and can move along the polymer chain by delocalization of double and single bonds. This change in oxidation state results in the formation of new energy states, called bipolarons. The energy levels are accessible to some of the remaining electrons in the valence band, allowing the polymer to function as a conductor. The extent of this conjugated structure is dependent upon the polymer chains to form a planar conformation in the solid state. This is because conjugation from ring-to-ring is dependent upon π-orbital overlap. If a particular ring is twisted out of planarity, the overlap cannot occur and the conjugation band structure can be disrupted. Some minor twisting is not detrimental since the degree of overlap between, for example, thiophene rings varies as the cosine of the dihedral angle between them.

Performance of a conjugated polymer as an organic conductor can also be dependant upon the morphology of the polymer in the solid state. Electronic properties

can be dependent upon the electrical connectivity and inter-chain charge transport between polymer chains. Pathways for charge transport can be along a polymer chain or between adjacent chains. Transport along a chain can be facilitated by a planar backbone conformation due to the dependence of the charge carrying moiety on the amount of double-bond character between the rings, an indicator of ring planarity. This conduction mechanism between chains can involve either a stacking of planar, polymer segment, called π-stacking, or an inter-chain hopping mechanism in which excitons or electrons can tunnel or "hop" through space or other matrix to another chain that is in proximity to the one that it is leaving. Therefore, a process that can drive ordering of polymer chains in the solid state can help to improve the performance of the conducting polymer. It is known that the absorbance characteristics of thin films of conducting polymers reflect the increased re-stacking, which occurs in the solid state.

To effectively use a conducting polymer, it is advantageously prepared by a method that allows the removal of organic and ionic impurities from the polymeric matrix. The presence of impurities, notably metal ions, for example, in this material may have serious deleterious effects on the performance of the conducting polymer. These effects include, for example, charge localization or trapping, quenching of the exciton, reduction of charge mobility, interfacial morphology effects such as phase separation, and oxidation or reduction of the polymer into an uncharacterized conducting state, which may not be suitable for a particular application. There are several methods by which impurities may be removed from a conducting polymer. Most of these are facilitated by the ability to dissolve the polymer in common organic and polar solvents.

Derivatives of a conducting polymer can be modified polymers, such as a poly(3-substituted thiophene), which retain an essential backbone structure of a base polymer, but are modified structurally over the base polymer. Derivatives can be grouped together with the base polymer to form a related family of polymers. The derivatives generally retain properties such as electrical conductivity of the base polymer.

In addition, the regioregular conducting polymers that are block copolymers can comprise the conducting block, having conjugated structures which may or may not be

doped, and the nonconducting block. The non-conducting block can include a variety of synthetic polymers including condensation, addition, and ring-opened polymers including for example, urethanes, polyamides, polyesters, polyethers, vinyl polymers, aromatic polymers, aliphatic polymers, heteroatom polymers, siloxanes, acrylates, methacrylates, phosphazene, silanes, and the like. Inorganic and organic polymers can be used as the non-conducting part.

If desired, the regioregular conducting polymers can be blended with other components including inorganic glasses and metals as well as other polymers including inorganic polymers and organic polymers, as well as other conducting polymers either of the same type (e.g., two polythiophene types) or of different type (e.g., a polythiophene with a nonpolythiophene). The block copolymer can be used as a compatibilizing agent.

Polymerization of polythiophenes and block copolymers for other types of non-thiophene polymers are described in, for example, Yokozawa et al., *Polymer Journal*, **36(2)**, 65 (2004). Block copolymers are generally known in the art. See, for example, Yang (Ed.), *The Chemistry of Nanostructured Materials*, pages 317-327 ("Block Copolymers in Nanotechnology") (2003). Also block copolymers are described in, for example, *Block Copolymers, Overview and Critical Survey*, by Noshay and McGrath, Academic Press, 1977. For example, this text describes A-B diblock copolymers (chapter 5), A-B-A triblock copolymers (chapter 6), and -(AB)n-multiblock copolymers (chapter 7), which can form the basis of block copolymer types in the present invention. Additional block copolymers including polythiophenes are described in, for example, Francois et al., *Synth. Met.*, **69**, 463-466 (1995), Yang et al., *Macromolecules*, **26**, 1188-1190, (1993), Widawski et al., *Nature*, **369**, 387-389 (1994), Jenekhe et al., *Science*, **279**, 1903-1907 (1998), Wang et al., *J. Am. Chem. Soc.*, **122**, 6855-6861 (2000), Li et al., *Macromolecules*, **32**, 3034-3044 (1999), and Hempenius et al., *J Am. Chem. Soc.*, **120**, 2798-2804 (1998).

Regioregular Poly(3-Substituted Thiophenes)

Materials with superior π-conjugation, electrical communication, and solid state morphology can be prepared by using regiospecific chemical coupling methods that

produce greater than 95% 2,5'-couplings of poly(3-substituted thiophenes) with alkyl substituents.

Like regio-random poly(3-substituted thiophenes) with alkyl, aryl, and alkyl/aryl substituents, regio-regular poly(3-substituted thiophenes) with alkyl, aryl, and alkyl/aryl substituents are soluble in common organic solvents and demonstrate enhanced processability in applications by deposition methods such as spin-coating, drop casting, dip coating, spraying, and printing techniques (such as ink-jetting, off-setting, and transfer-coating). Therefore, these materials can be better processed in large-area formats compared to regio-random poly(3-substituted thiophenes). Furthermore, because of the homogeneity of their 2,5'-ring-to-ring couplings, they exhibit evidence of substantial π-conjugation and high extinction coefficients for the absorption of visible light corresponding to the π-π * absorption for these materials. This absorption determines the quality of the conducting band structure, which may be utilized when a regioregular poly(3-substituted thiophene) with alkyl, aryl, or alkyl/aryl substituents is used in an organic electronic device and, therefore, determines the efficiency and performance of the device.

Another benefit of the regio-regularity of poly(3-substituted thiophenes) is that they can self-assemble in the solid state and form well-ordered structures. These structures tend to juxtapose thiophene rings systems through a π-stacking motif and allow for improved inter-chain charge transport through this bonding arrangement between separate polymers, enhancing the conducting properties compared to regio-random polymers. Therefore, one can recognize a morphological benefit to these materials.

As is the case with the use poly(thiophene) it has been shown that various poly(3-substituted thiophenes) with alkyl, aryl, and alkyl-aryl substituents are soluble in common organic solvents such as toluene and xylene. These materials share a common conjugated π-electron band structure, similar to that of poly(thiophene) that make them suitable p-type conductors for electronic applications, but due to their solubility they are much easier to process and purify than poly(thiophene). These materials can be made as oligomer chains such as $(3\text{-alkythiophene})_n$, $(3\text{-arylthiophene})_n$, or $(3\text{-alkyl/arylthiophene})_n$, in which n is the number of repeat units with a value of 2-10 or as

polymers in which n is 11-350 or higher, but for these materials, n most typically has a value of 50-200.

