Kinetics of oxygen doping and oxidation of poly(1,6-heptadiyne), a conducting polyene

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The oxidative stability of poly(1,6-heptadiyne) (a free-standing dopable polyene) has been studied via conductivity measurements. A kinetic model of degradation has been applied to the results and it has been shown that the degradation is first order with an activation energy of $\sim$13 kcal mol^{-1}. It is also shown that solvent wash during polymerization affects degradation rate but not activation energy. Simultaneous oxygen uptake–conductivity experiments are also described. The effect of light on degradation rates is presented. Results of these experiments are compared with earlier work on polyacetylene.

INTRODUCTION

Polymers such as polyacetylene[1-3] and poly(1,6-heptadiyne)[4,5] have received a great deal of scientific interest because of their ability to be doped to highly conductive levels. Unfortunately, these materials are not oxidatively or hydrolytically stable and decompose with concomitant loss of electrical conductivity. We have undertaken a systematic study of the effects of oxygen on these two polyene systems in order to understand the chemistry and the salient molecular features which control their chemistry. In a recent publication it was shown that the oxidative degradation of $(\text{–CH}=\text{CH–})_n$ can be kinetically modelled via a conductivity experiment[6]. This model provided information concerning the kinetic barriers to oxidation as well as the effect of *cis/trans* ratio of $(\text{–CH}=\text{CH–})_n$ on these barriers. Recently we reported the synthesis of poly(1,6-heptadiyne)[4,5], (P-1,6), a derivative of $(\text{–CH}=\text{CH–})_n$ whose structure is shown in *Figure 1*. Here, we report on the oxidative stability of P-1,6 as determined via conductivity measurements and compare our results with those for $(\text{–CH}=\text{CH–})_n$.

EXPERIMENTAL

P-1,6 was synthesized via Ziegler–Natta catalysis[4,5]. After synthesis, samples were washed repeatedly in an oxygen-free environment with either toluene, benzene, or pentane until no colour was extracted from the sample. The free-standing films were then stored in oxygen-free ($\leqslant$0.8 ppm) argon until use.

Conductivity measurements were carried out by the two electrode method with either brass or stainless steel pressure contacts which have been shown to provide ohmic contacts[6,7]. Transfer of P-1,6 samples to a stainless steel cell with ports to permit circulation of gasses was accomplished in an oxygen-free environment ($\leqslant$0.8 ppm). The cell was transferred to a Delta Design environmental oven and argon flow was initiated. The cell was then thermally equilibrated with flowing argon. Voltage was applied and current measured with a Keithley 616 digital electrometer. After thermal equilibration, pure oxygen was introduced to the flow system and current monitored as a function of time. The gases used in these experiments were circulated in the environmental oven prior to cell entry to ensure thermal equilibrium. With the exception of one experiment, all experiments were conducted in the dark to ensure triplet oxygen interaction with the polyene[8].

Additional experiments to monitor conductivity and oxygen uptake were done by replacing the stainless steel cell with a glass vacuum system with electrical feed-through to monitor current as described above. A known pressure of oxygen was introduced into the cell and current and pressure monitored simultaneously. As oxygen is absorbed, the pressure drops and the number of sorbed moles can be calculated via the ideal gas law. Pressure in this system was monitored with an MKS Instruments Inc. Baratron with a 0–1000 torr pressure head. Change in pressure during the sorption experiment was less than 1%, thus minimizing the effects of pressure changes upon sorption and diffusion. Additional weight uptake experiments by direct weight measurement on a Cahn balance in air were also undertaken.

