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(54) **Reversible electrochemical doping of conjugated polymers.**

(57) Reversible electrochemical doping of conjugated polymers is carried out in an electrochemical cell wherein the polymer to be doped is employed as one or both of the electrodes, and the electrolyte is a compound which is ionizable into ionic dopant species. Upon operation of the cell, the conjugated polymers are doped with the ionic dopant species to a preselected room temperature electrical conductivity ranging from that characteristic of semiconductor behavior to that characteristic of metallic behavior.

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Reversible electrochemical doping of conjugated polymers

This invention relates to electrochemical doping procedures for the selective modification of the room temperature electrical conductivity properties of conjugated polymers.

For use in a wide variety of electrical and electronic device applications, it is highly desirable to have available electrically conducting materials having a preselected room temperature electrical conductivity varying over a broad range extending from slightly conducting to highly conducting. Furthermore, particularly for use in semiconductor device applications, requiring one or more p-n junctions, such materials should advantageously be available with both p-type and n-type electrical conductivities.

It has recently been found that semiconducting acetylene polymers, such as polyacetylene, can be chemically doped in a controlled manner with electron acceptor and/or electron donor dopants to produce a whole family of p-type and n-type electrically conducting doped acetylene polymers whose room temperature electrical conductivity may be preselected over the entire range characteristic of semiconductor behavior and into the range characteristic of metallic behavior. Such doping procedures, as described i.a. in J. Amer. Chem. Soc. (1978) Vol. 100, 1013; J. Chem. Soc., Chem. Comm. (1978) 1066; and J. Chem. Phys. (1978) Vol. 69, 5098, involve merely contacting the acetylene polymer with the dopant, which may be either in the vapor phase or in solution, whereby uptake of the dopant into the acetylene polymer occurs by chemical reaction and/or charge transfer to a degree proportional with both the dopant concentration and the contacting period, such concentration and contacting period being coordinated and controlled so that the corresponding degree of doping will be such as to provide the resulting doped acetylene polymer with the preselected room temperature electrical conductivity. A p-type material is obtained with electron acceptor dopants, and an n-type material is obtained with electron donor dopants. The resulting room temperature electrical conductivity of the doped acetylene polymer increases with increasing degree of doping up to a certain point at which the maximum conductivity is obtained for any given dopant, such maximum conductivity generally being obtained at a degree of doping not greater than about 0.30 mol of dopant per -CH- unit of the polyacetylene.

While such chemical doping procedures are generally effective for achieving the desired result, they are subject to certain limitations. First of all, it is rather difficult with these procedures to obtain a reliably precise control of the degree and uniformity of doping so as to ensure commercial scale production of a doped polymer product with a consistent and uniform room temperature electrical conductivity. Secondly, the fact that these procedures require a doping material which is chemically reactive with the acetylene polymer and/or capable of forming a charge transfer complex therewith is a limiting factor in the selection of suitable doping materials for optimum properties and economy. Thirdly, these procedures require the use of two totally different doping materials and, consequently, separate doping systems for carrying out p-type and n-type doping. Hence, the development of more efficient and economical doping procedures would greatly enhance the commercial attractiveness of doped acetylene polymers as substitutes for the more conventional electrically conductive materials.

It is, accordingly, an object of the present invention to provide a more efficient and economical procedure for the doping of acetylene polymers and other dopable conjugated polymers, which enables a more precise control of the degree and uniformity of doping than the prior art procedures so as to ensure production of a doped polymer product with a consistent and uniform preselected room temperature electrical conductivity and which in particular enables the use of a greater variety of compounds as suitable doping materials so as to produce new and advantageous doped polymer materials.

The above and other objects are achieved in accordance with the present invention by means of electrochemical doping procedures which enable acetylene polymers and other dopable conjugated polymers to be electrochemically doped to a controlled degree with a wide selection of ionic dopant species to either a p-type or n-type material exhibiting a preselected room temperature electrical conductivity ranging from that characteristic of semiconductor behavior to that characteristic of metallic behavior.

Electrochemical doping of conjugated polymer in accordance with the present invention is carried out in an electrochemical cell wherein at least one of the two electrodes thereof includes the conjugated polymer to be doped as its electrode-active material, and the electrolyte comprises a compound which is ionizable into one or more ionic dopant species. When p-type doping is desired, the polymer is used as the anode-active material of the electrochemical cell, and the dopant species is an anionic species. The p-type doping proceeds by a mechanism in which operation of the electrochemical cell effects an increase in the oxidation state of the polymer by electron transfer from the carbon atoms on the conjugatedly unsaturated polymer backbone chain, imparting a positive charge thereto and consequently attracting the dopant anions as counter ions to maintain electrical neutrality in the polymer.