Substituent Effects

Since the electronic properties of a conducting polymer arise from the conjugated band structure of the polymer backbone, any factors that increase or decrease the electron density within the backbone π-structure directly affect the band gap and energy levels of the conducting polymer. Therefore, substituents that are attached to the backbone and contain electron withdrawing substituents will reduce the electron density of the conjugated backbone and deepen the HOMO of the polymer. Substituents that are attached to the backbone and contain electron releasing functionality will have the opposite effect. The nature of the effects of substitution is known to any skilled in the art and is well documented in general texts on organic chemistry (*see*, e.g., March, J., Advanced Organic Chemistry, Third Edition, John Wiley & Sons, New-York, Inc. 1985 and references incorporated therein). In both cases, the magnitude of the change in energy levels of the polymer depend upon the specific functionality of the substituent, the proximity or nature of attachment of the functionality to the conjugated backbone, as well as the presence of other functional characteristics within the polymer.

In the case of poly(3-alkyl thiophenes), the alkyl substituents that are typically included to increase solubility have an electron releasing effect, raising the HOMO of the polymer relative to that of poly(thiophene). It has been shown, for example, that a fluorine substituent either as a component of 3-substituent or as the 4-substituent of a poly(thiophene) will withdraw electrons from a poly(thiophene) polymer, lowering the HOMO of the conducting polymer. It can be seen that alkoxy substituents on the 3-position may be used to decrease the band gap of a regioregular poly(3-substituted thiophene). In each of these cases, the manipulation of the energy levels has been accomplished by modification of the backbone of a polymer. In many instances, it is important to incorporate a particular functionality into a conducting polymer to impart a specific property. For example, the alkyl substituent of a poly(3-hexyl-thiophene) is included to make the polymer soluble in common organic solvents. However, for an

application in which a deep HOMO is required, this electron-releasing functionality actually imparts the opposite of the desired electronic effect.

Therefore, a flexible synthetic method through which electronic, optical, and physical properties of the conducting polymer may be balanced and tuned to offer a material that satisfies diverse performance requirements offers a real advantage in organic device development.

The improved regioregular conducting polymers, for example, HT polythiophenes prepared by the methods disclosed herein can be unsubstituted HT poly(thiophene), HT poly(3-substituted-thiophene), or HT poly(3,4-disubstituted-thiophene). These substituents can be any of the groups recited under the definition of substituents above. In one embodiment, the thiophene is a 3-substituted thiophene, wherein the substituent is an alkyl, alkylthio, alkylsilyl, or alkoxy group. The substituent can be optionally substituted with other functional groups, for example, and with out limitation, about one to about five esters, ketones, nitriles, amines, halogens, aryl groups, heterocyclyl groups, and heteroaryl groups. One or more of the carbon atoms of alkyl chain of the alkyl, alkylthio, alkylsilyl, or alkoxy group can also be exchanged by one or more heteroatoms, such as O, S, NP groups (wherein P is a substituent or a nitrogen protecting group), or combinations thereof.

It is often preferable to include substituents that improve the solubility of the regioregular conducting polymer, for example, a HT polythiophene. Such substituents can preferably include groups that include at least about five or six carbon atoms, such as hexyl, hexoxy, hexylthio, and hexylsilyl groups. In another aspect of the invention, it can be preferable that the substituent directly attached to the 3-position is a heteroatom, such as a sulfur, silicon, oxygen, or nitrogen atom. The heteroatoms can be substituted with other appropriate groups, such as are described above in the definition of substituted. Heteroatoms at the 3-position of the thiophenes can further enhance the conductivity of the HT polythiophene by, for example, allowing for delocalization of the aromatic electrons of the thiophene ring systems and/or allowing for improved packing and optimized microstructure of the polymer, leading to improved charge carrier mobility. In a further aspect of the invention, it can be preferable to separate an aryl, heteroaryl, or heterocyclyl substituent from the thiophene ring by one or more

(e.g., one to ten, one to five, or one to three) methylene groups, optionally exchanged by one or more heteroatoms (e.g., a polyethylene or polyethyleneimine group wherein the group includes about 2 to about 10 repeating units. Substituents at the 3-position of the thiophene monomer can improve the regioregularity of the product HT polythiophene by providing steric bulk that influences the regiochemistry of the polymerization.

The terminal groups of the regioregular conducting polymer, for example, the group at the 2- or 5-position of the terminal thiophene of the polymer on the product HT polythiophene can be a hydrogen or a halogen. The terminal group of the regioregular conducting polymer, for example, HT polythiophene can also be an alkyl or functionalized alkyl group, which can be provided for by quenching the polymerization with an organometallic species, such as an organo-zinc reagent.

The average weight molecular weight of the regioregular conducting polymers prepared by the methods described herein can be about 5,000 to about 200,000, preferably about 20,000 to about 80,000, and more preferably about 40,000 to about 60,000, as determined by GPC using a polystyrene standard in tetrahydrofuran. The polydispersity index (PDI) can be about 1 to about 2.5, or preferably about 1.1 to about 2.4, or more preferably about 1.2 to about 2.2.

The regioregularity of the conducting polymers prepared by the methods described herein are typically at least about 87% without any purification after work-up. It was surprisingly discovered that by employing 1.2 equivalents of a metal halide salt, for example, a zinc halide salt, a higher percent of regioregularity can be obtained. For example, by employing 1.2 equivalents of $ZnBr_2$, based on the amount of 3-substituted thiophene starting material, an HT polythiophene of at least about 92% regioregularity was obtained. Simple purification techniques, such as Soxhlet extraction with hexanes can improve the regioregularity to greater than about 94%, preferably greater than about 95%, more preferably greater than about 97%, yet more preferably greater than about 98%, or even more preferably greater than about 99%. The crude regioregular conducting polymer can be isolated after polymerization by precipitation in methanol followed by simple filtration of the precipitated polymer. The crude polymer has superior properties relative to the crude products of the art. The crude regioregular conducting polymer has higher regioregularity that the known preparatory methods,

which reduces the amount of purification necessary to provide a usable material for electronic applications.

Higher regioregularity results in higher conductivity of the regioregular conducting polymer, for example, HT polythiophene. When doped, a regioregular conducting polymer, for example, a regioregular HT 3-substituted polythiophene, can have a conductivity of about 1,000 S/cm, +/- about 400 S/cm. Regiorandom 3-substituted polythiophenes typically conduct at only about 5-10 S/cm. Furthermore, undoped regioregular conducting polymers, for example, regioregular 3-substituted polythiophenes, can conduct at about 10^{-5} to about 10^{-6} S/cm (the semiconductor range), and undoped regiorandom polythiophenes conduct at about 10^{-9} S/cm.

Doping

In a preferred embodiment, the conducting polymer can be oxidatively or reductively doped. The addition of the dopant results in an expansion of the extent of the conjugated π system in the individual polymer molecule. It is not necessary to extend the conjugated π system over the full extent of the molecule. It is necessary to sufficiently extend the π conjugated system of an individual molecule so that after the solvent is removed the π conjugated part of an individual molecule is adjacent to a part of the π conjugated part of an adjacent molecule. In the π conjugated system an electron is delocalized over the entire π conjugated bonds. These electrons are more loosely bond and are available for electrical conduction. When an electric field is applied, and electron can flow along an individual molecule and hop from one molecule to an adjacent molecule in a region where the π conjugated parts of the adjacent molecules overlap.

