Consequently, the material elements in the twisted specimen are subjected to a state of secondary stresses which are more complex than those arising from shearing of a cube[14], and it is probably these secondary stresses which are responsible for the dimensional and volumetric changes observed by Poynting and by us in metals and polymers. However, while the dimensional and volumetric behaviour in torsion may be accounted for by the nonlinear character of the material, it remains unclear why metals undergo expansion while most of the polymers develop contraction of volume. We wish to pursue this subject further in a future study.

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References

1 Whitney, W. and Andrews, R. D. *J. Polym. Sci. C* 1967, **16**, 2981
2 Bowens, J-C. *J. Polym. Sci. A-2* 1970, **5**, 1145
3 Duckett, R. A., Rabinowitz, S. and Ward, I. M. *J. Mater. Sci.* 1970, **5**, 909
4 Benham, P. P. and McCammond, D. *Plast. Polym.* 1971, **39**, 130
5 Matsuoka, S., Aloisio, C. J. and Bair, H. E. *J. Appl. Phys.* 1973, **44**, 4265
6 Spitzig, W. A. and Richmond, O. *Polym. Eng. Sci.* 1979, **19**, 1129
7 Matsuoka, S. *Polym. Eng. Sci.* 1981, **21**, 000
8 Rivlin, R. S. *J. Rat. Mech. Anal.* 1953, **2**, 53
9 Murnaghan, F. D. 'Finite Deformation of an Elastic Solid', Dover, New York, 1951, p. 130
10 Poynting, J. H. Collected Pap. 1913, pp. 309, 404
11 Swift, H. W. *Engineering* 1947, **163**, 253
12 Foux, A. Proc. IUTAM symp. on Second Order Effects etc., Haifa, Pergamon Press, New York, 1962, p. 228
13 Rivlin, R. S. *J. Appl. Phys.* 1947, **18**, 444
14 Lord Kelvin and Tait, P. G. 'Treatise on Natural Philosophy', Cambridge University Press, 1883, Part 2, footnote of §679

A kinetic study of the interactions of *trans*-polyacetylene $(CH)_x$ with oxygen

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The kinetics of doping and degradation of all *trans*-polyacetylene by oxygen, have been studied over the temperature range 70°–110°C. Doping and degradation have first-order kinetics with the observed Arrhenius parameters $E = 11.52$, $E = 13.45$ kcal mol^{-1} and log A (s^{-1} = 4.19, log A (s^{-1}) = 4.49 respectively. The observations support the view that the reactions proceed *via* an intermediate-complex mechanism. Initially oxygen reduced the resistivity of $(CH)_x$ by formation of a charge transfer complex and subsequently reacted with $(CH)_x$ with an increase in resistivity.

Keywords Polyacetylene; kinetics; oxygen; doping; degradation

Introduction

Polyacetylene $(CH)_x$ is a unique material of considerable technological interest. Upon doping with both electron donating or accepting species, its electronic transport properties cover the entire range from insulators to semi-conductors and metals[1,2]. However, both pure and doped $(CH)_x$ are sensitive to air and oxygen. In particular the mechanical[3], electrical[4] and magnetic properties[5,6,7] of $(CH)_x$ can be drastically modified by contact with oxygen.

It has been reported that exposure of polyacetylene to oxygen for a longer period caused irreversible chemical changes in the material (compressed powder pellets) but complications arose in the extrapolation of continuous films[8].

The kinetics of doping and degradation of polyacetylene with oxygen were studied by Pochan *et al.*[9] with various *cis–trans* compositions at elevated temperatures. They reported that the kinetics of the degradation is first-order leading to consecutive reactions. However the thermal behaviour of the intermediate complex and the thermodynamic parameters were not studied in detail. After plotting $\log\frac{R_t}{R_0}$ against time, these authors obtained a curve which gave two different straight lines, i.e. two different rate values probably related to the various transformations of polyacetylene (*cis* to *trans* isomerization, doping and degradation processes). To avoid the effects of *cis* to *trans* isomerization on the kinetics, only pure *trans* $(CH)_x$ was used here and thus this study is related to the effect of oxygen on *trans* $(CH)_x$.