When n-type doping is desired, the polymer is used as the cathode-active material of the electrochemical cell and the dopant species is a cationic species. The n-type doping proceeds by a mechanism in which operation of the electrochemical cell effects a decrease in the oxidation state of the polymer by electron transfer to the carbon atoms on the conjugatedly unsaturated polymer backbone chain, imparting a negative charge thereto and consequently attracting the dopant cations as counter ions to maintain electrical neutrality in the polymer.

In each case, the polymer thereby becomes doped with the ionic dopant species to a degree dependent upon the degree of change effected in the oxidation state of the polymer and the dopant species concentration in the electrolyte, which are coordinated and controlled so that the corresponding degree of doping will be such as to provide the resulting doped polymer with the preselected room temperature electrical conductivity. The charge imparted to the carbon atoms of the polymer by means of their electrochemical oxidation or reduction is highly stable, thereby enabling the polymer to form stable ionic compounds of charge transfer complexes with a wide selection of possible dopant counter ions.

In comparison with known chemical doping procedure for conjugated polymers, the electrochemical doping procedures of the present invention enable a more reliably precise control of the degree and uniformity of doping so as to ensure production of a doped polymer product with a consistent and uniform room temperature electrical conductivity. Furthermore, since electrochemical doping is not dependent on the chemical reactivity of the doping material with the polymer nor its ability to form charge transfer complexes therewith, it enables greater versatility in the selection of suitable doping materials for optimum properties and economy. Moreover, it is possible with electrochemical doping to selectively or simultaneously effect p-type or n-type doping employing the same electrolyte as the doping material, depending upon the type of electrochemical cell employed and whether the polymer is used as the anode-active material, the cathode-active material, or both, of the electrochemical cell.

In a particular embodiment, which is of further advantage over the prior art doping procedures, the present invention relates to electrochemical doping procedures for the preparation of novel n-type doped conjugated polymers having a preselected room temperature electrical conductivity ranging from that characteristic of semiconductor behavior to that characteristic of metallic behavior, and wherein the cationic dopant species is non-metallic. Such novel n-type electrically conducting polymeric materials provided by the present invention are conjugated polymers doped to a controlled degree with organic dopant cations selected from the group consisting of $R_{4-x}MH_x{}^+$ and R_3E^+, wherein R is alkyl or aryl, M is N, P or As, E is O or S, and x is 0 or an integer ranging from 1 to 4.

The polymer which is used as the base material in the electrochemical doping procedures of the present invention may be any conjugated polymer which is dopable with an ionic dopant species to a more highly electrically conducting state. For the purposes of this invention, the term "conjugated polymers" is intended to encompass, as mentioned above, organic polymers having conjugated unsaturation along their main back bone chain. A number of conjugated organic polymers which are suitable for the purpose of this invention are known in the art and include, for example, acetylene polymers, poly (p-phenylene), poly (m-phenylene), poly (phenylene sulfide), $\leftarrow C_6H_4CH{=}CH \rightarrow_x$, polypyrrole, and the like. Such conjugated polymers may be employed in the present invention in any suitable form, such as, for example, in the form of films, foams, compressed films, compacted powders, or powders dispersed in a suitable carrier matrix, e.g., another organic polymeric material. Acetylene polymers have been found to be particularly suitable.

The term "acetylene polymer", as used herein throughout the Specification and in the appended Claims, is intended to encompass polyacetylene, i.e., $(CH)_x$, as well as substituted polyacetylenes in which at least some of the hydrogen atoms on the polymer chain have been replaced by halogen, alkyl (e.g., up to about 20 carbon atoms), aryl (e.g., phenyl, halophenyl, or alkylphenyl), or combinations thereof. Such acetylene polymers may suitably be prepared for use in the present invention in the form of films, foams, compressed films, or powders, by methods known in the art. For example, the synthesis of high quality, uniformly thin, flexible polycrystalline films of polyacetylene and their characterization are described in detail in a series of papers by Shirakawa, et al., [Polymer Journal, Vol. 2, No. 2, pp. 231-244 (1971); Polymer Journal, Vol. 4, No. 4, pp. 460-462 (1973); Journal of Polymer Science, Part A-1, Polymer Chemistry Edition, Vol. 12, pp. 11-20 (1974), and Journal of Polymer Science, Part A-1, Polymer Chemistry Edition, Vol. 13, pp. 1943-1950 (1975)] all of which are incorporated herein by reference. The synthesis procedures described by Shirakawa, et al., involve polymerizing acetylene monomer in the presence of a $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$ catalyst system, employing a critical catalyst concentration to avoid the formation of polyacetylene powder to obtain, depending on the polymerization temperature, polycrystalline polyacetylene films having an all cis structure (polymerization temperatures lower than -78°C), and all trans structure (polymerization temperatures higher than 150°C), or a mixed cis-trans structure (polymerization temperatures between -78 and 150°C).

