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# Thermal and optical studies on hexa-2,4-diyne-1,6-diyl-bis(4-*n*-hexoxybenzoate)

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As part of a programme investigating mesogenic diacetylenes a symmetrically disubstituted diacetylene has been synthesized and polymerized. Thermal, thermo-optical and IR studies have been carried out to investigate the different crystalline forms of the diacetylene.

## 1. Introduction

As part of our research programme on the synthesis and properties of diacetylenes and polydiacetylenes with mesogenic groups in their side chains, several new classes of materials have been reported together with the results of thermal analysis and hot stage polarising microscopy [1–3]. Although there are examples [4–7] of polymer main chain liquid crystals containing diacetylene units, these are either polyesters or polyurethanes. Only a small number of liquid-crystalline polydiacetylenes have been reported [3, 8, 9] (see figure 1). In this paper we report on the synthesis and structural, thermoanalytical and hot stage polarizing microscopy studies of hexa-2,4-diyne-1,6-diyl-bis(4-*n*-hexoxybenzoate).

## 2. Experimental

Hexa-2,4-diyne-1,6-diyl-bis(4-hexoxybenzoate) was prepared by the two-stage synthesis shown in Schemes I–IV. 4-*n*-Hexoxybenzoic acid (I) (27·7 g, 0·125 mol) was dissolved in benzene. *N*,*N*-Dimethylformamide (DMF) (1 cm$^3$) was added, the temperature increased to 50–60°C and a solution of thionyl chloride (11 cm$^3$, 0·14 mol) in benzene (11 cm$^3$) added slowly. The gases evolved were absorbed in DMF. After evolution had ceased, the reaction mixture was maintained at 50–60°C for a further 30 min, then the solution concentrated *in vacuo*.

The residual acid chloride (II) was dissolved in benzene (100 cm$^3$) and the solution added dropwise to a benzene solution of hexa-2,4-diyne-1,6-diol (III) (6·6 g, 0·06 mol) and triethylamine (57 cm$^3$, 0·4 mol) at 40° C. After 3 hours, the precipitated triethylammonium chloride was filtered off and the solution concentrated *in vacuo*. The oily residue was recrystallised five times from diethyl ether/methanol mixture (50 : 50 v/v) to give the product (IV). (Found: C, 73·96 per cent; H, 7·55 per cent, $C_{32}H_{38}O_6$ requires C, 74·13 per cent; H, 7·33 per cent). During purification, two products were

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¶Deceased.

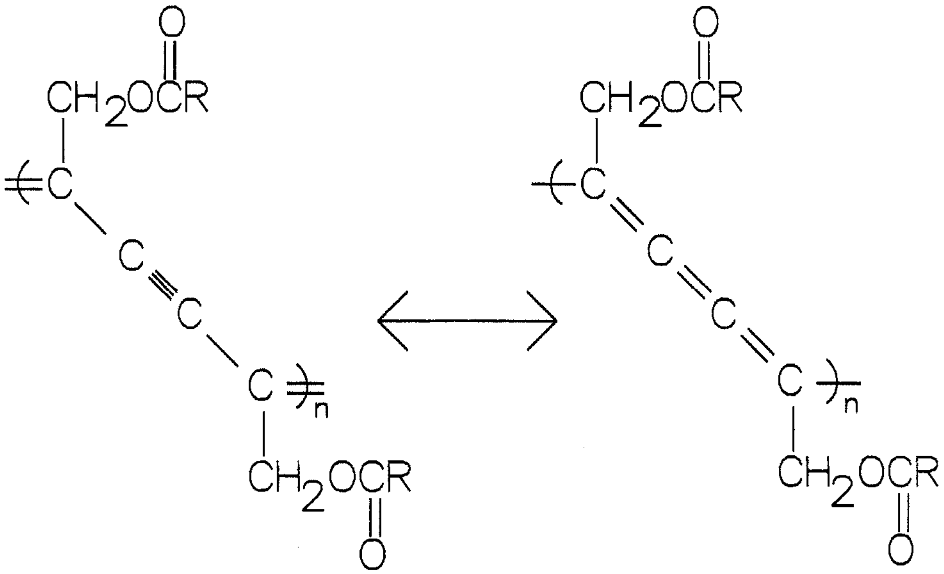
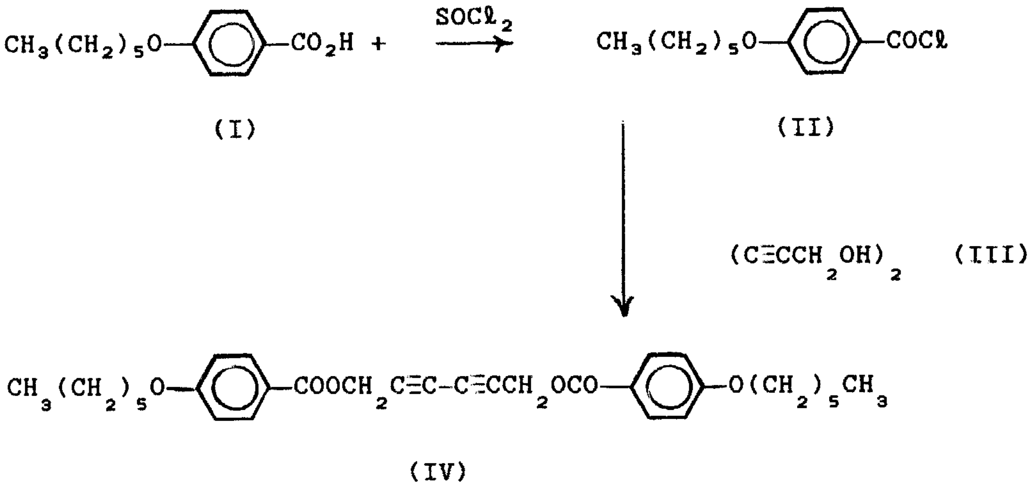


