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The thermal polymerisation of a diacetylenic liquid crystal

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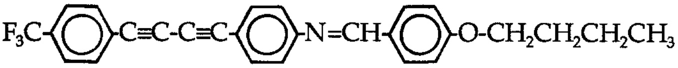
Summary

In this paper, the polymerisation of a conjugated liquid crystalline diacetylene is reported. The structure of the polymer is discussed in relation to results from spectroscopic studies and molecular weight determinations. The polymer has a backbone structure analogous to that of other polydiacetylenes.

Introduction

As part of our work on the synthesis, polymerisation and optoelectronic properties of conjugated, unsymmetrically disubstituted diphenyldiacetylenes(1-5), we have recently reported(5) the synthesis of compound I:



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This material was found to polymerise thermally in the liquid crystalline state to form a polymer of low solubility in common organic solvents.

In this paper we report some additional analytical data on compound I and the corresponding polymer.

Experimental

The synthesis of I has been reported elsewhere.(5) The material was recrystallised twice from absolute ethanol.

Infrared spectra were recorded as KBr discs on a Perkin Elmer 1600 Fourier-Transform spectrophotometer. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a VARIAN VXR 400 S spectrometer operating at 399.952 MHz and 100.577 MHz respectively. UV/Vis spectra were recorded in chloroform on a Perkin Elmer 330 spectrophotometer. Elemental (CHN) analyses were performed using a Carlo Erba 1106 elemental analyser equipped with a Spectra Physics SP4100 computing integrator. Studies of thermal polymerisation were carried out using a Perkin Elmer DSC7 differential scanning calorimeter. Thermogravimetric analysis results were obtained using a Stanton Redcroft STA-780 thermal analyser. Molecular weight distribution studies on the polymer were performed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) solution on a VISCOTEK instrument equipped with three columns of PL-gel of pore sizes 10^4, 10^2 and 50 nm respectively (Polymer Laboratories Ltd.). Measurements were carried

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out at room temperature using a flow rate of 1.0 cm^3 min^{-1}. A GPC calibration graph was obtained using a series of polystyrene standards. The purity of I was confirmed by HPLC using an ODS column with THF as solvent at room temperature and with a flow rate of 1 cm^3 min^{-1}. A single, narrow peak was obtained.

Discussion

The thermal polymerisation of I from a liquid crystalline state has been previously considered(3) and is believed to be a C_1-C_4 addition process similar to polymerisation from the solid state(6).

$$\begin{array}{c}\text{solid}\\ \text{monomer}\end{array} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \begin{array}{c}\text{liquid crystal}\\ \text{monomer}\end{array} \xrightarrow{\text{heat}} \text{polymer}$$

Further confirmation of this process for this material is evident from the results discussed below.

For the purpose of this study all samples (unless otherwise indicated) were polymerised by heating under nitrogen to 300 C at 10 C min^{-1} . The polymer obtained by the liquid crystalline state polymerisation of I had a black metallic appearance and gave elemental analysis results consistent with the homopolymerisation of this compound. Thermogravimetric analysis showed that the material is stable to temperatures up to about 325 C.

Samples of the polymer from **I** were dissolved in THF and the molecular weight distribution determined by GPC. For fully polymerised samples, a number average molecular weight of the order of 50,000 was obtained. Figure 1 compares the chromatogram of a sample of **I** heated from room temperature to 300 C at 10 C min^{-1} with that of a sample of **I** heated from room temperature to 290 C at the same rate. It is evident that not only is more monomer converted to the polymer on heating to the higher temperature, but that the polymer chains also increase in length. A monomer sample heated under identical conditions to 305 C resulted in the formation of a polymer which was completely insoluble in THF.

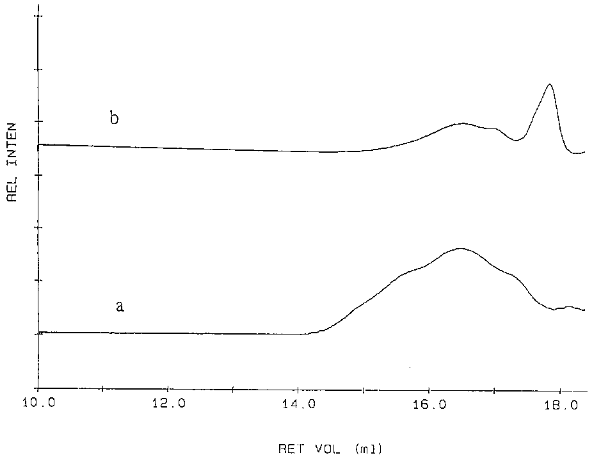


Figure 1
Molecular weight distribution (GPC trace) for thermally polymerised samples of I.

