Effects of oxidation on I_2 doping of *trans*-polyacetylene as studied *via* e.s.r. and conductivity measurements

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Oxidation of *trans*-polyacetylene lowers the activation energy for conduction from 16 kcal mol^{-1} to 11 kcal mol^{-1} for oxidation levels of $(C_2H_2O_n)_x$, $n = 0.144$, 0.207 and 0.550. Maximum conductivity levels for $0 < x < 0.144$ doped with I_2 were almost identical. At long I_2 doping times all samples exhibited some loss of conductivity. E.s.r. experiments indicate that: (1) linewidth is directly proportional to oxygen content, and (2) iodine doping is not diffusion controlled. All data are consistent with a molecular picture of PAC consisting of highly reactive localized spin states that are selectively oxidized, and less reactive delocalized states that affect conductivity more strongly *via* doping.

Keywords Conductivity; oxidation; doping; electron spin resonance; polyacetylene

INTRODUCTION

The effect of oxygen on the dopable polymers such as polyacetylene (PAC)[1,2] and poly(1,6-heptadiyne)[3] (P-1,6) is extremely important, because oxygen is pervasive and effects the ultimate properties of these materials[4]. It can also effect the *cis/trans* ratio in PAC[5]. We have conducted experiments on PAC[1,6,7] which show that: (1) oxidative degradation can be monitored *via* conductivity experiments, (2) psuedo first order kinetics control this oxidation, (3) the oxidation has activation energies of 13 kcal mol^{-1} for *trans*-PAC and ~9 kcal mol^{-1} for samples containing *cis* material (30 to 70%) and, (4) a parallel crosslinked network can be used to describe the degradation process.

The effect of oxidation on the dopability of PAC was not addressed in this initial work. This issue could be of paramount importance in any practical application. It would be of interest to know what exposure to ambient conditions can be tolerated with desired dopability maintained. The following is the report of such a study. This study is distinct from our previous reports which described the change in conductivity in an oxygen atmosphere. Samples in the present study were exposed to oxygen, then vacuum pumped, thus eliminating the effects of sorbed oxygen. Furthermore, the initially formed oxygen adducts, presumed to be peroxy radicals generated *via* triplet oxygen in the absence of ultraviolet light, have been given sufficient time for conversion to carbonyl and hydroxyl functionalities.

The present paper will describe four experiments. First, the effect of oxidation upon the undoped conductivity and its activation energy will be described. It will be shown that low levels (<15%) of oxidation enhance the conductivity when measured shortly after oxidation, while heavy oxidation reduces the conductivity. Exposure to oxygen also lowers the activation energy for conduction. Second, the effect of oxidation upon e.s.r. linewidth will be examined, with the result that linewidth is directly proportional to extent of oxidation. Third, iodine doping of lightly (<15%) oxidized polyacetylene will be shown to yield almost the same ultimate conductivity as unoxidized polyacetylene. Fourth, *in situ* doping of oxidized polyacetylene in the e.s.r. spectrometer will be described. The spin population shows a very rapid initial decrease, followed by a slower pseudo first order behaviour. This is taken as evidence that the doping is not diffusion controlled.

EXPERIMENTAL

Samples of polyacetylene were synthesized in the standard way[8]. The samples were washed repeatedly with toluene and stored and handled in an oxygen free environment (⩽0.8 PPM) either at room temperature or 195K. *Trans* samples were made by heating in vacuum 98 min at 473K. The infra-red spectrum showed the sample to be greater than 98% *trans*. Oxidation of the sample was carried out during a combined oxidation/conductivity experiment in the absence of ultraviolet light at 364K with samples thermally equilibrated in flowing argon and then exposed to pure thermally equilibrated flowing oxygen. The current–time relationship for the experiment is shown in *Figure 1*. Samples were chosen for oxygen exposure at $t = 0$, at the current maximum, at a time so that the current level approximates the initial current and at a time when the sample appeared completely oxidized in terms of the conductivity measurement. The samples were then evacuated (10^{-5} mm Hg-24h) and stored for further measurement and portions sent for elemental analysis. The compositions obtained are shown in *Table 1*.

