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REDUCTION POTENTIALS: KEY TO DOPING PHENOMENA IN POLYACETYLENE, $(CH)_x$

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Abstract

When $(CH)_x$ is p-doped (oxidized) or n-doped (reduced) chemically or electrochemically the "dopant" ion may or may not be derived from the oxidizing or reducing agent as dictated by the nature of the specific doping reaction involved. The reduction potentials of neutral $(CH)_x$ and its various oxidized or reduced states have been determined electrochemically and have been used, together with known standard reduction potentials of a variety of redox couples, to rationalize the doping of $(CH)_x$ to the metallic regime by a number of dopant species, including gaseous O_2 or benzoquinone (both in aqueous HBF_4 solution), aqueous $HClO_4$ and aqueous H_2SO_4. Reduction potentials can be used to predict new p- or n-dopants which are thermodynamically capable of doping $(CH)_x$ to the metallic regime. The p-doped polyacetylene is remarkably stable in the aqueous solutions in which it is synthesized.

Polyacetylene, synthesized by the catalytic polymerization of acetylene, HC≡CH, is the simplest conjugated organic polymer.[1] It can be prepared in the form of planar _cis_- or _trans_- chains as shown in Figure 1.

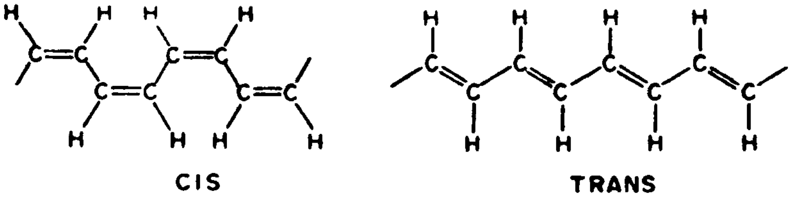


FIGURE 1: _Cis_ and _trans_ isomers of $(CH)_x$

Both cis- and trans-$(CH)_x$ can be "p-doped", (partly oxidized) or "n-doped" (partly reduced) through the semiconducting to the metallic regime with certain chemical "dopants" (oxidizing or reducing agents) or by electrochemical oxidation or reduction.[2,3] p-Doped $(CH)_x$ consists of a delocalized polycarbonium ion, $(CH^{+y})_x$ in combination with a stable counter anion, A^-, which makes the material $(CH^{+y}A^-_y)_x$, electrically neutral. Analogously, n-doped $(CH)_x$ consists of a delocalized polycarbanion, $(CH^{-y})_x$ in combination with a stable counter cation, M^+, which imparts electrical neutrality to the material, $[M^+_y(CH^{-y})]_x$.

This paper will be devoted to a discussion of the concept of doping in polyacetylene, the prototype conducting polymer since this polymer has been far more extensively investigated than any other conducting polymer. However, it seems likely that the principles laid forth will be applicable to most, if not all other conducting polymer systems with appropriate modification as dictated by fundamental differences in chemical composition, molecular structure and morphology. It will be shown that the doping behavior of known p- and n-dopants for $(CH)_x$ can be rationalized on the basis of their standard reduction potentials and that in addition, reduction potentials can be used to predict new potential dopants.

I. THE CONCEPT OF DOPING

When it was first discovered that the conductivity of $(CH)_x$ could be increased by up to 12 orders of magnitude by reaction with small quantities of electron-accepting or electron-donating species, the phenomenon was termed "p-doping" and "n-doping" respectively by analogy with the doping of a classical semiconductor such as silicon which results in a large increase in conductivity. Phenomenologically this designation is correct but as a better understanding of the nature of the doping process in $(CH)_x$ has developed, it has become apparent that the designation is mechanistically misleading.

For example, in the p-doping of a crystal of silicon, in which each silicon atom has four valence electrons, a silicon site in the crystal lattice is replaced by a boron atom which possesses only three valence electrons. Hence, even if there should be no charge transfer between neighboring silicon atoms and the boron atom, i.e. the silicon and boron atoms are electrically neutral, the boron site is electron deficient insofar as the crystal lattice is concerned. It, therefore, represents a positive "hole" in the crystal lattice. Conversely, if a crystal of silicon is doped by replacing a silicon site in the lattice by a phosphorus atom, which has five valence electrons, this constitutes a negative site insofar as the crystal lattice is concerned, i.e. there are five valence electrons in a site normally occupied by a silicon atom which has only four valence electrons. These positive and negative sites in the crystal lattice exist regardless of whether there is or is not significant charge transfer between the silicon and the dopant atom caused by differences in electronegativity between the silicon and the dopant atoms.