Figure 1. Molecular structure of a polydiacetylenic ester.

obtained, one white and one red. The white product is obtained by dissolving (IV) in diethyl ether and adding a large excess of methanol (8–10 times) to the boiling solution. Colourless well-formed rectangular crystals appeared on cooling to room temperature. The red product is obtained by dissolving (IV) in a mixture of diethyl ether/methanol (1 :4 – 1 : 5 v/v) at the boiling point followed by rapid cooling in ice-water.

## 3. Instrumentation

I.R. spectra were recorded as KBr discs on a Perkin Elmer 881 spectrophotometer and as crystals on a Perkin-Elmer 1760-X infrared Fourier transform spectrometer



Schemes I–IV.

linked to a Spectra Tech. I.R.-Plan infrared microscope accessory and a Perkin-Elmer 7700 professional computer. U.V./Vis spectra were recorded on a Perkin–Elmer $\lambda$7 spectrophotometer. Elemental analyses were obtained using a Carlo Erba 1106 elemental analyser equipped with a Spectra Physics SP4100 computing integrator. TA, DSC and melting behaviour were carried out respectively on a Stanton Redcroft STA-780 thermal analyser, a Mettler DSC 30 low temperature cell connected to a Mettler TC 10A automated data processor and on a Nikon Optiphot-Pol polarizing microscope equipped with a Linkam THM 600 hot stage.

## 4. Results and discussion

The white product has a sharp melting point at 57·7–58·3°C but the original needle-like crystals did not reappear on cooling. Instead, a marbled pink material formed. This indicates that polymerization has taken place after melting. DTA measurements show that after endothermic melting, an exothermic process occurs corresponding to polymerization (see figure 2) while TG shows no change in mass of the sample until the temperature exceeds 200°C.

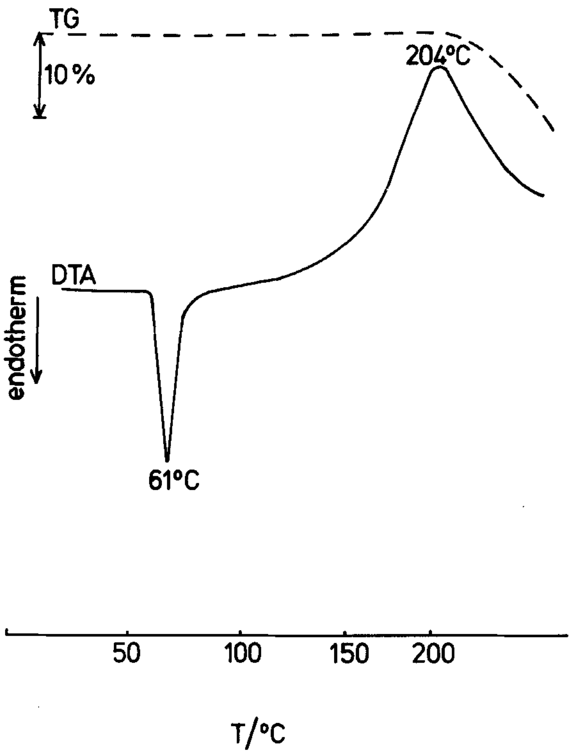


Figure 2. TG/DTA analysis of the white product.

DTA investigations of the red product show two endothermic peaks below 100°C (see figure 3). The first corresponds to melting of the residual monomer (IV) while the second may be due to a liquid-crystalline transition or to the melting of oligomers. The red product is less stable than the white since the peak in the exothermic process is at 176°C, some 28°C below the corresponding peak for the white product. A slight increase in weight occurs at 157°C followed by a decrease at 185°C.

