A kinetic study of the Durham precursor route to polyacetylene

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The processes involved in the thermal transformation of 'Durham polyacetylene precursor', poly[[5,6-bis(trifluoromethyl)-bicyclo[2,2,2]octa-5,7-diene-2,3-diyl]-1,2-ethenediyl], to all-*trans* polyacetylene have been studied. Above about 100°C the reactions are virtually concurrent, but at 50°C one can distinguish a first-order elimination ($k = 7.6 \times 10^{-4}$ s^{-1}), effusion of the elimination product ($D = 4 \times 10^{-9}$ cm^2 s^{-1}), and a first order *cis–trans* isomerization ($k = 1.5 \times 10^{-5}$ s^{-1}). The isomerization is very sensitive to traces of oxygen below 80°C, but at higher temperatures this is less pronounced and the reaction becomes approximately second order. Isomerization is generally more facile in the less ordered Durham polymer than in polymers from the Shirakawa route.

(Keywords: Durham polyacetylene; precursor polymer; isomerization kinetics)

INTRODUCTION

Polyacetylene (PA), like most conducting polymers, has the practical disadvantages of being infusible and insoluble in normal solvents. For this reason, a new preparation, via a processible precursor polymer, has been devised[1,2], and the reactions leading to the conversion of this prepolymer into polyacetylene are illustrated in *Figure 1*.

A previous study of this material by differential scanning calorimetry (d.s.c.) has indicated[2,3] that the following (partly overlapping) thermal transitions occur in the transformation reaction scheme shown in *Figure 1*:

(i) Chemical elimination to give *cis–trans* polyacetylene (**II** and **III**) plus a fluorinated xylene, 1,2-bis(trifluoromethyl)benzene (**V**).

(ii) Vaporization of the fluoroxylene from the bulk polymer.

(iii) Isomerization of the *cis–trans* initial product to all-*trans* polyacetylene (**IV**).

In the present work, we have been able to separate these stages, and to make a kinetic study of the processes in isolation. The work seems timely because the new 'Durham' polyacetylene prepared by this route is fully-dense, rather than being fibrillar like the standard Shirakawa polymer[4]. It is therefore possible to make much more reliable measurements of bulk transport properties.

EXPERIMENTAL

Samples of the pre-polymer (**I**) were stored at −20°C to minimise unwanted decomposition. Films were normally cast from solutions in dry, deoxygenated acetone in a glove-box under flowing nitrogen or argon, and transformed by heating under dynamic high vacuum.

The fluoroxylene product accounts for over 80% of the precursor weight and is reasonably volatile ($SVP = 20$ torr at ambient temperature), so the elimination reaction was followed by weight-loss measurements. Free-standing precursor films of 10–150 μm thickness were suspended from a fine silica spring, and the isothermal weight-losses in the temperature range 50°C to 80°C were determined by observing the contraction of the spring using a cathetometer.

Since it was found necessary to use even thinner films to avoid diffusive limitations in the weight-loss curves, films of sub-micron thickness were cast onto a standard 6 MHz quartz crystal and their weight changes during transformation were measured as proportionate shifts in
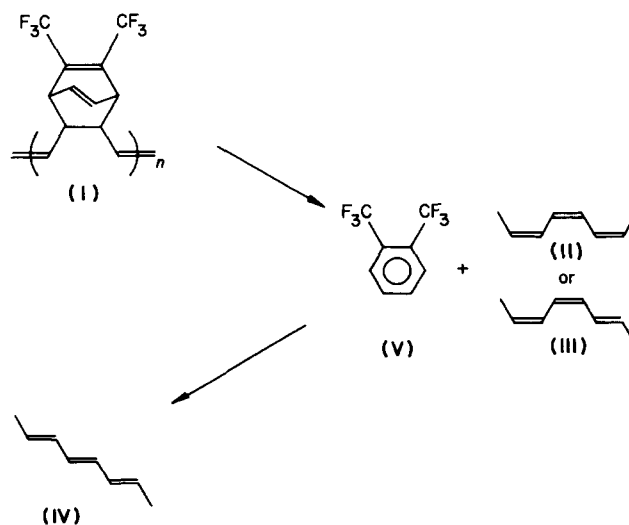

Figure 1 Reaction sequence for conversion of Durham precursor (I) to all *trans*-polyacetylene

the resonance frequency. Such a 'piezoelectric microbalance' has been described[5] by Warner and Stockbridge, and uses an AT-cut crystal to minimise the effect of small temperature fluctuations on the mass resolution. The crystal was incorporated into a conventional Colpitts oscillator circuit, which was connected via a buffer stage to a digital frequency-meter.