Doping can also be achieved electrochemically by confining the conducting polymers to an electrode surface and subjecting it to an oxidizing potential in an electrochemical cell.

Dopants that may be included in the conducting polymer matrix include, for example, iodine (I_2), bromine (Br_2), ferric chloride, and various arsenate or antimony salts. Other dopants may include, for example, various known onium salts, iodonium salts, borate salts, tosylate salts, triflate salts, and sulfonyloxyimides. The conducting

polymers may be doped, for example, by dissolving the polymer in a suitable organic solvent and adding the dopant to the solution, followed by evaporation of the solvent. Many variations of this technique can be employed and such techniques are well known to those of skill in the art. *See* for example, U.S. Patent No. 5,198,153, which is hereby incorporated by reference.

In a conductive thin-film application, the conductivity can range from about 1 x 10^{-8} S/cm to about 10^{4} S/cm, but most typically it is in the range of about 1 S/cm to about 500 S/cm. In the case of conducting polymers that are regio-regular poly(3-substituted thiophenes) in which the 3-substitutent is an alkyl, aryl, or alkyl/aryl moiety with an oxygen substitution in either the α- or β-position of the 3-substituent or a hetero atom in either the α- or β-position of the 3-substituent, the desirable characteristics of the conductive thin film are that they retain their conductivity for thousands of hours under normal use conditions and meet suitable device stress tests at elevated temperatures and/or humidity. This facilitates an operational range of robust charge mobility and allows the tuning of properties by controlling the amount and identity of the doping species and complements the ability to tune these properties by the tuning of the primary structure.

There are many oxidants, which may be used to tune conductive properties as described above. By controlling the amount of exposure of the dopant to the conducting polymer, the resulting conductive thin film can be controlled. Because of their high vapor pressure and solubility in organic solvents, halogens may be applied in the gas phase or in solution. Oxidation of the conducting polymer greatly reduces the solubility of the material relative to that of the neutral state. Nevertheless, various solutions may be prepared and coated onto devices.

Suitable dopants may also include, for example, iron trichloride, gold trichloride, arsenic pentafluoride, alkali metal salts of hypochlorite, protic acids such as benzenesulfonic acid and derivatives thereof, propionic acid, and other organic carboxylic and sulfonic acids, nitrosonium salts such as $NOPF_6$ or $NOBF_4$, or organic oxidants such as tetracyanoquinone, dichlorodicyanoquinone, and hypervalent iodine oxidants such as iodosylbenzene and iodobenzene diacetate. Conducting polymers may also be oxidized by the addition of a polymer that contains acid or oxidative

functionality, for example, poly(styrene sulfonic acid).

The solvents used in adding the dopants are not particularly limited. One or multiple solvent compounds, or mixtures, can be used. Organic solvents can also be used. For example, ethers, esters, and alcohols can be used. Water can be used. Polar solvents can be used. Aprotic solvents can be used. Solvents having molecular weights of under 200, or under 100 g/mol can be used.

Suitable solvents for adding dopants include, for example, dimethyl formamide (DMF), dioxolane, methyl ethyl ketone, MIBK, ethylene glycol dimethyl ether, butonitrile, cyclopentanone, cyclohexanone, pyridine, chloroform, nitromethane, 2-nitromethane, trichloroethylene tetrachloroethylene, propylene carbonate, quinoline, cyclohexanone, 1,4-dioxolane, dimethyl sulfoxide (DMSO), nitrobenzene, chlorobenzene, and 1-methyl-2-pyrrolidinone.

Other Components

In a preferred embodiment, the conducting polymers can also include one or more other suitable components such as, for example, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers or oligomers, surface active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, diluents, colorants, dyes, pigments, or dopants. These optional components can be added to a conducting polymer composition by dissolving the conducting polymer in a suitable organic solvent and adding the component to the solution, followed by evaporation of the solvent. In certain embodiments, the conducting polymer are significantly useful as substantially pure polymers or as a doped polymers.

Thin films

In a preferred embodiment, the conductive polymer may be in the form of a film. Highly conductive thin films of soluble, conducting polymers are useful in a variety of applications, including, for example, many types of diodes. In their neutral or undoped form, soluble conducting polymers offer the ability to be applied by spin casting, drop casting, screening, ink-jetting, and standard printing techniques such as

transfer or roll coating. Conductivity can be tuned from the neutral or semi-conductive state to a highly conductive state depending upon the amount of dopant added, making the material specifically suitable for a given application. Generally speaking, conductive films of doped conducting polymers can be made transparent in the visible region. This makes them suitable for use as transparent conductors. This combination of properties makes them suitable for use in electronic devices such as diodes and light emitting diodes.

Conducting polymers, in particular doped polythiophenes, have been shown to function suitably as positive charge carriers, also known as hole injection layers, in diodes as well as in light emitting diodes and solid-state lighting. This is a function of their facile oxidation as well as their stability in the doped state. A commercial example of this type of application is poly(3,4-ethylenedioxythiophene), which is available from H. C. Stark GmbH of Goslar, Germany. This material has limited applicability in that it is synthesized in an oxidized form, low in pH, and insoluble. It is available as an aqueous dispersion.

Performance of conductive thin films is gauged by evaluation of their high electrical conductivity value, good electrical performance, and high thermal stability. Conductivity is typically measured by: $\sigma = I/(4.53\ VW)$, where conductivity, σ, is measured in S/cm, I = current in amps, V = voltage, V, and W = film thickness in cm. Typically this value is measured by the standard, four point probe method, wherein current is passed between two electrodes and potential is measured through another pair of electrodes. Thickness can be determined by various methods such as SEM and profilometry.

The use of soluble conducting polymers, such as poly(3-alkylthiophenes), to build conductive layers or films offers in diodes several advantages such as ease of processability of materials and components during device production. In their neutral or undoped form, conducting polymers offer the ability to use spin casting, drop casting, screening, ink-jetting, and standard printing techniques such as transfer or roll coating to apply the conducting polymer layer. These methods allow for facile *in-situ* processing and precise control over the volume of conductive material applied. In general, methods can be used, which are used for printable or printed electronics.

Microlithography and nanolithography methods can be used.

The use of conducting polymers, for example, regio-regular poly(3-heteroatomic substituted thiophenes) offer several advantages in this application. Paramount among these advantages is the ability to tune the conductivity of the device through control of the morphology of the film, the selection of oxidant used, and the amount of oxidant used. As these materials are formed in the neutral or undoped state, conductivity may be carefully tuned by the amount of oxidation. Another key benefit of the use of these materials compared to the use of other conducting polymers is the stability of the oxidized or "doped" conductive state of the poly(3-heteroatomic substituted thiophene). The selective solubility of these materials also allows for selective application and removal of films of these materials in devices.

In addition, electrically conducting polymers are described in The Encyclopedia of Polymer Science and Engineering, Wiley, 1990, pages 298-300, including polyacetylene, poly(p-phenylene), poly(p-phenylene sulfide), polypyrrole, and polythiophene. This reference also describes blending and copolymerization of polymers, including block copolymer formation.