The Shirakawa et al. polymerization procedure can similarly be employed for preparing films of the above defined substituted polyacetylenes by using as the starting monomer a substituted acetylene monomer having the formula $RC\equiv CH$ or $RC=CR'$ wherein R and R' are halogen, alkyl, or aryl. Such substituted acetylene monomers may be used either alone or in appropriate mixture with each other and/or with acetylene monomer in carrying out the polymerization reaction to obtain the desired substituted polyacetylene.

In an alternative procedure for preparing such substituted polyacetylene, the starting material is a bromine-doped polyacetylene film prepared, for example, by the methods described in the U.S. Patent 4,222,903. When this film is heated in vacuo to a temperature within the range of from 120°C--150°C in a sealed container, HBr and Br_2 are first evolved. This gaseous mixture is then permitted to react further with the film at room temperature and is then reheated to within the aforementioned temperature range. After this procedure has been repeated several times, all the Br_2 is absorbed and HBr is the only gaseous material formed. The resulting product is a substituted polyacetylene in which some of the hydrogen atoms on the polymer chain have been replaced by bromine atoms. Subsequent treatment of this substituted polyacetylene with alkyl or aryl organometallic reagents, e.g., methyl lithium, phenylmagnesium bromide, or Friedel-Craft--type reagents, will lead to replacement of the bromine atoms by the organic group in the organometallic reagent employed. In the substituted polyacetylenes prepared in this manner, some of the CH bonds in the original polyacetylene polymer may be converted to C-C or C=C.

While the acetylene polymers employed in carrying out the present invention are preferably in the form of films, prepared as described above, they may also suitably be in the form of compacted or matrix-dispersed powders prepared, for example, as described by Berets et al., Trans. Faraday Soc., Vol. 64, pp. 823-828 (1968), incorporated herein by reference; or in the form of foams or compressed films prepared from intermediate gels, as described by Wnek et al., Polymer Preprints, Vol. 20, No. 2, pp. 447-451, September 1979, also incorporated herein by reference.

In accordance with the electrochemical doping procedures of the present invention, p-type doping of the conjugated polymer is effected with anionic dopant species, while n-type doping of the polymer is effected with cationic dopant species. A wide variety of anionic and cationic dopant species may suitably be employed, either individually or in combination, for effectively modifying the room temperature electrical conductivity of the conjugated polymer in accordance with the present invention.

Suitable anionic dopant species for effecting p-type doping include, for example, I^-, Br^-, Cl^-, F^-, ClO_4^-, PF_6^-, AsF_6^-, AsF_4^-, $SO_3CF_3^-$, BF_4^-, BCl_4^-, NO_3^-, POF_4^-, CN^-, SiF_5^-, $CH_3CO_2^-$ (acetate), $C_6H_5CO_2^-$ (benzoate), $CH_3C_6H_4SO_3^-$ (tosylate), SiF_6^{--}, SO_4^{--} or the like.

One class of cationic dopant species particularly suitable for effecting n-type doping are metallic cations of a metal whose Pauling electronegativity value is no greater than 1.6. A complete list of such metals and their corresponding electronegativity values are provided in Table I below.

Table I

Metal	Electronegativity Value
Cs	0.7
Rb	0.8
K	0.8
Na	0.9
Ba	0.9
Li	1.0
Sr	1.0
Ca	1.0
Mg	1.2
Y	1.3
Sc	1.3
Be	1.5
Al	1.5
Zr	1.6
Ti	1.6

The above list of metals includes all of the alkali metals, all of the alkaline earth metals, and certain of the metals from Group 3 (Y, Sc and Al) and Group 4 (Zr and Ti) of the Periodic Table.