RESULTS AND DISCUSSION

Effects of oxygen–kinetic model

An example of a typical current-time relationship for P-1,6 exposed to pure oxygen is shown in *Figure 2*. It is seen that upon initial exposure to oxygen, the current level increases, indicating doping of the material. At longer times, however, the current drops precipitously until it can no longer be measured. In our oxidative study on $(\text{–CH}=\text{CH–})_n$ such behaviour was modelled as a consecutive reaction sequence and a simple parallel series

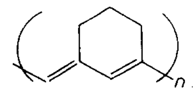

Figure 1 **Structure of poly(1,6-heptadiyne)**

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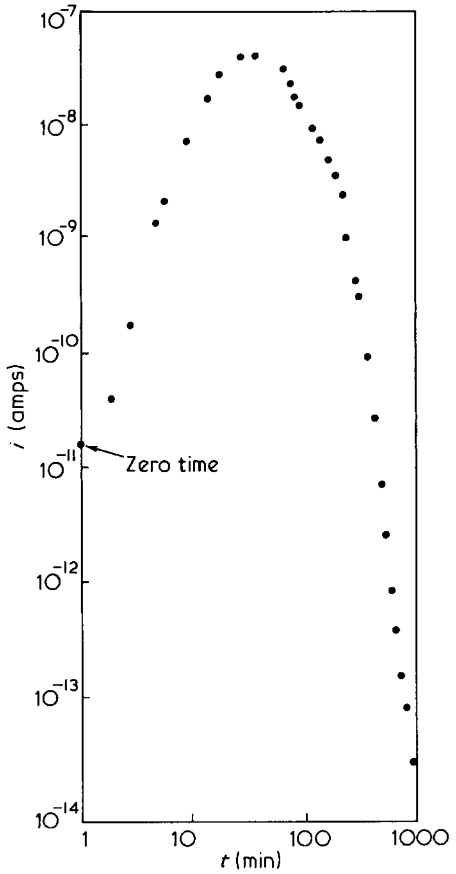


Figure 2 Log (current at 100 volts) ***versus*** log (exposure time to pure oxygen) for a P-1,6 sample at 279.2K. Note the equivalent conductivity for this system at 10^{-9} amps is 10^{-11} (ohm cm)$^{-1}$

resistance model[9]. Equation (1) demonstrates the rate equation as applied to P-1,6:

$$\text{P-1,6}+0_2\xrightarrow{k_1}[\text{P-1,6}/0_2]\xrightarrow{k_2}\text{Products} \qquad (1)$$

where k_1 and k_2 represent the rate constants for the reaction of P-1,6 with oxygen to form a conducting complex and the degradation of the complex to insulative products, respectively. In the case where $k_1 \gg k_2$, i.e. the concentration of conductive complex reaches a maximum prior to any significant degradation, the second step of equation (1) reduces to a first order rate equation whose solution is:

$$[\mathrm{C}]=[\mathrm{C}]_0e^{-t/\tau} \qquad (2)$$

where the bracketed terms [C] and $[\mathrm{C}]_0$ are the concentration of complexed species at any time and the time at which the complex reaches a maximum, respectively. Further, a parallel resistance model is used to describe the observed data:

$$\frac{1}{R_T}=\frac{X_u}{R_u}+\frac{X_c}{R_c}+\frac{X_{Pr}}{R_{Pr}} \qquad (3)$$

where the Xs are the molar average concentrations of the uncomplexed polymer (u), the complexed polymer (c) and the oxidative reactant products (Pr) and the Rs are the respective resistances of these components. From data such as those shown in *Figure 2*, $R_c \ll R_{Pr}$ and at least two orders of magnitude smaller than R_u and therefore once oxygen is introduced to the polymer, the term X_c/R_c in equation (3) is dominant. Since these experiments measure current, equation (3) can be rewritten:

$$i=\frac{V}{R}=\frac{VX_c}{R_c} \qquad (4)$$

Equation (4) can be written:

$$i=\frac{VX_c}{R_c}\sim\frac{V}{R_c}[\mathrm{C}]_0e^{-t/\tau} \qquad (5)$$

which predicts that a plot of log *i versus* time will be linear if the oxidative product is the result of a first order decay of the P-1,6/0_2 complex.