Portions of each sample were sealed in an evacuated e.s.r. tube (10^{-5} mm Hg ~15h) and joined *via* a break seal to an evacuated tube (10^{-4} mm Hg at 195K) containing I_2 crystals. For conductivity measurements, two platinum

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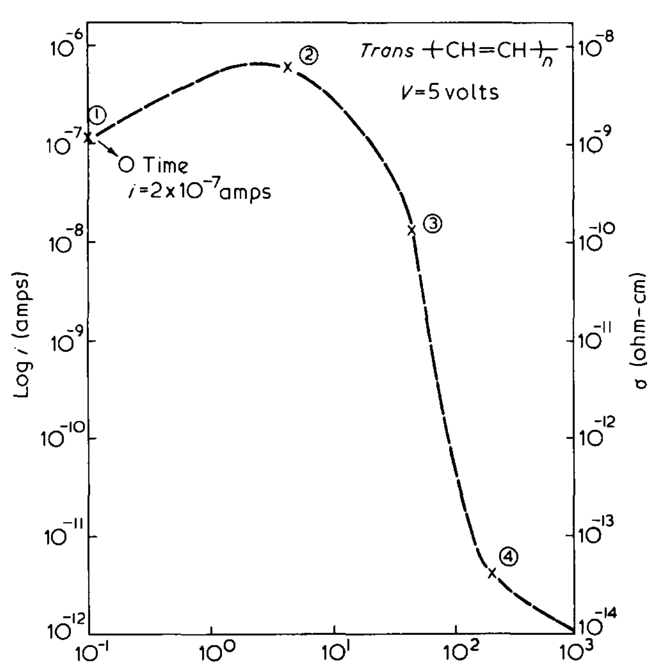

Figure 1 Conductivity-time relationship for exposure of polyacetylene to oxygen at 364K. Samples 1–4 correspond to the points marked (X)

wires were attached with Electrodag^R to the sample 8 to 10 mm apart. Current was monitored as a function of time at constant applied voltage ($E = 0.002$ V/μ). Ohmic response was observed with fields up to an order of magnitude larger.

Doping experiments were conducted at room temperature by breaking the glass seal separating the I_2 crystals from the sample. During the doping process the Q factor of the e.s.r. cavity changed with the initial addition of I_2; however, the amplitude of a reference nitroxide free radical did not change after an initial change of 10–15%. I_2 was not the cause of this initial change as doping of other less conductive materials did not affect the Q of the cavity.

E.s.r. measurements were conducted in a Varian E 109 spectrometer operating at a frequency of 9.6 gHz and power levels of 1 to 10 mW. A power study indicated no saturation effects of the e.s.r. signal at these power levels.

Conductivity-temperature data were obtained by connecting the sample with pressure contacts[1] in series with a Keithley regulated voltage supply and a Keithley 616 Electrometer. A constant voltage was applied and current was monitored as a function of temperature. Temperature control was achieved with a Delta Design Environmental Oven (accuracy ±1°C) scan rate: 1°/min. Temperature was monitored with copper-constantin thermocouple mounted within 1 cm of the sample.

RESULTS AND DISCUSSION

Conductivity of oxidized samples

Results of conductivity measurements on *trans*-PAC and the oxidized samples (*Figure 2*) show: (1) two thermally activated regions with a transition between them in the 250–270K range and (2) increased conductivity at low oxygen content [$(C_2H_2O_{0.144})_x$ vs. $(C_2H_2)_x$] and decreased conductivity at high oxygen content [$(C_2H_2O_{0.207})_x$ and $(C_2H_2O_{0.550})_x$ vs. $(C_2H_2)_x$] as previously reported[1].

In the high temperature region ($T > 270$K) unoxidized *trans*-PAC exhibits an E_a [calculated from $i = i_0 \exp(E_a/kT)$ of 16 kcal mol^{-1} (0.7 eV). This value is higher than those normally reported for *trans*-PAC[10] and may the result of two effects: (1) a lower impurity content than in previous samples and (2) a longer annealing time than that needed to obtain maximum conductivity in the sample[11]. The low temperature regime yields a lower activation of ~9 kcal mol^{-1}. These two temperature regions of conductivity have not been discussed previously, although there is some evidence in the literature that a change is taking place in 'pristine' PAC in this temperature region[12,13].