Another class of cationic dopant species particularly suitable for effecting n-type doping are non-metallic cations selected from the group consisting of $R_{4-x}MH_x^+$ and R_3E^+, wherein R is alkyl (e.g., up to about 20 carbon atoms), aryl (e.g., phenyl, halophenyl, or alkylphenyl), or combinations thereof; M is N, P or As; E is O or S; and x is 0 or an integer from 1 to 4. In such organic cations having more than one R group, the various R groups may be the same or different. Such organic cations which are particularly suitable are those wherein R is a C_1 to C_{10} alkyl group, and X is 0, i.e., tetraalkyl ammonium, tetraalkyl phosphonium, tetraalkyl arsonium, trialkyl oxonium, and trialkyl sulfonium cations.

Each of the anionic and cationic dopant species set forth above will effect an increase, to varying degrees, in the room temperature electrical conductivity of the starting conjugated polymer. For the widest range in selectivity as to achievable conductivities, the preferred cationic dopant species are tetraalkyl ammonium and alkali metal cations, particularly Li^+; and the preferred anionic dopant species are halide ions, ClO_4^-, PF_6^-, AsF_6^-, AsF_4^-, $SO_3CF_3^-$ and BF_4^-.

A compound which is ionizable into one or more of the above-described ionic dopant species is employed as the active material of the electrolyte of the electrochemical cell in carrying out the electrochemical doping procedures in accordance with the present invention, and thereby serves as the dopant ion source. Such ionizable compound may suitably be a simple salt of one of the cationic species of dopant ions with one of the anionic species of dopant ions, in which case the electrolyte has the versatility of being usable for selectively or simultaneously effecting p-type or n-type doping, depending upon the type of electrochemical cell employed and whether the conjugated polymer is used as the anode-active material, the cathode-active material, or both, of the electrochemical cell. Halide, perchlorate, or hexafluorophosphate salts of either an alkali metal or a tetraalkyl ammonium cation are particularly useful examples of this type of ionizable compound. Other types of ionizable compounds, which are ionizable into only one species of dopant ions, are also suitable for use in carrying out the electrochemical doping procedures in accordance with the present invention, in those instances wherein only one type of doping, i.e., either p-type or n-type, is desired.

The ionizable compound, which is used as the active electrolyte material of the electrochemical cell in carrying out the electrochemical doping procedures may suitably be employed in the form of a solid, fused solid (i.e., molten salt, e.g. $Na_{0.5}K_{0.5}[AlCl_4]$), or dissolved in a suitable solvent for the ionizable compound which is inert with respect to the electrode materials and which will permit the migration of the dopant ions to the electrode-active materials. Alkali metal halides, such as lithium iodide, are particularly suitable for use as solid electrolytes. Suitable solvents for use in preparing electrolyte solutions include water, methylene chloride, acetonitrile, alcohols (e.g., ethyl alcohol), ethers (e.g., monoglyme, diglyme, or solid polyethylene oxide), cyclic ethers (e.g., tetrahydrofuran or dioxane), hexamethylphosphoramide, propylene carbonate, methyl acetate, dioxolane, or the like. When using an electrolyte solution for carrying out n-type doping with Li^+, Na^+, or K^+, it is generally preferred to employ ethers or cyclic ethers as the solvent due to the high reactivity of the resulting doped material with many of the other solvents. The concentration of the ionizable compound when employed in the form of an electrolyte solution may suitably be within the range of from about 0.01 to about 2.0 molar. The solutions of lower molarity are preferably employed when the doped polymer being prepared is to have a relatively low room temperature electrical conductivity, while the solutions of higher molarity are preferably employed when such doped polymer is to have a relatively high conductivity.

Depending upon whether p-type or n-type doping is to be effected, the electrochemical cell employed for carrying out the electrochemical doping procedures of the present invention may be either an electrolytic cell (i.e., wherein the anode and cathode are electrically connected to the positive and negative terminals, respectively, of an external dc power source), or a voltaic cell (i.e., wherein the external circuit electrically connecting the anode and cathode does not include any external power source). Either p-type or n-type electrochemical doping may suitably be carried out in an electrolytic cell, while n-type electrochemical doping may alternatively be carried out in a voltaic cell.