A plot of log (normalized current) (taken continuously) *versus* exposure time to oxygen for a given P-1,6 sample is shown in *Figure 3*. Three temperatures are indicated in the Figure. It is seen that all plots are linear, verifying the first order hypothesis and that rate increases with increasing temperature. A plot of log (rate) (the linear slopes of *Figure 3*) *versus* inverse temperature is shown in *Figure 4* for samples washed with toluene or pentane. It is seen that all pentane-washed samples exhibit Arrhenius behaviour with an activation energy of ~13 kcal mol^{-1}. The toluene-washed samples appear to be randomly scattered at lower rates than those observed for the pentane-washed materials. These differences can now be resolved.

Pentane versus *toluene wash*

Like polyacetylene, P-1,6 can exist in two isomeric forms, at least for the double bonds exo to the six-

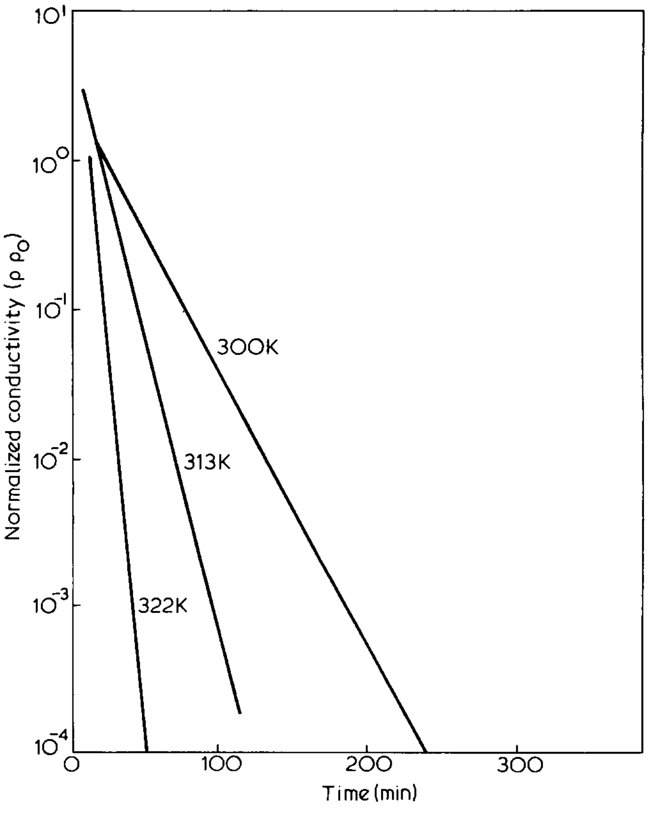


Figure 3 Log (current at 10 volts) ***versus*** exposure time to pure oxygen for a toluene-washed P-1,6 sample at various temperatures

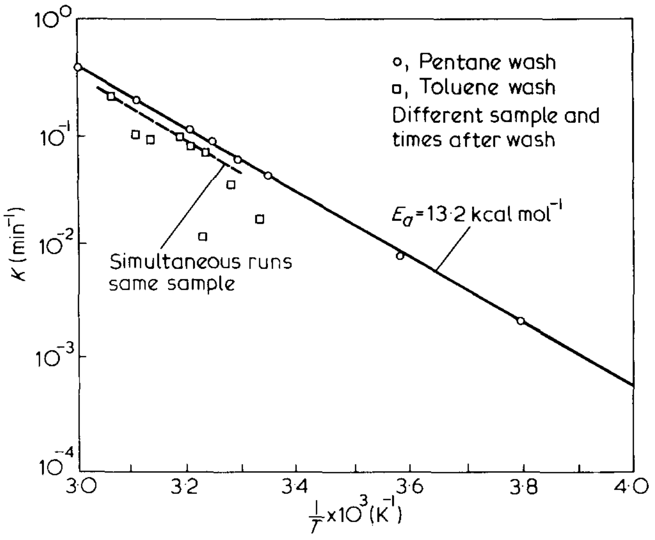


Figure 4 Log (rate) *versus* inverse temperature for samples of P-1,6 washed with pentane or toluene