When oxygen, which is a weak electron acceptor, is added to the sample the activation energy decreases to 11 kcal mol^{-1} (0.5 eV). This decrease is expected with doping but persists even for oxygen contents as high as 0.55. Thus, the effect of oxidation is to lower the activation energy and to ultimately decrease conductivity to

Table 1 Elemental analysis of oxidized *trans* polyacetylene $(C_2H_2O_n)_x$

Sample number	n
1	0.0
2	0.144
3	0.207
4	0.550

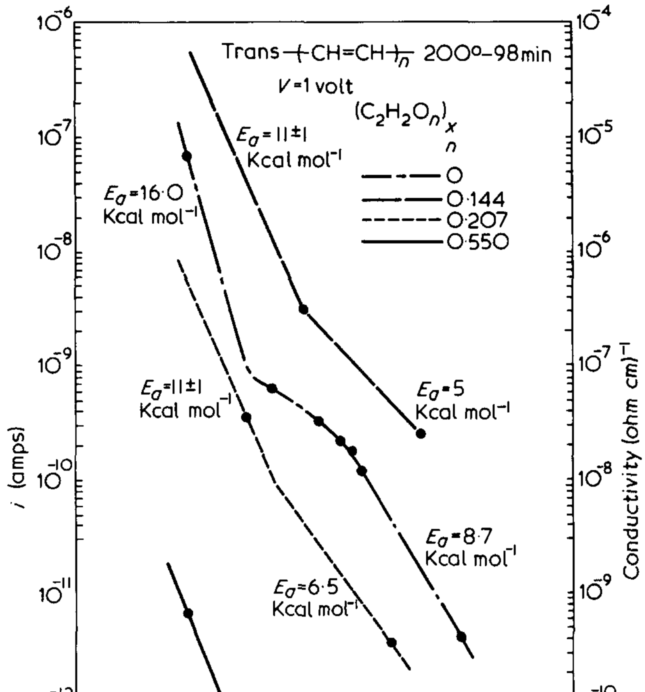

Figure 2 Log i or conductivity *versus* inverse temperature for unoxidized *trans*-PAC and various levels of oxidation. Note: Data taken continuously during these experiments

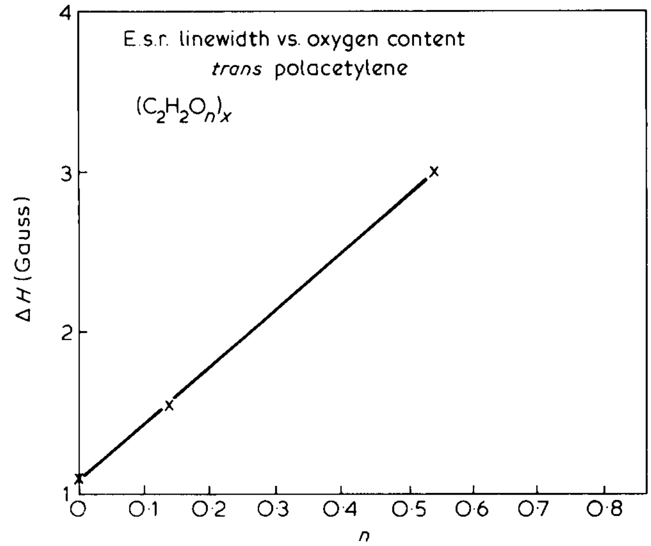

Figure 3 E.s.r. linewidth *versus* oxygen content for oxidized *trans* polyacetylene. Power level = 8 mW

insulating-type values. This is to be expected since oxidation to carbonyl and hydroperoxide moieties has been observed[1,2]. The fact that the activation energy does not change in the high temperature regime with increased oxidation is puzzling. At a level of 1 oxygen atom for every other double bond it might be expected that the physics of transport would be affected. These experiments indicate that either the mobility and/or the number of charge carriers is being affected, but that the transport barriers are not. These results are not unlike those for CF_3SO_3H doping of PAC which produces a constant activation for doping levels $(C_2H_2X_y)_x y \geqslant 0.02$.[14] These results lend credence to the parallel resistance model used to describe conductivity and oxidation in this system[1].