The doping of conducting polymers is conceptually completely different from the doping of a classical semiconductor such as silicon. p-Doping of a conducting polymer refers to the partial oxidation of the conducting polymer, e.g.,

$$(CH)_x \rightarrow (CH^{+y})_x + (xy)e^- \qquad (1)$$

This may be accomplished either chemically or electrochemically. In order to preserve electrical neutrality in the system a counter anion, A^-, must also be provided:

$$(CH^{+y})_x + (xy)A^- \rightarrow (CH^{+y}A^-_y)_x \qquad (2)$$

To date, all counter anions used have been monovalent. Analogously, n-doping refers to the partial reduction of the conducting polymer, e.g.,

$$(CH)_x + (xy)e^- \rightarrow (CH^{-y})_x \qquad (3)$$

Again, in order to preserve electrical neutrality, a counter cation, M^+, must be provided:

$$(CH^{-y})_x + (xy)M^+ \rightarrow [M^+_y(CH^{-y})]_x \qquad (4)$$

To date, all counter cations have been monovalent species.

The counter ions may be completely different chemically from the oxidizing or reducing species or they may be derived from them. For example, in the n-doping of $(CH)_x$ by sodium naphthalide, the strongly reducing naphthalide radical anion made by dissolving metallic sodium in a solution of naphthalene in tetrahydrofuran[4] is used. An electron is transferred to the lowest energy antibonding π^* molecular orbital in the naphthalene and the Na^+ ion so formed acts as the counter cation. The lowest energy antibonding π^* molecular orbital in $(CH)_x$ is apparently of lower energy than the π^* orbital of the naphthalene containing the unpaired electron, since the electron is spontaneously transferred from the π^* orbital of the naphthalene to the π^* orbital of the $(CH)_x$ when $(CH)_x$ is placed in the solution of sodium naphthalide. The naphthalide radical anion acts as the reducing agent:

$$(CH)_x + (xy)\dot{Nphth}^- \longrightarrow (CH^{-y})_x + (xy)Nphth \qquad (5)$$

while the Na^+ ion acts as the counter "dopant" cation:

$$(CH^{-y})_x + (xy)Na^+ \longrightarrow [Na_y^+(CH^{-y})]_x \qquad (6)$$

The reducing agent is not related chemically to the dopant cation. If, however, metallic sodium is used in, for example, the form of a liquid amalgam, the reaction may be regarded as consisting of two hypothetical parts. The sodium first acts as a reducing agent:

$$(CH)_x + (xy)Na \longrightarrow (CH^{-y})_x + (xy)Na^+ \qquad (7)$$

and the Na^+ so formed, then acts as the dopant cation:

$$(CH^{-y})_x + (xy)Na^+ \longrightarrow [Na_y^+(CH^{-y})]_x \qquad (8)$$

In this case the dopant ion, Na^+, is chemically derived directly from the reducing agent. If, however, $(CH)_x$ is n-doped electrochemically, the reduction is carried out electrochemically and any convenient counter cation may be used as the dopant ion. For example, if $(CH)_x$ is placed in a solution of $(n\text{-}Bu_4N)^+(ClO_4^-)$ in tetrahydrofuran and is held at a potential less positive than +1.8V (vs. Li)* it will become reduced:[5]

$$(CH)_x + (xy)e^- \longrightarrow (CH^{-y})_x \qquad (9)$$

---

*The convention used in this discussion is that the standard reduction potential, E°_{red}, for the electrode reaction: $Li^+ + e^- \rightleftarrows Li$ is -3.05 volts with respect to the Standard Hydrogen Electrode (see also Table I).

and the $(n\text{-}Bu_4N)^+$ ion will then act as the dopant counter anion:

$$(CH^{-y})_x + (xy)(n\text{-}Bu_4N)^+ \rightarrow [(n\text{-}Bu_4N^+)_y(CH^{-y})]_x \qquad (10)$$

When $(CH)_x$ is p-doped with iodine, the iodine acts as the oxidizing agent and the dopant counter anion, I_3^- is derived from the oxidizing agent:

$$(CH)_x + 1/2(xy)I_2 \rightarrow (CH^{+y})_x + (xy)I^- \qquad (11)$$

$$(xy)I^- + (xy)I_2 \rightarrow (xy)I_3 \qquad (12)$$

$$(CH^{+y})_x + (xy)I_3^- \rightarrow [CH^{+y}(I_3^-)_y]_x \qquad (13)$$

Examples of p-doping where the oxidizing agent is different from the dopant anion are given in Section III.