The high purity conducting polymers prepared by the methods described herein can be used to form thin films. The thin films can be formed using standard methods known to those of skill in the art, such as spin coating, casting, dipping, ink jet coating, bar coating, roll coating, air knife coating, curtain coating, extrusion slot die coating, and the like, using a solution of a conducting polymer dissolved in a solvent. *See* for example U.S. Patent Nos. 5,892,244, 6,337,102, 7,049,631, 7,037,767, 7,025,277, 7,053,401, and 7,057,339 for methods of preparing thin films and organic field effect transistors, which are hereby incorporated by reference.

In one embodiment, a thin film of conducting polymer may be formed, for example, by forming a Langmuir-Blodgett film of the polythiophene precursor, and converting the polythiophene precursor into a polythiophene. Likewise, a thin film may be formed, for example, by vapor depositing a polythiophene precursor, and converting the polythiophene precursor into a polythiophene.

In one embodiment, a thin film of conducting polymer may be formed, for example, by spin coating. A solution of the conducting polymer is placed on the

substrate, which is rotated at high speed in order to spread the fluid by centrifugal force. The rotation of the substrate is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. Further, the higher the angular speed of spinning, the thinner the film will be produced. The thickness of the film also depends on the concentration of the solution and the solvent.

In one embodiment, a thin film of a conducting polymer may be formed, for example, by casting. Molten conducting polymer is introduced into a mould, allowed to solidify within the mould, cooled, and the mould disassembled to afford the thin film.

In one embodiment, a thin film of a conducting polymer may be formed, for example, by dip coating in which a substrate is immersed into a tank containing polythiophene, removing the substrate from the tank, and allowing it to drain. The coated substrate can be air-dried or baking.

In one embodiment, a thin film of a conducting polymer may be formed, for example, by ink jet coating in which a solution of polythiophene is ejected from a piezoelectric ink jet onto a substrate. The coated substrate can be air-dried or baking.

The thin films can have a wide range of thickness. A typical thin film is in the range of about 1 μm to about 1 mm. The thin film can include a coloring agent, a plasticizer, or a dopant. The conducting polymers can be electrically conductive, particularly when a dopant is included in the polymer matrix.

Applications

The applications of the conducting polymers are not particularly limited but include optical, electronic, energy, biomaterials, semiconducting, electroluminescent, photovoltaic, LEDs, OLEDs, PLEDs, sensors, transistors, field effect transistors, batteries, flat screen displays, organic lighting, printed electronics, nonlinear optical materials, dimmable windows, RFID tags, fuel cells, triodes, rectifiers, and others. *See*, for example, Kraft et al., *Angew. Chem. Int Ed.*, **37**, 402-428 (1998). *See*, also, Shinar, *Organic Light-Emitting Devices*, Springer-Verlag, (2004). Hole-injection layers can be fabricated. Multilayer structures can be fabricated and thin film devices made. Thin films can be printed. Patterning can be carried out. Printing on consumer products can

be carried out. Small transistors can be fabricated. In many applications, the composition is formulated to provide good solution processing and thin film formation. Blends with other polymers including conductive polymers can be prepared. The nanowire morphology of the block copolymers can be exploited in nanoscale fabrication. The following is a brief description of exemplary applications for the conducting polymers.

Organic Light-Emitting Diodes

In one preferred embodiment, the conducting polymers prepared by the methods described herein may be used in, for example, an organic light-emitting diode. For example, regioregular polythiophenes, which can be employed in the manufacture of organic light-emitting diodes (OLEDs). Organic light-emitting diodes (OLEDs) are used in electronic applications or as backlight of, for example, liquid crystal displays. Common organic light-emitting diodes are fabricated using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/or hole-transport layers. By applying an electric voltage, electrons and holes as charge carriers move towards the emission layer, where their recombination leads to the excitation and luminescence of the lumophore units contained in the emission layer. The conducting polymers may be employed in one or more of the charge transport layers and/or in the emission layer, corresponding to their electrical and/or optical properties. Furthermore, their use within the emission layer is especially advantageous, if the conducting polymers show electroluminescent properties themselves or comprise electroluminescent groups or compounds. In such case, luminescence can be obtained by injection of charge carriers into the conducting polymer itself. The selection, characterization as well as the processing of suitable monomeric, oligomeric, and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art (*see*, e.g., Meerholz, *Synthetic Materials*, **111-112**, 31-34 (2000) and Alcala, *J. Appl. Phys.*, **88**, 7124-7128 (2000) and the literature cited therein).

According to another use, the conducting polymers, especially those showing photoluminescent properties, may be employed as materials of light sources, for

example, of display devices such as described in European Patent Application Publication No. EP 0 889 350 A1 or by C. Weder et al., *Science*, **279**, 835-837 (1998).

Field Effect Transistors

In a preferred embodiment, the conducting polymers may also be used in, for example, field effect transistors (FETs). In a field effect transistor, an organic semiconductive material is arranged as a film between a gate-dielectric, a drain, and a source electrode (*see*, e.g., U.S. Patent No. 5,892,244, PCT Patent Application Publication No. WO 00/79617, and U.S. Patent No. 5,998,804). Due to the advantages associated with these materials, like low cost fabrication of large surfaces, preferred applications of these field effect transistors are, for example, integrated circuitry, thin film transistor (TFT) displays, and security applications.

In security applications, field effect transistors and other devices with semiconductive materials, like transistors or diodes, may be used for radio frequency identification (RFID) tags or security markings to authenticate and prevent counterfeiting of documents of value. Documents of value may include, for example, banknotes, credit cards, identification (ID) cards, passports, licenses, or any other product with monetary value (e.g., stamps, tickets, shares of stock, bonds, checks, and the like).

Photovoltaic cells

In a preferred embodiment, the conducting polymers may also be used in, for example, photovoltaic cells. A photovoltaic cell is an electrochemical device that converts electromagnetic radiation to electrical energy. Although not limited by theory, the conversion of electromagnetic radiation to electrical energy may be accomplished through a charge separation event, which occurs after absorption of a photon. This causes the creation of an excited state, which can be referred to as an exciton, in a p-type semiconductor, which is in intimate contact with an n-type semiconductor. Typically the semiconductor domains are sandwiched in one or more active layers between two electrodes, wherein at least one electrode is sufficiently transparent to allow for the passage of the photon. A photovoltaic cell can be used to charge batteries

or operate electronic devices. It offers advantages to any electrical application, which is electrically driven by an electrical distribution grid, either as a replacement for a battery or as means to restore the charge on a battery which is used to power a device. Finally, it can be used to supplement power supplied on the electrical distribution grid or to replace power supplied from the electrical distribution grid.