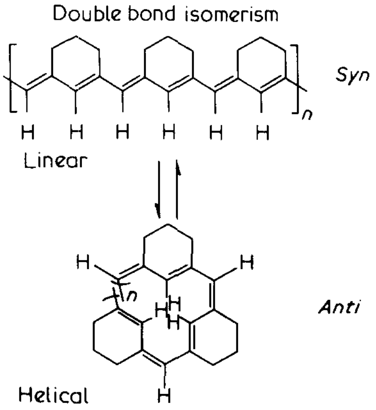
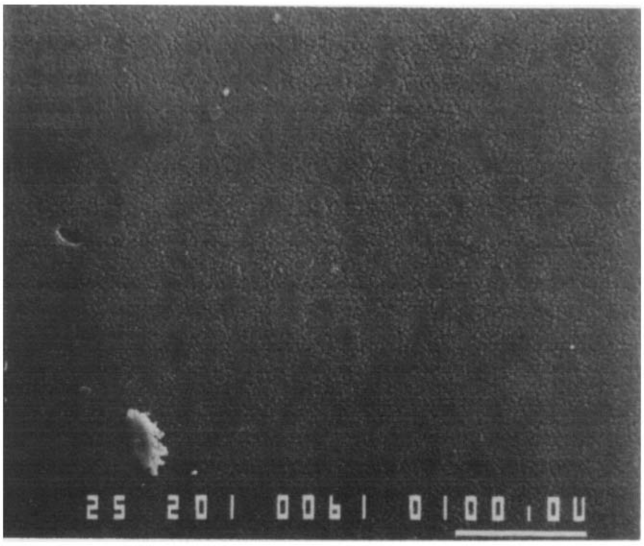


Figure 5 Proposed *syn* and *anti* structures of P-1,6

membered ring. These structures are the *syn* and the *anti* forms as shown in *Figure 5*. With all *syn* configurations of the double bonds exo to the ring, the polymer takes on a helical type configuration due to steric interference of the rings. The *anti* configuration allows the polymer to assume a nearly planar extended-chain structure. We believe that the reported exotherm observed for P-1,6[4] at ~380K is the *syn*→*anti* conversion. This exothermic process is a function of solvent wash. Pentane-washed samples exhibit a much larger exotherm than their toluene-washed counterparts. Furthermore, washing with toluene or benzene removes additional material from pentane-washed polymer. This is readily seen in *Figure 6*, a scanning electron micrograph of a P-1,6 film first washed with pentane and subsequently with benzene. It is seen that additional material is removed during the secondary wash. These data indicate that the aromatic solvents are probably better solvents for the polymer and remove more low molecular weight polymer. Based on this and the observed rate constants, it can be argued that the insoluble portion (higher molecular weight analogues?) are more stable to oxidation. Note is also made that thermal conversion of the material at 400K had little effect on the degradation rates.

Also shown in *Figure 4* is a curve for toluene-washed film at slightly lower absolute rates than the pentane-washed sample, but with an identical activation energy. These experiments, run consecutively with little time between them, indicate that the oxidative process in benzene- or toluene-washed material is identical to that for pentane-washed samples, but that the absolute rate is lower. We have noted that a toluene-washed sample that initially provides a much lower rate of oxidation than a



Pentane wash

Monomer temperature=47°±2°C
Reactor temperature=20°±1°C
Identical catalyst

Benzene wash

Figure 6 Scanning electron micrograph of a P-1,6 sample initially washed with pentane and subsequently washed with benzene. Bars are 1 μm markers

Table 1 Activation energy for oxidation

Sample	E_a (kcal mol^{-1})
Poly(1,6-heptadiyne)	13.2 ± 0.2
~98% *Trans* $(-CH{=}CH-)_n$	13.8 ± 1.1
60% *Trans* $(-CH{=}CH-)_n$	9.4 ± 1.4
30% *Trans* $(-CH{=}CH-)_n$	10.4 ± 1.4