For carrying out the electrochemical doping procedures in accordance with the present invention in an electrolytic cell, the conjugated polymer to be doped is employed as the electrode-active material of one or both of the electrodes, depending upon the type of doping desired. If only p-type doping is to be effected, the polymer will be used as the anode-active material, and a suitable electrolyte will be chosen so as to comprise a compound which is ionizable at least into an anionic dopant species. If only n-type doping is to be effected, the polymer will be used as the cathode-active material, and a suitable electrolyte will be chosen so as to comprise a compound which is ionizable at least into a cationic dopant species. In each of these two cases, the other electrode may suitably comprise any metal which is inert to the electrolyte employed, such as, for example, platinum, palladium, ruthenium, rhodium, gold, iridium, aluminum, or the like. If it is desired to effect both p-type and n-type doping simultaneously in the same electrolytic cell, a conjugated polymer can be employed both as the anode-active material and as the cathode-active material of the cell, and a suitable electrolyte chosen so as to comprise a compound which is ionizable into both an anionic dopant species and a cationic dopant species.

The electrical energy source for powering the electrolytic cell in carrying out the electrochemical doping procedures in accordance with the present invention, may suitably be any dc power supply, such as, for example, a battery, which is capable of delivering an electrical potential sufficiently high to initiate electrochemical oxidation and/or reduction of the conjugated polymer, or electron transfer from and/or to the polymer, but sufficiently low so as not to produce electrochemical degradation of the polymer or of the solvent. Such electrical potential may suitably be, for example, within the range of from about 2 to 25 volts, with about 9 volts being found to be particularly suitable.

For producing a doped conjugated polymer exhibiting a preselected p-type or n-type room temperature electrical conductivity by means of the electrochemical doping procedures, the electrolytic cell is first assembled in the appropriate manner for obtaining the desired type of doping as described above, i.e., with the polymer or polymers at the appropriate electrode position and with the appropriate electrolyte and dc power supply. The cell is then operated by applying an electrical potential thereto sufficient to effect a change in the oxidation state of the polymer. Doping of the polymer with the dopant ions consequently occurs by migration of the anionic dopant ions into the anode-active polymer to produce a p-type material and/or by migration of the cationic dopant ions into the cathode-active polymer to produce an n-type material, by means of the doping mechanisms described more fully above. The degree of such doping will be dependent upon the degree of change effected in the oxidation state of the polymer (which will be a function of the voltage and time period of the applied potential) and the dopant ion concentration in the electrolyte, all of which variables are properly coordinated and controlled so that the corresponding degree of doping will be such as to provide the resulting doped polymer or polymers with the preselected room temperature electrical conductivity. In general, the required degree of doping can suitably be obtained with applied potentials ranging from about 2 to 25 volts for a time period ranging from about a few minutes to about a few hours and with dopant ion concentrations equivalent to an electrolyte solution having an ionizable compound concentration within the range of from about 0.01 to about 2.0 molar. Within these broad operating ranges, the proper combination of the voltage and time period of the applied potential and the dopant ion concentration in the electrolyte to obtain the desired degree of doping can generally be predetermined by trial and error procedures. For example, employing as the electrolyte a 0.5 molar solution of either potassium iodide or tetra-n-butyl ammonium perchlorate, and an applied potential of about 9 volts, polyacetylene can be electrochemically doped with I_3^- or ClO_4^-, respectively, to a highly conductive metallic state in a time period ranging from about 0.5 to about 1.0 hour.

For carrying out n-type electrochemical doping in accordance with the present invention in a voltaic cell, the conjugated polymer to be doped is employed as the cathode-active material, and the anode-active material is a metal whose Pauling electronegativity value is no greater than 1.0. As indicated by the values listed in Table 1, above, the anode-active metals contemplated for use in this embodiment thus include all of the alkali metals, Ba, Ca and Sr. All of these metals have standard oxidation electrode potentials greater than 2.70. The preferred anode-active metal is lithium, which has the highest standard oxidation electrode potential. The electrolyte comprises a compound which is ionizable at least into a cationic dopant species. If the dopant cations are of a different species than the anode-active metal, a suitable separator means, e.g., a glass frit, is preferably employed for preventing mixing of the dopant cations with the metallic cations released from the anode as a result of the anode reaction during cell discharge.

The voltaic cell is operated by discharging it through the external circuit electrically connecting the anode and cathode so as to effect a reduction in the oxidation state of the polymer by electron transfer thereto from the anode-active metal. Doping of the polymer with the dopant cations to an n-type material consequently spontaneously occurs by means of the n-type doping mechanism described more fully above.