The photovoltaic cells typically include at least four components, two of which are electrodes. One component is a transparent first electrode such as indium tin oxide coated onto plastic or glass which functions as a charge carrier. This component is typically the anode, and allows ambient light to enter the device. A second electrode can be made of a metal, for example, calcium or aluminum. In some cases, this metal may be coated onto a supporting surface such as a plastic, glass sheet, sapphire, aluminum nitride, quartz, or diamond. This second electrode also carries current. Between these electrodes are either discrete layers or a mixture of p- and n-type semiconductors, the third and fourth components. The p-type material can be called the primary light harvesting component or layer. This material absorbs a photon of a particular energy and generates a state in which an electron is promoted to an excited energy state, leaving a positive charge or "hole" in the ground state energy levels. This is known as exciton formation. The exciton diffuses to a junction between p-type and n-type material, creating a charge separation or dissociation of the exciton. The electron and "hole" charges are conducted through the n-type and p-type materials, respectively, to the electrodes. This results in the flow of electric current out of the cell. In addition to the conducting polymers described herein, the p-type semiconductor can also comprise conjugated polymers including, for example, mixtures or blends of materials including use of poly-phenylenevinylene (PPV) or poly (3-hexyl)thiophene (P3HT). The n-type component can comprise materials with a strong electron affinity including, for example, carbon fullerenes, titanium dioxide, cadmium selenium, and polymers and small molecules that are specifically designed to exhibit n-type behavior.

Performance of photovoltaic cells can be determined by measurement of the efficiency of conversion of light energy to electrochemical energy as measured by the quantum efficiency (number of photons effectively used divided by the number of

photons absorbed) and by the peak output power generated by the cell (given by the product $I_{pp}V_{pp}$, where I_{pp} is the current and V_{pp} is the voltage at peak power).

Electroluminescent Devices

In one preferred embodiment, the conducting polymers may also be used as, for example, hole injection or hole transport layers in organic or polymer electroluminescent devices. The use of the conducting polymers in electroluminescent devices offers several desirable properties such as increased luminescence of the device, lower threshold voltage, longer lifetime, electron blocking, ease of processability of materials and components during device production, the ability to use spin casting, drop casting, ink-jetting, and other printing techniques to apply the hole injection or hole transport layer in electroluminescent devices, the ability to prepare more flexible electroluminescent devices, the ability to prepare low-weight electroluminescent devices, and the ability to prepare low-cost electroluminescent devices.

An electroluminescent device is a device that converts electric current to a photon flux. This is accomplished when an electron and a positive charge or "hole" meet in an electroluminescent material creating an excited state species or exciton which emits a photon when it decays to the ground state. The device is an efficient way to produce light at low voltage and minimal radiant heat. These devices currently find uses in many consumer electronics.

One example of an electroluminescent device includes four components. Two of these components are electrodes. The first component can be a transparent anode such as indium tin oxide, coated onto a plastic or glass substrate, which functions as a charge carrier and allows emission of the photon from the device. The second electrode, or cathode, is frequently made of a low work function metal such as calcium or aluminum or both. In some cases, this metal may be coated onto a supporting surface such as a plastic, glass sheet, sapphire, aluminum nitride, quartz, or diamond. This second electrode conducts or injects electrons into the device. Between these two electrodes are the electroluminescent layer and the hole injection or hole transport layer.

The third component is an electroluminescent layer material. The electroluminescent layer can comprise, for example, materials based on the conducting

polymers, other conducting polymers, and organic-transition metal small molecule complexes. These materials are generally chosen for the efficiency with which they emit photons when an exciton relaxes to the ground state through fluorescence or phosphorescence and for the wavelength or color of the light that they emit through the transparent electrode.

The fourth component is an hole injection or hole transport layer material. The hole injection or hole transport layer is a conducting material that is able to transfer a positive charge or "hole" from the transparent anode to the electroluminescent layer, creating the exciton which in turn leads to light emission. The hole injection or hole transport layers are typically p-doped or oxidized conductive materials that are generally chosen for the facility with which they are able to transfer a positive charge to the electroluminescent layer and their overall efficiency.

Organic and polymer electroluminescent devices can take a variety of forms. Where the electroluminescent layer includes, for example, small molecules, typically vacuum deposited, the devices are commonly referred to as OLEDs (Organic Light Emitting Diodes). Where the electroluminescent layer includes, for example, electroluminescent polymers, typically solution processed and deposited, the devices are commonly referred to as PLEDs (Polymer Light Emitting Diodes). Some electroluminescent layers may not conveniently fit either description, such as mixtures of an electroluminescent material and a solid electrolyte to form a light-emitting electrochemical cell. Electroluminescent layers can be designed to emit white light (i.e., a balanced mixture of primary colors)either for white lighting applications or to be color filtered for a full-color display application. Electroluminescent layers can also be designed to emit specific colors, such as red, green, and blue, which can be combined to create the full spectrum of colors.

The light emitting diodes (LEDs) can be combined to make flat panel displays, either monochrome (single color) or full color (large number of colors typically created by combinations of red, green and blue). They may be passive matrix displays, where strips of anode material are deposited orthogonally to strips of cathode material with hole injection or hole transport layer and electroluminescent layers in between, such that current flowing through one anode and one cathode strip causes the intersection

point to luminesce as a single pixel in a display. They may also be active matrix displays where transistors at each pixel control whether the individual pixel luminesces and how brightly. Active matrix displays can be either bottom emitting, where the light shines through or beside the transistor circuitry or top emitting where the light shines out in the opposite direction of the layers that contain the transistor circuitry.

Other Diodes

In one preferred embodiment, the conducting polymers may also be used in, for example, diodes, which are not light emitting or photovoltaic. Diodes are described in, for example, Ben G. Streetman, *Solid State Electronic Devices*, 4th Ed., 1995 (see, e.g., Chapters 5 and 6). This book describes, for example, fabrication of junctions and diodes. In one type of diode, a p-type material is placed against an n-type of material. Examples of semiconductor junction types of diodes include normal p-n diodes, gold doped diodes, Zener diodes, avalanche diodes, transient voltage suppression (TVS) diodes, light-emitting diodes (LEDs), photodiodes, Schottky diodes, snap diodes, Esaki or tunnel diodes, IMPATT diodes, TRAPATT diodes, BARITT diodes, and Gunn diodes. Other types of diodes include point contact diodes, tube or valve diodes, gas discharge diodes, and varicap or varactor diodes. One skilled in the art can prepare non-light emitting and non-photovoltaic diodes.

These on-light emitting and non-photovoltaic diodes can be fabricated by methods known in the art. For example, a p-n junction can be fabricated by (i) providing a p-type material, (ii) providing an n-type material, and (iii) combining the p-type material and the n-type material so that they contact each other by methods known in the art. The p-type material can be the conducting polymers as described herein. Similarly, an additional step can be provided for providing an additional p-type material and combining it with the p-n junction to provide a p-n-p sandwich structure.

The conducting polymers can further be used in, for example, liquid crystal and/or semiconducting materials, devices, or applications. The increased conductance of these polymers compared to conventional syntheses allows for improved conductance, and therefore, improved function of these applications and devices.

The polymers described herein are also useful in, for example, reflective films, electrode materials in batteries, and the like. Accordingly, an electronic device including a circuit constructed with a polymer as described herein, such as a polymer prepared as described in Examples 7-12 may also be useful.

Furthermore, compositions of the present invention may be generally described and embodied in forms and applied to end uses that are not specifically and expressly described herein. For example, one skilled in the art will appreciate that the present invention may be incorporated into electronic devices other than those specifically identified herein. Other devices that may be fabricated include (depending on the properties of the present polymers) include, for example, unipolar transistors (e.g., FETs, BJTs, and JFETs), heterojunction transistors (e.g., HEMTs and HBTs), detectors (e.g., PIN, MSM, HPT, focal plane arrays, CCDs, and active pixel sensors), diodes (e.g., Peltier and piezoelectric), optical devices (e.g., waveguides, external cavity lasers & resonators, WGM lasers, optical amplifiers, and tunable emitters), and quantum structures (e.g., quantum wires, quantum dots, and nanowires).