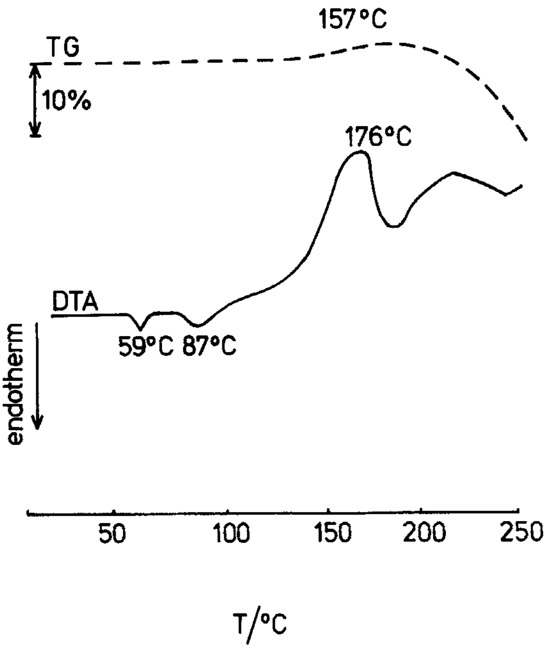


Figure 3. TG/DTA analysis of the red product.

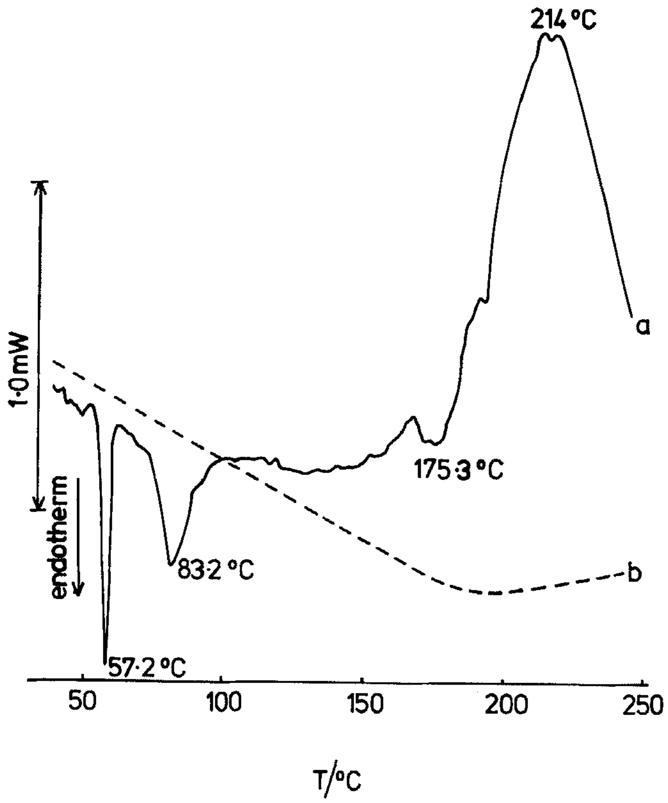


Figure 4. DSC thermogram of the red product.

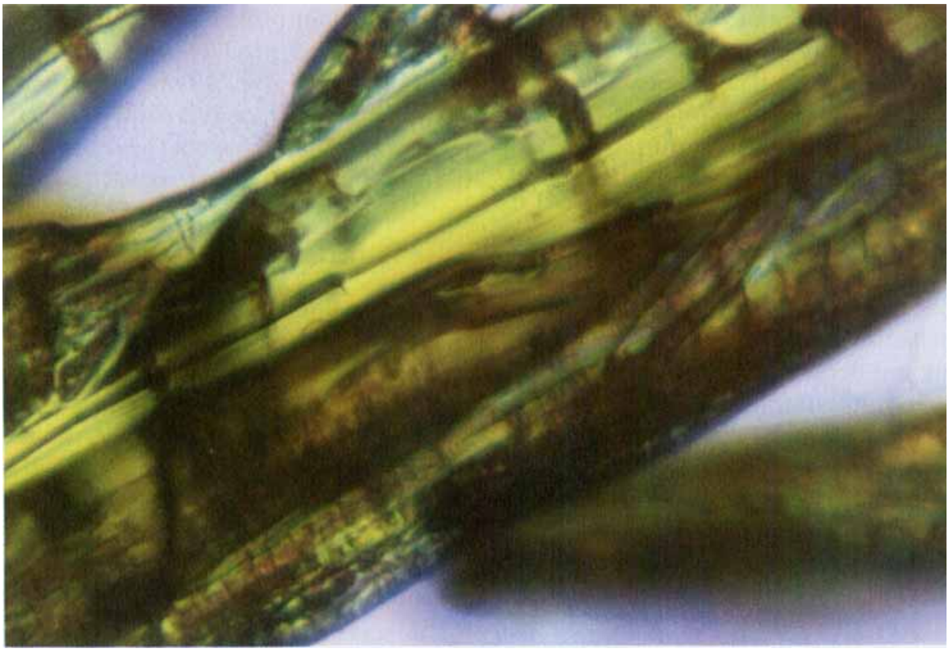


Figure 5. Photomicrograph ( × 620) of the red product at 113°C.