The balances described above were contained in evacuable glassware with thermostatically controlled jackets through which water or poly(ethylene glycol) was pumped at temperatures from 25°C to 80°C. The weight-loss at higher temperatures (up to 350°C) was determined under flowing nitrogen by thermogravimetric analysis (t.g.a.) on a Stanton–Redcroft balance.

The *cis–trans* isomerization was initially studied by infra-red absorption spectroscopy using a Perkin–Elmer 1430 grating spectrophotometer. Precursor films of thickness 5 to 15 μm were cast onto thin KBr windows and transformed and isomerized in an evacuable infra-red cell after extensive pre-pumping. Pinhole formation was occasionally observed at first, but was subsequently avoided by using a 50:50 acetone–ethyl acetate mixture to dissolve the precursor, by drying the solvents well with 3 Å molecular sieves and by covering the KBr window with a Petri dish after applying the solution. This gave slow, uniform evaporation and films of homogeneous appearance.

The evacuated cell was heated in a thermostatically controlled oven or (more rapidly) in an oil-bath, and the isomerization was followed by observing the changing absorbances of the *cis* vibrations at 740 and 440 cm^{-1} and the *trans* vibration at 1010 cm^{-1}.[6]

Later results were obtained using evacuable high-temperature cells, enabling the reaction to be followed *in situ*. Samples as thin as 1 μm were examined by a grating i.r. instrument, whilst a Nicolet 7199B FTIR spectrometer was used to allow higher accuracy with more optically-dense films.

The effect of oxygen, as a possible impurity, on the isomerization rate was examined by comparing the kinetics under 'oxygen-free' conditions of varying stringency with those in the presence of added oxygen (as dry air). A sample was also thermally isomerized at 25°C under visible illumination from a 60 W tungsten lamp at 25 cm from the polymer film, to identify the possible role of photo-isomerization in the other experiments.

RESULTS AND DISCUSSION

Elimination of the hexafluoroxylene

For a 20 μm film on the silica spring balance, the logarithm of the relative weight-loss at 68°C was a linear function of time. This indicates that a first-order elimination reaction limited the rate of fluoroxylene loss, rather than diffusion of the aromatic from the polymer film. At lower temperatures, however, diffusion was slow and there was no simple kinetic behaviour, whilst at 80°C the weight loss was too rapid to measure and heat-transfer was too slow to study the whole reaction isothermally.

The use of thinner films on the piezoelectric balance enabled the reaction to be studied without diffusive limitation down to 10% remaining fluoroxylene, even at 25°C. Strictly first-order kinetics was observed throughout—which is somewhat surprising, since it indicates a random elimination of individual units or

short sequences with an initiation probability that is apparently unaffected by the extent of reaction. First-order rate constants, obtained in the range 25°C to 80°C, are summarized in *Table 1* and are shown as an Arrhenius plot in *Figure 2*, from which an activation energy of 94.9 kJ mol^{-1} may be calculated. A very similar value of 95 kJ mol^{-1} was obtained using differential scanning calorimetry (d.s.c.)[3].

To check whether complete elimination was possible from samples of more convenient thickness, free-standing precursor films around 25 μm thick were studied by t.g.a. *Figure 3* depicts two typical weight-loss curves, with an initially sharp decline followed by a much more gradual one. Largely complete chemical and physical elimination of the fluoroxylene were obtained by fairly slow (1°C min^{-1}) heating to 120°C, but isothermal weight loss at 100°C was only complete after 5 h. (The instrumental resolution only allows the final weight loss to be quoted as 99 ± 0.5% of the theoretical value.) Above 120°C, the sample mass was constant until beyond 250°C, when a catastrophic decrease due to pyrolysis occurred.

Table 1 First-order rate constants for the elimination reaction

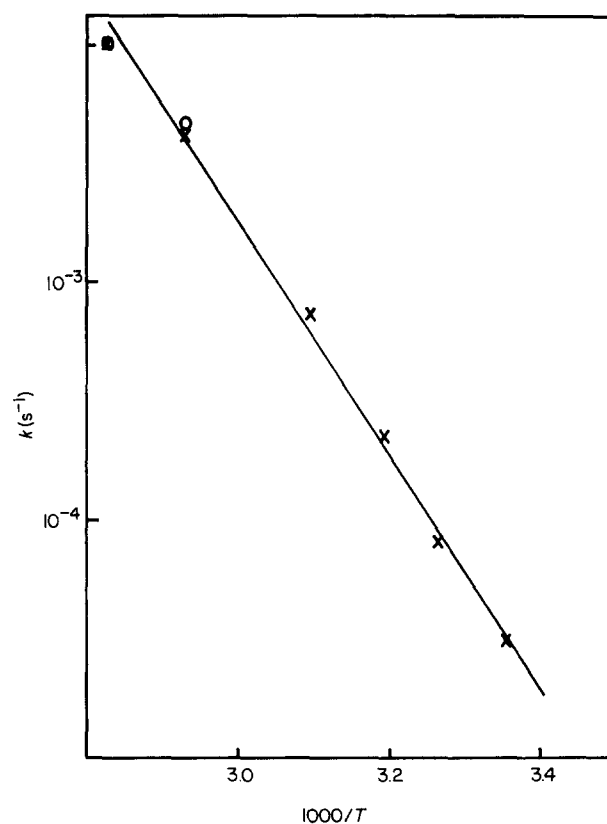| Temperature (°C)	$10^5 \, k \, (\text{s}^{-1})$
25	3.0
33	8.0
40	22.0
50	76
68	440
80	1000