Experimental and Results

For all the experimental runs, the polyacetylene used was prepared by a modification of the method described by Ito *et al.*[10] using a Ziegler–Natta catalyst. The *cis* rich $(CH)_x$ obtained was heated to give *cis* to *trans* isomerization at 150°C for 30 min. All-*trans* films of thickness *ca* 100 μ were used in this investigation.

The reaction was studied in the following manner: in a reactor the Pt-electrodes were kept vertical, sealed in a

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Table 1 Apparent first-order rate constants with O_2 doped *trans*-polyacetylene

Run temperature (°C)	Temperature coefficient	$\bar{k}\times 10^3$ (s^{-1})
70	–	0.872
90	1.10	1.920
110	1.11	4.260

Table 2 Calculated activation parameters from *Table 1*

E (kcal. mol^{-1})	11.52
Log A (s^{-1})	4.19
ΔH^* (kcal. mol^{-1})	10.76
ΔF^* (kcal. mol^{-1})	27.78
ΔS^* (cal. mol^{-1} deg^{-1})	–44.42

Table 3 Apparent first-order rate constants for the degradation of *trans*-polyacetylene with oxygen

Run temperature (°C)	Temperature coefficient	$\bar{k}\times 10^4$ (s^{-1})
70	–	0.906
80	1.766	1.600
90	1.555	2.480
100	1.625	4.030
110	1.714	6.908

Table 4 Calculated activation parameters from *Table 3*

	This study	Earlier results[9]
E (kcal. mol^{-1})	13.45	13.8 to 14.90
Log A (s^{-1})	4.49	6.11 to 8.78
ΔH^* (kcal. mol^{-1})	12.72	11.01 to 14.20
ΔF^* (kcal. mol^{-1})	27.46	24.90 to 24.90
ΔS^* (cal. mol^{-1} deg^{-1})	–42.94	–39.95 to –30.73

pyrex glass tube with a cup at the top which could be easily fitted on the tube of the apparatus. The apparatus was firstly evacuated then kept under an argon atmosphere in a glove-bag. The thin film of *trans*-polyacetylene was fixed on the platinum electrodes with electrodrag. The apparatus was connected to the vacuum line and all the argon pumped out. When a good vacuum was obtained, the upper parts of the electrodes were connected to a digital multimeter (Keithley 179) to record the change in resistance. Purified dry oxygen, supplied by Air-liquide, France, was used. A mercury manometer was fixed on the line to determine the oxygen pressure and the volume of the reactor occupied by oxygen.

After assembly of the system and placement of the reactor in a thermostat (±0.05) 30 min were allowed for thermal equilibrium to be established; oxygen was introduced into the line and manometer (31.5 mm), and allowed to come in contact with the $(CH)_x$ film. The fast doping of polyacetylene was observed by a fast decrease in resistance. After a certain time, the degradation started with an increase in resistance. Several experiments were conducted at various temperatures for the doping and degradation study of *trans*-polyacetylene. The rate of doping of polyacetylene was very rapid and therefore very difficult to study, however, we succeeded in obtaining results at low temperatures (*Table 1*).

The degradation study of *trans*-polyacetylene was made over the temperature range 70°–110°C. The ratio of resistances at time t and at zero time (R_t/R_0) plotted against time gave a smooth curve. The $\log\left(\frac{R_t}{R_0}\right)$ vs. t plot from representative points on the smoothed experimental plots resulted in straight lines for all the experiments. *Figure 1* shows a typical curve obtained at 110°C. The average rate constants were calculated in the usual manner from the slopes of the experimental logarithmic plots and are tabulated in *Tables 1* and *3*. The activation parameters, based upon the data of *Tables 1* and *3*, are cited in *Tables 2* and *4* respectively, along with the results of Pochan *et al.* that we have calculated from their data in *Table 3*. Our runs were at 70°, 80°, 90°, 100° and 110°C. At room temperature many more deviations were observed and these may be due to temperature fluctuations as the reaction was continued over a couple of days. However constant temperature is quite essential, hence an oil-thermostat was used throughout for all the experimental runs at all temperatures and the results were found to be reproducible.