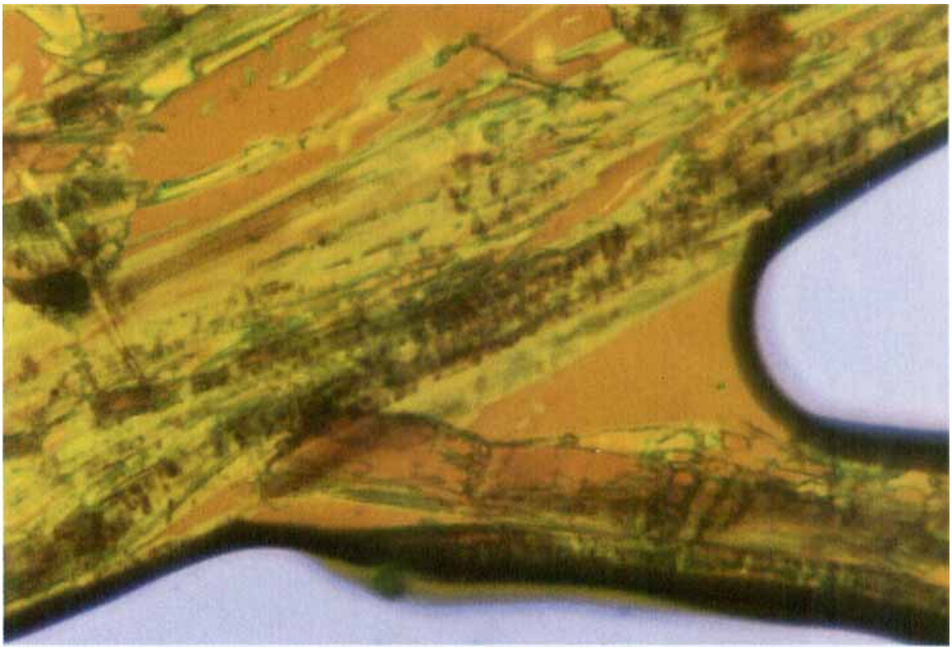


Figure 6. Photomicrograph ( × 620) of the red product at 191·7°C.

DSC studies of the red product also show these transitions (see figure 4). The first endothermic transition, from 48°C to 68°C, is sharp and unsymmetrical; this corresponds to melting of the residual monomer. The peak melting temperature is 57·2°C with $\Delta H$ of $3{\cdot}1\,\mathrm{J\,g^{-1}}$.

DSC studies of the white product gives $\Delta H$ (melting) of 95 J g$^{-1}$. Thus, assuming the white product is pure monomer (IV), the red product contains about 3 per cent by weight of monomer. The second transition gives a symmetrical peak between 70°C and 110°C with a peak temperature at 83·2°C and $\Delta H$ of 19·6 J g$^{-1}$. Polymerization occurs during and after these transitions since the peaks do not reappear during a second heating cycle after the sample has been cooled to room temperature.

The red product was also investigated by optical microscopy between crossed polars. The sample was heated on a hot stage at 5 K min$^{-1}$ and photomicrographs were taken at temperatures corresponding to the transitions shown in figure 4. Two of these photomicrographs are shown in figures 5 and 6. No major changes are noticed between photomicrographs recorded at 35·4°C and 63·5°C although a small change in birefringence occurred. The change between 63·5°C and 113·4°C is much greater with the disappearance of the sharp edges and the appearance of dark lines across the sample (see figure 5). On further heating these lines disappeared and a fibrillar structure could be seen (see figure 6). This texture disappeared at 208°C and degradation of the sample then occurred.