Figure 2 Arrhenius plot for the elimination of fluoroxylene from a thin film of precursor: (×) crystal oscillator method; (○) quartz spring balance
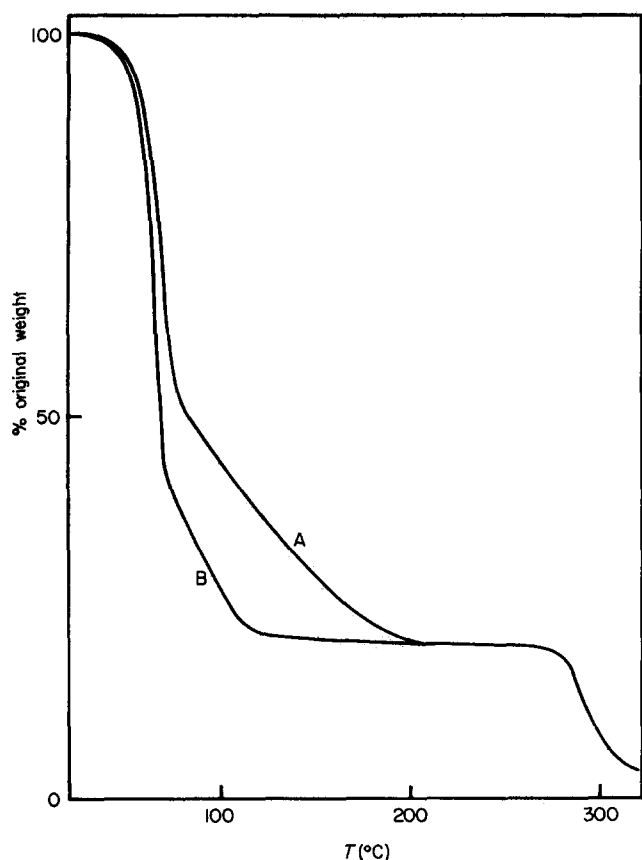
Figure 3 Weight loss curves for fluoroxylene loss from thick precursor films, measured by t.g.a. (A) 5°C min^{-1}; (B) 1°C min^{-1}

Diffusion

A 35 μm thick piece of precursor film was allowed to transform completely to polyacetylene for 6 days at 20°C in a sealed tube of argon, and was then quickly transferred to the spring balance. The subsequent loss of weight *in vacuo* at 50°C was initially rapid, though diffusion-controlled with a coefficient, D, of 4×10^{-9} cm^2 s^{-1}. When over 60% loss had occurred however, the rate of effusion became much slower ($D < 1 \times 10^{-11}$ cm^2 s^{-1}), suggesting that the process had originally been enhanced by the plasticizing effect of the fluoroxylene itself, whilst towards the end the remaining xylene was becoming trapped in a matrix of increasing rigidity. In support of this, it was found that while 80% transformed polymer was unaffected by exposure to liquid fluoroxylene, after 40% transformation at 50°C the same treatment resulted in rapid swelling.

The change in the infra-red spectrum of the pre-polymer with heat treatment is exemplified in *Figures 4* and *5*. There was clearly a rapid diminution of the intense CF$_3$ stretching bands at 1155, 1190 and 1300 cm^{-1} after initial heating, but the rate of disappearance soon decreased sharply. A limiting concentration of about 1.5% of the original CF$_3$ was indicated for the 80°C transformation, but it is not possible to say whether the residual CF$_3$ was just physically entrained in the matrix, or whether a few incipient fluoroxylene groups had failed to eliminate, for example because of accidental prior addition to their double bonds. Nevertheless, the band seen at 1680 cm^{-1} in the precursor, due to the F$_3$C.CR:CR.CF$_3$ chromophore, did disappear completely during transformation; despite its having less intensity than the CF$_3$ stretching modes, the removal of

this band (even from quite thick films) implies over 99% complete chemical elimination. This of particular importance because precursor residues on the polyacetylene chain could ultimately limit the conjugation length of the polymer, and thus have a bearing on the electronic transport properties. Previous work on the Durham polymer has indicated a conjugation length of only about 30 double bonds[7], which, in the light of these results, clearly cannot be explained on the basis of incomplete elimination of fluoroxylene.

