The Concept of `Doping' of Conducting Polymers: The Role of Reduction Potentials [and Discussion]

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The concept of 'doping' of conducting polymers: the role of reduction potentials

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The conductivity of certain organic polymers can be raised to metallic levels by chemical or electrochemical 'p-doping' (oxidation), or 'n-doping' (reduction). Polyacetylene, $(CH)_x$, the prototype conducting polymer, has been studied more extensively than any other conducting polymer and the doping concepts involved appear to be applicable to other polymer systems. The doping of an organic polymer to achieve certain metallic properties is phenomenologically similar to the doping of a classical inorganic semiconductor in that very large increases in conductivity are observed when the material takes up very small amounts of certain chemical species. However, mechanistically it is different in that the doping of an organic polymer involves simply the partial oxidation or reduction of the polymer, each oxidation state exhibiting its own characteristic reduction potential. The dopant ion incorporated may be derived from the chemical dopant species or it may be completely unrelated to it.

The reduction potentials of neutral *trans*-$(CH)_x$ and its various oxidized or reduced states, and also the band gap of *cis*- and *trans*-$(CH)_x$ have been determined electrochemically. The reduction potentials have been used, together with known standard reduction potentials of a variety of redox couples, to rationalize the doping of $(CH)_x$ to achieve metallic conductivity by using a number of dopant species, including I_2, Li, $AgClO_4$, gaseous O_2, H_2O_2 or benzoquinone (the last three species in aqueous HBF_4) and aqueous $HClO_4$, etc. The stability of p-doped polyacetylene in aqueous acidic media is ascribed to the fact that a positive charge on a CH unit in *trans*-$(CH)_x$ is delocalized over approximately fifteen carbon atoms in what is termed a 'positive soliton'. This reduces the ease of nucleophilic attack of the partly oxidized polymer chain. The O_2-doping of $(CH)_x$ permits the use of $(CH)_x$ as an electrocatalytic electrode for the spontaneous reduction of oxygen at one atmosphere pressure and at room temperature in strong aqueous HBF_4 solutions.

It is concluded that reduction potentials can be used to rationalize the ability of certain dopants to increase the conductivity of selected organic polymers by many orders of magnitude and that they may also be used to predict new chemical species that are thermodynamically capable of acting as p- or n-dopants.

1. Introduction

Polyacetylene, synthesized by the catalytic polymerization of acetylene, $HC \equiv CH$ (Ito *et al.* 1974), is the simplest conjugated organic polymer. It can be prepared in the form of planar *cis* or *trans* chains as shown in figure 1. Both *cis*- and *trans*-$(CH)_x$ can be 'p-doped' (partly oxidized) or 'n-doped' (partly reduced) through the semiconducting to the metallic scale of conductivity with certain chemical 'dopants' (oxidizing or reducing agents) (MacDiarmid & Heeger 1979), or by electrochemical oxidation or reduction (MacInnes *et al.* 1981). 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,
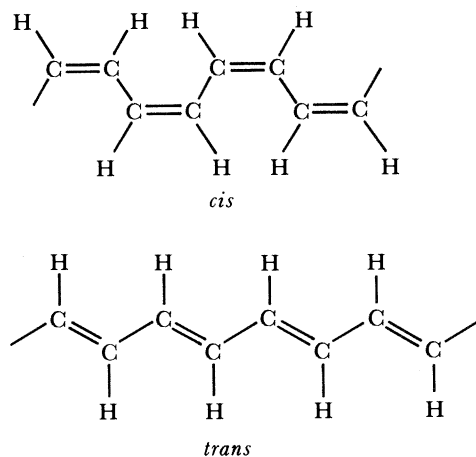
FIGURE 1. *Cis* and *trans* isomers of $(CH)_x$

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 $[M_y^+(CH)^{y-}]_x$. The conductivity of *cis*- and *trans*-$(CH)_x$ together with a few selected examples of the compositions and conductivities of materials obtained by p- or n-doping $(CH)_x$ are given in table 1. Isomerization occurs during the doping process; hence similar conductivities are obtained regardless of whether the *cis* or *trans* isomer is used.

TABLE 1. SELECTED DOPANTS FOR $(CH)_x$

|	conductivity $\dfrac{}{\Omega^{-1}\,\mathrm{cm}^{-1}}$
cis-$[CH]_x$	1.7×10^{-9}
trans-$[CH]_x$	4.4×10^{-5}
p-doping (oxidation)	
(1) I_2 vapour: $[(CH)^{0.07+}(I_3)^-_{0.07}]_x$	5.5×10^2
(2) AsF_5 vapour: $[(CH)^{0.1+}(AsF_6)^-_{0.1}]_x$	1.2×10^3
(3) $HClO_4$ (liquid or vapour): $[(CH\{OH\}_{0.08})^{0.12+}(ClO_4)^-_{0.12}]_x$	5×10^1
(4) Electrochemical: $[(CH)^{0.1+}(ClO_4)^-_{0.1}]_x$	1×10^3
n-doping (reduction)	
(1) Li naphthalide: $[Li^+_{0.2}(CH)^{0.2-}]_x$	2×10^2
(2) Na naphthalide: $[Na^+_{0.2}(CH)^{0.2-}]_x$	2.5×10^1
(3) Electrochemical: $[Li^+_{0.1}(CH)^{0.1-}]_x$	$10^1 - 10^2$

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

2. 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 reacting it with small quantities of electron-accepting or electron-donating species, this was termed 'p-doping' or 'n-doping' respectively by analogy with the doping of a classical semiconductor, such as silicon. Phenomenologically this designation is correct, in that large increases in conductivity are observed when the material takes up very small quantities of certain chemical species. However, as a better understanding of the nature of the doping process in $(CH)_x$ developed, it has become apparent that the description is mechanistically misleading.

