Thermal and photo-oxidative degradation of poly(5′,6′-bis(trifluoromethyl)-bicyclo[2.2.2]octa-5′,7′-diene-2′,3′-diyl)-1,2-ethenediyl, the Durham polyacetylene precursor polymer, and polyacetylene

Peter I. Clemenson* and W. James Feast†
IRC in Polymer Science and Technology, Chemistry Department, Durham University, South Road, Durham DH1 3LE, UK

and Munir M. Ahmad, Philip C. Allen‡, David C. Bott§, Chris S. Brown, Lucy M. Connors, Nick S. Walker and Jeremy N. Winter§
BP Research Centre, Sunbury-on-Thames, Middlesex TW16 7LN, UK
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The photo-oxidation of the precursor polymer to Durham polyacetylene has been studied by thermal analysis and ultra-violet, infra-red and solid-state nuclear magnetic resonance spectroscopies. It is concluded that the process that is involved in the photolithographic formation of relief images in polyacetylene is initiated by singlet oxygen attack on the polymer film followed by classical auto-oxidation and crosslinking. Polyacetylene was studied as a related model.

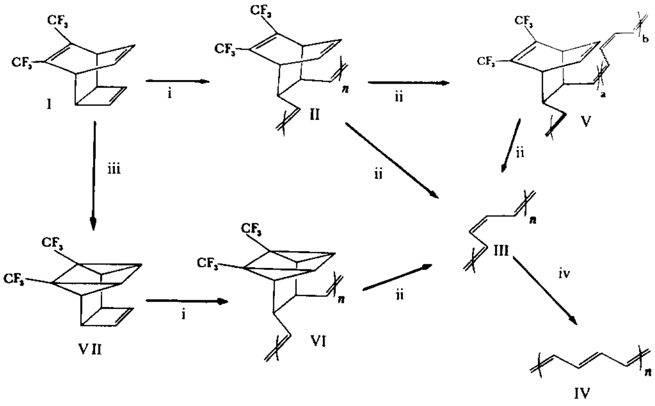
(Keywords: thermal degradation; photo-oxidative degradation; polyacetylene; precursor)

INTRODUCTION

We have previously described precursor routes to polyacetylene[1,2] that have some practical advantages over the direct synthesis from acetylene in terms of ease of manipulation and control of morphology in the final product. This approach has been exploited in the investigation of the materials properties of well defined polyene samples[3–12]. Also we have reported that photo-oxidative modification of the Durham polyacetylene precursor polymer followed by heating allows the fabrication of high-resolution relief images[13], an observation that may be important with respect to possible applications of this material in electronic and optical devices.

The most commonly used version of the precursor route to polyacetylene is shown in *Scheme 1*. The tricyclic triene (**I**) undergoes ring-opening metathesis polymerization (ROMP) with any of several different initiator systems to give the soluble and processable precursor polymers (**II**, the Durham polyacetylene precursor polymer, poly(5′,6′-bis(trifluoromethyl)-bicyclo[2.2.2]octa-5′,7′-diene-2′,3′-diyl)-1,2-ethenediyl), which in turn undergo a symmetry-allowed elimination of hexafluoro-orthoxylene to yield polyacetylene (**III**) with a minimum concentration of *cis*-vinylene units of 50 mol%, the exact *cis*/*trans* content depending on the initiator system used to prepare the precursor polymer (**II**); this material is thermally equilibrated to give the more stable *trans*-polyacetylene (**IV**). These three steps overlap in time and space and the protocol adopted for the formation of polyacetylene by this route is an important determinant of the final form of the product.