The structural changes obtained on heating were confirmed by I.R. A KBr disc of the white product was heated to 70°C and maintained at this temperature for five

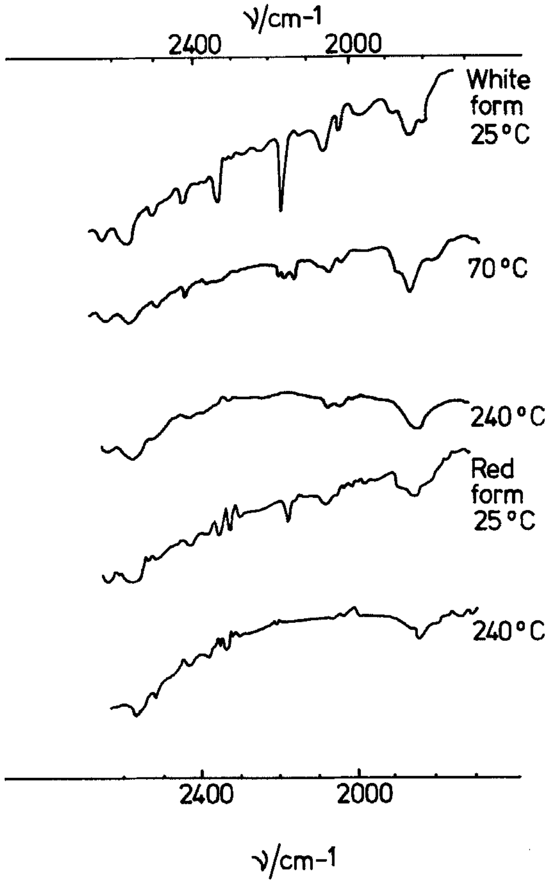


Figure 7. I.R. spectrum of the heat treated white product.

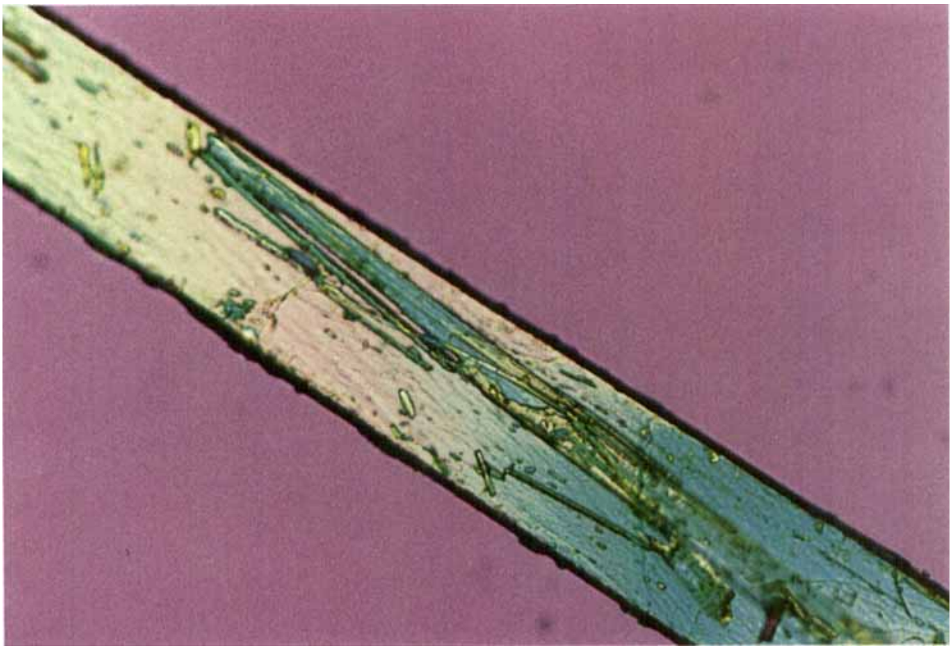


Figure 8. Photomicrograph (×620) of needles of the white product IV grown from toluene.

