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## Liquid Crystals

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### thermotropic Liquid-Crystalline Polyesters Containing Cyclooctyl Units III. Effect of Mesogen Length and the Dual Role of the Cyclooctyl Ring

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## Thermotropic liquid-crystalline polyesters containing cyclooctyl units

### III. Effect of mesogen length and the dual role of the cyclooctyl ring

by J. M. G. COWIE and H. H. WU

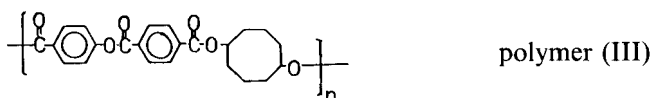
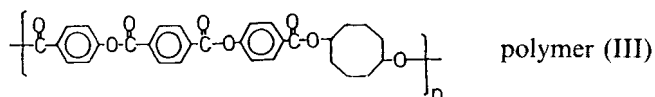
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Three polyesters have been prepared which incorporate the cyclooctyl unit in the main chain. The number of phenyl rings in the repeat unit was varied from one to three and in each case the polymer exhibited a liquid-crystalline phase. It has been shown that the cyclooctyl ring may act both as a semi-flexible spacer as well as an integral part of the mesogenic unit. This dual role is of considerable interest and has not been reported previously.

#### 1. Introduction

Thermotropic liquid-crystalline polyesters generally contain either two or three aromatic units linked in the para-positions with or without linear spacers [1-5]. It has been reported that polymers with a common spacer but with mesogenic groups of various length exhibit different textures [1, 2]. Here we describe the synthesis and phase behaviour of a series of liquid-crystalline polyesters in which the cyclooctyl group acts as common unit linking mesogenic cores consisting of one, two and three aromatic units:



#### 2. Experimental

The synthesis of the triad bis-phenol monomer for polymer III has already been reported [6]. The preparation of the diad monomer for polymer II involved standard literature methods [7, 8]. Cis-1,5-cyclooctane diol (Aldrich Chemical Company Ltd) was used without purification and the polymerization conditions have been described elsewhere [6]. The average molar weight of the products has not been measured. However, their viscosities suggest an average degree of polymerization in the range of 20 to 40 repeat units.

Transition temperatures were measured using a Perkin-Elmer DSC-2 at a scan rate of 20 K/min. A Reichert Thermovar polarizing microscope equipped with a hot-stage was used to identify the liquid-crystalline phases.

### 3. Results and discussion

#### 3.1. Polymer III

Figure 1 shows the D.S.C. thermograms of polymer III. Both the melting point ( $T_{CN}$ ) and the mesophase to isotropic transition temperature ( $T_{NI}$ ) were obtained from the first heating scan because the sample tended to decompose at high temperatures. The glass transition temperature ( $T_g$ ) was determined from the second heating cycle. The values of  $T_g$ ,  $T_{CN}$  and  $T_{NI}$  obtained from the heating scan are 358 K, 442 K and 517 K respectively.

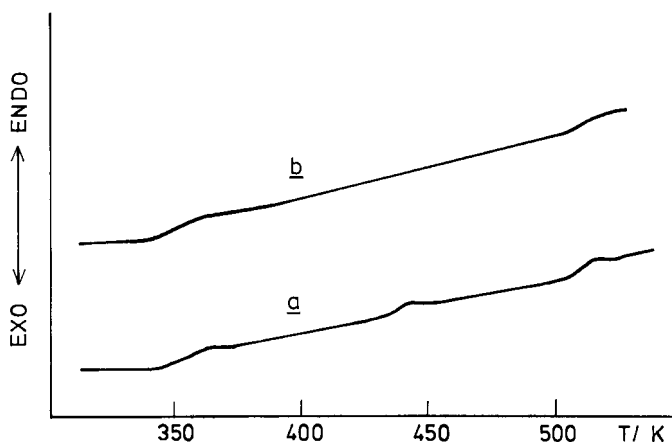


Figure 1. The D.S.C. thermograms of polymer III; (a) first heating scan, showing  $T_g$ ,  $T_{CN}$  and  $T_{NI}$  at increasing temperatures; (b) second heating scan, showing only  $T_g$  and  $T_{NI}$ .