Cis-trans isomerization

Infra-red determination of the relative concentrations of cis and trans polyacetylenes relies upon the truth of the following assumptions:

(i) The total number of (cis + trans) double bonds remains constant after fluoroxylene elimination (i.e. crosslinking and accidental oxidation are absent).

(ii) The absorption bands measured are characteristic of individual double bonds rather than conjugated sequences of any particular type.

(iii) The molar absorbances of the cis and trans chromophores either do not change with composition over a wide range, or else any slight variations affect both bands equally.

These assumptions may be tested by a plot of the absorbance for trans (A_{trans}) vs. that for cis (A_{cis}); this is found to be linear over a wide range for the bands at 740 and 1010 cm^{-1} (*Figure 6*), as would be expected from the above. (Assumption (i) is also true for Shirakawa PA samples below 140°C in well-pumped systems[8], and is indirectly supported by our own e.s.r. observations on Durham PA[9].

The proportion of cis isomer remaining in a sample is given by:

$$\%cis = 100 S A_{cis}/(S.A_{cis} + A_{trans})$$

where

$$S = -(\varepsilon_{trans})/(\varepsilon_{cis})$$

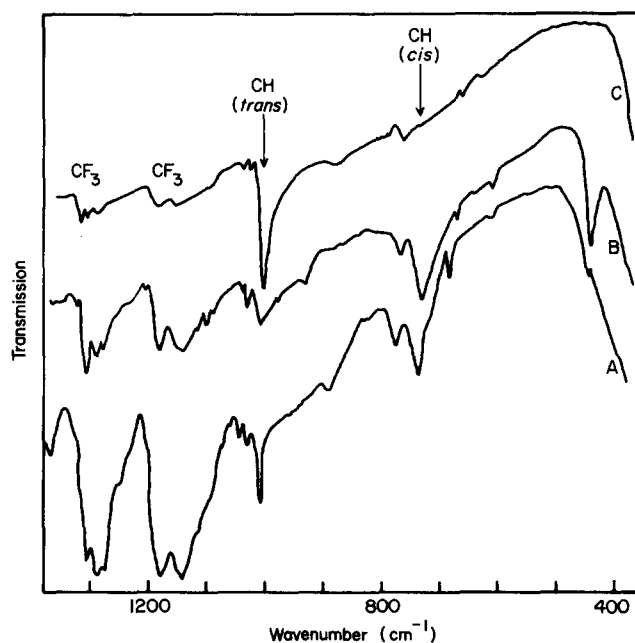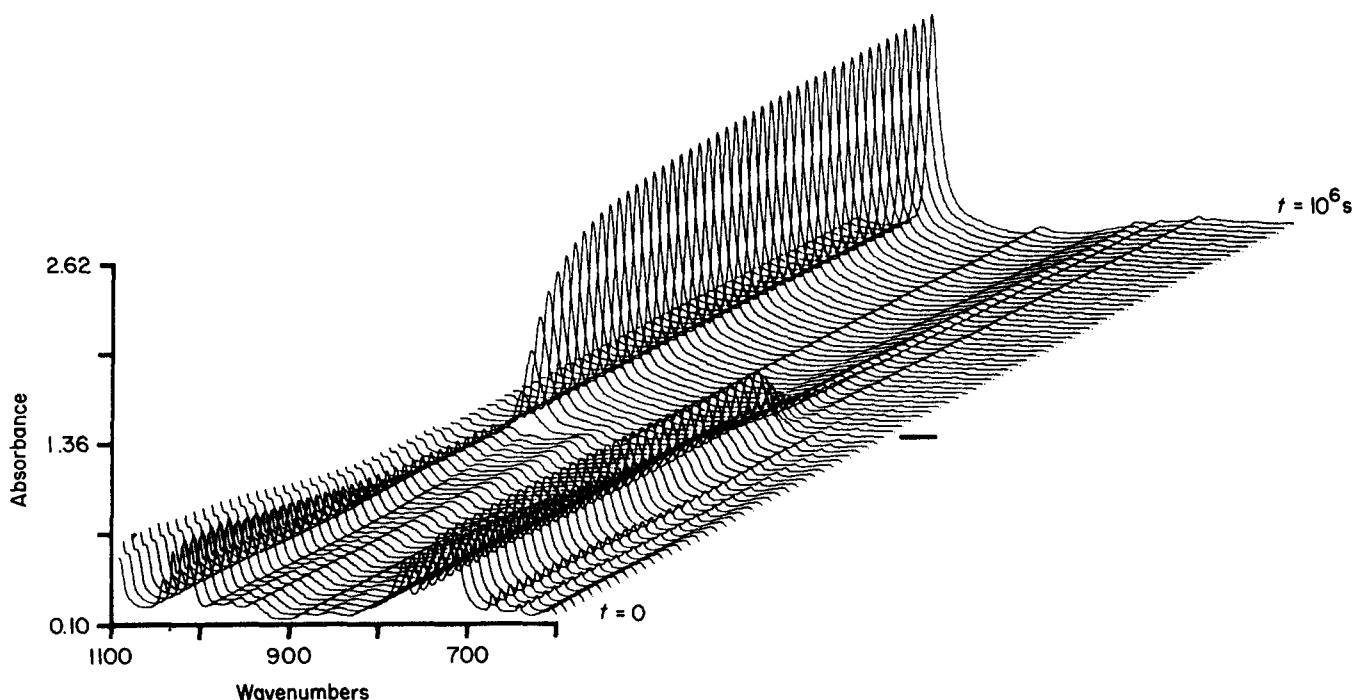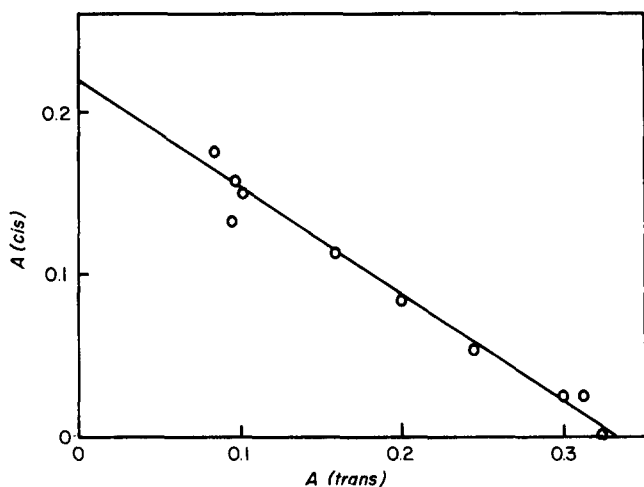**Figure 4** I.r. spectra of (A) precursor polymer; (B) after 3 h at 50°C; (C) after 12 h at 80°C