In practice this picture of the process only applies when a rigorous regime of temperature regulation is applied during *all* stages of synthesis, purification and manipulation of the precursor polymer **II**. If the temperature is maintained at or below 0°C, the precursor **II** has the structure indicated and is colourless. This is not difficult to achieve but is fairly time-consuming and,



Scheme 1 Precursor routes to polyacetylene

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*Current address: Department of Chemical and Physical Sciences, The Polytechnic of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK
†To whom correspondence should be addressed
‡Current address: Thorn EMI Central Research Laboratories, Dawley Road, Hayes UB3 1HH, UK
§Current address: Courtaulds Research, PO Box 111, Lockhurst Lane, Coventry CV6 5RS, UK

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since for most practical purposes this route is used to obtain thin films of polyacetylene via conventional spinning from a viscous solution of **II**, one of the main criteria for a useful polyacetylene precursor sample is that it is soluble and not oxidatively degraded. It is experimentally found that the **II** to **III** elimination reaction can be allowed to proceed to the stage where the polymer solution is yellow to orange-red without seriously affecting this required processability. Thus the actual precursor polymer used in this process is not strictly **II** but is more properly represented as **V** (see *Scheme 1*), that is a copolymer of the repeat unit of **II** and short polyene sequences. It seems reasonable to assume that this is a statistical copolymer and that the polyene moieties are predominantly of three or five vinylene units since significant concentrations of longer polyene sequences would result both in a darker product and insolubility. Earlier investigations of the conversion of **II** to **III** indicated that the elimination reaction was a first-order process, implying the absence of any neighbouring group or chain reaction[3].

It is precursor polymers of the type represented by structure **V** that have been used in the photolithographic process referred to above[13]. When exposed to u.v. irradiation in the presence of dioxygen, such polymers are bleached and the bleached polymer cannot be converted to polyacetylene. Thin films of polyacetylene also undergo photobleaching on exposure to air and light. This paper reports an investigation of the processes involved in the photobleaching of films of precursor polymer **V** and, as a related model, polyacetylene.

EXPERIMENTAL

Photolithography using precursor polymer **V** is a two-stage process that occurs in the solid state using thin films; usually thicknesses in the 1 to 3 μm range were used. The films are spun cast onto a substrate from a viscous solution of the polymer in acetone or butan-2-one. Successful photolithography requires that these thin films have a colour in the yellow to orange-red range for the reasons outlined in the introductory section. The thin films are selectively irradiated through a mask in the presence of air in order to produce an image that is developed by heating in a vacuum oven at 80°C.

Preparation of photobleached precursor polymer

In order to prepare sufficient photobleached precursor polymer to investigate its structure the following procedure was repeated 15 times. A thin film of polymer **V** was spun cast onto a glass disc approximately 7.5 cm in diameter using a Dynapert Precima PRS 14E Photoresist spinner operating at 2000–4000 rpm for 60 s. Film thicknesses were not routinely monitored, but this procedure gives films with thicknesses in the range 1 to 3 μm. The films were irradiated in air for 2–3 h using a Hanovia 1000 W medium-pressure Hg lamp 15 cm above the polymer sample; the temperature at the sample surface was between 50 and 60°C. The samples were then heated in a vacuum oven at 80°C and 10^{-2} mmHg to give clear films; unirradiated samples gave films of polyacetylene when heated. A few samples exhibited faint black flecks presumably of polyacetylene; and when thicker films were used, the concentration of these 'polyacetylene flecks' became more noticeable, and such samples were discarded. The films were scraped from the glass discs using a razor blade, which introduces the possibility of polytetrafluorethylene (PTFE) contamination since the blades were coated with PTFE. However, our subsequent investigations revealed no evidence for such contamination.

Wavelength dependence of photobleaching

In an attempt to assess the wavelength dependence of the photobleaching process, thin films were irradiated in a Rayonet 208 Photochemical Reactor using sets of RPR2500 lamps providing a band at 254 nm with a bandwidth at half height of ±2.5 nm, RPR3000 lamps providing a band at 300 nm with a bandwidth at half height of ±18 nm, and RPR3500 lamps providing a band at 360 nm with a bandwidth at half height of ±25 nm. The films were all spun onto silica discs from the same batch of a yellow solution of precursor **V** in butan-2-one. ^{19}F n.m.r. spectroscopic analysis (Brucker AC/250 operating at 235 MHz) of the solution immediately prior to film casting indicated a ratio of hexafluoroxylene (^{19}F shift -58.9 ppm) to polymer-bound CF_3 (^{19}F shift -60.7 ppm with respect to C_6F_6) units of 1:2.3; thus in this material at least one in three of the repeat units of the pristine polymer **II** had undergone the elimination reaction. Half of each film was masked with an opaque material in order to act as a reference, and after heating in the vacuum oven all the masked areas were converted to polyacetylene. Photo fluxes were computed using an Applied Photophysics digital voltmeter with photocell. The samples were maintained in the temperature range 20 to 30°C by cooling with a flow of nitrogen; nevertheless there was sufficient air at the polymer surface to allow photo-oxidative modifidation. The results are summarized in *Table 1*.