In order to have a p- or n-doped conducting polymer which is stable it is essential that the dopant cation or anion does not react chemically in an irreversible manner with the carbonium ion or with the carbanion. For example, iodine-doped $(CH)_x$, i.e., $[CH^{+y}(I_3^-)_y]_x$ loses its conductivity[6] slowly when standing in a vacuum for several weeks because the I_3^- ion reacts irreversibly and destructively with the $(CH^{+y})_x$ ion to form HI and a complex mixture of unknown insulating products:

$$I_3^- + (CH^{+y})_x \rightarrow HI + C_xH_pI_q \qquad (14)$$

If a doped conducting polymer is to be stable in air, (O_2 and H_2O), then, in addition to the necessity of its being chemically stable to its own dopant counter ion, it is absolutely necessary that the counter ion be unreactive towards oxygen and water. The more difficult problem is, however, to obtain a polycarbonium ion or carbanion which is also stable to oxygen and water. However, as is shown in Section III, each of these three critical stability criteria have been attained for p-doping of $(CH)_x$ at least under certain experimental conditions.

In summary, the use of the term "doping" when referring to the increase in conductivity of polymers by many orders of magnitude by the incorporation of a few percent of a different chemical species is phenomenologically correct. However, it is conceptually very different from the doping of a classical semiconductor. As will be shown in Sections II and III it is necessary to remember that the doping of conducting polymers is a simple chemical oxidation-reduction (redox) reaction and that the role of the "dopant" species differs from that in classical semiconductors. With this in mind, it is then possible to rationalize why certain species can act as p- or n-dopants and to predict new p- and n-dopants for potentially conducting organic polymer systems.

II. REDUCTION POTENTIAL OF POLYACETYLENE

The standard reduction potential of a redox couple is measured with respect to the potential of the standard hydrogen electrode, which is defined as zero at 25°C. All substances must be at unit activity. A conventional standard reduction potential cannot be measured for a polyacetylene couple since two separate states, the oxidized state and the reduced state, each at unit activity, cannot be obtained in the same piece of (solid) polyacetylene. Also, polyacetylene is insoluble in all solvents regardless of its oxidation state. In addition, its polymeric nature dictates that its oxidation state will change in a continuous manner, not in integral steps as is the case when discreet ions or molecules are oxidized or reduced. The reduction potentials for the polyacetylene couples are, therefore, here defined as the potentials for a given level of oxidation or reduction of the polyacetylene such that the application of an infinitesimally small potential greater or smaller than that of the couple will result in the removal or addition, respectively, of an infinitesimally small amount of negative charge, $(ax)e^-$, from or to the couple.

The open circuit voltage, V_{oc}, measured between a piece of pure trans-$(CH)_x$ film and a piece of lithium metal both immersed in a 1.0 molar solution of $LiClO_4$ in propylene carbonate will lie somewhere in the range between +2 to +3 volts[7] depending on the slightly different ways in which the film has been previously stored or handled. This is unusual since a pure oxidizable or reducable material will usually exhibit a given fixed potential under these conditions. Electrochemical oxidation (p-doping) of the $(CH)_x$ can be accomplished by attaching the positive terminal of a d.c. power supply to the $(CH)_x$, the negative terminal being attached to any convenient counter electrode, e.g. a piece of platinum wire. As the applied potential is increased it is found that significant current only begins to flow, i.e. significant oxidation (withdrawal of electrons from the $(CH)_x$) only begins to occur when the potential of the $(CH)_x$ versus a lithium metal reference electrode is more positive than +3.1 volts.[8] The lithium reference electrode is also immersed in the electrolyte and is attached to the $(CH)_x$ electrode via a voltmeter. Conversely, electrochemical reduction (n-doping) of the $(CH)_x$ can be accomplished by attaching the $(CH)_x$ to the negative terminal of a d.c. power supply and the counter electrode to the positive terminal. As the applied potential is decreased it is found that a significant current only begins to flow i.e. significant reduction (addition of electrons to the $(CH)_x$) only begins to occur when the potential of the $(CH)_x$ versus a lithium metal reference electrode is less positive than +1.8 volts.

The above observations may be understood by referring to the density of states diagram given for trans-$(CH)_x$ in Figure 2.

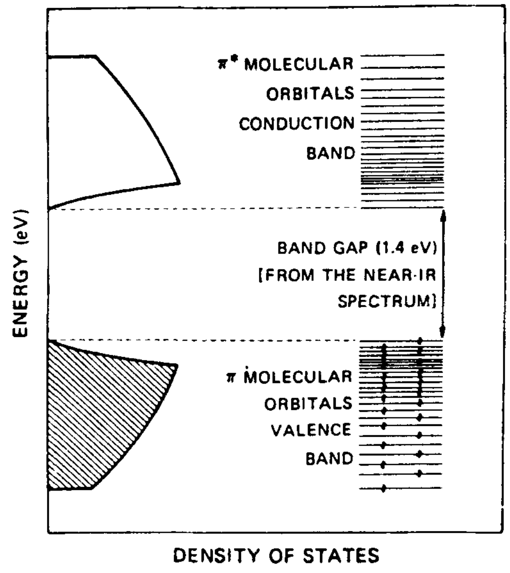


FIGURE 2:[9] The left-hand diagram is the conventional density of states diagram for trans-$(CH)_x$. The right-hand diagram depicts this in terms of π and π^* molecular orbitals.