Figure 5 I.r. spectra during transformation to Durham polyacetylene

Figure 6 Absorbance of *cis* ($1010\,\text{cm}^{-1}$) and *trans* ($740\,\text{cm}^{-1}$) bands during isomerization

with ε_{trans} and ε_{cis} being the respective extinction coefficients at the temperature of measurement. S is also the slope of a plot such as that shown in *Figure 6*, for which a value of $S = 1.5 \pm 0.1$ was obtained for experiments at 20°C.

By this means, when transformation was carried out under conditions expected to lead to little isomerization, the initial composition of all the samples after 95% transformation was found to be 75% to 85% *cis*. A value of 75% was expected because the precursor contains about 50% *cis* and *trans* linkages in random distribution and the fluoroxylene elimination necessarily occurs *cis* to the chain.

At the highest temperatures used (80°C, 90°C and 100°C), the isomerization data fit well to a second-order kinetic analysis (*Figure 7*). This has also been observed by Gibson *et al.*[10] for Shirakawa PA, but only for
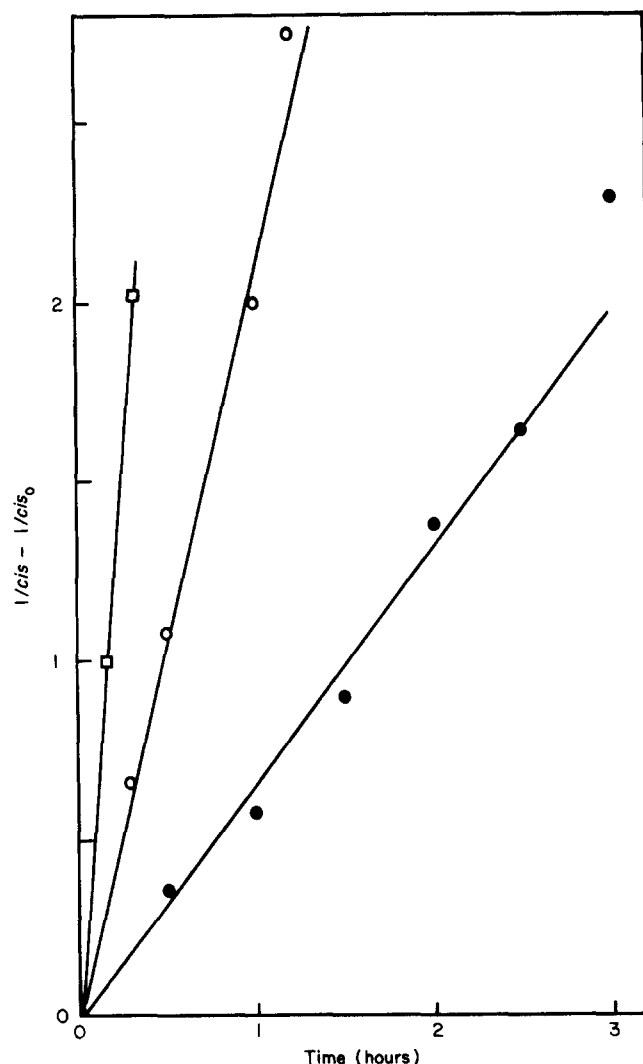
Figure 7 Second-order plots of isomerization kinetics. (□) 100°C; (○) 90°C; (●) 80°C