The degree of such doping will be dependent upon the degree of reduction effected in the oxidation state of the polymer (which will be a function of the time period of the cell discharge and the standard oxidation electrode potential of the anode-active metal) and the dopant ion concentration in the electrolyte, all of which variables are properly coordinated and controlled so that the corresponding degree of doping will be such as to provide the resulting doped polymer with the preselected room temperature electrical conductivity. Similarly as with the electrolytic cell embodiment described above, and within similar broad operating ranges of time periods and concentrations, the proper combination of the time period of the cell discharge, the standard oxidation electrode potential of the anode-active metal, and the dopant ion concentration in the electrolyte, to obtain the desired degree of doping, can generally be predetermined by trial and error procedures. For example, employing lithium as the anode-active metal, and a 0.3 molar solution of lithium perchlorate in tetrahydrofuran as the electrolyte of the voltaic cell, polyacetylene can be electrochemically doped with Li^+ to a highly conductive metallic state in a time period ranging from about 0.5 to about 1.0 hour.

Simplification of the coordination and control of the operating condition variables of the electrochemical doping procedures so as to enable precise achievement of the desired degree of doping, is made possible by the fact that the progressive conversion of the conjugated polymer to a more highly conductive state with increasing degree of doping is accompanied by a correspondingly progressive change in the current flow through the electrochemical cell. Thus, once the correlation between such current flow and the degree of doping has been established for any given electrochemical doping system, monitoring of such current flow, for example, by means of an ammeter connected into the external circuitry of the electrochemical cell, provides a direct monitoring of the degree of doping in that system. Furthermore, provided that the electrolyte employed is one which is normally chemically unreactive with the polymer so that the doping reaction is entirely electrochemical in nature, such reaction is terminable with a sharp cutoff point precluding any over-doping of the polymer, merely by switching off the operation of the electrochemical cell. These two features combine to provide the electrochemical doping procedures of the present invention with a reliably precise control of the degree and uniformity of doping so as to ensure production of a doped polymer product with a consistent and uniform room temperature electrical conductivity.

The maximum degree of doping and the corresponding maximum level of room temperature electrical conductivity of the resulting doped polymer, which are achievable by means of the electrochemical doping procedures of the present invention, will vary with the particular type and form of conjugated polymer and the particular species of dopant ions employed. Up to such maximum level, the resulting conductivity will increase with increasing degrees of doping. With acetylene polymers, for example, a degree of doping ranging from less than about 0.001 to about 0.1 mol of dopant ion per carbon atom of the acetylene polymer main chain will increase the room temperature electrical conductivity of the starting acetylene polymer to a value ranging from slightly in excess of that of the undoped acetylene polymer up to on the order of 10^3 $ohm^{-1}cm^{-1}$. Since the conductivity of the undoped acetylene polymer will typically be on the order of about 10^{-9} to 10^{-5} $ohm^{-1}cm^{-1}$ depending upon its composition and method of preparation, and since the semiconductor-metal transition of the doped polymer will generally be reached at a conductivity of approximately 1 $ohm^{-1}cm^{-1}$, the electrochemical doping procedures of the present invention provide a broad range of selectivity in the resulting room temperature electrical conductivity of the doped polymer, extending over the entire semiconductor regime and into the metallic regime.

As described more fully above, the electrochemical doping procedures proceed by mechanisms which impart a positive or negative charge to the carbon atoms on the conjugatedly unsaturated polymer backbone chain, which charge attracts the dopant anions or cations as counter ions to maintain electrical neutrality in the polymer. Due to the presence of the conjugated unsaturation along the main backbone chain of the polymer, making a large number of resonance forms available, the charge imparted to the carbon atoms becomes delocalized along the carbon atom chain over a very large number of carbon atoms. Such delocalization of the charge renders the charge highly stable, thereby enabling the polymer to form stable ionic compounds or charge transfer complexes with a wide selection of possible dopant counter ions, which selection is substantially broader in scope than that permitted with the prior art chemical doping procedures.