(a) polymerised by heating to 300C at 10C min^{-1}.

(b) partially polymerised by heating to 290C at 10C min^{-1}

The infrared spectrum of I and that of the corresponding polymer are shown in figures 2a and 2b respectively. In common with diacetylenes which polymerise in the solid state,(7) the major difference between the spectra of the monomer and the polymer is the disappearance of the $\nu(C{\equiv}C)$ stretching vibration at 2211 cm^{-1} in the monomer and the appearance of a very weak broad absorption at the same wavenumber in the polymer. This is a common observation during the conversion of unsymmetrical diacetylenes to the corresponding polydiacetylenes. All the other spectral features are retained in the polymer, but most of the signals are broadened. In particular, the three distinct monomer absorptions in the region 1569 cm^{-1} to 1623 cm^{-1} merge into a broad band with four shoulders in the polymer. The absorption of the monomer at 1623 cm^{-1} is attributed to the (C=N) stretching vibration and in the spectrum of the polymer, this stretching vibration appears as a shoulder of the 1599 cm^{-1} band.

The occurrence of the new absorption at about 1642 cm^{-1} on polymerisation and which is partially masked by the stretching vibration at 1623 cm^{-1} may be explained in terms of the double bond character which develops in the polymer backbone as illustrated below. This is considered further in the discussion of ^{13}C NMR results.

$$n\ R_1C{\equiv}C\text{-}C{\equiv}CR_2 \rightarrow \text{-}(R_1C{=}C{=}C{=}CR_2)\text{-}_n \quad \text{or} \quad {=}(R_1C\text{-}C{\equiv}C\text{-}CR_2){=}_n$$

UV/Vis spectra for **I** and the corresponding polymer, both recorded in chloroform, are shown in figure 3. The polymer was insufficiently soluble to enable accurate determination of the solution concentration. The monomer shows an

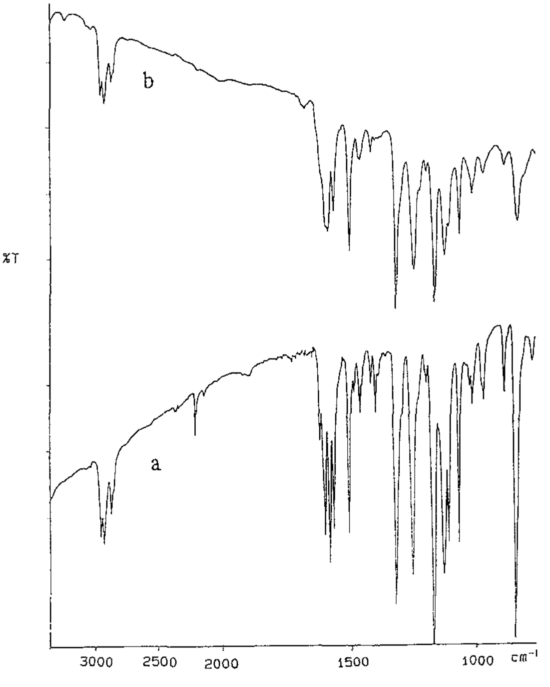


Figure 2
Transmission (KBr discs) FTIR spectra.
(a) monomer
(b) polymer

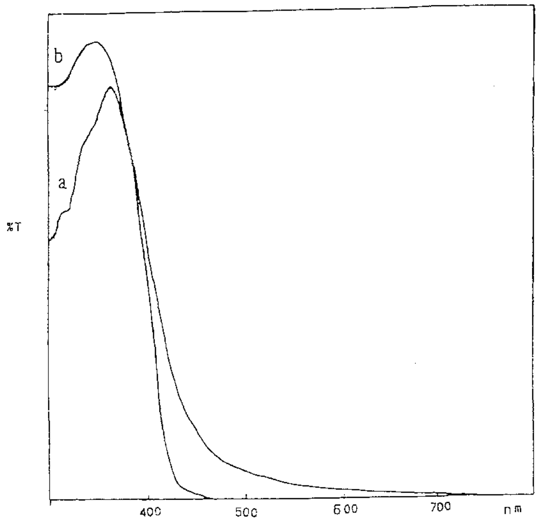


Figure 3
UV-Vis spectra
chloroform solutions
(a) monomer
(b) polymer

absorption limit of about 450 nm whereas the polymer shows some absorption above 600 nm. The broader absorption profile of the polymer is attributed to transitions in the π-electron system along the polymer backbone.(8)

Solution ^{1}H NMR spectra for I and the corresponding polymer are shown in figures 4a and 4b respectively. A detailed assignment of the proton resonances is given in Table 1. The protons on aromatic carbon atoms adjacent to the diacetylene unit in the monomer become non-equivalent in the polymer. This results in a change from the pseudo AB system observed in the spectrum of the monomer to a rather complex system of multiplets in the spectrum of the polymer.