Effect of oxidation upon e.s.r. spectra

Oxidation of the *trans*-PAC causes an increase in e.s.r. linewidth as shown in *Figure 3*. Oxidation to a level $n = 0.55$ increases the line width by a factor of three. The results are similar to those of Goldberg *et al.*[15]. The data indicate a linear relationship between the mol fraction oxygen incorporated into the system and the e.s.r. linewidth (ΔH). This linear observation is in agreement with Holczer and co-workers[16], who postulate the linewidth to be a function of diffusive spin populations with narrow ΔH (~ 0.2G) and localized spins with large ΔH (5–10G) but dominated by the localized spins. In fact, they postulate that ΔH would be a rough indication of the oxygen content of these samples. Our evidence bears this out and suggests that localized oxygen based radicals (perhaps peroxy radicals) are involved[17].

I_2 doping of oxidized PAC

Conductivity. Results for I_2 doping of the samples are shown in *Figure 4*. Although there is some variation in the unoxidized samples, all the samples show a sigmoidal shape in the log–log representation. The curves shift to longer times with increasing degree of oxidation. With 14.4 mol percent of the double bonds in PAC affected by oxygen, I_2 doping produces conductivity levels within a half order of magnitude of the unoxidized PAC. A rather large degree of oxidation can thus take place with little effect on the ultimate conductivity derived *via* I_2 doping. At higher oxidation levels doping still increases conductivity but to lower ultimate values.

In comparing *Figures 2* and *4* it is seen that the starting conductivities for the $n = 0.144$ sample are quite different. The current–temperature experiments were run immediately after the samples were made and the doping experiments two weeks later. It appears that during that time further degradation has taken place. This could possibly be due to conversion of peroxy radicals to carbonyl and hydroxyl functionalities[17,18].

At very long times, the samples exhibit a maximum in the conductivity and begin showing decreases. Such a maximum could be either the result of iodination chemistry causing loss of conjugation[18] or reaction of the contacting paste with iodine, decreasing its conductivity. We favour the chemical addition of I_2 to the conducting material because reaction of the contacting paste should have the same time dependence for all samples studied, contrary to the observed time dependence. A normalized conductivity vs. time plot of the data in *Figure 4* beyond the maximum is shown in *Figure 5*. In the pure PAC material it is obvious that the data is described by single time constant (2×10^6 s), indicating that psuedo first order kinetics are controlling the conductivity in this time regime. Other samples show similar pseudo first order behaviour with rate constants decreasing with increasing levels of oxidation.

E.s.r. Iodine addition initially reduces line intensity of these samples very quickly (too quickly to be measured), as shown in *Figure 6*, and has only a slight effect on the linewidth except at very long times where ΔH increases slightly. These oxidized samples have been vacuum evacuated prior to these experiments and, as such, would exhibit a narrower linewidth that samples in an oxygen containing environment[15].

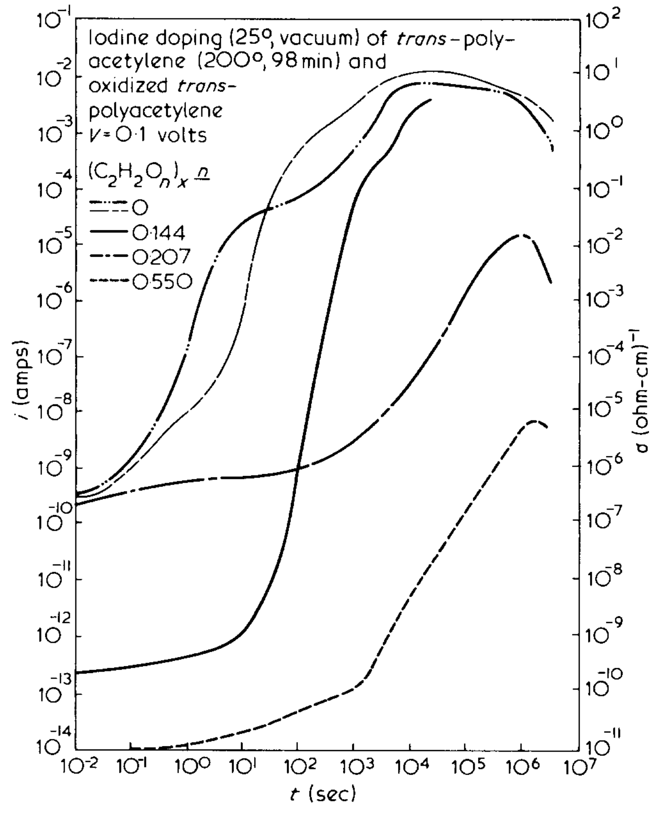

Figure 4 Log current *versus* log exposure time to I_2 vapour at 293K for various oxidized samples of *trans* PAC