The broader selection of suitable dopant species made possible by the electrochemical doping procedures of the present invention, enables the preparation of novel n-type doped conjugated polymers of varying levels of room temperature electrical conductivity ranging up into the metallic regime, and wherein the cationic dopant species is non-metallic in nature. Such novel n-type electrically conducting polymeric materials provided by the present invention are conjugated polymers doped to a controlled degree with organic dopant cations selected from the group consisting of $R_{4-x}MH_x^+$ and R_3E^+, wherein R is alkyl or aryl, M is N, P or As, E is O or S, and x is 0 or an integer ranging from 1 to 4. These organic dopant cations are more fully described above. The molecular size of these organic dopant cations and their solubility properties in various organic solvents may be varied over a rather broad range merely by varying the size and number of their R groups. Since the molecular size of the dopant species may be an important factor in determining the electrical conductivity and various other properties imparted to the doped polymer, the novel organic cation-doped n-type conjugated polymers provided by the present invention offer a wider range of flexibility in this regard than the metallic cation-doped n-type conjugated polymers previously described.

The electrochemical doping procedures of the present invention may thus suitably be employed as an efficient and economical means for the production of various p-type or n-type doped polymer stock materials of varying levels of room temperature electrical conductivity for use in a wide variety of electrical and electronic device applications.

The invention is further illustrated by way of the following examples.

Example 1

A 1 cm x 3 cm x 0.01 cm strip of polyacetylene film composed of approximately 82% cis-isomer and having a room temperature electrical conductivity of about 1 x 10^{-8} $ohm^{-1}cm^{-1}$, was employed as the anode of an electrolytic cell having a platinum cathode and a 0.3 M solution of $[Pr^{n}{}_{3}NH]^{+}[AsF_{6}]^{-}$ in methylene chloride. The electrolytic cell was powered by a 9-volt battery, and an ammeter was connected into the external circuit of the cell. The 9-volt potential was applied for a period of 0.75 hour, during which time the current as measured by the ammeter increased from 0.4 to 1.02 mA. The resulting p-type doped polyacetylene film was found by elemental analysis to have a composition corresponding to $[CH(AsF_{4})_{0.077}]_{x}$, and a room temperature electrical conductivity of 553 $ohm^{-1}cm^{-1}$. It is believed that the AsF_{4}^{-} ion is formed by a reaction sequence involving proton abstraction from $[Pr^{n}{}_{3}NH]^{+}$ by fluorine atoms from AsF_{6}^{-} during the electrolysis process.

Example 2

The procedure of Example 1 was repeated, but this time employing as the electrolyte a 0.3 M solution of $[Bu^{n}{}_{4}N]^{+}[SO_{3}CF_{3}]^{-}$ in methylene chloride. The 9-volt potential was applied for a period of 0.5 hour, during which time the current as measured by the ammeter increased from 1.6 to 2.35 mA. The resulting p-type doped polyacetylene film was found to have the composition $[CH(SO_{3}CF_{3})_{0.06}]_{x}$, and a room temperature electrical conductivity of 255 $ohm^{-1}cm^{-1}$.

Example 3

The procedure of Example 1 was repeated, but this time employing the poacetylene film as the cathode, and the platinum electrode as the anode of the electrolytic cell and employing as the electrolyte a 1.0 M solution of $[Bu^n{}_4N]^+[ClO_4]^-$ in tetrahydrofuran, and an applied potential of 4 volts for a period of about 0.25 hour. This procedure resulted in the polyacetylene film becoming doped with $[Bu^n{}_4N]^+$ to an n-type material having the composition $[(Bu^n{}_4N)_{0.003}CH]_x$.

Claims

1. A reversible electrochemical method for modifying the electrical conductivity properties of a conjugated polymer having conjugated unsaturation along its main back bone chain and which is dopable with a cationic dopant to a more highly electrically conducting state, comprising the steps of:

   a) providing an electrochemical cell comprising an anode, a cathode, and an electrolyte, said cathode including said conjugated polymer as its cathode-active material, said electrolyte comprising a compound which is ionizable into an organic cationic dopant of $R_{4-x}MH_x^+$ and R_3E^+, wherein R is alkyl or aryl, M is N, P or As, E is O or S, and x is 0 or an integer ranging from 1 to 4;

   b) operating said electrochemical cell so as to effect a change in the oxidation state of said polymer whereby said polymer becomes doped with said organic cationic dopant; and

   c) coordinating and controlling the degree of change effected in said oxidation state of said polymer and the dopant concentration in said electrolyte so that the corresponding degree of doping will be such as to provide the resulting doped polymer with said preselected room temperature n-type electrical conductivity.