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 that possesses only three valence electrons. Even if there is no charge transfer between neighbouring silicon atoms and the boron atom (i.e. the silicon and boron atoms are electrically neutral), the boron site is electron-deficient so far 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 so far as the crystal lattice is concerned, i.e. there are five valence electrons in a site normally occupied by a silicon atom that 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 species.

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 polymer, for example,

$$(CH)_x \rightarrow [(CH)^{y+}]_x + (xy)\, e^-. \tag{1}$$
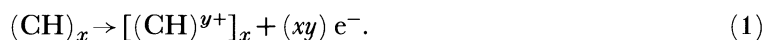
This may be accomplished either chemically or electrochemically. To preserve electrical neutrality in the system a counter-anion, A^-, must also be provided,

$$[(CH)^{y+}]_x + (xy)\, A^- \rightarrow [(CH)^{y+} A_y^-]_x. \tag{2}$$
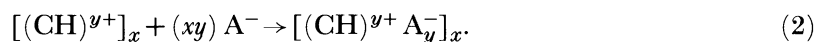
To date, all counter-anions used have been monovalent. Analogously, n-doping refers to the partial reduction of the conducting polymer, for example,

$$(CH)_x + (xy)\, e^- \rightarrow [(CH)^{y-}]_x. \tag{3}$$
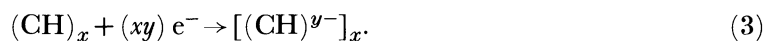
Again, to preserve electrical neutrality, a counter-cation M^+ must be provided,

$$[(CH)^{y-}]_x + (xy)\, M^+ \rightarrow [M_y^+ (CH)^{y-}]_x. \tag{4}$$
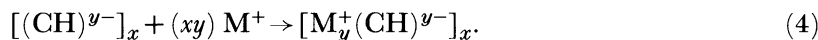
All counter-cations used up to the present time have been monovalent species.

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 (Chiang *et al.* 1978), is used. The lowest energy π^* molecular orbital in $(CH)_x$ is apparently of lower energy than the π^* orbital of the naphthalide radical anion containing the unpaired electron, because 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,

$$(CH)_x + (xy) \, nphth^{-\cdot} \rightarrow [(CH)^{y-}]_x + (xy) \, nphth, \tag{5}$$
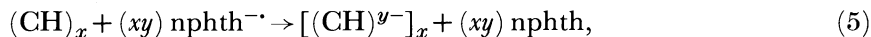
while the Na^+ ion acts as the counter 'dopant' cation,

$$[(CH)^{y-}]_x + (xy) \, Na^+ \rightarrow [Na_y^+ (CH)^{y-}]_x. \tag{6}$$

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

$$(CH)_x + (xy) \, Na \rightarrow [(CH)^{y-}]_x + (xy) \, Na^+, \tag{7}$$
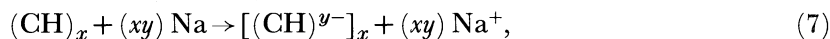
and the Na^+ so formed then acts as the dopant cation,

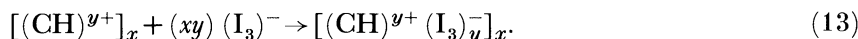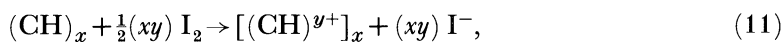$$[(CH)^{y-}]_x + (xy) \, Na^+ \rightarrow [Na_y^+ \, (CH)^{y-}]_x. \tag{8}$$

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 can be carried out by using electrons supplied by a d.c. power source 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 $+1.8$ V (measured against a reference electrode Li^+/Li) it will become reduced (MacInnes et al. 1981),

$$(CH)_x + (xy) \, e^- \rightarrow [(CH)^{y-}]_x, \tag{9}$$
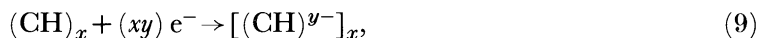
and the $(n\text{-}Bu_4N)^+$ ion will then act as the dopant counter-cation,

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

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

$$(CH)_x + \tfrac{1}{2}(xy) \, I_2 \rightarrow [(CH)^{y+}]_x + (xy) \, I^-, \tag{11}$$

$$(xy) \, I^- + (xy) \, I_2 \rightarrow (xy) \, (I_3)^-, \tag{12}$$

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

Examples of p-doping where the oxidizing agent is different from the dopant anion are given in §4.