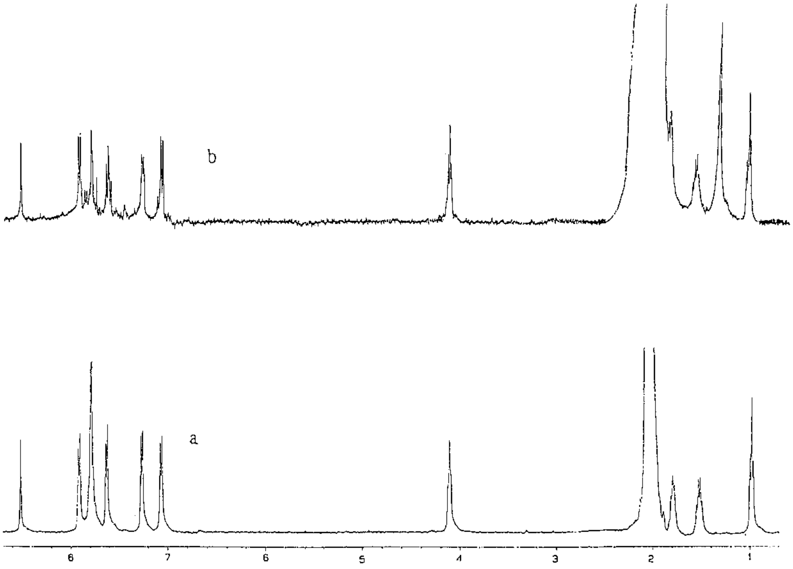
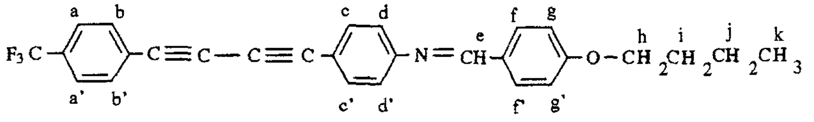


Figure 4 - ^{1}H NMR (acetone-d_6) spectra (a) monomer, (b) polymer

Table 1: Assignment of the ^{1}H-NMR spectrum of I and the corresponding polymer

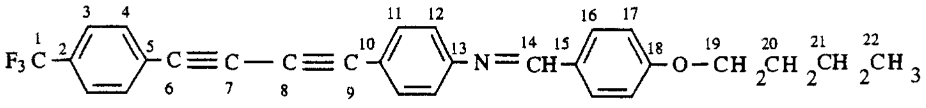


proton	monomer shift/ppm	polymer shift/ppm
H_e	8.52(s,1H)	8.52(s,1H)
H_g	7.92(d,2H)	7.92(d,2H)
$H_{c,c',d}$	7.80(pseudo AB,4H)	7.80(m,4H)
H_a	7.63(d,2H)	7.63(m,2H)
$H_{b,b'}$	7.26(d,2H)	7.26(m,2H)
H_f	7.07(d,2H)	7.07(d,2H)
H_h	4.11(t,2H)	4.11(t,2H)
H_i	1.79(m,2H)	1.79(partially masked)
H_j	1.52(m,2H)	1.52(m,2H)
H_k	0.99(t,3H)	0.99(t,3H)

The solution ^{13}C NMR spectra of I in deuterated chloroform and that of the polymer in deuterated benzene are shown in figures 5a and 5b respectively. Solutions of the polymer in deuterated acetone or chloroform were of insufficient concentration to allow the determination of the ^{13}C NMR spectrum even after a total acquisition time of 42 hours. Assignment of the signals of both monomer and polymer are given in Table 2. The main difference between the spectra of the monomer and the polymer is that the four acetylenic resonances of the monomer in the region 84.00 ppm to 73.61 ppm are replaced by two in the polymer at 82.75 ppm and 67.89 ppm.

The interpretation of the ^{13}C NMR spectrum and to a lesser extent the ^{1}H NMR spectrum of the polymer can be inferred using Figure 6. Previous ^{13}C NMR studies on symmetrical diacetylenes and the corresponding polymers have shown that a substantial shift occurs from 80 ppm to about 110 ppm for the single signal assigned to the two acetylenic carbon atoms in the main chain.(9) This shift has been attributed to the contribution of a possible cumulene resonance structure. Our results imply that such a contribution is minimal in the polymer formed in this study. The alkenic carbon atoms in the polymer main chain are expected to have shift values near 130 ppm and are masked by the deuterated benzene solvent.