compositions from 100 down to 50% *cis* isomer. Their observation was rationalized on the basis of a mechanism in which the outer two members of a *cis–cis–cis* combination isomerize by forming biradicals and allowing a 'crankshaft' rotation of the central *cis* unit. Such a process would result in efficient conversion to a *trans–cis–trans* combination, despite the constraints of a solid matrix, but it requires the presence of at least three consecutive *cis* units, so that it is statistically limited to 50% isomerization. To explain the slow continuation of the reaction after this stage in Shirakawa PA, Gibson *et al.* have proposed more complex mechanisms in keeping with an observed change to 4th-order kinetics and an increased activation energy.

More recently however, Jing and co-workers[11] have found that a 3rd-order analysis could be successfully applied to their infra-red data on Shirakawa PA over a wide range of isomerization. They attributed this to a mechanism in which the bonding configuration in three adjacent *cis* units changes from *cis–transoid* to *trans–cisoid*, which then allows free rotation about the single bonds to give an all-*trans* section. However, this seems a less probable process than the sequence of events proposed by Gibson[10] and there is little direct evidence to support it. Furthermore the compositional data of Jing *et al.* are much more sparse than those of Gibson.

Our high-temperature results for Durham PA (90°C and 100°C) showed clear second-order kinetics, which persisted well beyond the 50% limit reported by Gibson *et al.*, and in fact extended to at least 70%. This cannot be rationalized by the mechanisms of Gibson or of Jing.

If we compare the data for initial isomerization rates at various temperatures in the form of an Arrhenius plot of times for isomerization from 75 to 50% *cis*, a roughly linear graph is obtained above 50°C with a slope equivalent to an activation energy of about $105\,kJ\,mol^{-1}$ (*Figure 8*). This energy is almost equal to that obtained by Shirakawa and co-workers[12] and might be taken to indicate the same electronic barrier to isomerization, but with a larger pre-exponential factor for Durham PA because of more favourable statistics. However, more
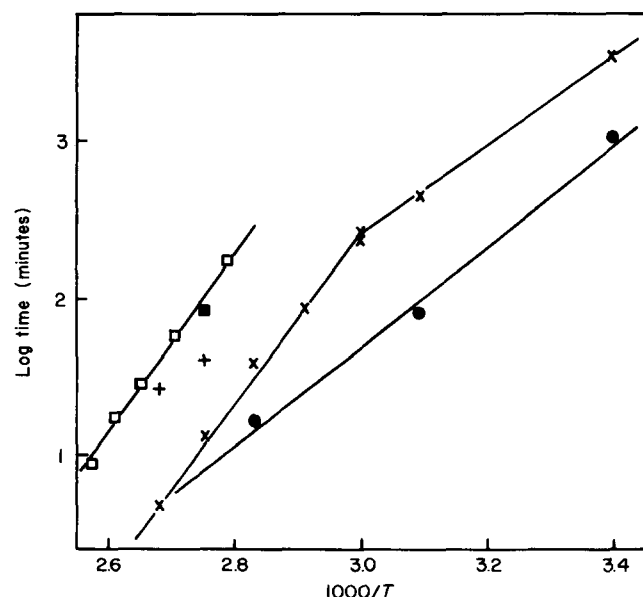
detailed analysis of our low-temperature data (for 21°C, 50°C and 60°C) shows a change to first-order reaction with a lower activation energy of around $55\,kJ\,mol^{-1}$. (The measured 1st and 2nd-order rate parameters are summarised in *Table 2*.) Overall, the data appear to show a continuously increasing activation energy which approaches $140\,kJ\,mol^{-1}$, the value obtained from d.s.c. data over the range $110°C–150°C^3$.