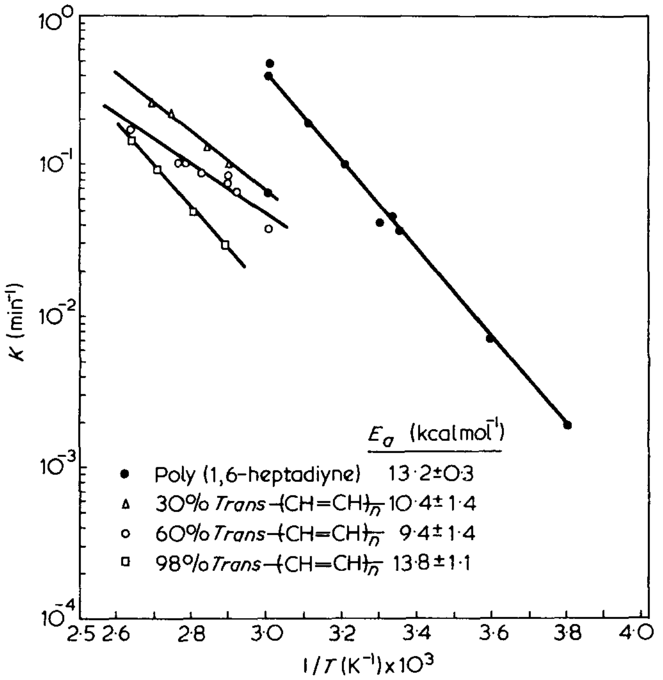


Figure 7 Log (rate) *versus* inverse temperature for pentane-washed P-1,6 (●), *trans* (–CH=CH–)$_n$ (□), 60% *trans* (–CH=CH–)$_n$ (▵), and 30% *trans* (–CH=CH–)$_n$ (▵)

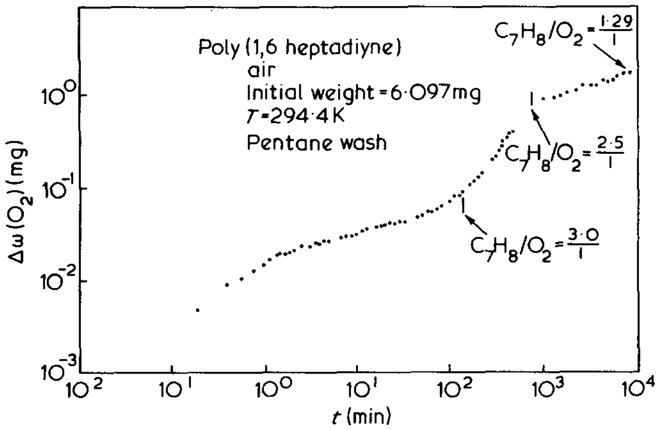


Figure 8 Log(moles uptake oxygen) *versus* log (exposure time) for a pentane-washed P-1,6 sample exposed to 200 torr oxygen at 324K

pentane-washed sample will slowly change and approach the reaction rates of the pentane-washed material. Based on this observation and the difference in solubility described above, it can be speculated that after toluene wash the polymer slowly changes *Mw* or structure and approaches that originally attained with pentane wash. This is supported by the fact that a sample rigorously washed with toluene upon standing for a week or two yields a coloured extract with toluene. Since the activation energy observed for both wash solvents is identical, the chemistry occurring during reaction must be identical; only the relative amounts of reactive species differ. A comparison of the degradation rate constants for P(1,6) and various *cis*/*trans* ratios of polyacetylene is shown in *Figure 7*.

Simultaneous oxygen uptake—conductivity experiments

Oxygen uptake experiments were carried out simultaneously with conductivity measurements as described above and with a Cahn balance in air. The results of these two types of experiments on pentane-washed samples are shown in *Figures 8* and *9*. Both experiments provide similar data: an initial slowly rising uptake, an intermediate region with a slope of one and a levelling region at long times. In *Figure 9* it is seen that the oxidation is proceeding to a polymer repeat unit–oxygen ratio of one, indicating that there is enough oxygen present for oxidation of every double bond (see below). If the data in *Figure 9* are plotted on a linear scale, the result is *Figure 10*. It is interesting to note that the shaded area of the insert of the Figure coincides with the observed doping of the sample, i.e. this area corresponds only to the increasing current portion of the *i–t* curves. Above approximately 150 min, conductivity begins to drop.