An Arrhenius plot of log k against $1/T$, yielded a straight line for both doping and degradation (results from *Tables 1* and *3*) from which the energy of activation was calculated. A plot of log k vs. $1/T$ for degradation is shown in *Figure 2*.

Discussion

As the polyacetylene was exposed to oxygen, the resistivity initially decreased remarkably quickly, but then increased with time. A typical curve at 110°C (*Figure 1*) is characteristic of all polyacetylene samples exposed to oxygen. The decrease in resistance is attributed to the doping and the increase in resistance to the degradation. Since the doping and degradation are first-order reactions, it can be predicted that the reaction proceeds *via* an intermediate complex mechanism and may be displayed in the following form

$$\mathrm{PA}+\mathrm{O}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{complex}}{|\mathrm{PA}-\mathrm{O}_2|} \xrightarrow{k_2} \text{product}$$

PA = polyacetylene

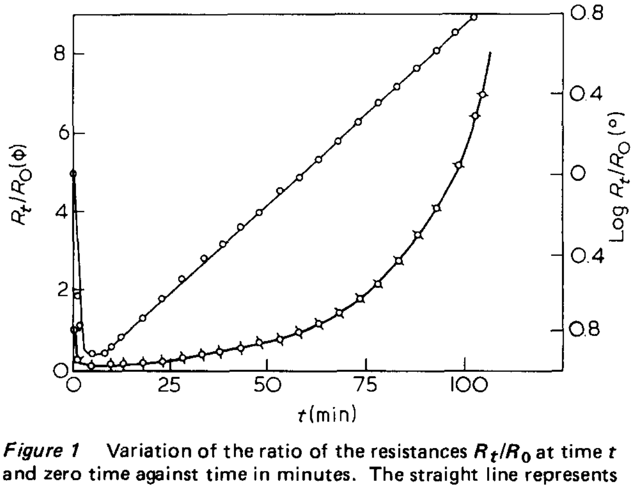

Figure 1 Variation of the ratio of the resistances R_t/R_0 at time t and zero time against time in minutes. The straight line represents the variation of the logarithmic ratio of resistances (R_t/R_0) against time in minutes

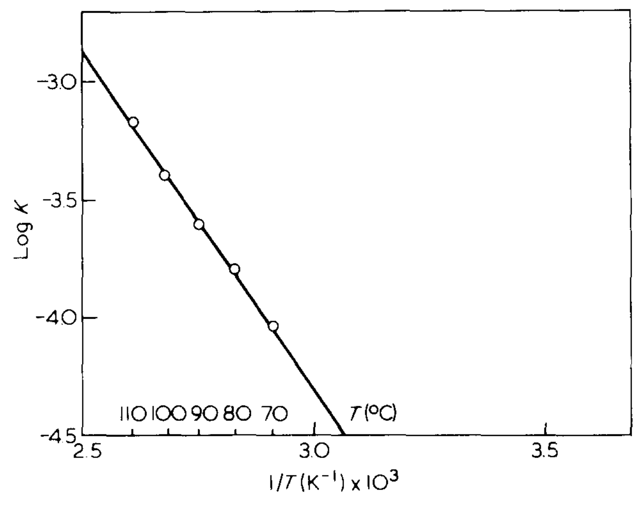

Figure 2 Logarithm of the rate constants against the reciprocal of the absolute temperature T

where k_1 is the rate of formation of polyacetylene–oxygen complex which causes the decrease in resistivity, k_{-1} is the reverse process which is dominated by k_1, hence k_{-1} is negligibly small and k_2 is the rate constant for the degradation of the intermediate transition complex.