3. Reduction potentials of polyacetylene in oxidized and reduced forms

The reduction potentials of polyacetylene in oxidized and reduced forms may be measured conveniently by placing a strip of $(CH)_x$ film and a Li metal electrode in an appropriate electrolyte such as a solution of $LiClO_4$ in propylene carbonate or tetrahydrofuran. Application of a suitable potential between the $(CH)_x$ and Li electrode results in the removal (oxidation; p-doping) or the addition of electrons (reduction; n-doping) from or to the $(CH)_x$, respectively. The applied potential is removed and the open circuit voltage, V_{oc}, of the oxidized or reduced

film is measured after approximately 24–48 h. This time interval permits equilibration of the dopant counter-ions throughout the material. 'Undoping' of the film is also done potentiostatically and returns the polyacetylene to its original, neutral form. The charge involved in this undoping process gives the degree of oxidation or reduction of the polyacetylene corresponding to the measured V_{oc} value obtained under these quasi-equilibrium diffusion conditions. The above procedure is then repeated with $(CH)_x$ film in a number of different oxidized or reduced states, the V_{oc} values being recorded in each case. The reduction potential for a polyacetylene couple is therefore here defined as the potential 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 (see table 2). The relation between the open circuit voltage and the oxidation state of polyacetylene oxidized or reduced up to 8 mol % is given in figure 2.

TABLE 2. REDUCTION POTENTIALS OF SELECTED COUPLES

couple	E_{red} (against Li^+/Li)	E_{red} (against H^+/H_2)
1. $Li^+ + e^- \rightleftharpoons Li$	0.00	-3.05[a]
2. $Na^+ + e^- \rightleftharpoons Na$	$+0.33$	-2.71[a]
3. $[(CH)^{-0.1+a}]_x + (ax)\,e^- \rightleftharpoons [(CH)^{0.1-}]_x$	$+0.9$	-2.2
4. $[(CH)^{-q+a}]_x + (ax)\,e^- \rightleftharpoons [(CH)^{q-}]_x$	$+1.81$	-1.24
5. $[(CH)^{0+a}]_x + (ax)\,e^- \rightleftharpoons [(CH)^{0}]_x$	$+2.48$	-0.57
6. $Pb^{2+} + 2e^- \rightleftharpoons Pb$	$+2.92$	-0.13[a]
7. $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$	$+3.05$	0.00[a]
8. $[(CH)^{+q+a}]_x + (ax)\,e^- \rightleftharpoons [(CH)^{q+}]_x$	$+3.15$	0.10
9. $I_2 + 2e^- \rightleftharpoons 2I^-$	$+3.59$	$+0.54$[a]
10. $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	$+3.73$	$+0.68$[a]
11. $O{=}(C_6H_4){=}O + 2H^+ + 2e^- \rightleftharpoons HO\,(C_6H_4)\,OH$	$+3.75$	$+0.70$[a]
12. $[(CH)^{+0.1+a}]_x + (ax)\,e^- \rightleftharpoons [(CH)^{0.1+}]_x$	$+3.8$	$+0.7$
13. $Ag^+ + e^- \rightleftharpoons Ag$	$+3.85$[b]	$+0.80$[a]
14. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	$+4.28$	$+1.23$[a]
15. $(ClO_4)^- + 8H^+ + 8e^- \rightleftharpoons Cl^- + 4H_2O$	$+4.42$	$+1.37$[a]
16. $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$+4.82$	$+1.77$[a]

[a] The values given are standard reduction potentials (Weast 1975).
[b] Experimentally measured value against Li in a $Li\,|\,LiClO_4$ (1 M in P.C.) $\|\,AgClO_4$ (1 M in P.C.) $|\,Ag$ cell was $+3.74$ V (MacDiarmid et al. 1984).
(Note that couples 4–8 are for neutral $(CH)_x$.)

The measured reduction potentials of n-doped polyacetylene are independent (within experimental error) of the nature of the dopant cation, at least in the case of $[Li_y^+(CH)^{y-}]_x$ and $[Na_y^+(CH)^{y-}]_x$, which have been examined in detail (Kaner et al. 1985). The effect of incorporating different dopant anions to give species such as $[(CH)^{y+}(ClO_4)_y^-]_x$ and $[(CH)^{y+}(PF_6)_y^-]_x$, although not yet examined in such great detail, appears to cause no significant change in the reduction potentials of p-doped polyacetylene. Similarly, different electrolytes, particularly those most commonly used such as propylene carbonate (for oxidation) and tetrahydrofuran (for reduction), appear to have no significant effect on the reduction potentials measured.

The oxidation and reduction processes involved may be understood by referring to the density of states diagram for trans-$(CH)_x$ given in figure 3. The density of states, i.e. the number of π molecular orbitals in undoped trans-$(CH)_x$ between the top of the π bonding orbitals
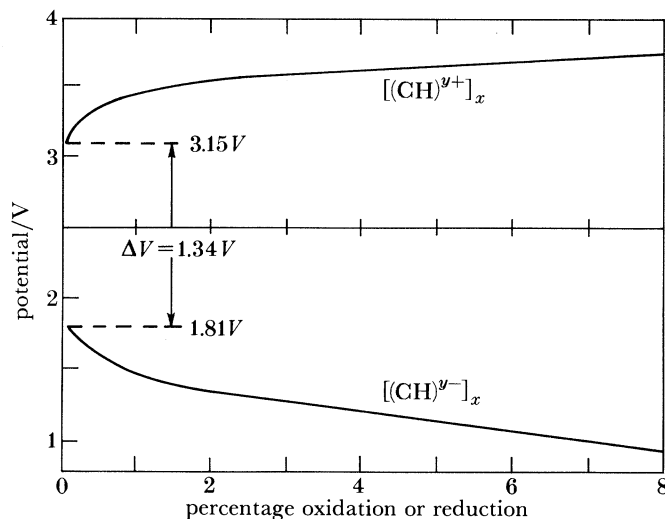
FIGURE 2. Relation between the potential (open circuit voltage V_{oc} against the Li$^+$/Li couple) and the percentage oxidation and reduction of $trans$-(CH)$_x$.