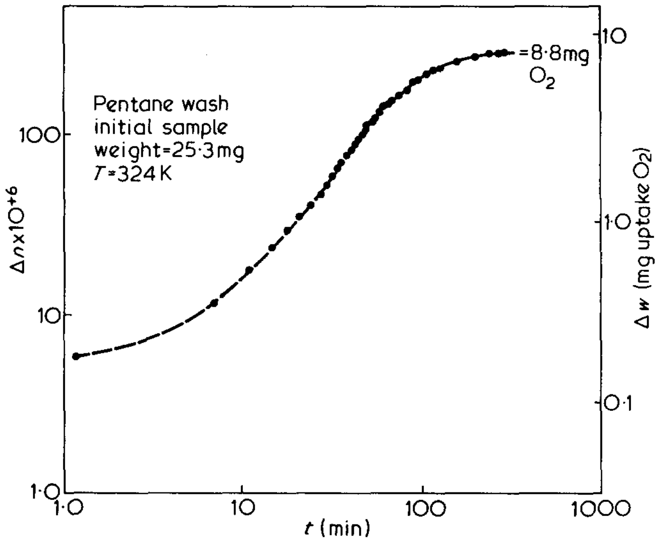


Figure 9 Log (weight uptake oxygen) *versus* log (exposure time) for a P-1,6 pentane-washed sample exposure to air, T = 294.4K. P (1,6) monomer to O$_2$ ratio shown on Figure

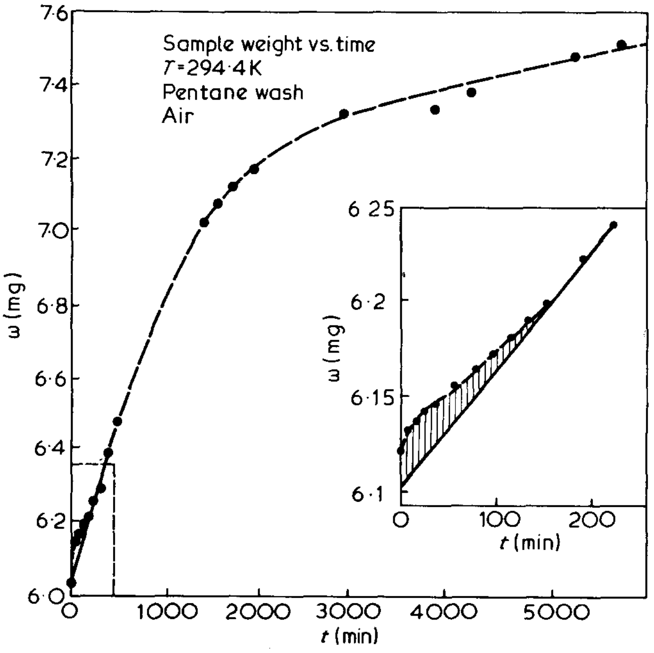


Figure 10 Weight *versus* exposure time to air for a pentane washed sample of P-1,6