The density of states i.e. the number of pi molecular orbitals in undoped trans-$(CH)_x$ between the top of the pi bonding orbitals (valence band) and bottom of the pi antibonding orbitals (conduction band) is extremely small. Hence, when electrons are first removed from $(CH)_x$ they will be removed in any significant amount only from the top of the valence band. Experimentally this occurs only when the potential of the $(CH)_x$ is more positive than +3.1 volts versus a lithium metal reference electrode. This value, therefore, defines the energy of the top of the valence band with respect to lithium. Analogously, electrons can only be added to the $(CH)_x$ in any significant amount by injecting them into the empty antibonding π^* molecular orbitals at the bottom of the conduction band. This only begins to occur when the potential of the $(CH)_x$ is less positive than +1.8 volts versus a lithium metal reference electrode. This value, therefore, defines the energy of the bottom of the conduction band with respect to lithium. Hence neutral $(CH)_x$ has a "floating" potential versus the Li^+/Li couple. The midpoint between +3.1 volts and +1.8 volts i.e. +2.4 to +2.5 volts, therefore, defines a potential which can be regarded as characteristic of pristine, undoped $(CH)_x$, (see Table I).

The relationship between the cell potential (open circuit voltage) of trans$(CH)_x$ and the percent oxidation of the p-doped $(CH)_x$ is given by the upper curve in Figure 3.[8] Oxidation was carried out electrochemically using the $(ClO_4)^-$ dopant anion. The analogous relationship between the open circuit voltage and the percent reduction is given by the lower curve. This was obtained by electrochemical reduction using the Li^+ dopant cation. Subsequent studies showed that more exact values of the onset of oxidation and reduction could be obtained in a computer-controlled study in which the applied potential was increased in a series of very small increments, dV, the number of coulombs passed at each increment, dQ, being recorded when the current which flowed after each increment had decreased to a very small value. The results of this study are given in the inset to Figure 3.[7] It can be clearly seen that essentially no coulombs are passed on changing the applied potential in the range +3.1 to +1.75 volts. This is consistent with the very small density of states within the band gap and moreover, the difference between these values (1.35 volts) gives the value of the band gap of trans-$(CH)_x$ as determined electrochemically.

It is in close agreement with the value of ~ 1.4eV determined for the band gap of trans-$(CH)_x$ by measurement of its visible-near I/R absorption spectrum.[10]

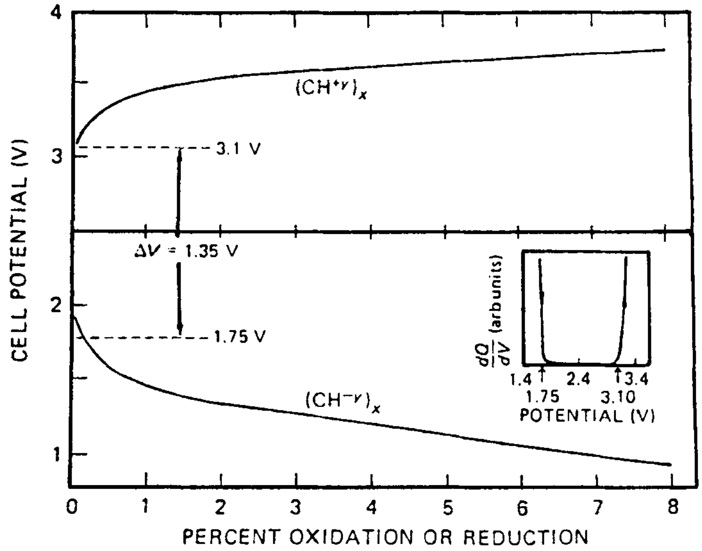


FIGURE 3: Relationship between the cell potential (open circuit voltage) (versus the Li^+/Li couple) and the percent oxidation and reduction of trans-$(CH)_x$. The inset shows the onset potentials of oxidation and reduction using dQ/dV measurements.