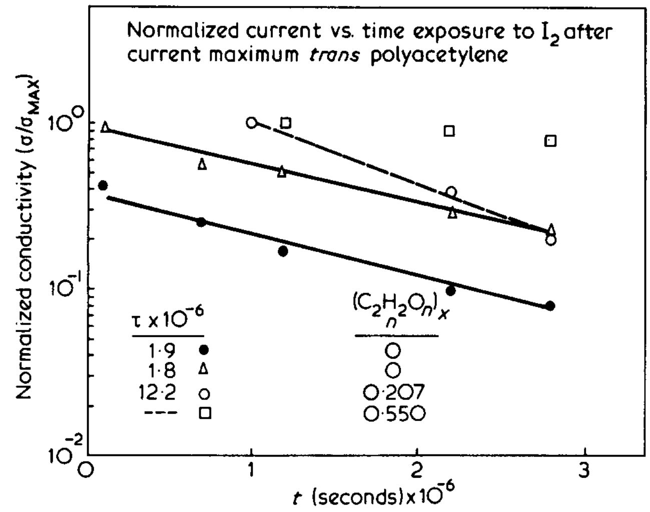

Figure 5 Log current *versus* exposure time to I_2 vapour at 293K for various oxidized samples of *trans* PAC

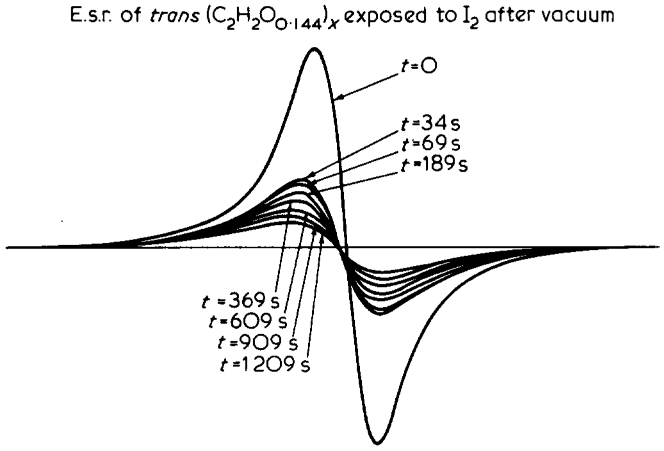

Figure 6 E.s.r. signal for a partially oxidized *trans*-PAC sample as a function of time after I_2 exposure at room temperature

The e.s.r. data can be analysed in two ways as shown in *Figure 7*. Peak intensity obtained *via* double integration is plotted *versus* exposure time and peak height is also plotted *versus* exposure time. Both methods yield single linear time plots over the time frame of observation after an initial sharp decrease in signal. The calculated time constants agree within a factor of two. The peak height method of analysis probably introduces less error (due to detuning of the spectrometer during initial doping).

Peak height data for all samples is shown in *Figure 8*. Three effects are discerned from the data: (1) After a rapid initial drop in signal, which is ~50% in all samples except the most highly oxidized, the signals exhibit simple first order decay, (2) The decay time increases with oxidation, and (3) There is no abrupt change in the highly oxidized sample when iodine is introduced.

RATIONALIZATION OF RESULTS

The state of the free radicals in the *trans*-PAC samples prior to and after oxidation can be used to explain the observed data. In general, the PAC sample is made up of delocalized and localized free radicals. Holczer and coworkers[16] have deduced this from magnetic resonance and e.s.r. measurements. The localized spins are most likely in a higher energy state than their delocalized counterparts. These different energy states could be nothing more than variations in conjugation length. Since oxidation will most likely occur *via* triplet oxygen insertion at free radical positions[1,3,15,19], these higher energy (less stable) localized spins will oxidize more readily than the delocalized spins and, hence, the greater the extent of oxidation the less the population of localized polyene free radical states. Since the rate of removal of spins by dopants such as iodine is dependent upon their energy, the more highly oxidized PAC samples should dope more slowly (*Figure 4*). The data in *Figure 8* can also be explained with such a model. The lower levels of oxidation (n=0.144 and 0.207) do not remove all the localized spins and addition of I_2 (a stronger electron acceptor than O_2) causes the less stable spin states to react, quickly reducing the e.s.r. population. The more delocalized spins react with the I_2 on a much longer time scale. The more highly conjugated, lower energy states affect the ultimate conductivity to a greater extent than the less conjugated, higher energy states. Therefore, it