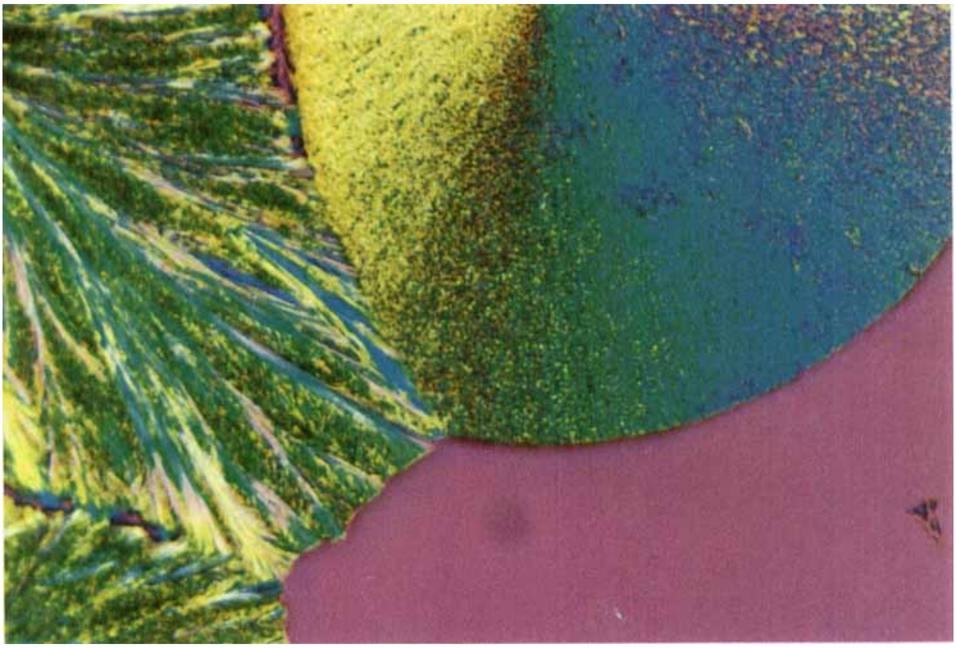


Figure 9. Photomicrograph (×620) of two types of spherulites grown from toluene (early stage).

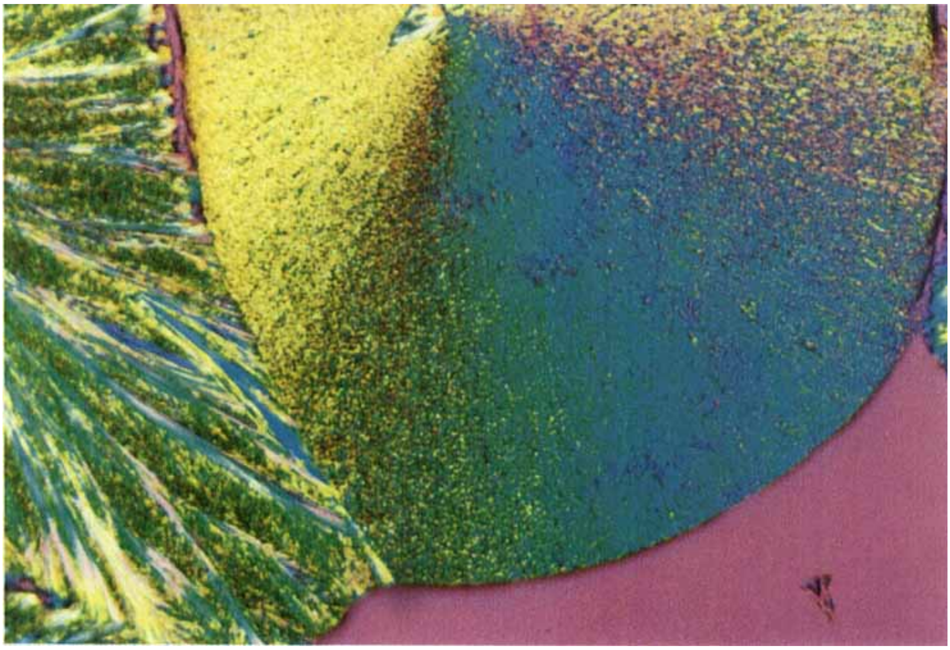


Figure 10. Photomicrograph ( × 620) of two types of spherulites grown from toluene (middle stage).

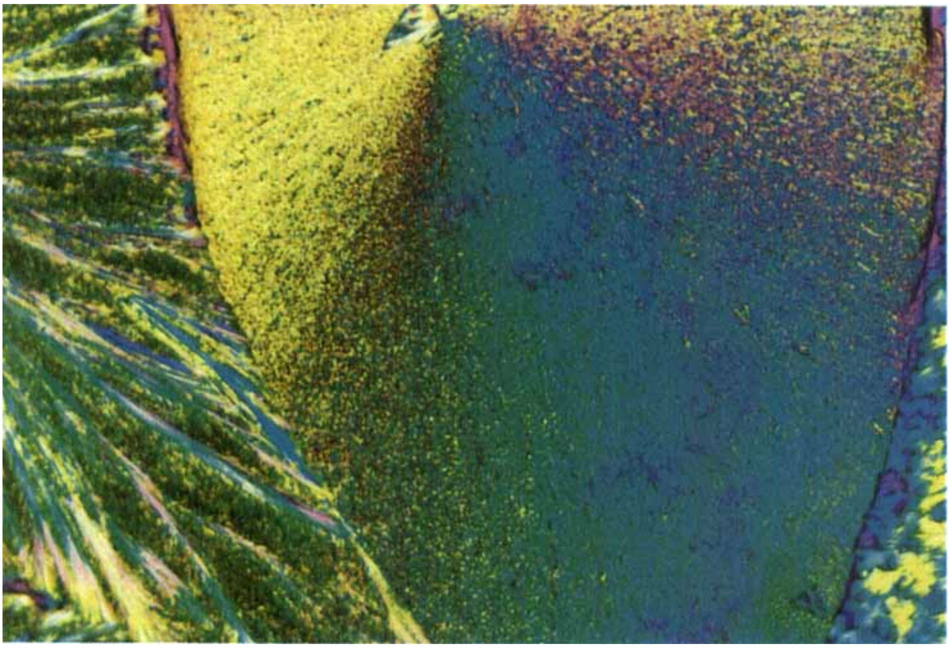


Figure 11. Photomicrograph ( × 620) of two types of spherulites grown from toluene (late stage).