The sample irradiated at 254 nm gave a clear film, which did not convert to polyacetylene on heating in the vacuum oven; the samples irradiated at 300 and 360 nm did display conversion to polyacetylene after irradiation and heating but the quality of the material produced was not as good as that produced from the unirradiated (masked) areas of the sample, showing a blotchy texture indicative of partial photo-oxidative modification.

Related systems that failed to undergo photo-oxidative modification

Samples of the precursor polymer **II**, which were colourless and presumably consisted essentially of bis(trifluoromethyl)bicyclo[2.2.2]octadiene vinylene units with few if any triene and pentaene sequences, were found to be photo-inactive. Freshly prepared polymer **II** was dissolved in butan-2-one at -10°C to give a colourless viscous solution, and thin films were spun cast onto silica discs. The bottom side of the discs was maintained at -10°C while the film of **II** on the top surface was irradiated for 2 h in a current of dry air (to

Table 1

Wavelength (nm)	Duration of irradiation (s)	Total number of incident photons/cm^2
254	1962	6.66×10^{19}
300	2280	6.53×10^{19}
360	1800	10.3×10^{19}

prevent condensation of moisture) with the 1000 W lamp 15 cm from the surface. The films remained clear throughout this process, so it may be concluded that the cooling technique had effectively prevented the thermal elimination of orthohexafluoroxylene. Films exposed to u.v. radiation and air in this way gave polyacetylene when heated in the vacuum oven. Films cast from samples of precursor polymer that had become deep red also failed to undergo photobleaching under standard irradiation conditions (2 h at 15 cm from the 1000 W lamp and 50–60°C). Thin films prepared from an alternative precursor polymer **VI** (see *Scheme 1*), which is prepared via ROMP of **VII**, the photoisomer of **I**, and which has a bis(trifluoromethyl)quadricyclo $[6.0.0^{2,4}.0^{3,6}.0^{5,7}]$octane vinylene repeat unit, failed to undergo photo-oxidative modification under these conditions, but prolonged irradiation (>7 h) had a small effect inasmuch as mottled films of polyacetylene were obtained on heating in the vacuum oven. Three fresh samples of colourless copolymers containing bis(trifluoromethyl)quadricyclo$[6.0.0^{2,4}.0^{3,6}.0^{5,7}]$octane vinylene and bis(trifluoromethyl)bicyclo[2.2.2]octadiene vinylene units (monomer ratio of 95:5, 90:10 and 85:15 respectively) were also unreactive towards photo-oxidative modification under these conditions. Thin films of these copolymers were also examined after they had been stored at room temperature for several hours in order to allow the bis(trifluoromethyl)bicyclo [2.2.2]octadiene vinylene units to convert to polyene sequences prior to irradiation. These films showed no tendency to undergo photo-oxidative modification even after prolonged irradiation; all samples gave polyacetylene on heating in the vacuum oven.

Photobleaching of polyacetylene films

Samples of polyacetylene film prepared by the precursor route from **II** were exposed to air and light for a period of up to 2 years. The films bleached unevenly; colourless sections were cut from the film and ground to a powder in liquid nitrogen. The powder obtained was dried under continuous pumping at 10^{-3} mmHg for several hours.

Analytical techniques

The samples whose preparation is described above were studied by: solid-state cross-polarization magic-angle spinning (c.p./m.a.s.) ^{13}C n.m.r. spectroscopy using a Varian XR 300 n.m.r. spectrometer; thermal analysis using a Perkin–Elmer DSC-2 and a Stanton–Redcroft TG-760; infra-red spectroscopy using a Perkin–Elmer 580 spectrophotometer; ultra-violet/visible spectroscopy using a Perkin–Elmer 330 u.v./vis. spectrophotometer; differential thermal pyrolysis (d.t.p.) using the heated direct insertion probe on a VG Analytical 7070E Mass Spectrometer; and C, H and N elemental analysis using a Carlo–Erba Elemental Analyser 1106.