Methods of Making the Compositions

The compositions described herein can be prepared by any of the applicable techniques of organic synthesis. Many such techniques are well known in the art. However, many of the known techniques are elaborated in Compendium of Organic Synthetic Methods (John Wiley & Sons, New York) Vol. 1, Ian T. Harrison and Shuyen Harrison (1971); Vol. 2, Ian T. Harrison and Shuyen Harrison (1974); Vol. 3, Louis S. Hegedus and Leroy Wade (1977); Vol. 4, Leroy G. Wade Jr., (1980); Vol. 5, Leroy G. Wade Jr. (1984); and Vol. 6, Michael B. Smith; as well as March, J., Advanced Organic Chemistry, 3rd Edition, John Wiley & Sons, New York (1985); Comprehensive Organic Synthesis. Selectivity, Strategy & Efficiency in Modern Organic Chemistry, In 9 Volumes, Barry M. Trost, Editor-in-Chief, Pergamon Press, New York (1993); Advanced Organic Chemistry, Part B: Reactions and Synthesis, 4th Ed.; Carey and Sundberg; Kluwer Academic/Plenum Publishers: New York (2001); Advanced Organic Chemistry, Reactions, Mechanisms, and Structure, 2nd Edition, March, McGraw Hill (1977); Protecting Groups in Organic Synthesis, 2nd Edition, Greene, T.W., and Wutz,

P.G.M., John Wiley & Sons, New York (1991); and Comprehensive Organic Transformations, 2nd Edition, Larock, R.C., John Wiley & Sons, New York (1999).

EXAMPLES

The following Examples are illustrative of the above invention. One skilled in the art will readily recognize that the techniques and reagents described in the Examples suggest many other ways in which the present invention could be practiced. It should be understood that many variations and modifications may be made while remaining within the scope of the invention.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

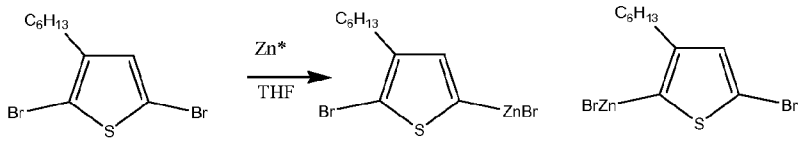
Reactions were typically carried out on a dual manifold vacuum/argon or nitrogen system. The handling of air-sensitive materials was performed under argon or nitrogen in a dry box when necessary. Chemical reagents were primarily purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI), and were used as received unless indicated otherwise.

EXAMPLES 1-6

Preparation of Thienylzinc Bromide

Organozinc I and II as listed in Example 1 in Table 1 were prepared using the method described in U.S. Patent No. 5,756,653 (*see*, e.g., column 54, lines 15-40) which is hereby incorporated by reference, and shown below in Scheme 5. Examples 2-6 are variations on the method of Example 1.

Scheme 5



I II

Table 1

Example	Conditions*	Ratio of Organozinc I and II**
	Temperature Time	
1	0°C for 6 hours	90:10
2	a. -78°C for 1 Hour b. Room Temperature for 4 Hours	92:8
3	a. -78°C for 2 Hours b. Room Temperature for 2 Hours	93:7
4	0°C for 3 hours	92:8
5	a. -40°C for 3 Hours b. Room Temperature for 2 Hours	93:7
6	a. -78°C for 1.5 Hours b. -40°C for 3 hours c. Room Temperature for 2 Hours	94:6

* After the period of time at -78°C or -40°C, the reaction temperature is allowed to warm to the next temperature gradually and proceed at the temperature for the remainder of the recited time.

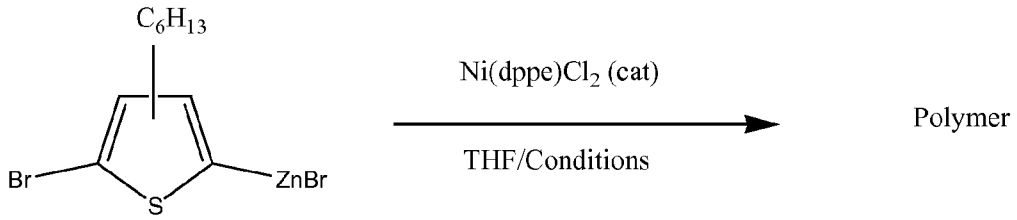
** As determined by ^{1}H NMR.

EXAMPLES 7-12

Polymerization of Thienylzinc Bromide

These examples were prepared according to Scheme 6.

Scheme 6



EXAMPLE 7

Standard Addition Procedure

(Zn-Thiophene to Nickel Catalyst)

A five liter (L) (three-necked) round bottom flask containing a magnetic stirring bar was placed under argon atmosphere. In a separate 100 milliliter (mL) single-necked round bottom flask was added 0.36 mole percent (mol %) of Ni (dppe)Cl_2 (based on organozinc). The 100 mL single-necked round bottom flask was fitted with a rubber septa and 100 mL of tetrahydrofuran was added by cannula into the 100 mL single-necked round bottom flask. The Ni (dppe)Cl_2/ tetrahydrofuran slurry was added by cannula into the single-necked round bottom flask. The organozinc solution from Example 1 was added by cannula over six hours into the five-thousand milliliter (mL) (three-necked) round bottom flask using a 16" gauge cannula at a fast drip rate. After the internal temperature achieved 40°C, the addition was slowed to maintain a temperature of 40°C. The reaction was stirred for an additional 18 hours.

The reaction mixture was divided into three parts and each part was worked up by the following procedure. One liter (L) of polymer solution was added with stirring into a four liter beaker containing 1 liter of methanol. The stirring was continued for 30 minutes and the precipitate was allowed to settle for at least thirty minutes. The precipitate was filtered with a Buchner funnel fitted with course filter paper under

vacuum. The crude polymer was placed in a Soxhlet thimble and extracted with hexanes for 24 hours. The polymer was dried under high vacuum to afford the L-Grade polymer of Example 7 in Table 2.

EXAMPLES 8-12

General Reverse Addition Procedure

(Nickel Catalyst to Zn-Thiophene)

To a three-thousand milliliter (mL) round bottom flask containing a magnetic stirring bar under argon atmosphere was added 1.0 liter thienylzinc bromide solution (0.5 mol in a 0.5 M solution in tetrahydrofuran). To this was added 1000 ml of fresh tetrahydrofuran to afford a 0.25 M thienylzinc bromide solution. The flask was cooled in an ice-bath and 0.26 g Ni (dppe)Cl_2 (0.1 mol % based on organozinc) was added in one portion. The mixture was stirred at 0°C for six hours, the ice bath was removed, and the mixture was allowed to warm to room temperature. After stirring for eighteen hours at room temperature, the mixture was poured into three liters of methanol. The mixture was stirred for twenty minutes. The precipitate was filtered with a Buchner funnel fitted with course filter paper under vacuum. The precipitate was washed with methanol and dried in a vacuum to afford 70 gm (84%) of crude polymer.