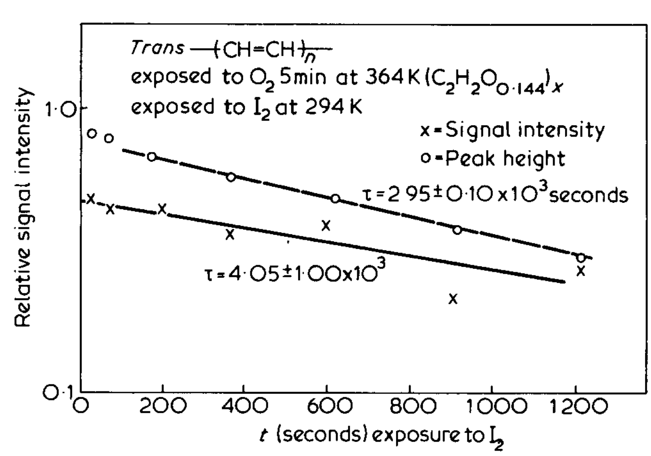

Figure 7 E.s.r. signal intensity and peak height for $(C_2H_2O_{0.144})_x$ sample *versus* exposure time to iodine vapour after vacuum treatment

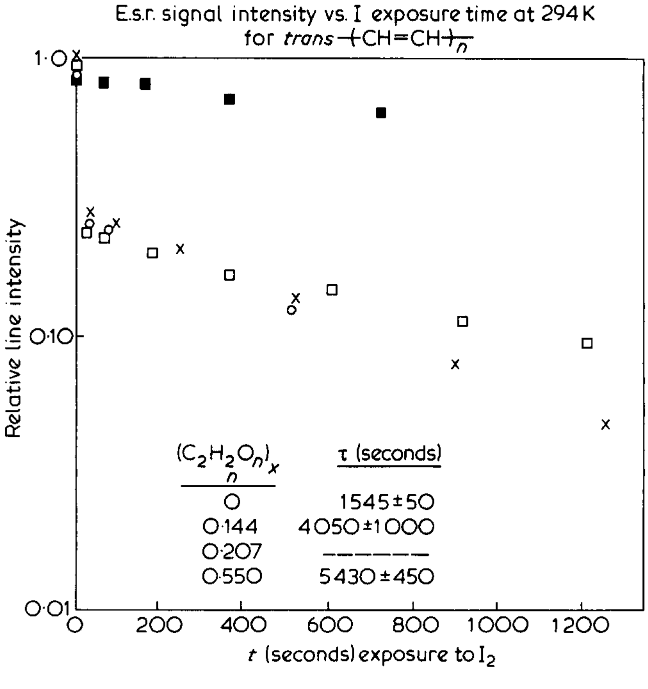

Figure 8 E.s.r. line intensity for PAC with various oxidation levels *versus* exposure time to I_2 vapour