RESULTS AND DISCUSSION

Ultra-violet/visible spectroscopy

A thin film of precursor **V** was spun from a yellow solution in butanone onto the quartz window of a demountable gas cell. The cell was assembled with the precursor polymer film on the inside and evacuated; the spectrum of this sample was recorded (trace a, *Figure 1*). The sample was irradiated under vacuum for 20 min using a medium-pressure Hg lamp and the spectrum re-recorded (trace b, *Figure 1*). Next the quartz window was removed from the cell and the polymer film was irradiated face up in the air for 10 min. The cell was reassembled, evacuated and heated at 100°C for 100 min and the spectrum recorded (trace c, *Figure 1*). Finally the cell was re-evacuated and the spectrum re-recorded (trace d, *Figure 1*). It is clear from this set of spectra that the precursor displays the multiple absorption bands in the 300 to 500 nm region anticipated for a conjugated polyene mixture; irradiation under vacuum (trace b) does not have a particularly spectacular effect on the nature of the spectrum: the bands move to longer wavelengths but the general appearance is unchanged, a result consistent with a slight increase in the average conjugation length of the polyene sequences present and possibly some *cis* to *trans* isomerization. After exposure in air and heating, the spectrum (trace c) of the film is completely changed: the multiple polyene bands have disappeared and there is a residual featureless tail showing increasing absorption to short wavelength, at least part of which must be due to volatile components produced during the heating stage, since a significant part of the intensity of the tail absorption is lost on re-evacuating the cell. The spectrum of precursor polymer left in the dark at room temperature changes slowly, with the polyene bands gradually increasing in intensity.

This set of observations make it clear that the photolithographic process in polymer **V** involves both light and air, and is correctly described as a photo-oxidative modification. During the photobleaching all the polyene sequences are destroyed and, since heating the bleached film does not result in the generation of new polyene sequences, it is likely that there are few sequences of the repeat unit **II** present at this stage. This implies either that the repeat units in **II** are affected by the photo-oxidation or that there are very few adjacent units of structure **II** in samples of precursor film that undergo photo-oxidative modification; the former hypothesis can, however, be ruled out since pure precursor polymer **II** is not susceptible to photo-oxidative modification as evidenced by the fact that samples exposed to u.v. and air do undergo thermal conversion to polyacetylene (see 'Experimental' section). Thus, it appears likely that in samples of precursor suitable for the photolithographic

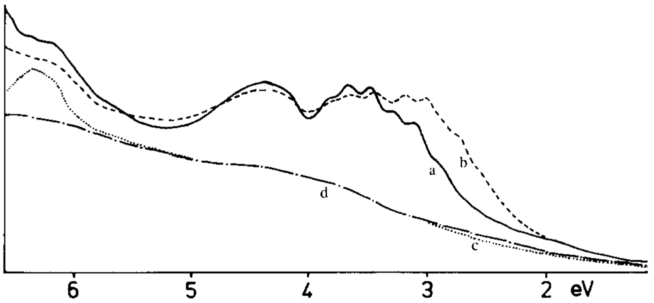

Figure 1 U.v./vis. spectra for thin films of: (a) precursor polymer V spun onto the silica window of a demountable gas cell and examined under vacuum at room temperature; (b) sample (a) after irradiation with a medium-pressure Hg lamp for 20 min; (c) sample (b) after the cell has been demounted, the sample irradiated in air, the cell reassembled and heated at 100°C for 100 min; and (d) sample (c) after the cell has been evacuated to remove volatile components