The crude polymer was placed in a Soxhlet thimble and extracted with hexanes for 24 hours. The polymer was dried under high vacuum to afford the L-Grade polymers of Examples 8-12 in Table 2.

Table 2

Example	Organozinc Ratio*	Conditions	Yield (ratio)#	
			Crude	L-Grade
7	90:10	Room Temperature to 40°C for 24 hours		84% (90:10)
8	90:10	0°C for 2 hours, Room Temperature for 22 Hours @ 0.2 M concentration	88% (94:6)	77% (97:3)
9	92:8	0°C for 6 hours, Room Temperature for 18 Hours @ 0.25 M concentration and 0.5 mol	84% (95:5)	80% (96:4)
10	94:6	0°C for 7 hours @ 0.2 M concentration	67% (97:3)	64% (96:4)
11	>99:1**	0°C for 1 hour, Room Temperature for 23 Hours @ 0.2 M concentration	82% (92:8)	
12	92:8	Room Temperature for 2 Hours @ 0.5 M concentration		85% (95:5)

* = Ratio of 5-thienylzinc bromide to 2-thienylzinc bromide

** = Ratio of 5-thienylzinc iodide to 2-thienylzinc iodide

= Regiochemistry (by ^{1}H NMR)

There are two surprising improvements to the above process in which the thiophene-zinc complex was added to the flask containing a solution of the nickel (II) catalyst. First, the thiophene-zinc complex is formed by combining a 3-substituted thiophene having at least two leaving groups with Rieke zinc (Zn*) commencing at a temperature of less than 0°C, for example, -78°C, and allowing the reaction to proceed

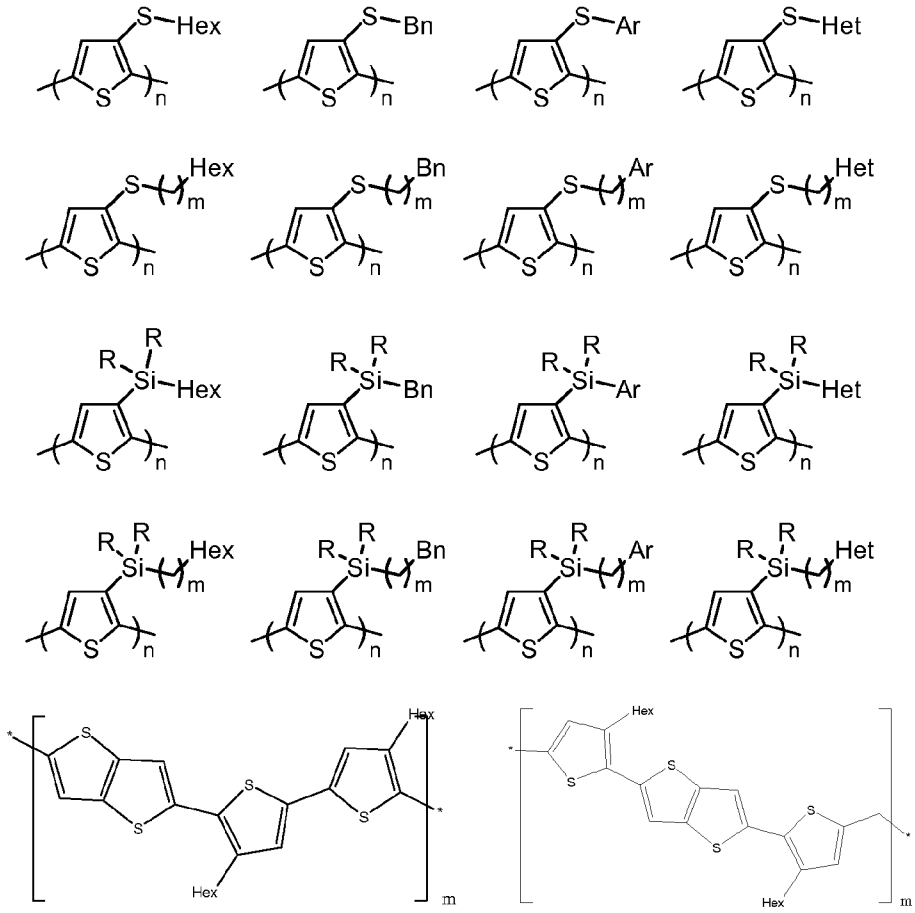
from about -78°C to ambient or room temperature in an inert solvent (e.g., tetrahydrofuran). This affords a higher ratio of 5-thienylzinc bromide than when the reaction can be carried out between about 0°C and ambient or room temperature as shown above in Table 1. Second, when the Ni (II) catalyst is added to the thiophene-zinc complex to initiate polymerization at about ambient or room temperature, a polymer with greater than about 97% regioregularity can be formed versus 90% regioregularity in which the thiophene-zinc complex is added to the Ni (II) catalyst as shown by Examples 7-8 in Table 2 below. This increase in regioregularity may be a result of the thermodynamic control of the formation of the 5-thienylzinc intermediate, which is lacking in the previous process. This is very advantageous because it is very difficult to raise the ratio of the regioregular to regiorandom polymer. Further, as described above, higher regioregularity results in higher conductivity of the HT polythiophenes.

EXAMPLE 13

Exemplary Regioregular Conducting Polymers

Scheme 7 illustrates several of the regioregular conducting polymer that can be prepared by the methods described herein, wherein n is a value such that the polythiophene polymer as a molecular weight of about 10,000 to about 200,000; "Hex" is hexyl but can be any alkyl group as described herein; "Bn" is benzyl which can be optionally substituted as described herein; "Ar" is aryl as described herein; "Het" is heteroaryl or heterocycle as described herein; m is 1 to about 20; and R is alkyl as described herein.

Scheme 7.



All publications, patents, and patent documents are incorporated by reference herein, as though individually incorporated by reference. The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

What is claimed is:

1. A method of preparing a regioregular conducting polymer comprising adding a nickel (II) catalyst to a solution of a monomer-metal complex to provide the regioregular conducting polymer,

wherein the monomer-metal complex is prepared by a method comprising combining a dihalo-monomer together with an activated metal, a Grignard reagent, or a RZnX, R_2ZnX, or R_3ZnM reagent, wherein R is a (C_2-C_{12})alkyl group, M is magnesium, manganese, lithium, sodium, or potassium, and X is F, Cl, Br, or I;

wherein the dihalo-monomer is an aromatic or heteroaromatic group substituted by two halogens wherein the halogens are the same or different.

2. The method of claim 1, wherein the aromatic or heteroaromatic group is benzene, thiophene, pyrrole, furan, aniline, phenylene vinylene, thienylene vinylene, bis-thienylene vinylene, acetylene, fluorene, arylene, isothianaphthalene, p-phenylene sulfide, thieno[2,3-b]thiophene, thieno[2,3-c]thiophene, thieno[2,3-d]thiophene, naphthalene, benzo[2,3]thiophene, benzo[3,4]thiophene, biphenyl, or bithiophenyl, and

wherein the aromatic or heteroaromatic group has from zero to about three substituents other than halogen.