Selected characteristic potentials of neutral, oxidized and reduced polyacetylene couples obtained from the curves given in Figure 3 are given in Table I together with the standard reduction potentials of certain other couples obtained from the literature.[11] Reference works give standard reduction potentials with respect to the standard hydrogen electrode, H^+/H_2, i.e. S.H.E., in aqueous solution whose potential is defined as zero. The potential of the Li^+/Li couple differs from that of the H^+/H_2 couple by 3.05 volts. Since potentials are frequently determined in non-aqueous solutions by reference to the Li^+/Li couple, values are listed for convenience in Table I versus the H^+/H_2 couple and also versus the Li^+/Li couple. These values can be interconverted by addition or subtraction of 3.05 volts. Since reduction potential values will vary somewhat according to the solvent in which they are measured the values obtained by the simple addition or subtraction of 3.05 volts on going from one solvent system to another must be used with caution. However, in the nonaqueous solvents commonly used to date in studies on conducting polymers, it appears that the value obtained by subtracting 3.05 volts from a value obtained experimentally in aqueous solution will not differ by more than ~ 0.1 volt from the value obtained experimentally in the non-aqueous solvent systems. Hence, the standard reduction potentials of couples determined in aqueous solution (when all components are at unit activity) can be applied qualitatively to rationalizations and predictions in non-aqueous solution, as described below, so long as the difference in reduction potentials being compared is more than a few tenths of a volt. Similar arguments apply to aqueous and non-aqueous solutions when activities differ from unity.

III. THE ROLE OF REDUCTION POTENTIALS IN RATIONALIZING AND PREDICTING p- AND n-DOPANTS

The electrons in the redox couples in Table I may be loosely regarded as a "chemical species" in the given equilibrium reactions. Similarly, the reduction potentials are a function of the equilibrium constant for the reactions. The less positive the reduction potential the more the equilibrium tends to lie to the left. Hence, when the components of two couples are mixed, the couple with the less positive reduction potential tends to move from right to left, releasing electrons, while the couple with the more positive potential tends to move from left to right, taking in the electrons released by the less positive couple. For example, when the components of couples 6 and 7 i.e. the Cr^{+2}, Cr^{+3}, Pb^{+2} ions and Pb are mixed, the thermodynamically predicted reaction is:

$$Cr^{+2} + Pb^{+2} \rightarrow Cr^{+3} + Pb \qquad (15)$$

<u>not</u>

$$Pb + Cr^{+3} \rightarrow Pb^{+2} + Cr^{+2} \qquad (16)$$

Whether or not a given reaction predicted from reduction potential values will or will not occur, depends on whether or not the activation energy for the reaction is small or large. However, if reduction potentials predict that a reaction cannot occur thermodynamically, then such a reaction need not be investigated experimentally.

In the past the selection of p- or n-dopants for conducting polymers has been carried out on a haphazard trial and error basis. It now appears that selection of dopants can be made in a scientific, logical manner by use of reduction potentials of likely dopant systems. Several examples will be given below illustrating the use of this approach. Many more can be cited to rationalize known dopants for $(CH)_x$ and new dopant systems can be predicted, assuming favorable kinetics.

From couples 5 and 11 (Table I) it would be predicted that excess I_2 should p-dope (oxidize) $(CH)_x$ according to the equation:

$$(CH)_x + 1/2(xy)I_2 \rightarrow (CH^{+y}I_y^-)_x \qquad (17)$$

In the presence of excess I_2, the I^- ion is known to coordinate with an I_2 molecule to form the I_3^- ion. This reaction does not involve oxidation or reduction. The final expected product would, therefore, be $[CH^{+y}(I_3^-)_y]_x$. Experimentally it is found that iodine does dope $(CH)_x$ to the metallic regime and that the iodine exists primarily as the I_3^- ion with smaller quantities of the I_5^- ion formed by the addition of an I_2 molecule to the I_3^- ion. In the presence of excess iodine the reduction potential of the oxidized polyacetylene should be identical with that of the iodine at equilibrium conditions. This value is +3.59 volts (vs. Li^+/Li) (Table I) when the activity of the I_2 and I^- are both unity. Using the empirical equation:[8]

$$V_{oc} = 3.43 + 0.14 \ln y \qquad (18)$$

(where y is the percent oxidation) relating the extent of oxidation of $(CH)_x$ to its V_{oc} (open circuit voltage vs. Li^+/Li), the above value would predict an oxidation level of 3.14%. Compositions of $[CH^{+0.05}(I_3^-)_{0.05}]_x$ corresponding to 5% oxidation are obtained experimentally[2] when $(CH)_x$ doped with iodine vapor is pumped in vacuum to remove excess iodine. Hence remarkably good agreement is obtained between the predicted and experimental levels of doping considering that the reduction potential of the I_2/I^- couple measured in aqueous solution is here applied to the doping of $(CH)_x$ with iodine vapor.