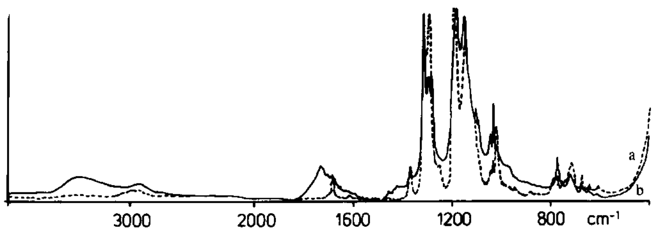

Figure 2 Infra-red spectra for thin films of: (a) precursor polymer **V** spun onto the KBr window of a demountable gas cell and examined under vacuum at room temperature; and (b) sample (a) after irradiation with a medium-pressure Hg lamp for 13 min in air, the spectrum being recorded after reassembly and evacuation of the cell

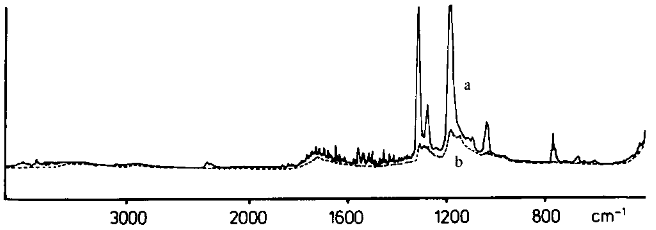

Figure 3 Infra-red spectra for thin films of: (a) the sample from *Figure 2b* after the cell had been heated at 100°C for 67 min; and (b) the same sample after evacuation of the cell

process units with structure **II** occur predominantly as single isolated features between short polyene sequences.

Infra-red spectroscopy

Thin films of precursor **V** were spun cast from a yellow solution in butanone onto the polished KBr window of a demountable gas cell; the cell was assembled with the polymer film on the inside, evacuated and the spectrum recorded (trace a, *Figure 2*). The window was then removed from the cell and the polymer film exposed to air and radiation from a medium-pressure Hg lamp for 13 min; the cell was assembled, evacuated and the spectrum recorded (trace b, *Figure 2*). It is clear from these spectra that the original precursor film has undergone extensive oxidation; thus, there is a new broad featureless band at 3700–3100 cm^{-1}, which is consistent with the presence of hydroxyl or hydroperoxide groups. There is also a new broad absorption band at 1850–1550 cm^{-1}, which is consistent with a series of overlapping carbonyl absorptions. The positions of two of the bands associated with the CF_3 groups are shifted, 1295 to 1315 cm^{-1} and 1195 to 1185 cm^{-1}, while the band at 1150 cm^{-1} is unchanged. Despite these changes it is clear that the CF_3 units remain intact in the photo-oxidized film. The band at 1018 cm^{-1} in the precursor disappears and there is a reduction in intensity of the band at 720 cm^{-1}; both of these absorptions can be associated with out-of-plane bending modes of vinylic C–H bonds. There are a number of other minor changes consistent with substantial changes in structure during photo-oxidation of precursor **V**.

The cell containing the photo-oxidized precursor film under vacuum was heated in an oven for 67 min at 100°C and the spectrum recorded (trace a, *Figure 3*). The cell was evacuated and the spectrum re-recorded (trace b, *Figure 3*). It can be seen that heating the photo-oxidized film under vacuum releases volatile materials. Comparison with reference spectra allows the assignment of the bands removed on evacuation to a mixture of water (4000 to 3500 cm^{-1}, 1975 to 1350 cm^{-1} and 600 to 400 cm^{-1} regions), carbon dioxide (weak doublet at 2350 cm^{-1} and band at 670 cm^{-1}) and hexafluoroorthoxylene (1320, 1280 and 1185 cm^{-1}). The hexafluoroorthoxylene must originate from residual units of **II** and the carbon dioxide and water from the decomposition of the groups produced during the photo-oxidation process.

Figure 4 shows the spectrum of a free-standing film of polyacetylene prepared by the precursor route, which has been allowed to photobleach in the normal laboratory atmosphere over a period of 2 years. It shows several features that are similar to photobleached precursor **V** (*Figure 2*, trace b) but in a more intense form; thus, the bands in the –OH and >C=O stretching regions dominate the spectrum, and in this case the broad –OH stretching region extends from 3600 to 2500 cm^{-1} consistent with the presence of carboxylic acid units.