In the low-temperature region, it was suspected that 'extrinsic' factors such as accidental doping were responsible for the unexpectedly fast reaction. No evidence for photo-isomerization was detected. Oxygen was known from previous work[13-15] to be a potential isomerization catalyst, and in fact the lowest-temperature data were only found to be reproducible if the precursor films were pumped under high vacuum for several hours prior to transformation.

The isomerization rate was also reduced somewhat by equilibrating films of precursor with diethylamine before transformation, although a proper kinetic analysis was prevented by the presence of residual amine in the product. (The amine acts by compensating the effects of *p*-type dopants; these could include oxygen traces, or alternatively catalyst residues such as tungsten (VI) which are potential electron acceptors.) However, the deliberate addition of 50 Torr of air to Durham PA (also shown in *Figure 8*) produced a clear increase in isomerization rate at 21°C (*Figure 9*), 50°C and 80°C. The activation energy was $61\,kJ\,mol^{-1}$, and, as was recently found for Shirakawa PA[14], the oxygen-catalysed isomerization was first-order.

The highest temperature isomerizations (90°C and 100°C) were much less sensitive to the effects of added oxygen, and an attempt to change the reaction order by increasing the oxygen pressure merely led to a competing oxidation of the polymer. Thus, at 80°C and below, isomerization was virtually complete before substantial carbonyl absorption appeared in the infra-red spectra, but at higher temperatures strong absorptions around $1700\,cm^{-1}$ were seen at an early stage of isomerization in the presence of air.

Measurements were also made on isomerization of very thin films ($<1\,\mu m$) at 90°C and 100°C under continuous pumping. The isomerization kinetics of the films appear to be second-order but are significantly slower than those for thicker films (*Figure 8*). This observation apparently reflects the plasticization of the thicker films by trapped fluoroxylene and illustrates the effect of molecular mobility on the isomerization rate. This also explains the
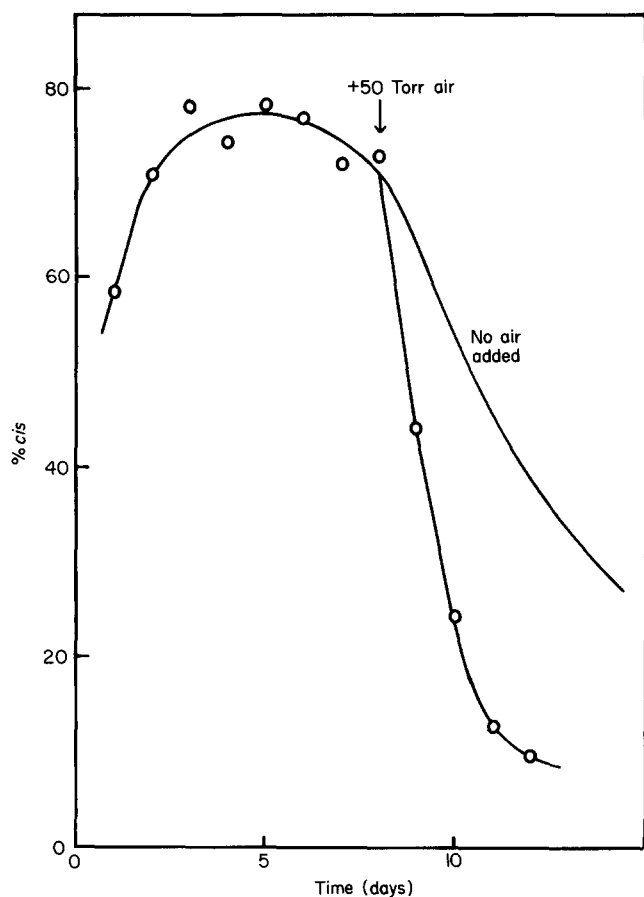
Table 2 First- and second-order rate constants for isomerization of Durham PA

Temperature (°C)	Order	$10^5 k_1$ (s^{-1})	$10^4 a_0 k_2$ (s^{-1})
21	1	0.20	–
50	1	1.54	–
60	1	2.51	–
60	1	3.0	–
70	1 or 2	3.9	1.1
80	1 or 2	13.0	2.1
90	2	–	6.1
90	2	–	7.5
90^a	2	–	2.15
100	2	–	17.9
100^a	2	–	2.97

^{a} Results obtained from very thin film (see text)

Figure 8 Isomerization times for 75% *cis* to 50% *cis*. (×) this work; (●) 50 Torr oxygen; (+) very thin films; (□) Shirakawa *et al.*[12]; (■) Gibson *et al.*[10]

Figure 9 Effect of oxygen on isomerization at 21°C

structure of the polyacetylene with temperature and degree of isomerization. In Durham polyacetylene the isomerization reaction is accelerated by the higher mobility of the plasticized amorphous structure. In the denser materials produced at high temperature the mobility becomes rate limiting. The further collapse of the structure as isomerization proceeds leads to higher order kinetics. This collapse is also seen as a sharpening of the X-ray peaks during isomerization, particularly at high temperatures. This would be consistent with either random or sequential isomerization, but our own X-ray studies[19] lead us to believe that sequential processes operate in Durham polyacetylene.