It has been found that $(CH)_x$ is p-doped to a conductivity of ~ 3 $ohm^{-1} cm^{-1}$ when placed in a solution of $AgClO_4$ in toluene, viz.,

$$(CH)_x + 0.018xAgClO_4 \rightarrow [CH^{+0.018}(ClO_4)^-_{0.018}]_x + 0.018xAg \qquad (19)$$

Metallic silver particles were observed by electron microscopy on the $(CH)_x$ fibrils.[12] Again this is consistent with what is expected from couples 5 and 16 in Table I. The Ag^+ ion oxidizes the $(CH)_x$ to (CH^{+y}) and is itself reduced to metallic silver while the $(ClO_4)^-$ ion acts as the necessary dopant counter anion. The value of the Ag^+/Ag couple in aqueous solution is +0.80 volts (vs. H^+/H_2). This converts to a value of +3.85 volts versus Li^+/Li on adding 3.05 to the +0.80 volt value. The value determined experimentally in propylene carbonate (P.C.) solution (see Table I) is +3.74 volts (vs. Li^+/Li).[13] In the presence of excess $AgClO_4$ it is expected that the potential of the doped polyacetylene will also be +3.74 volts when equilibrium conditions are reached. Using equation 18 this value would predict a doping level of 9.25%. The attainment of equilibrium conditions in 200Å $(CH)_x$ fibrils can take up to approximately eight days due to the slow diffusion of dopant ions into the $(CH)_x$ during doping.[14] Since the doping period was undoubtedly less than this it seems likely that the smaller level of doping obtained may have been due to the fact that the experiment was terminated before equilibrium conditions were reached.

This doping system has been studied in a U-cell divided by a sintered glass frit containing a $(CH)_x$ electrode immersed in a 1.0 molar solution of $LiClO_4$ in propylene carbonate in one compartment and a silver metal electrode immersed in a 1.0 molar solution of $AgClO_4$ in propylene carbonate in the other compartment. A lithium metal reference electrode was used to measure the reduction potential of the $(CH)_x$ (+2.08 volts) and the silver electrode (+3.74 volts).[13] The potential difference between the $(CH)_x$ and Ag electrodes is therefore 1.66 volts. When the two electrodes were connected by an external wire, a current flowed. The electrochemical reactions occuring were:

At $(CH)_x$ $$(CH)_x + (xy)(ClO_4)^- \rightarrow [CH^{+y}(ClO_4)_y^-]_x + (xy)e^- \qquad (20)$$

At Ag $$(xy)Ag^+ + (xy)e^- \rightarrow (xy)Ag \qquad (21)$$

to give the net reaction, identical with that given by equation 19.

$$(CH)_x + (xy)AgClO_4 \rightarrow [CH^{+y}(ClO_4)_y^-]_x + (xy)Ag \qquad (22)$$

A key difference in this reaction, however, is that the reaction given by equation 19 has been broken down into two separate half reactions and that the $[CH^{+y}(ClO_4)_y^-]_x$ obtained contains no silver metal particles. The silver metal, in this experiment is deposited on the silver metal electrode. This experiment illustrates how the p-doping of $(CH)_x$ by an apparently "strange" dopant can be broken down into simple oxidation-reduction steps which are consistent with the known reduction potentials of the species involved.

The n-doping of $(CH)_x$ can be similarly understood by means of reduction potentials. Thus from couples 1 and 5 (Table I) it would be predicted that metallic lithium should spontaneously n-dope (reduce) $(CH)_x$. Because $(CH)_x$ and Li are both solids the doping of solid $(CH)_x$ using solid Li by physically placing them together cannot be conveniently studied. However, if a piece of Li metal and a piece of $(CH)_x$ are placed in a solution of $LiClO_4$ in tetrahydrofuran and an external wire is placed between them an open circuit voltage of ~ +2.4 volts is observed and a spontaneous electric current will flow.[7] The electrochemical reactions occuring are:

At Li: $$(xy)Li + (xy)(ClO_4)^- \rightarrow (xy)Li^+(ClO_4)^- + (xy)e^- \qquad (23)$$

At $(CH)_x$: $$(CH)_x + (xy)e^- + (xy)Li^+ \rightarrow [Li_y^+(CH^{-y})]_x \qquad (24)$$

The net reaction which occurs is, therefore:

$$(CH)_x + (xy)Li \rightarrow [Li_y^-(CH^{-y})]_x \qquad (25)$$

In the presence of excess lithium one would expect the polyacetylene to attain the potential of Li (0.0 volts) when equilibrium was reached. However, when the $[Li_y^+CH^{-y}]_x$ which is formed reaches a potential of ~ +0.3 volt it be-