Table 2: Assignment of the ^{13}C-NMR spectrum of I and the corresponding polymer.



nucleus	monomer shift/ppm (chloroform-D)	monomer shift/ppm (acetone-D_6)	polymer shift/ppm (benzene-D_6)
13	162.36	163.35	162.15
14	160.35	161.63	159.82
2	153.54	154.90	153.69
18	133.50	134.52	133.89
17	133.64	134.52	133.87
3	132.66	133.89	133.87
11	130.78	131.71	131.07
12	130.74	130.71	131.07
5	128.83	130.07	masked
10	125.34	126.72	masked
1	masked	masked	masked
4	121.19	122.37	121.55
15	118.18	118.48	118.25
16	114.86	115.68	115.05
8	83.21	84.00	82.75
7	79.92	80.63	67.89
6	77.52	76.90	masked
9	74.10	73.61	masked
19	68.01	68.70	63.85
20	31.24	32.01	31.45
21	19.21	19.87	19.41
22	13.74	14.04	13.80

NOTE: The masked -CF_3 signal is expected to appear as a low intensity quartet in the region 115 - 130 ppm.

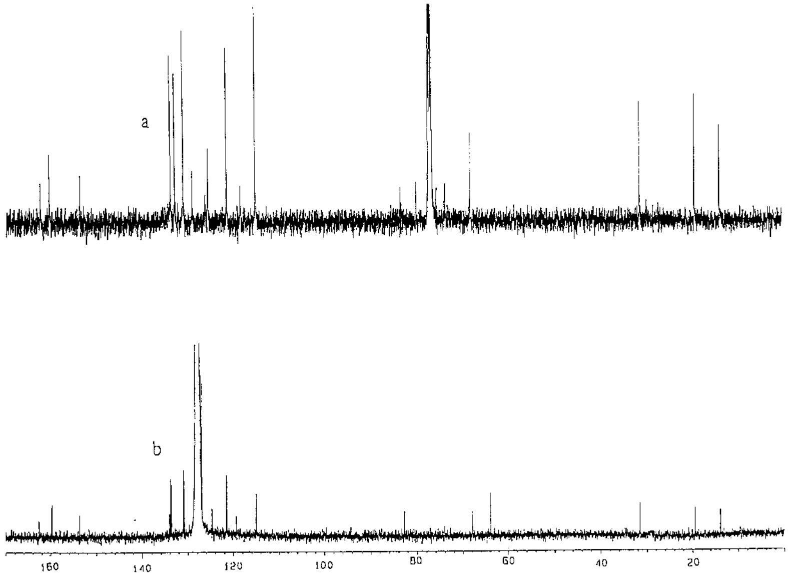


Figure 5 - ^{13}C NMR (a) monomer in chloroform-d (b) polymer in benzene-d_6

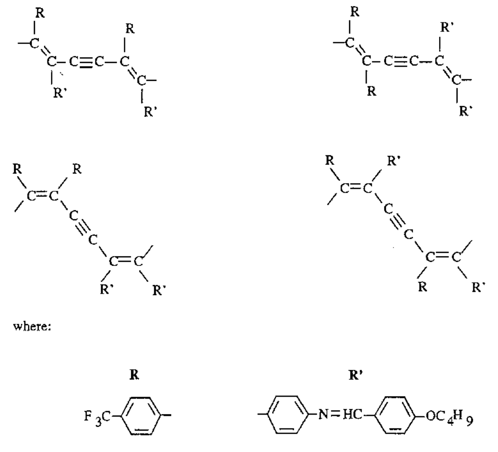


Figure 6
Possible Structures

Figure 6 shows the four possible ways in which the polymer can be formed from the monomer. Polymerisation of diacetylenes in the solid state yields trans isomers but the possibility of cis isomers occurring in solution of certain polydiacetylenes has been reported.(10) Polymerisation from the liquid crystal state may therefore produce cis as well as trans isomers.(11)

Studies using ^{13}C NMR on low molecular mass model compounds akin to sections of polydiacetylene chains have shown that the differences in positions of signals in the ^{13}C NMR spectra of cis and trans isomers is very small.(12,13) Thus ^{13}C NMR studies on the polymer from I does not establish that the polymer adopts a definite cis or trans configuration and further studies are in progress.

Conclusion

The thermal polymerisation of the liquid crystalline diacetylene (I) results in the formation of a polymer which has a backbone structure analogous to that obtained by the solid state polymerisation of other diacetylenes.

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