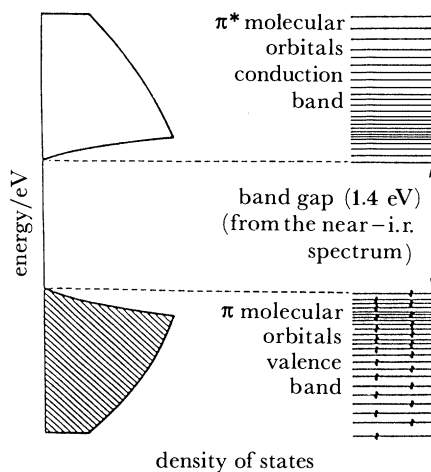
FIGURE 3. The left-hand diagram is the conventional density of states diagram for $trans$-(CH)$_x$. The right-hand diagram depicts this in terms of π and π^* molecular orbitals (MacDiarmid $et\ al.$ 1984).

(valence band) and the bottom of the π antibonding (π^*) orbitals (conduction band), is extremely small. Hence, when electrons are first removed from (CH)$_x$ they will be removed in a 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 $+3.15$ V measured against a Li$^+$/Li 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 a significant amount by injecting them into the empty π^* molecular orbitals at the bottom of the conduction band. This only begins to take place when the potential of the (CH)$_x$ is less positive than $+1.81$ V against a Li$^+$/Li 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 against the Li$^+$/Li couple. The midpoint between $+3.15$ and $+1.81$ V (i.e. $+2.48$ V) defines a potential that can be regarded as characteristic of pristine, undoped (CH)$_x$ (see table 2).

Electrochemical oxidation removes electrons from the top of the valence band and electrochemical reduction adds electrons to the bottom of the conduction band. When carried out extremely slowly, under quasi-equilibrium conditions, the potentials at which these processes first begin to occur can be determined very accurately by the electrochemical techniques described above. For *trans*-$(CH)_x$ the difference between these values, 3.15 and 1.81 V, (i.e. 1.34 V) gives a value of the band gap. This is in excellent agreement with the value of *ca.* 1.4 eV observed spectroscopically. The band gap for *cis*-$(CH)_x$ can be determined in a similar manner. The value of the band gap so obtained, 1.93 V, is also in excellent agreement with that observed spectroscopically, *ca.* 1.9 eV. Band edges and band gaps determined electrochemically for *cis* and *trans*-$(CH)_x$ are depicted diagrammatically in figure 4.
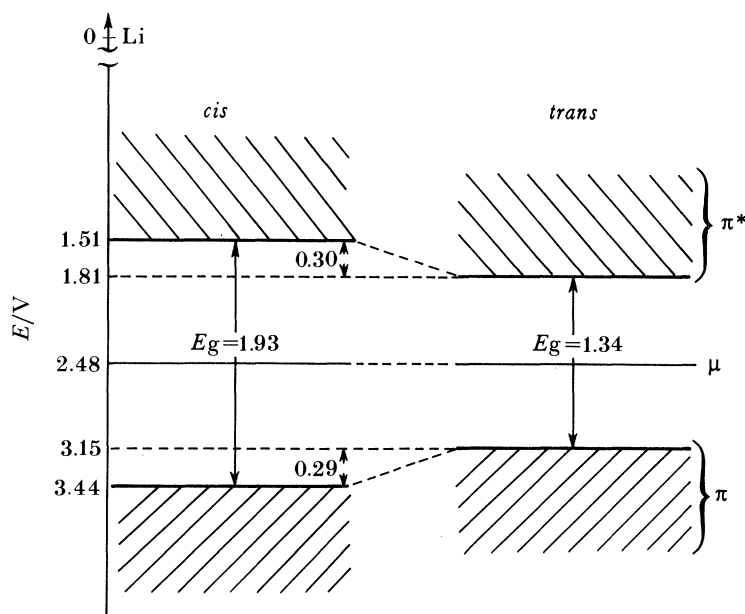

FIGURE 4. Relationship between band edges and band gaps in *cis*- and *trans*-$(CH)_x$ as determined electrochemically. Potentials measured against Li^+/Li reference electrode.

An advantage of the electrochemical studies is that absolute values (against the Li^+/Li couple) of the band edges in the two isomers are obtained. Spectroscopic studies give only the energy difference between the top of the valence band and the bottom of the conduction band in each case.