Polymer III was heated into the isotropic phase (*c.* 600 K) and then gradually cooled to 500 K on the hot stage microscope, at which temperature tiny droplets began to form in a homeotropic background indicating the existence of a nematic phase. When the temperature was decreased to 490 K and the sample annealed for about 20 minutes, these nematic droplets began to coalesce. However, a brownish charred region developed and this was probably thermal decomposition of the sample.

#### 3.2. Polymer II

The DSC thermograms of polymer II are shown in figure 2. The higher temperature endotherm (408 K) was assigned as the mesophase to isotropic transition while the one at the lower temperature (385 K) was the melting transition. Subsequent thermal cycles were rather featureless apart from a glass transition at about 335 K. The cooling scan did not provide any further information. However, optical observations revealed that there was a mesophasic transition between 390 K to 410 K. In order to investigate this, the sample was cooled from 420 K to 390 K and annealed overnight. The sample was then cooled at 20 K/min to 300 K. On reheating to 420 K, two

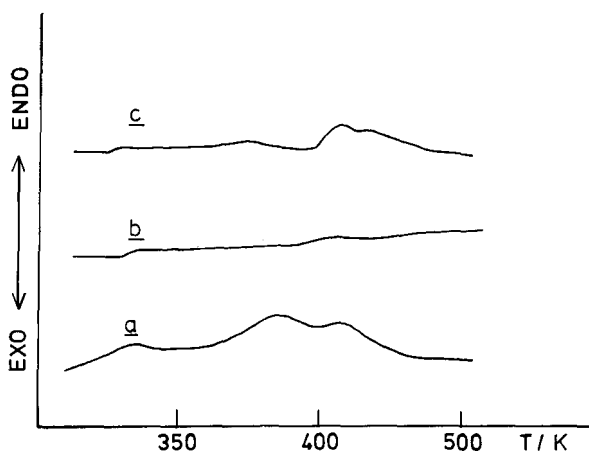


Figure 2. The D.S.C. thermograms of polymer II; (a) first heating scan, showing  $T_g$  at 335 K,  $T_{CS}$  at 385 K and  $T_{Sl}$  at 410 K; (b) second heating scan; (c) third heating scan after annealing at 390 K overnight.

endotherms were obtained at temperatures of 406 and 375 K. There was little change in the clearing temperature (ca 2 K) whereas the melting temperature obtained from the annealed sample was 10 K lower than that of a fresh sample. This suggests that the polymer had, to some extent, aligned during the annealing process and this is in accord with the optical observations.

When heated on a hot stage microscope, the sample began to melt at approximately 370 K and the last of the crystalline phase disappeared at 400 K. After that, the sample transformed into a homeotropic texture and the stir-opalescence effect vanished at 420 K. When quenched from the isotropic melt rapidly to room temperature, no identifiable texture could be observed and instead the sample was transparent. As a result, the sample was heated to 20 K above its clearing temperature, cooled to 390 K and annealed at this temperature for 24 hours. After two hours, a yellow fan-like texture began to develop from the homeotropic phase and four hours later, a spherulite-like texture also started to appear. Figure 3 shows the coexistence of the fan-like texture and the spherulites. Similar fan-like textures are usually observed in the smectic phases of low molar mass liquid crystals but the origin of the spherulites is unknown. Shaffer and Percec [9] have observed a similar texture in a series of polythioethers and on the basis of D.S.C. and optical observations concluded that this spherulite-like texture was a highly ordered smectic mesophase although the possibility of a crystal phase should not be excluded. A similar interpretation could also be applied to this system but from the evidence available it is impossible to state unequivocally whether there is only one smectic phase or two.

### 3.3. Polymer I

The D.S.C. thermograms for polymer I are shown in figure 4. The second heating scan clearly showed three endotherms, at 457 K, 462 K and 492 K, respectively, and subsequent scans were reasonably reproducible.