Nuclear magnetic resonance spectroscopy

The c.p./m.a.s. ^{13}C n.m.r. spectrum of a sample of the photo-oxidized and heated precursor **V**, accumulated as described above and ground to a powder under liquid nitrogen, was recorded at 75.43 MHz (*Figure 5*). There are at least seven distinguishable carbon environments in the material and the chemical shifts observed are consistent with a highly oxidized system. Assignments may be made as follows: carboxylic acid (203.3 ppm), ketone carbonyl (175.0 ppm), vinylic carbons (133.7 ppm), saturated carbon carrying one oxygen atom (76.6 ppm) and allylic carbons (41.7 ppm), with one signal at 101.0 ppm of uncertain origin.

The c.p./m.a.s. ^{13}C n.m.r. spectrum of a sample of powdered photo-oxidized polyacetylene film was also

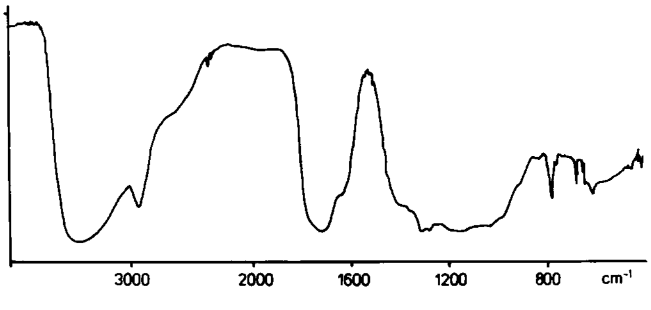

Figure 4 Infra-red spectrum of a free-standing film of polyacetylene prepared by the precursor route which has been allowed to photobleach in the normal laboratory atmosphere over a period of several months

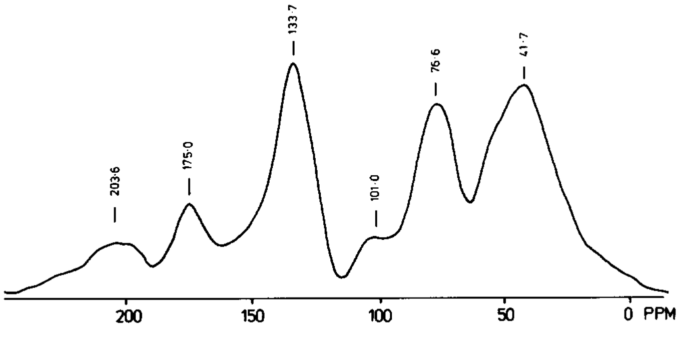

Figure 5 C.p./m.a.s. ^{13}C n.m.r. spectrum of a sample of the photo-oxidized and heated precursor **V**, accumulated as described in the text and recorded at 75.43 MHz

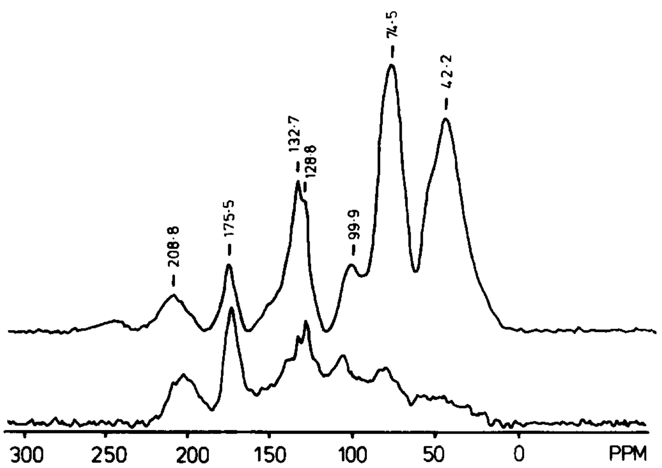

Figure 6 C.p./m.a.s. ^{13}C n.m.r. spectrum of a sample of powdered photo-oxidized polyacetylene film recorded at 75.43 MHz. Upper spectrum records all nuclei; lower spectrum non-quaternary carbon signals suppressed

recorded (*Figure 6*). The spectra shown in *Figures 5* and *6* are very similar and the signals in *Figure 6* may be assigned to the same set of carbon environments postulated to account for the earlier spectrum. In this case the non-quaternary suppressed spectrum gives further support to the assignments.