Selected characteristic potentials of neutral, oxidized and reduced polyacetylene couples obtained from the curves in figure 2 are given in table 2 together with standard reduction potentials of certain other couples. The potential of the Li^+/Li couple differs from that of the H^+/H_2 couple by 3.05 V. Because potentials are frequently determined in non-aqueous solutions by reference to the Li^+/Li couple, values are listed for convenience in table 2 against the H^+/H_2 couple and also against the Li^+/Li couple. These values can be interconverted by addition or subtraction of 3.05 V. Because 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 V on going from one solvent system to another must be used with caution. However, in the non-aqueous solvents commonly used to date in studies on conducting polymers, it appears that the value obtained by adding 3.05 V to the value (against H^+/H_2)

obtained experimentally in aqueous solution will not differ by more than *ca.* 0.1 V from the value (against Li^+/Li) obtained experimentally in the non-aqueous solvent systems. Hence the standard reduction potentials of couples determined in aqueous solutions (when all components are at unit activity) can be applied qualitatively to rationalizations and predictions in non-aqueous solutions, as described below, provided the difference in reduction potentials being compared is more than a few tenths of a volt.
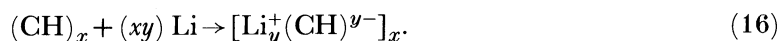
4. The role of reduction potentials in rationalizing and predicting p- and n-dopants

In the past the selection of chemical p- or n-dopants for conducting polymers has been made on a haphazard trial and error basis. It now appears that selection of dopants can be made in a logical, scientific manner by using reduction potentials of likely dopant systems (MacDiarmid *et al.* 1984; Mammone & MacDiarmid 1984). The reduction potentials of polyacetylene, determined as described in §3, together with the standard reduction potentials of known redox couples can be used to rationalize the doping ability of known dopants for $(CH)_x$ and to predict new dopants, assuming favourable kinetics. It appears that a similar approach can be used for other potentially dopable polymer systems. 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. Whether or not a given reaction predicted from reduction potential values will or will not occur, depends of course 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. Several representative examples will be given below to illustrate the use of this approach.

The n-doping of $(CH)_x$, by Li or Na, for example, can be readily understood by means of reduction potentials. Thus, from couples 1 and 5 for Li or couples 2 and 5 for Na (table 2), it would be predicted that metallic Li or Na should spontaneously n-dope (reduce) $(CH)_x$. Because $(CH)_x$, Li and Na are solids, the doping of solid $(CH)_x$ using solid Li or Na by physically placing them together cannot be conveniently studied. However, if, for example, a piece of Li metal and a piece of $(CH)_x$ are placed in a solution of $LiClO_4$ in tetrahydrofuran, an open circuit voltage of *ca.* $+2.5$ V is observed. If an external wire is then placed between the two electrodes a spontaneous electric current will flow. The electrochemical reactions occurring are,

at Li: $$(xy) \, Li \rightarrow (xy) \, Li^+ + (xy) \, e^-; \tag{14}$$

at $(CH)_x$: $$(CH)_x + (xy) \, e^- \rightarrow [(CH)^{y-}]_x. \tag{15}$$
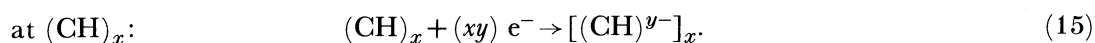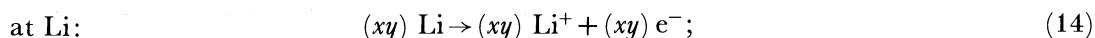
The net reaction that occurs is therefore,

$$(CH)_x + (xy) \, Li \rightarrow [Li_y^+(CH)^{y-}]_x. \tag{16}$$

An analogous reaction occurs with Na. It is of interest to note that this reaction may also be regarded as the discharge reaction of a rechargeable battery cell, the charging reaction being the electrochemical conversion of $[Li_y^+(CH)^{y-}]_x$ back to $(CH)_x$ and Li. Intense industrial

interest is presently being shown in this and related types of reversible electrochemical reactions involving $(CH)_x$ and other conducting polymers. It is believed that conducting polymers might have potential technological use as electrode-active materials in rechargeable batteries.

p-Doping of $(CH)_x$ can also be rationalized by means of reduction potentials. For example, from couples 5 and 9 (table 2) it would be predicted that I_2 should p-dope (oxidize) $(CH)_x$,

$$(CH)_x + \tfrac{1}{2}(xy)\,I_2 \rightarrow [(CH)^{y+}I_y^-]_x. \tag{17}$$
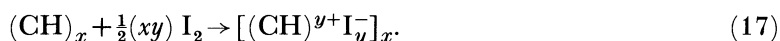
In the presence of excess I_2, the I^- ion is known to coordinate with an I_2 molecule to form the $(I_3)^-$ ion. The latter reaction does not involve oxidation or reduction. The final expected product would, therefore, be $[(CH)^{y+}(I_3)_y^-]_x$. Experimentally it is found that iodine does dope $(CH)_x$ to give metallic behaviour and that the iodine exists primarily as the $(I_3)^-$ ion. The dopant ion in this case is the reduced form of the oxidizing agent.