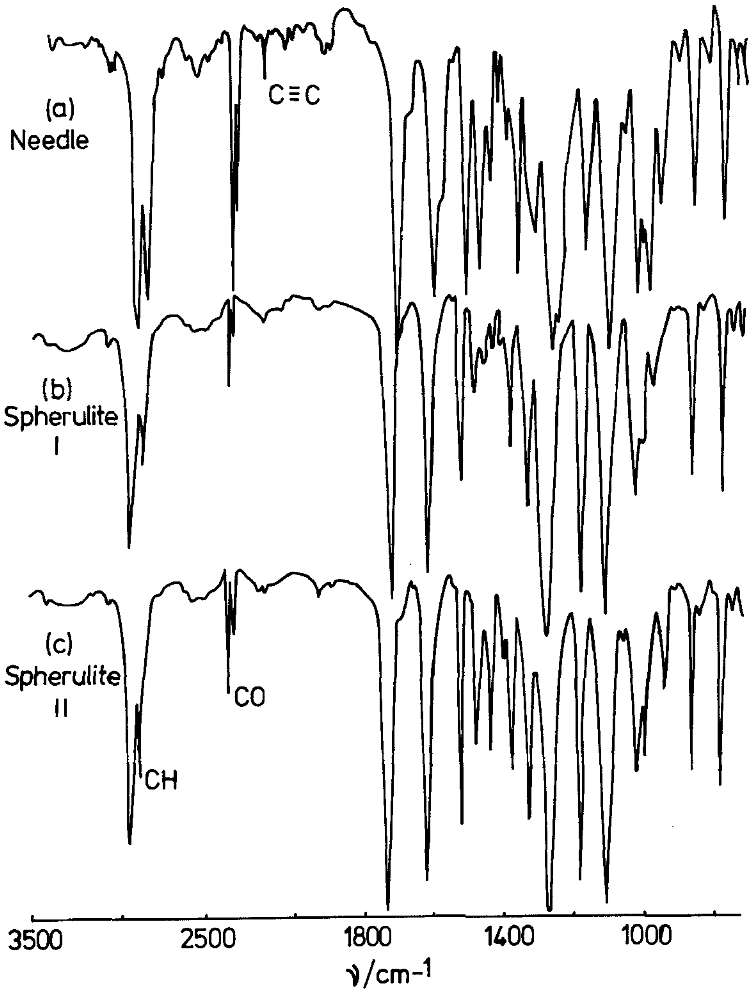


Figure 12. FTIR spectrum of (*a*) needles of the white product IV grown in toluene, (*b*) spherulite I, (*c*) spherulite II.

minutes then cooled to room temperature. The disc was then reheated to 240°C and held at this temperature for 5 min before cooling.

The I.R. spectra from 2600–1900 cm$^{-1}$ of the heat treated and original material are shown in figure 7. The spectrum of the original white product shows absorption at 2170 cm$^{-1}$ corresponding to the C≡C bond. On heat treatment, this peak decreases and disappears at 240° C, suggesting that thermal polymerization has occurred. The weight loss on heating is due to the formation of volatile products, and is characteristic of polymer degradation. The insolubility in common solvents infers crosslinking during polymer degradation.

The white product shows interesting behaviour when dissolved in toluene. Rapidly growing needles, together with two types of spherulite, growing at different rates, crystallize from the solution. Figure 8 shows the needles and figures 9–11 the two types of spherulite at different stages of crystallization with curved edges indicating the different growing rates [10]. Birefringence of the spherulites disappears at 53–54°C