The similarity of the carbon environments in photo-oxidized precursor **V** and photo-oxidized polyacetylene suggests that the materials have similar compositions and probably arise by similar processes, namely oxidation of conjugated polyene sequences. This hypothesis is in agreement with the infra-red evidence that hexafluoroorthoxylene is thermally eliminated from photo-oxidized **V**, which implies that at least some of the units of structure **II** are present after photobleaching **V**. The presence of carbon dioxide and water in the volatile thermolysis products from photobleached precursor **V** can be postulated to arise from carboxylic acid, hydroxyl and hydroperoxy groups.

Thermal analysis

In differential thermal pyrolysis (d.t.p.) a sample of the material under examination is coated onto the direct insertion probe of a mass spectrometer. After insertion into the source region the probe temperature is raised from ambient to 200°C while the mass spectrum of the evolved volatiles is continuously monitored. Examined in this way, precursor polymers **II** and **V** gave exclusively hexafluoroorthoxylene as expected; precursor **VI** decomposed explosively in all of several attempts to record a d.t.p. trace, the only significant new peak detected in the wake of these explosions occurring at mass 91. The d.t.p. of photo-oxidized **V** revealed only carbon dioxide and hexafluoroorthoxylene as volatile thermolysis products, and photobleached polyacetylene evolved a trace of hexafluoroorthoxylene at first and then only carbon dioxide. As water is not detected by this technique, these results are in agreement with the infra-red spectroscopic analyses reported above.

Samples of the various materials discussed above were also examined by differential scanning calorimetery and thermogravimetric analysis. The results were consistent with the picture of the processes occurring during photo-oxidation which emerged from the spectroscopic analyses; two sets of traces are presented in *Figures 7* and *8* by way of illustration.

The upper trace in *Figure 7* and the broken curve in *Figure 8* were recorded for samples cut from a film of polyacetylene that had been prepared by the precursor route and allowed to photobleach in air over a period of 2 years; the broad endothermic process observed in d.s.c. between 320 and 420 K is attributed to decomposition reactions and is consistent with the initial weight loss observed in the thermogravimetric analysis in the same temperature range. Samples of photo-oxidized precursor polymer show a similar but less marked endothermic decomposition pathway in this temperature range. In the d.s.c. record the photobleached material appears relatively stable in the temperature range 420 to 600 K, at which point a large endothermic process dominates. These observations are consistent

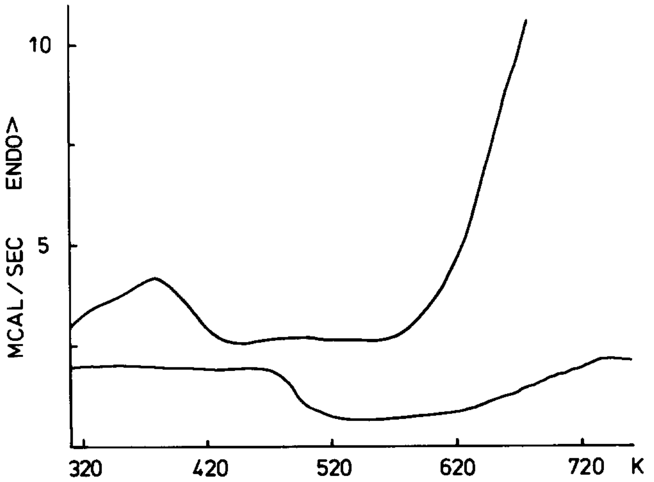

Figure 7 D.s.c. analysis record for photo-oxidized polyacetylene (5.22 mg, upper curve) and photo-oxidized precursor polymer **V** which has been heated at 100°C for 1 h (0.834 mg, lower curve)