CONCLUSIONS

Chemical elimination of hexafluoroxylene from the Durham precursor was found to be first order with a rate constant given by

$$k = 1.41 \times 10^{12}\exp(-11416/T)\ s^{-1}$$

in the range 298 to 353 K. Although diffusion of the xylene from the transforming polymer was initially rapid, there was a tendency for some of the product to be trapped in films thicker than a few microns. Thermal isomerization of Durham polyacetylene is significantly faster than for Shirakawa PA, with second-order kinetics at 70°C to 100°C. There is a first order reaction at lower temperatures, with a low activation energy of about 55 kJ mol^{-1}. Very thin films isomerize more slowly at 90°C and 100°C as they lack the plasticizing effect of the trapped fluoroxylene that occurs in thicker films. The change in the order of the reaction with temperature is believed to be caused by changes in the chain packing decreasing the mobility of the chains as isomerization proceeds.
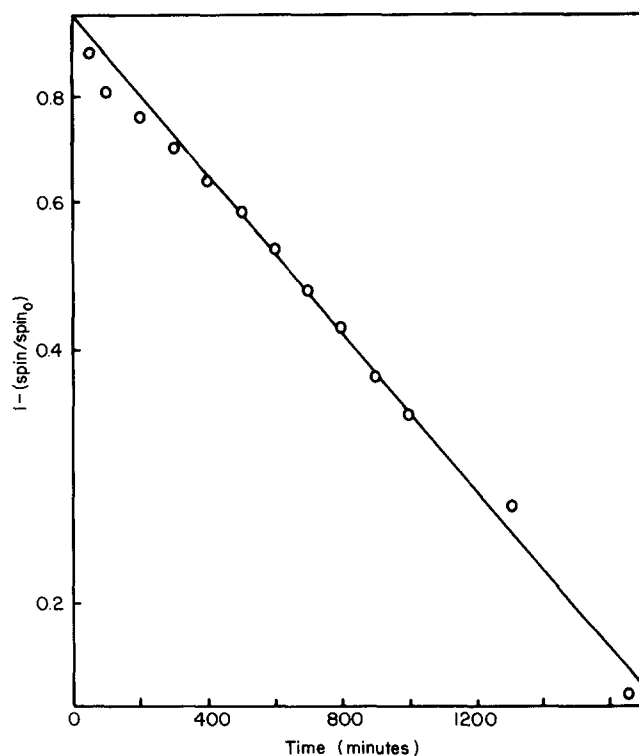
faster isomerization kinetics of Durham polyacetylene when compared with the Shirakawa polymer. Similarly the apparent activation energy change in *Figure 8* at about 80°C is due to the decreasing amount of fluoroxylene trapped in the films at the higher transformation temperatures.

Using X-ray diffraction, Robin *et al.*[16] conclude that the isomerization occurs by random rotation of individual units, while Perego *et al.*[17] suggest that the isomerization occurs by conversion of long sequences. This could involve a random initiation event, such as the formation of a biradical, which then propagates along the chains in both directions converting them to the *trans* conformation. The kinetics for such a process would be expected to be analogous to the degradation of a polymer chain by random initiation followed by 'unzipping', as is observed for poly(methyl methacrylate)[18]. The kinetics should then be first-order if the kinetic chain length is greater than the molecular chain length, so that termination occurred at the ends of the molecules, and 3/2 order if termination occurred by radical-radical reaction. Such a mechanism would be consistent with the appearance of the spin signal which we observe by e.s.r. We find that the number of spins rises, following first-order kinetics, to a concentration of about one spin per chain at times corresponding to the end of isomerization (*Figure 10*). The activation energy for this process is about 50 kJ mol^{-1}. It is tempting to ascribe the observed kinetics to a change from first to 3/2 order, as predicted by the chain propagation model, with increasing temperature. In fact the data are more consistent with a slow shift from first to second-order over the range from 50°C to 100°C. It seems most probable that this is due to the changing

Figure 10 Increase of spin concentration with isomerization time at 60°C

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