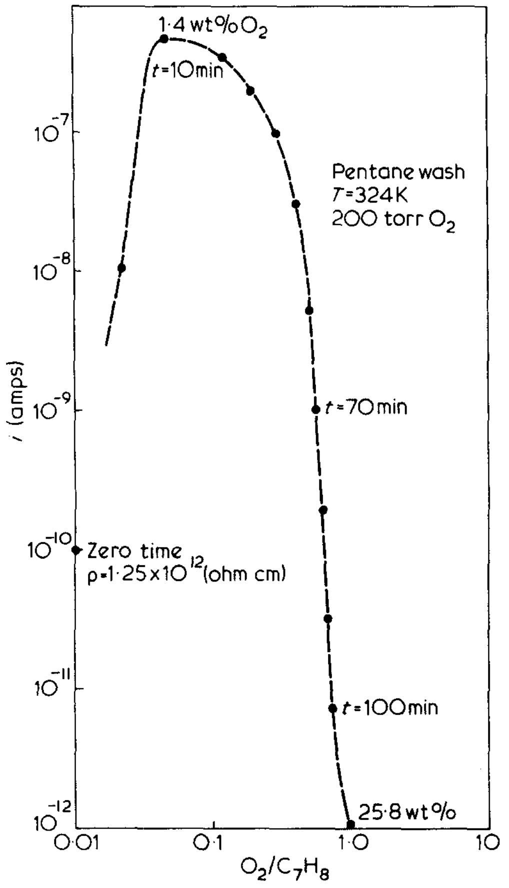


Figure 11 Log (current) ***versus*** log (oxygen—P-1,6 monomer ratio) for exposure to 200 torr oxygen, V = 100 volts

Simultaneous current (conductivity): O_2/C_7H_8 ratio data at 324K are shown in *Figure 11*. The maximum in the curve occurs at 1.4 wt% oxygen at a molar ratio of 0.07. This is obseved after 10 min exposure at 324K. In a time slightly greater than 200 min, the sample contains enough oxygen to oxidize every double bond. The results are replotted on a linear scale in *Figure 12* and indicate that at a molar ratio of approximately 0.5, conductivity is only slightly affected. Beyond this sorption ratio, however, the conductivity drops precipitously. By comparing these data with a current–time relationship for oxidation, it is found that the parallel resistance model describes the observed results quite well in the 0.5 to 1.0 molar ratio range. The results further illustrate the necessity for exclusion of oxygen from this material as exposure to oxygen not only causes doping but also caused degradation. In the 10 to 30 min exposure range there is only a slight effect on conductivity and yet the molar ratio of O_2/C_7H_8 increases from 0.07 to >0.4, indicating a large uptake of oxygen. Such effects were also observed for (–CH=CH–$_n$, but on a different time scale[9].

Poly(*1,6-heptadiyne*) versus *polyacetylene*

P-1,6 exhibits a single straight line log (current) vs. oxidation time plot. Polyacetylene, on the other hand, showed two such straight line positions during each experiment[9]. This latter effect was associated with either a morphological effect or the chemical kinetics of the system. In the former case it was assumed that two terms, interfibril contacts and fibril conductivity control measured conductivity. It was shown that by a random elimination (oxidation) of bonds or contacts between fibrils, the two rate processes result. In the latter case k_1 and k_2 are comparable in equation (1), thus permitting degradation and complexing to occur simultaneously, and producing the apparent double rate process curve. P(1,6) exhibits only one rate constant and is morphologically continuous[4–7]. Its absolute oxidation rates are also much larger than (–CH=CH–)$_n$ (see *Figure 7*). It is tempting to assign the differences observed in the oxidation of the two polymers to morphology and/or crystallinity. However, lack of knowledge of oxygen diffusion constant differences between P-1,6 and (–CH=CH–)$_n$ and absolute rates of complexation(k_1 in the rate equation) preclude this conclusion.

The activation energies for oxidation of P-1,6 and *trans* (–CH=CH̄)$_n$ are identical at ~14 kcal mol^{-1} while (–CH=CH–)$_n$ with 30 and 60% *trans* exhibits an activation energy of ~9 kcal mol^{-1} (see *Figure 7*). As shown, the absolute rates are much higher for P-1,6, indicating that the pre-exponential term in the rate expression is much larger in P-1,6 at any given temperature[10]. This difference in pre-exponential terms may be associated with the more easily removed allylic hydrogen atoms (those methylene groups alpha to the polyene chain) in P-1,6. In each monomer unit of P-1,6 there are four such hydrogen atoms whereas (–CH=CH–)$_n$ contains none of these with the exception of those that could exist at the phase kink, or soliton positions[11] or at crosslink sites. These allylic hydrogen atoms are readily abstracted to form free radicals which are susceptible to triplet oxygen attack[12].