It has been found that $(CH)_x$ is p-doped to 1.8 mol% ($y = 0.018$) and a conductivity of ca. $3\ \Omega^{-1}\,cm^{-1}$ is observed when placed in a solution of $AgClO_4$ in toluene (Clark et al. 1978; Clark & Street 1979),

$$(CH)_x + (xy)\,AgClO_4 \rightarrow [(CH)^{y+}(ClO_4)_y^-]_x + (xy)\,Ag. \tag{18}$$

Metallic silver particles were observed by electron microscopy on the $(CH)_x$ fibrils. Again this is consistent with what is expected from couples 5 and 13 in table 2. The Ag^+ ion oxidizes the $(CH)_x$ to $[(CH)^{y+}]_x$ and is itself reduced to metallic silver, while the $(ClO_4)^-$ ion acts as the necessary dopant counter-anion.

Another example of p-doping in which the oxidizing agent differs from the dopant ion involves the oxidation of $(CH)_x$ to the metallic level ($\sigma \approx 12\ \Omega^{-1}\,cm^{-1}$) by H_2O_2 in the presence of 48% (7.4 M) aqueous HBF_4. The reaction

$$2(CH)_x + (xy)\,H_2O_2 + 2(xy)\,HBF_4 \rightarrow 2[(CH)^{y+}(BF_4)_y^-]_x + 2(xy)\,H_2O \tag{19}$$
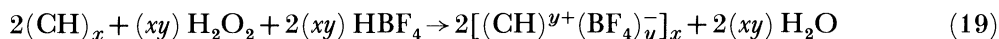
($y = 0.058$) is consistent with the reduction potentials of couples 5 and 16 (table 2).

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 an aqueous solutions of $HClO_4$, it becomes partly oxidized and at higher concentrations of $HClO_4$, it actually undergoes a semiconductor–metal transition (Mammone & MacDiarmid 1984). The net reaction is
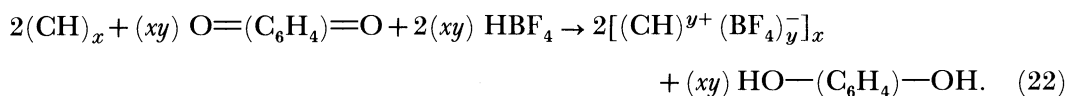
$$8(CH)_x + 9(xy)\,HClO_4 \rightarrow 8[(CH)^{y+}(ClO_4)_y^-]_x + (xy)\,HCl + 4(xy)\,H_2O. \tag{20}$$
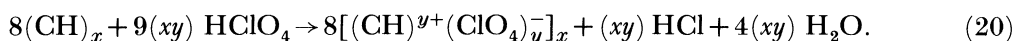
This reaction is consistent with the reduction potentials of couples 5 and 15 in table 2. One of the $HClO_4$ species oxidizes the $(CH)_x$ to $[(CH)^{y+}]_x$ and is itself reduced to HCl, while the $(ClO_4)^-$ ions in the other eight $HClO_4$ species act as the necessary stable dopant counter-anions for the $[(CH)^{y+}]_x$ ions. After treatment with 12 M aqueous $HClO_4$ and drying in vacuo, the elemental analysis is consistent with the composition $[(CH\{OH\}_{0.08})^{0.12+}(ClO_4)_{0.12}^-]_x$, suggesting that partial hydrolysis of the species $[(CH)^{0.2+}(ClO_4)_{0.2}^-]_x$ (presumably first formed) occurred during the doping process

$$[(CH)^{0.2+}(ClO_4)_{0.2}^-]_x + (0.08x)\,H_2O \rightleftharpoons [(CH\{OH\}_{0.08})^{0.12+}(ClO_4)_{0.12}^-]_x$$
$$+ (0.08x)\,HClO_4. \tag{21}$$
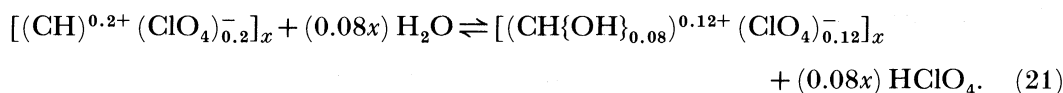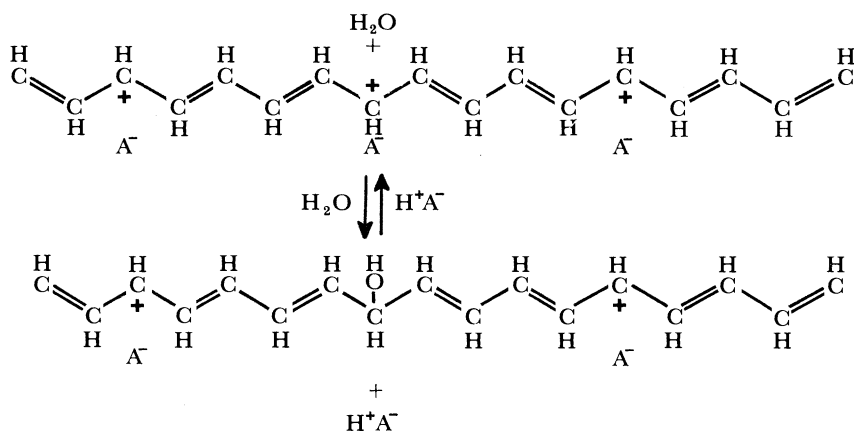
The introduction of an HC(OH) group, involving an sp³ hybridized carbon atom, would reduce the conductivity below that expected for $(CH)_x$ doped to a 12 mol% level. In the reversible hydrolysis reaction above, the positive charge has been depicted for simplicity as residing completely on one CH unit. However, it is believed that the charge is actually delocalized over approximately 15 CH units in what is termed a 'positive soliton'. This would stabilize the polycarbonium ion, $[(CH)^{y+}]_x$ towards nucleophilic attack and would reduce the extent of hydrolysis, particularly in acidic aqueous media.