Assuming that activation energy effects are not significant, then, thermodynamically, when $(CH)_x$ wetted with aqueous HBF_4 is exposed to gaseous oxygen, it can be seen from couples 5 and 17 that the reaction given by equation 28:

$$4(CH)_x + 4(xy)HBF_4 + (xy)O_2 \rightarrow 4[CH^{+y}(BF_4)^-_y]_x + 2(xy)H_2O \tag{28}$$

should occur spontaneously. The oxygen oxidizes the $(CH)_x$ to $(CH^{+y})_x$ while the HBF_4 supplies the $(BF_4)^-$ counter ion which makes the oxidized polymer electrically neutral. Moreover the $(BF_4)^-$ does not apparently react chemically with the (CH^{+y}) cation in an irreversible chemical reaction to destroy the conductivity of the film - at least in the time period during which the experiments have been carried out to date.

Certain chemical species can actually play a dual role - a portion can act as the oxidizing agent and a portion can act as the necessary stable counter anion. For example, when $(CH)_x$ film is placed in aqueous solutions of $HClO_4$ it becomes oxidized, "p-doped", and at the higher concentrations it actually undergoes a semiconductor/ metal transition. The net reaction which occurs is:

$$8(CH)_x + 9(xy)HClO_4 \rightarrow 8[CH^{+y}(ClO_4)^-_y]_x + (xy)HCl + 4(xy)H_2O \tag{29}$$

This reaction is consistent with the reduction potentials of couples 5 and 18 in Table I. One of the $HClO_4$ species oxidizes the $(CH)_x$ to $(CH^{+y})_x$ and acts, in effect, in lieu of the O_2 as given in equation 28. It is itself reduced to HCl while the the $(ClO_4)^-$ ions in the other eight $HClO_4$ species act as the necessary stable counter anion for the $(CH^{+y})_x$ ion.

A similar doping of $(CH)_x$ to the metallic regime is observed with aqueous H_2SO_4 solutions, again consistent with the reduction potential values (couples 5 and 10) given in Table I. However, this system is more complex because of the possible formation of a variety of different species on reduction of H_2SO_4.

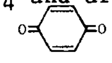
gins to react with the tetrahydrofuran.

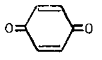
Since metal ions having an appropriate reduction potential can be used to oxidize $(CH)_x$ or reduce $(CH^{+y})_x$ it is not surprising to find that non-metal ions can also behave similarly. For example, although the reduction potentials of the nitrosyl ion, $(NO)^+$ and the nitryl ion, $(NO_2)^+$ are not known, salts of these ions, $(NO)^+A^-$ and $(NO_2)^+A^-$ act as good oxidizing agents, and are converted to gaseous NO and NO_2 respectively on removing an electron from another species. Thus solutions of $(NO)^+(SbF_6)^-$ and $(NO_2)^+(PF_6)^-$ in a CH_3NO_2/CH_2Cl_2 mixture react with $(CH)_x$ according to the equations below to give p-doped materials conducting in the metallic regime.[2,15]

$$(CH)_x + 0.017x(NO)^+(SbF_6)^- \rightarrow [CH^{+0.017}(SbF_6)^-_{0.017}]_x + 0.017xNO \qquad (26)$$

$$(CH)_x + 0.033x(NO_2)^+(PF_6)^- \rightarrow [CH^{+0.033}(PF_6)^-_{0.033}]_x + 0.033xNO_2 \qquad (27)$$

Until very recently it has been believed that extended exposure of $(CH)_x$ to O_2 or air results in the destruction of its conductivity and its concomitant conversion to an unknown mixture of compounds containing many carbonvl and other groups.[16] However, very recent studies[17] have shown that if a film of cis-$(CH)_x$ is first dipped in a 48% (7.M) aqueous solution of the non-oxidizing strong acid, fluoroboric acid, HBF_4, and is then exposed to one atmosphere of gaseous oxygen its resistance falls during a period of approximately four days to give a conductivity of ca. 1 $ohm^{-1}cm^{-1}$, just at the beginning of the metallic conducting regime. A control piece of $(CH)_x$ similarly treated with HBF_4 when exposed to an atmosphere of gaseous nitrogen shows only the expected immediate decrease in conductivity, due to the ionic conductivity of the HBF_4 solution wetting its surface. More recent studies have shown that somewhat higher conductivities, (ca. 5 $ohm^{-1}cm^{-1}$), are obtained if the $(CH)_x$ film is first "activated" by electrochemical p-doping followed by electrochemical undoping in $Li^+(BF_4)^-$/propylene carbonate solution.[17] Trans-$(CH)_x$ appears to require little or no preliminary activation. The film is simply suspended in the 7.4 M solution of aqueous HBF_4 through which O_2 is bubbled for ~ 24 hours.