The lower activation energy for (–CH=CH–)$_n$ with *cis* content is possibly due to oxygen catalysed *cis*→*trans* isomerization which produces a biradical that would be capable of oxygen insertion. This topic has already been discussed in detail[9].

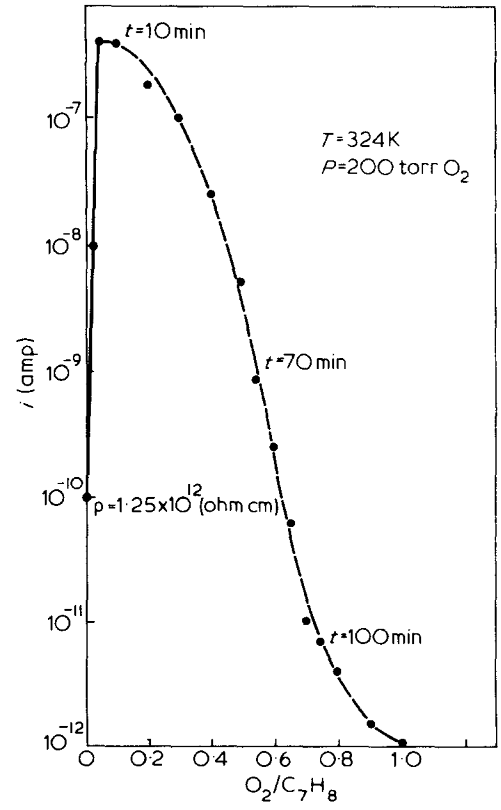


Figure 12 Log (current) ***versus*** oxygen—P-1,6 monomer ratio for exposure to 200 torr oxygen, V = 100 volts

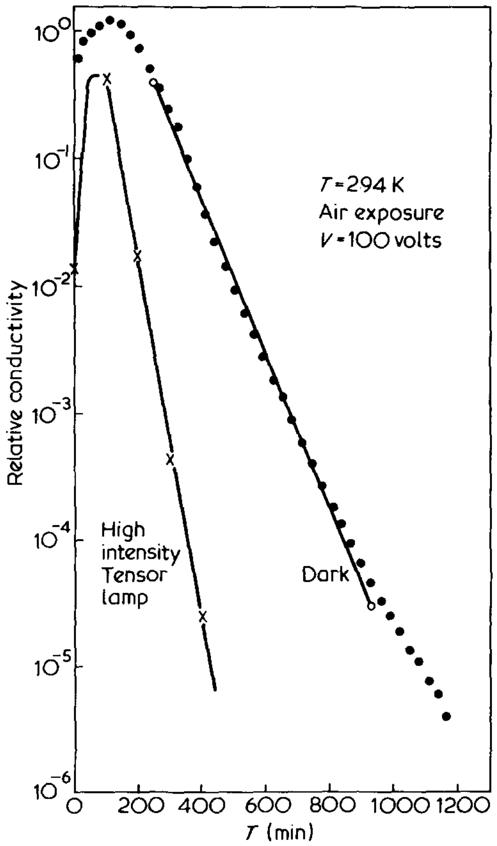


Figure 13 Log(current) *versus* exposure time to air for a pentane-washed P-1,6 sample exposed to a high intensity tensor lamp and in the dark

Effect of light

All oxidation experiments to calculate activation energies were carried out in the dark. Therefore, the possibility of singlet oxygen interactions with the P-1,6 samples was eliminated[8,12]. Additional experiments were conducted with a high intensity Tensor lamp (tungsten filament through glass) shining on the sample and the results of this experiment are shown in *Figure 13*. It is seen that light exposure increases the degradation rate. We cannot tell from these experiments whether the observed increased degradation results directly from singlet oxygen production or via excitation of the polyene. Such transfer has been observed in polystyrene[13]. Further experiments are in process to clarify this point.

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