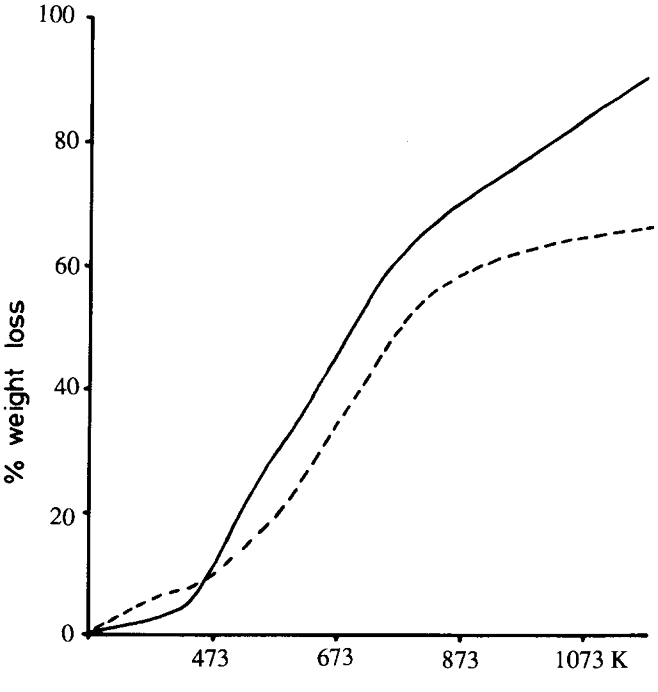

Figure 8 T.g. analysis record for photo-oxidized polyacetylene (8.70 mg, broken curve) and photo-oxidized precursor polymer **V** which has been heated at 100°C for 1 h (0.34 mg, full curve)

with the S-shaped t.g. record, the flat region in the d.s.c. trace corresponding with the minimum in the rate of weight loss and the large endothermic process corresponding with the rapid weight loss.

The lower trace in *Figure 7* and the full curve in *Figure 8* were recorded for a sample of a thin film of the precursor polymer **V** that had been photo-oxidized and then heated under vacuum. Again the two kinds of analysis are self-consistent. The material is stable up to 470 K when an exothermic process and rapid weight loss are observed in the d.s.c. and t.g. respectively.

These thermal analysis data taken as a whole are consistent with the hypothesis put forward to accommodate the spectroscopic evidence; namely, that both the precursor polymer **V** and polyacetylene undergo photo-oxidative modification, which leads to incorporation of a variety of oxygen-containing functionalities. In these experiments the modification of the precursor polymer **V** was generally not as extensive as that of polyacetylene as is illustrated in *Figure 8* where the t.g. curve appears to reach a plateau at about 60 to 70% weight loss, presumably because the highly functionalized material is able to form a highly crosslinked char. There are differences between the thermal behaviour of photo-oxidized precursor polymer **V** and photobleached polyacetylene films as would be expected on the basis of their different structures. Thus, all the decomposition processes observed for photo-oxidized polyacetylene are endothermic whereas photo-oxidized samples of the precursor polymer **V** undergo an endothermic decomposition process below 400 K and an exothermic process above 470 K; presumably the latter is associated with the elimination of hexafluoroxylene residues, which are not, of course, present in oxidized polyacetylene samples.

Elemental analysis

Elemental analysis of samples of the various materials described here gave variable results depending on the thickness of the film used and the duration of the exposure to oxidizing conditions. In all cases there was a significant decrease in carbon content consistent with the incorporation of oxygen into the samples; for example, a photobleached sample of polyacetylene gave C 49.6%, H 4.7% inferring an oxygen content of 45.7% and roughly one oxygen atom per carbon. These observations are consistent with the hypothesis of extensive oxidation but are otherwise not very informative.

CONCLUSIONS

The photolithographic process in the precursor polymer **V** has been shown to proceed most efficiently when trienes and pentaenes are the predominant conjugated sequences present in the copolymer. Pure precursor polymer **II** does not undergo photo-oxidative crosslinking and the presence of significant concentrations of longer polyene sequences reduces the efficiency of the process. The available evidence is consistent with the proposal that effective forms of the precursor polymer film **V** function in the lithographic process by sensitizing the production of singlet oxygen *in situ*, which then reacts with the film to give peroxides via reaction involving a vinylene and a tertiary allylic C–H bond and/or cyclic peroxides via 2 + 4 cycloaddition at *cis*-diene units, these two steps initiating the classic auto-oxidation process for unsaturated organic materials, a well established process that leads to extensive crosslinking[14–16].

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