The rate of formation of the complex is different from the rate of break down of the complex:

Thus
$$\frac{\mathrm{d}(\text{complex})}{\mathrm{d}t} \propto (\text{complex})$$
$$= k_2(\text{complex})$$

The above equation is a first-order equation. The reacting molecules, possessing sufficient energy, approach each other and there is a redistribution of the valence bonds so that the activated complex acquires a form in which it can alter the bonding to form the product.

The energy of activation, calculated from the graph (*Figure 2*) for the doping, is 11.52 kcal mol^{-1} and for degradation process is 13.45 kcal mol^{-1}. These values can be attributed to the fact that 11.52 kcal mol^{-1} is associated with the charge transfer complex and hence, the decrease in the energy of activation. When the polyacetylene double bond is attacked by the oxygen atom a carbonyl group is probably formed. More energy is needed in the formation of such a double bond, hence the higher the energy of activation compared with that of doping process. The theoretical heat of reaction for the formation of the carbonyl group from the polyacetylene unit, i.e. the enthalpy of activation was calculated as 50.1 kJ mol^{-1} and the experimental enthalpy of activation obtained was 52.0 kJ mol^{-1} for the degradation reaction; clearly both values are in close agreement. The frequency factor A from *Tables 2* and *4* (line 2), shows that a particular $(CH)_x$ molecule collides with O_2 with the same frequency but the rate of doping is ten times faster than that of degradation. A comparison of the thermodynamic parameters in *Tables 2* and *4* shows that both the doping and degradation have first order kinetics.

Using the results plotted by Pochan *et al.*, we have calculated and compared the thermodynamic functions for the degradation reaction. However Pochan *et al.* made their studies with different fixed *cis trans* compositions of $(CH)_x$ and their values are somewhat smaller and varied in range but our energy of activation value and the value reported by them are in close agreement (*Table 4*, line 1).

In our investigation it was noticed that the enthalpy of activation (*Table 2*, line 3 and *Table 4*, line 3: column 1) and the entropy of activation (*Table 2*, line 5 and *Table 4*, line 5, column 1) in the doping process were smaller than those for the degradation reaction, which would indicate that the charge transfer complex is more stable than that for the degradation complex. This conclusion does seem at odds with the finding that the doping rates, at all temperatures, are ten times faster than the degradation rates.

The study of the action of O_3 O_2 mixtures on $(CH)_x$ is now in progress and should give more information on and clarify the mechanisms of interaction of $(CH)_x$ with oxygen.

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References

1 MacDiarmid, A. G. and Heeger, A. J. 'Molecular Metals', Plenum Press, New York, 1979, p. 161
2 Bernier, P., Rolland, M., Galtier, M., Montaner, A., Regis, M., Candille, M., Benoit, C., Aldissi, M., Linaya, C., Schue, F., Sledz, J., Fabre, J. M. and Giral, L. J. *Phys. Lett.* 1979, **40**, L–297
3 Druy, M. A., Tsang, C. H., Brown, N., Heeger, A. J. and MacDiarmid, A. G. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 429
4 Berets, D. J. and Smith, D. S. *Trans. Faraday Soc.* 1968, **64**, 823
5 Goldberg, I. B., Crowe, H. R., Newman, P. R., Heeger, A. J. and MacDiarmid, A. G. *J. Chem. Phys.* 1979, **70**, 1132
6 Snow, A., Brant, P., Weber, D. and Yang, N. L. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 263
7 Bernier, P., Rolland, M., Linaya, C., Disi, M., Sledz, J., Schue, F., Fabre, J. M. and Giral, L. *Polym. J.* 1981, **13**, 3, 201
8 Luttinger, L. B. *Chem. Ind.* (*London*) 1960, **36**, 1135
9 Pochan, J. M., Pochan, D. F., Rommelmann, H. and Gibson, H. W. *Macromolecules* to be published
10 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci. Polym. Chem. Edn.* 1975, **13**, 1943
11 Haleem, M. A. and Hakem, M. A. *Aust. J. Chem.* 1976, **29**, 443