Even certain organic compounds can act as the oxidizing agent in lieu of oxygen.[17] They can oxidize $(CH)_x$ to the metallic regime in aqueous HBF_4 and are themselves reduced. For example, benzoquinone,  , reacts with $(CH)_x$ according to the equation:

$2(CH)_x + (xy)$  $+ 2(xy)HBF_4 \rightarrow 2[CH^{+y}(BF_4)^-_y]_x$

$+ (xy)$  (30)

and is reduced to hydroquinone,  . This reaction is consistent with the reduction potential values for couples 5 and 14 given in Table I.

It is important to note that the reactions given by equations 28, 29 and 30 were carried out in aqueous solution to produce highly conducting p-doped polyacetylene. The chemical stability of p-doped polyacetylene in these solutions is at first sight highly surprising. A possible explanation of this stability is given elsewhere.[18] The 48% (7.4M) aqueous HBF_4 employed in certain of the above studies has no effect on neutral $(CH)_x$; however, a concentrated non-oxidizing protonic acid such as "$BF_3 \cdot 2H_2O$", i.e. $[H_3O]^+[BF_3(OH)]^-$ rapidly dopes $(CH)_x$ to the metallic regime.[19] This "protonic acid doping", which is as yet very little understood, probably involves the formation of a pi complex between the carbon-carbon double bond and the proton of the acid. Although this would involve partial removal of electron density from the pi system of the $(CH)_x$ it is a type of oxidation which falls into a different category from the oxidation reactions described above where definite products resulting from reduction of the oxidizing agent can be identified.

The above studies show that in order to understand the phenomenon of p- and n-doping of $(CH)_x$ it is necessary to clearly distinguish between the oxidizing or reducing agent and the dopant anion or cation involved in the doping process. Also, the studies show the importance of determining the reduction potentials of polyacetylene in various oxidation states since the values so obtained then permit the rationalization of known, and prediction of new dopants. Preliminary studies indicate that this approach can readily be applied to other conducting polymer systems.

TABLE I: Reduction Potentials of Selected Polyacetylene Couples and Other Couples

		Couple	$E^\circ_{red.}$ (vs Li^+/Li)	$E^\circ_{red.}$ (vs H^+/H_2)
	1.	$Li^+ + e^- \rightleftarrows Li$	0.00	-3.05
	2.	$(CH^{-0.1+a})_x + (ax)e^- \rightleftarrows (CH^{-0.1})_x$	+0.9	-2.2
Neutral $(CH)_x$	3.	$(CH^{-q+a})_x + (ax)e^- \rightleftarrows (CH^{-q})$	+1.8	-1.3
	4.	$N_2 + 4H_2O + 4e^- \rightleftarrows N_2H_4 + 4OH^-$	+1.89	-1.16
	5.	$(CH^{+a})_x + (ax)e^- \rightleftarrows (CH)_x$	+2.4	-0.7
	6.	$Cr^{+3} + e^- \rightleftarrows Cr^{2+}$	+2.65	-0.40
	7.	$Pb^{+2} + 2e^- \rightleftarrows Pb$	+2.92	-0.13
	8.	$H^+ + e^- \rightleftarrows 1/2\ H_2$	+3.05	0.00
	9.	$(CH^{+q+a})_x + (ax)e^- \rightleftarrows (CH^{+q})_x$	+3.1	0.0
	10.	$SO_4^{-2} + 4H^+ + 2e^- \rightleftarrows H_2SO_3 + H_2O$	+3.25	+0.20
	11.	$I_2 + 2e^- \rightleftarrows 2I^-$	+3.59	+0.54
	12.	$(CH^{+0.06+a})_x + (ax)e^- \rightleftarrows (CH^{+0.06})_x$	+3.7	+0.6
	13.	$O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$	+3.73	+0.68
	14.	$O{=}(C_6H_4){=}O + 2H^+ + 2e^- \rightleftarrows HO(C_6H_4)OH$	+3.75	+0.70
	15.	$(CH^{+0.1+a})_x + (ax)e^- \rightleftarrows (CH^{+0.1})_x$	+3.8	+0.7
	16.	$Ag^+ + e^- \rightleftarrows Ag$	+3.85[a]	+0.80
	17.	$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	+4.28	+1.23
	18.	$ClO_4^- + 8H^+ + 8e^- \rightleftarrows Cl^- + 4H_2O$	+4.42	+1.37
	19.	$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	+4.82	+1.77

(a) Experimentally measured value versus Li in a Li/ $LiClO_4$ (1M in P.C.)//$AgClO_4$ (1M in P.C.)/Ag cell was +3.74V.[13]

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