Organic compounds can also act as oxidants for $(CH)_x$. Thus benzoquinone oxidizes $(CH)_x$ to 9.5 mol% ($y = 0.095$) in aqueous 7.4 M HBF_4 with a resulting metallic conductivity of *ca.* 130 ohm⁻¹ cm⁻¹,

$$2(CH)_x + (xy)\, O{=}(C_6H_4){=}O + 2(xy)\, HBF_4 \rightarrow 2[(CH)^{y+}\,(BF_4)_y^-]_x$$
$$+ (xy)\, HO{-}(C_6H_4){-}OH. \quad (22)$$

This reaction is consistent with the reduction potentials of couples 5 and 11 in table 2.

Until very recently it has been believed that prolonged exposure of $(CH)_x$ to O_2 or air results in the destruction of its conductivity and its conversion to an unknown mixture of compounds containing many carbonyl and other groups (Pochan *et al.* 1980; Pochan *et al.* 1981). However, studies have now shown that when gaseous oxygen is bubbled through a 48% (7.4 M) solution of aqueous HBF_4 in which pieces of $(CH)_x$ film are floating, the conductivity of the $(CH)_x$ increases from *ca.* $10^{-5}\,\Omega^{-1}$ cm⁻¹ to *ca.* $3\,\Omega^{-1}$ cm⁻¹. The reaction is consistent with the reduction potentials of couples 5 and 14 in table 2,

$$4(CH)_x + 4(xy)\, HBF_4 + (xy)\, O_2 \rightarrow 4[(CH)^{y+}\,(BF_4)_y^-]_x + 2(xy)\, H_2O. \quad (23)$$

The oxygen oxidizes the $(CH)_x$ to $[(CH)^{y+}]_x$ ($y \approx 0.02$), while the HBF_4 supplies the $(BF_4)^-$ counter-ion that makes the oxidized polymer electrically neutral.

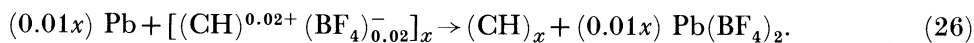If a piece of $[(CH)^{0.02+}\,(BF_4)_{0.02}^-]_x$ film and a strip of lead are placed in a 48% aqueous HBF_4 solution and are connected via an external wire, the lead dissolves with the liberation of electrons:

$$Pb \rightarrow Pb^{2+} + 2e^-. \quad (24)$$

The electrons flow through the wire and reduce the $[(CH)^{0.02+}]_x$ ion,

$$[(CH)^{0.02+}]_x + (0.02x)\, e^- \rightarrow (CH)_x, \quad (25)$$
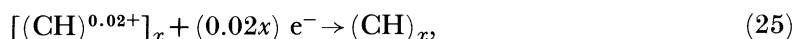
resulting in the net electrochemical reaction,

$$(0.01x)\ \text{Pb} + [(\text{CH})^{0.02+}(\text{BF}_4)^-_{0.02}]_x \rightarrow (\text{CH})_x + (0.01x)\ \text{Pb}(\text{BF}_4)_2. \tag{26}$$

These reactions are consistent with the reduction potential of couple 6 and with the reduction potentials of the polyacetylene couples in table 2.

If oxygen is constantly bubbled over the polyacetylene electrode it is possible to continuously chemically oxidize the polyacetylene to $[(\text{CH})^{0.02+}(\text{BF}_4)^-_{0.02}]_x$ as rapidly as it is reduced electrochemically according to (26), with the concomitant production of an electric current. Neither the chemical composition nor the total mass of the p-doped polyacetylene electrode changes during the reaction at steady state, i.e. the p-doped polyacetylene acts as a 'catalyst electrode', permitting the overall reaction expressed by (27) to take place:

$$\text{Pb} + \tfrac{1}{2}\text{O}_2 + 2\text{HBF}_4 \xrightarrow{(\text{CH})_x} \text{Pb}(\text{BF}_4)_2 + \text{H}_2\text{O}. \tag{27}$$
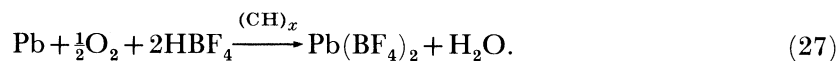
This reaction occurs only to a negligible extent in the absence of the $(\text{CH})_x$. When the oxygen stream is turned off the current stops; when it is turned on the current again flows as shown in figure 5. The top of the $(\text{CH})_x$ film ($1.1\ \text{cm}^2 \times 0.01\ \text{cm}$) was attached to a platinum wire clip covered with paraffin wax. At the conclusion of the experiment the film was severed from the clip by cutting through the wax and the film with a razor blade. As can be seen from figure 5, a negligible current was then observed when oxygen was bubbled over the current collector, thus showing that the observed effect was caused by the $(\text{CH})_x$ film. The polyacetylene is therefore acting as an electrocatalytic, 'fuel-cell type' electrode for the reduction of gaseous oxygen at room temperature and atmospheric pressure in an aqueous acidic medium.
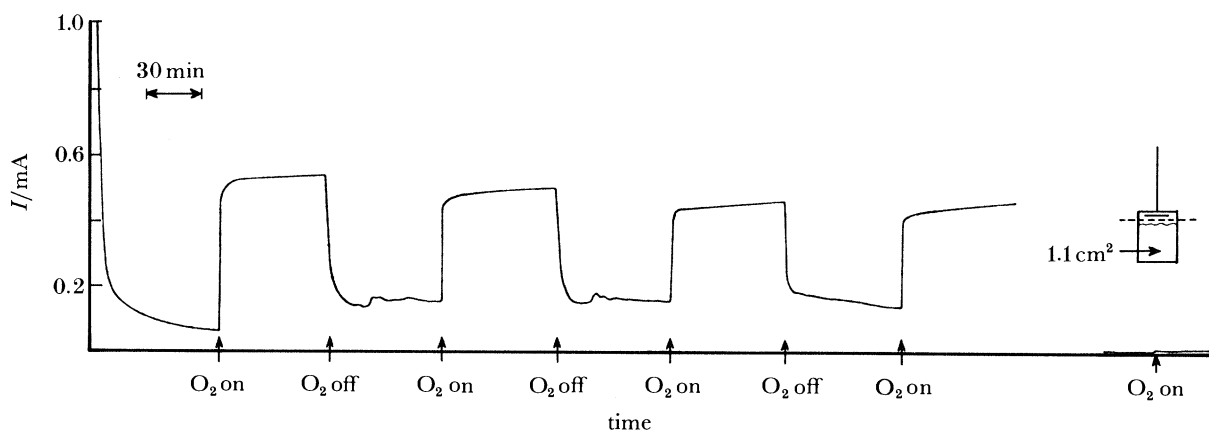

FIGURE 5. Change in current produced by a $\text{Pb}\,|\,\text{HBF}_{4(\text{aq})}\,|\,\text{O}_2\,|\,(\text{CH})_x$ cell when the oxygen stream bubbling over the $(\text{CH})_x$ electrode is turned on and off.

5. CONCLUSIONS

The above studies show that to understand the phenomenon of p- and n-doping of $(\text{CH})_x$ it is necessary to distinguish clearly 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, because the

values so obtained then permit the rationalization of known and the prediction of new dopants. Preliminary studies indicate that this approach can readily be applied to other conducting polymer systems.

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Discussion

R. Pethig (*School of Electronic Engineering Science, University College of North Wales, Bangor, U.K.*). Some of Professor MacDiarmid's doped samples exhibit conductivities of the order 10^3 mho cm^{-1}, and if we assume that the mobile charges are each spread over some 15 CH units, this implies an effective macroscopic charge carrier mobility of at least 2 cm^2 V^{-1} s^{-1}. This corresponds to a conduction mode on the borderline between a hopping-type and a band-type transport process. Could this imply that there is a very small barrier for charge transfer between polymer chains, and that inter-chain tunnelling or resonant transfer processes are possible?

A. J. HEEGER (*Institute for Polymers and Organic Solids, University of California, Santa Barbara, U.S.A.*). A more detailed analysis was presented by Park *et al.* (1980) with the conclusion that the mobility in the metallic state of doped $(CH)_x$ is in excess of $10\ cm^2\ V^{-1}\ s^{-1}$ and possibly as high as $60\ cm^2\ V^{-1}\ s^{-1}$. In my view, such high mobilities do indeed imply effective charge transfer between chains. Note, however, that at very dilute doping the infared mobility is orders of magnitude lower, which implies a major change in electronic structure at the semi-conductor–metal transition.

D. R. ROSSEINSKY (*Department of Chemistry, The University, Exeter, U.K.*). Spectroscopic and electrochemical estimates of the band gap in polyacetylenes are in close agreement, and it would be interesting to know how much the latter estimate depends on the electrolytes (ions and solvent) employed. Independence of solvent might imply zero solvent uptake by the polymer.

A. G. MACDIARMID. The measured reduction potentials of n-doped polyacetylene are indepen-dent (within experimental error) of the nature of the dopant cation, at least for $[Li_y^+\ (CH)^{y-}]_x$ and $[Na_y^+(CH)^{y-}]_x$, which have been examined in detail (Kaner *et al.* 1985). The effect of incorporating different dopant anions to give species such as $[(CH)^{y+}\ (ClO_4)_y^-]_x$ and $[(CH)^{y+}\ (PF_6)_y^-]_x$, although not yet examined in such great detail, appears to cause no significant change in the reduction potentials of p-doped polyacetylene. Similarly, different electrolytes, particularly those most commonly used, such as propylene carbonate (for oxidation) and tetrahydrofuran (for reduction), appear to have no significant effect on the reduction potentials measured. These observations therefore suggest that although the $(CH)_x$ fibrils swell during electrochemical p- or n-doping, effects related to solvation of the polycarbonium or polycarbanions so formed are not sufficient to modify significantly the potentials at which oxidation or reduction begins.