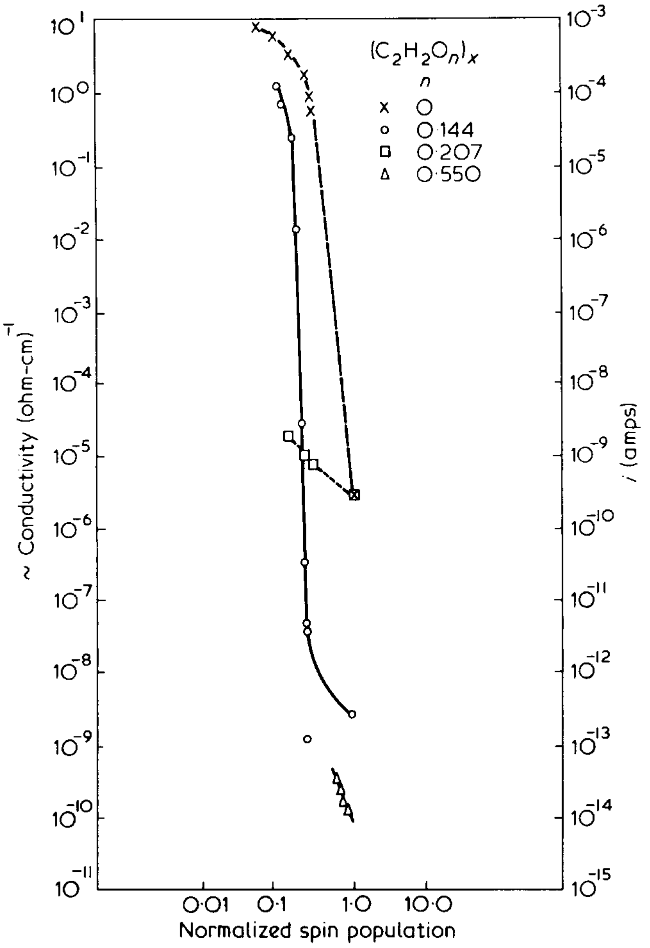

Figure 9 Conductivity *versus* normalized e.s.r. spin population of *in situ* iodine doped *trans*-polyacetylene (200°–98 min) and oxidized *trans* polyacetylene

might be expected that the $n = 0.144$ sample would dope to a level nearly identical with the unoxidized PAC, because the higher energy, more localized spins are removed during the earlier stages of oxidation.

The first order rate of the disappearance of e.s.r. signal with doping provides some insight into what is physically and chemically happening to the system. The first step of the reaction is probably that of equation 1.

$$\overset{\bullet}{\text{Polymer}} + I_2 \xrightarrow{k_1} \overset{+}{\text{Polymer}} + \overset{\bullet}{I_2}{}^{-} \qquad (1)$$

where k_1 is the rate constant for the abstraction of an electron associated with a free radical. This free radical position may be the so called neutral soliton position of the polymer and electron transfer to I_2 would produce the charged soliton. $\overset{\bullet}{I_2}{}^{-}$ may then undergo sugsequent conversion to I_3^- and I_5^-. If k_1 were large so that the kinetics of this reaction did not limit the rate of the e.s.r. signal loss, the diffusion of I_2 into the system would be rate limiting. Such a system (diffusion plus reaction) has been theoretically addressed for a different geometry than the fibrils of PAC and it has been shown that the number of moles of diffusant sorbed is linearly related to time[20,21]. In such a case the decay rate of the e.s.r. signal should also be related directly to time. The fact that it is not is an indication that the observed process is not limited by the diffusion of I_2 into PAC, but by the kinetics of I_2 reacting with polymer free radical. The result is plausible in terms of the delocalized nature of a portion of the spin population and in the case of the localized spins the need for proper overlap, or orientation of the free radical species to cause charge exchange[22,23]. Moreover, the loss of ~90% of the spins during doping is relevant to arguments concerning the homogeneity of doping. This result suggests either that the iodine diffuses rapidly through the fibrils as argued above or that the spins are mobile enough to diffuse to the surface of the fibrils where they react with the iodine. The latter possibility is considered unlikely in view of the breadth of the e.s.r. lines.

The data of *Figures 4* and *7* have been cross-plotted in *Figure* 9 to show the correlation of conductivity and relative e.s.r. population for the various PAC samples. The pure *trans*-PAC and partially oxidized *trans*-PAC $(C_2H_2O_{0.144})_x$ indicate almost complete doping with only an order of magnitude decrease in spin population. The implication of this result is that the formation of $\sim 10^{18}$ charged soliton states per gram in the *trans*-PAC is sufficient to cause the semi-conductor to metal transition in the polymer.

CONCLUSION

The effect of I_2 doping of preoxidized *trans*-polyacetylene has been investigated *via* e.s.r. and conductivity measurements. It has been shown that oxidation lowers the activation energy for conduction from 16 kcal mol^{-1} (pure *trans*-PAC) to 11 kcal mol^{-1} for oxidation levels of $(C_2H_2O_n)_x$, $n = 0.144$, 0.207 and 0.550. Conductivity levels for $n = 0$ to $n \leqslant 0.144$ doped with I_2 exhibited almost identical maximum values. At long I_2 doping times all samples exhibited degradation, leading to a lowering of conductivity. E.s.r. experiments indicate: (1) that iodine doping is not diffusion controlled and (2) that linewidth is directly proportional to oxygen content. Furthermore, all data are consistent with a molecular picture of PAC consisting of highly reactive localized spin states that are selectively oxidized and less reactive delocalized states that affect conductivity more strongly *via* doping.

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