3. The method of claim 2, wherein the substituents other than halogen are each independently (C_1-C_{24})alkyl, (C_1-C_{24})alkylthio, (C_1-C_{24})alkylsilyl, or (C_1-C_{24})alkoxy that may be optionally substituted with about one to about five ester, ketone, nitrile, amino, aryl, heteroaryl, or heterocyclyl groups, and one or more carbon atoms of the alkyl chain of the alkyl group may be optionally exchanged by about one to about ten O, S, or NH groups.

4. The method according to any of the preceding claims, wherein the dihalo-monomer is selected from the group consisting of a 2,5-dihalo-thiophene, a 2,5-dihalo-pyrrole, a 2,5-dihalo-furan, a 1,3-dihalobenzene, a 2,5-dihalo-3-substituted-thiophene, a

2,5-dihalo-3-substituted-pyrrole, a 2,5-dihalo-3-substituted-furan, a 1,3-dihalo-2-substituted-benzene, a 1,3-dihalo-4-substituted-benzene, a 1,3-dihalo-5-substituted-benzene, a 1,3-dihalo-6-substituted-benzene, a 1,3-dihalo-2,4-disubstituted-benzene, a 1,3-dihalo-2,5-disubstituted-benzene, a 1,3-dihalo-2,6-disubstituted-benzene, a 1,3-dihalo-4,5-disubstituted-benzene, a 1,3-dihalo-4,6-disubstituted-benzene, a 1,3-dihalo-2,4,5-trisubstituted-benzene, a 1,3-dihalo-2,4,6-trisubstituted-benzene, a 1,3-dihalo-2,5,6-trisubstituted-benzene, a 1,4-dihalo-2-substituted-benzene, a 1,4-dihalo-3-substituted-benzene, a 1,4-dihalo-5-substituted-benzene, a 1,4-dihalo-6-substituted-benzene, a 1,4-dihalo-2,3-disubstituted-benzene, a 1,4-dihalo-2,5-disubstituted-benzene, a 1,4-dihalo-2,6-disubstituted-benzene, a 1,4-dihalo-3,5-disubstituted-benzene, a 1,4-dihalo-3,6-disubstituted-benzene, a 1,4-dihalo-3,5,6-trisubstituted-benzene, a 2,5-dihalo-3,4-disubstituted-thiophene, a 2,5-dihalo-3,4-disubstituted-pyrrole, or a 2,5-dihalo-3,4-disubstituted-furan.

5. The method according to any of the preceding claims, wherein the regioregular conducting polymer is an unsubstituted or substituted poly(aromatic) homopolymer or a poly(heteroaromatic) homopolymer.

6. The method according to any of the preceding claims, wherein the regioregular conducting polymer is an unsubstituted or substituted polythiophene homopolymer, a poly(3-substituted-thiophene) homopolymer, or a poly(3,4-disubstituted-thiophene) homopolymer.

7. The method according to any of the preceding claims, wherein the regioregular conducting polymer is a regioregular HT poly(3-substituted-thiophene) or a regioregular HT poly(3,4-disubstituted-thiophene).

8. The method according to any of the preceding claims, wherein the activated metal is aluminum, manganese, copper, zinc, magnesium, calcium, titanium, iron, cobalt, nickel, indium, or a combination thereof.

9. The method according to any of the preceding claims, wherein the nickel (II) catalyst is added to the monomer-metal complex at about 0°C to about 40°C.

10. The method according to any of the preceding claims, wherein the regioregularity of the regioregular conducting polymer is greater than about 87%.

11. The method according to any of the preceding claims, wherein the regioregular conducting polymer is substituted with a straight-chain, branched-chain, or cyclic (C_1-C_{30})alkyl group.

12. The method according to any of the preceding claims, wherein the regioregular conducting polymer is substituted with a hexyl group.

13. The method according to any of the preceding claims, wherein a weight average molecular weight of the regioregular conducting polymer is about 5,000 to about 200,000.

14. The method according to any of the preceding claims, wherein a weight average molecular weight of the regioregular conducting polymer is about 40,000 to about 60,000.

15. The method according to any of the preceding claims, wherein the regioregular conducting polymer prepared has a polydispersity index of about 1 to about 2.5.

16. The method according to any of the preceding claims, wherein the nickel (II) catalyst is or is derived from Ni (dppe)Cl_2, Ni (dppp)Cl_2, Ni $(PPh_3)_2Br_2$, 1,5-cyclooctadienebis(triphenyl)nickel, dichoro(2,2'-dipyridine)nickel, tetrakis(triphenylphosophine)nickel, NiO, NiF_2, $NiCl_2$, $NiBr_2$, NiI_2, NiAs, Ni $(dmph)_2$, BaNiS, or a combination thereof.

17. The method according to any of the preceding claims, wherein about 0.1 mol % to about 5 mol % of nickel (II) catalyst is employed.

18. A method of preparing a regioregular HT poly(substituted-thiophene) comprising adding a nickel (II) catalyst to a substituted-thiophene-zinc complex to provide the regioregular HT poly(substituted-thiophene), wherein the substituted-thiophene-zinc complex is prepared by a method comprising contacting a 2,5-dihalo-substituted-thiophene with Rieke zinc (Zn*), and wherein the regioregular HT poly(substituted-thiophene) is a regioregular HT poly(3-substituted-thiophene) or a HT poly(3,4-disubstituted-thiophene).

19. The method of claim 18, wherein the regioregular HT poly(substituted-thiophene) is substituted with a hexyl group.

20. An electronic device comprising a circuit constructed with the regioregular conducting polymer obtainable by the method as defined in any of claims 1 to 19.

21. The electronic device of claim 20, wherein the device is a thin film transistor, a field effect transistor, a radio frequency identification tag, a flat panel display, a photovoltaic device, an electroluminescent display device, a sensor device, and electrophotographic device, or an organic light emitting diode.

22. A regioregular conducting polymer obtainable by a method as defined in any of claims 1 to 19.

23. The regioregular conducting polymer of claim 22, wherein the crude regioregular conducting polymer has a regioregularity of at least about 87%, preferably greater than about 92%, more preferably greater than about 95%.

24. The regioregular conducting polymer of claims 22 or 23, in the form of a thin film.

25. A regioregular conducting polymer having at least about 92% regioregularity; an average weight molecular weight of about 30,000 to about 70,000; and a conductance of about 10^{-5} to about 10^{-6} S/cm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/064452

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G61/10 C08G61/12
ADD. H01L51/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L C09D H01L H01B H05B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YOKOZAWA ET AL: "Catalyst-transfer condensation polymerization for the synthesis of well-defined polythiophene with hydrophilic side chain and of diblock copolythiophene with hydrophilic and hydrophobic side chains" HIGH PERFORMANCE POLYMERS, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 19, 1 January 2007 (2007-01-01), pages 684-699, XP009096332 ISSN: 0954-0083 abstract figures 1-3,6,7 tables 1,2 page 688, item 2.6 - page 689, item 2.8 page 690, item 3.2 - page 698, item 4. ----- -/--	1-7, 9-17, 20-25

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 February 2009	20/02/2009

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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