2. A reversible electrochemical method for modifying the electrical conductivity properties of a conjugated polymer having conjugated unsaturation along its main back bone chain and which is dopable with a cationic dopant to a more highly electrically conducting state, comprising the steps of:

   a) providing a voltaic cell comprising an anode, a cathode, and an electrolyte, said cathode including said conjugated polymer as its cathode-active material, said anode including as its anode-active material a metal whose Pauling electronegativity value is no greater than 1.0, and said electrolyte comprising a compound which is ionizable into said cationic dopant;

   b) operating said voltaic cell so as to effect a change in the oxidation state of said polymer, whereby said polymer becomes doped with said cationic dopant to a degree dependent upon the degree of change effected in said oxidation state of said polymer and the dopant concentration in said electrolyte; and

c) coordinating and controlling the degree of change effected in said oxidation state of said polymer and the dopant concentration in said electrolyte so that the corresponding degree of doping will be such as to provide the resulting doped polymer with said preselected room temperature n-type electrical conductivity.

3. A reversible electrochemical method for simultaneously effecting modification of the electrical conductivity properties of a conjugated polymer having conjugated unsaturation along its main back bone chain and which is dopable with ionic dopant to a more highly electrically conducting state, comprising the steps of:

a) providing an electrolytic cell comprising an anode, a cathode, and an electrolyte, said anode including said polymer as its anode-active material, said cathode including said polymer as its cathode-active material, and said electrolyte comprising a compound which is ionizable into an anionic dopant and a cationic dopant,

b) operating said electrolytic cell so as to effect a change in the oxidation states of said polymer, whereby said anode-active polymer becomes doped with said anionic dopant to a p-type electrically conducting material and said cathode-active polymer becomes doped with said cationic dopant to an n-type electrically conducting material; and

c) coordinating and controlling the degree of change effected in the oxidation states of said electrode-active polymers and the dopant concentration in said electrolyte so that the corresponding degree of doping will be such as to provide the resulting doped polymers with said preselected room temperature electrical conductivity.

4. The method of any one of claims 1 to 3, wherein said conjugated polymer is an acetylene polymer.

5. The method of any one of claims 2 to 4, wherein said cationic dopant species is a metallic cation of a metal whose Pauling electronegativity value is no greater than 1.6.

6. The method of any one of claims 2 to 4, wherein said cationic dopant species is an organic cation selected from the group consisting of $R_{4-x}MH_x^+$ and R_3E^+, wherein R is alkyl or aryl, M is N, P or As, E is O or S, and x is 0 or an integer ranging from 1 to 4.

7. The method of any one of claims 3 to 6, wherein said anionic dopant species is selected from the group consisting of halide ions, ClO_4^-, PF_6^-, AsF_6^-, $SO_3CF_3^-$, and BF_4^-.

8. The method of any one of claims 3 to 7, wherein the anode-active conjugated polymer and the cathode-active conjugated polymer are opposite surfaces of the same unitary mass of conjugated polymer, and said electrolyte is impregnated within said conjugated polymer.

9. An n-type electrically conducting polymeric material comprising a conjugated polymer doped to a controlled degree with a cationic dopant species characterized in that the conjugated polymer is doped with a non-metallic dopant cation selected from the group consisting of $R_{4-x}MH_x^+$ and R_3E^+, wherein R is alkyl or aryl, M is N, P or As, E is O or S, and x is 0 or an integer ranging from 1 to 4 according to the method of claim 6.

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})
A	JOURNAL DE CHIMIE PHYSIQUE, vol. 76, no. 4, 1979, pages 369,370; G. TOURILLON et al.: "Dopage électrochimique de films minces de polyTHF déposés sur électrode de platine: étude spectroscopique XPS et SIMS" * Whole document * ---	1	H 01 M 10/36 H 01 B 1/12 H 01 L 29/28
A	J.C.S. CHEM. COMM., 1979, pages 594-595; P.J. NIGREY et al.: "Electrochemistry of polyacetylene, (CH)x: Electrochemical doping of (CH)x films to the metallic state" * Whole document * ---	1-5,7	
P	C & EN, 26th January 1981, pages 39,40; R. DAGANI: "Organic battery uses polyacetylene electrodes" * Whole document * ---	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl. ^{3})
P	EP-A-0 022 271 (JAPAN SYNTHETIC RUBBER CO.) * Page 2, lines 14-28; page 4, lines 5-21 * ---	9	H 01 M 10/36 H 01 M 4/60 H 01 B 1/12 H 01 L 29/28
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-08-1984	DE VOS L.A.R.

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Page 2

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A	GB-A-1 216 549 (C.N.R.S.) * Claims 1,2,8 * -----		
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