Optical microscopy revealed that the sample cleared at 510 K and on cooling the isotropic melt to 483 K, a blurred texture began to develop. No obvious textural changes were observed even after annealing the sample for 4 hours. On cooling the

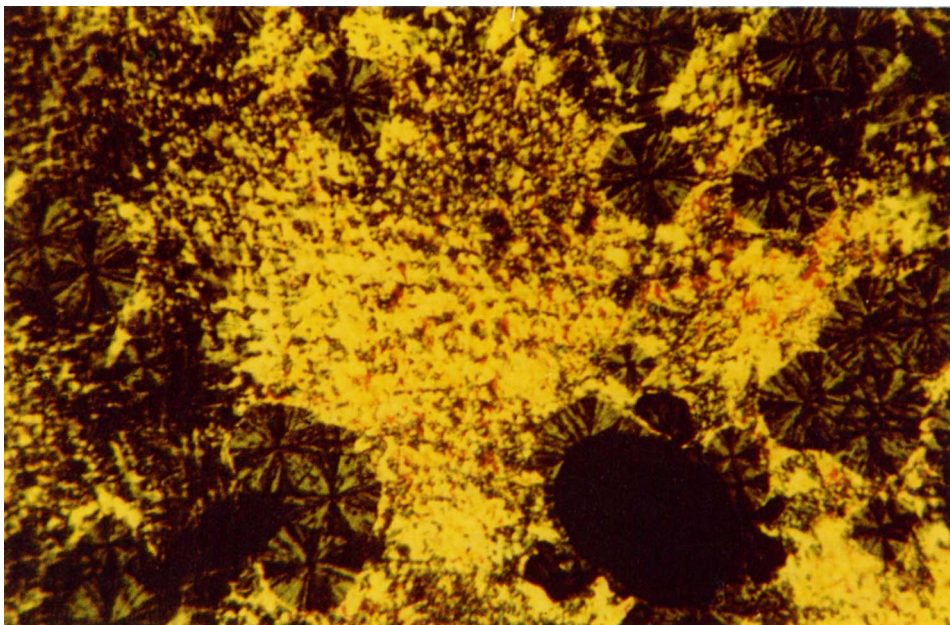


Figure 3. Microphotograph of polymer II taken at 390 K after annealing for 6 hours; this shows the coexistence of a fan-like texture and spherulites.

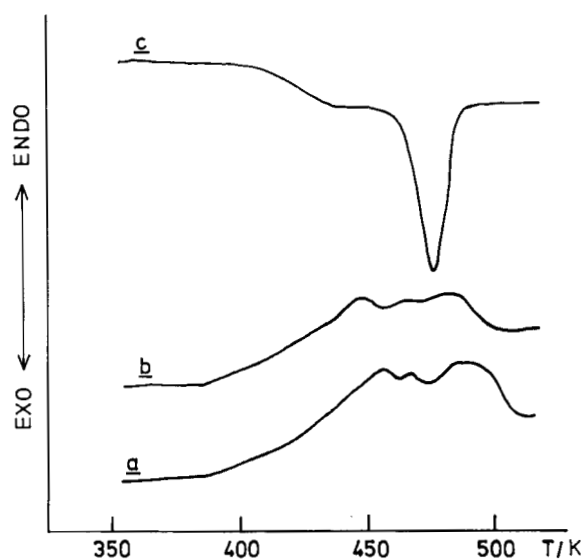


Figure 4. The D.S.C. thermograms of polymer I; (a) first heating scan, and (b) second heating scan, both showing three endotherms at 457 K, 462 K and 492 K; (c) first cooling scan.

sample slowly to room temperature a golden yellow coloured texture gradually started to appear that was reminiscent of the broken focal-conic texture of a smectic phase [10]. This suggested the possible formation of a smectic *C* phase but we require additional evidence to substantiate this assignment.

These results indicate an interesting dual role for the cyclooctyl ring. In polymers II and III it appears to act as a flexible spacer, linking the mesogenic units into a chain. In polymer I, however, the terephthalic acid residue is not mesogenic but when joined to the cyclooctyl ring the resulting structure possesses a smectic phase. In this example, the cyclooctyl ring now clearly forms part of the mesogenic unit. In all of the polymers studied, the cyclooctyl ring may then operate both as a semi-flexible spacer and as part of the mesogenic unit itself.

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