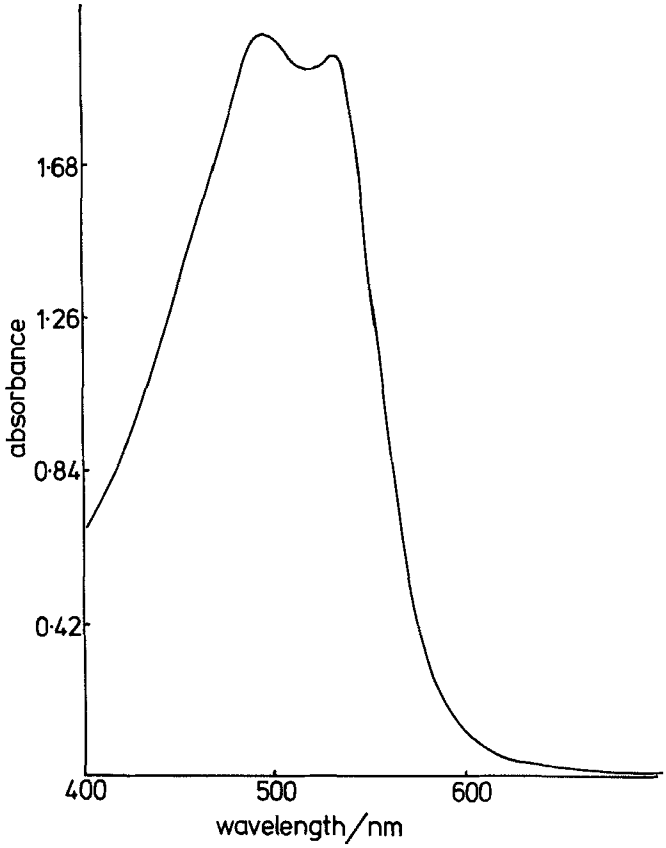


Figure 13. U.V./vis spectrum of the red product.

and the spherulites do not reappear on cooling. This suggests that polymerization is taking place at 53–54°C during melting. The needles and spherulites were also investigated by FTIR microscopy.

The spectrum (see figure 12 (*a*)) of the needle-like crystals has an absorption peak at 2180 cm$^{-1}$ (C≡C) showing the crystals to be pure (IV). This peak is almost absent from the spectra (see figures 12 (*b*), (*c*)) of the spherulites indicating that polymerization has occurred in toluene. A major difference in the spectra of the two types of spherulite is the relative intensity of the absorption peak at 1430 cm$^{-1}$. Spherulite I with the faster growth rate has a less intense peak at 1430 cm$^{-1}$ (see figure 12 (*b*)) than spherulite II (see figure 12 (*c*)). The morphology of the spherulites is thus related to the molecular structure of the material. The molecular structure of spherulite I is shown by FTIR to be identical to that of the red product, obtained by recrystallization (IV) from diethyl ether/methanol. Thus the red product always contains red polymeric fibrous material and white monomer. This is evident from U.V./vis spectra (see figure 13) where two absorption peaks are observed unless the monomer is extracted continuously with acetone over 24 hours. Complete polymerization occurs when the red residue from the extraction of monomer is heated for a further 24 hours. The U.V./vis absorption spectrum of the polymer shows only a single peak (see figure 14).

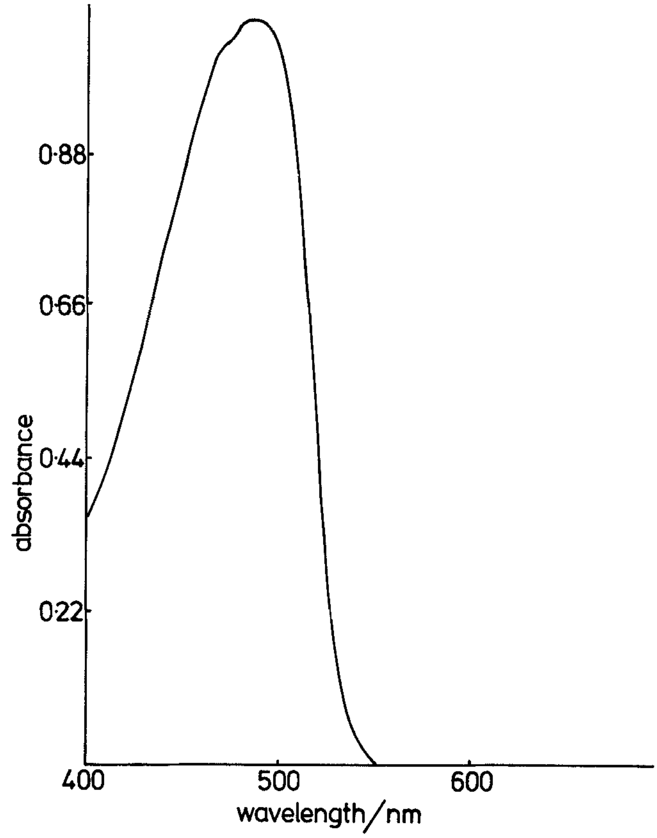


Figure 14. U.V./vis spectrum of the pure polymer.

In conclusion, in contrast to diacetylenic esters previously reported [3] this particular ester does not seem to form liquid crystals, but like many alkenes exhibits liquid state polymerization.

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