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Thermotropic liquid crystalline main-chain polymers containing cyclooctyl units

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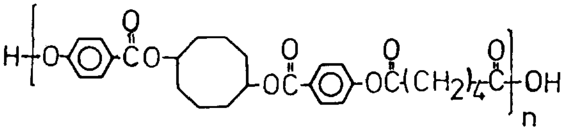
SUMMARY

A new LC main-chain polymer containing 1,5-cyclooctyl moieties in the mesogenic groups was prepared and its optical and thermal properties were studied. Preliminary results showed that this polymer exhibited two smectic mesophases.

INTRODUCTION

It is well known that fibres spun from anisotropic melts possess a high degree of molecular orientation (CIFERRI et al. 1982). This unique property of thermotropic main-chain liquid crystalline (LC) polymers is of interest both academically and industrially. To be liquid crystalline, polymers must bear mesogenic groups (rigid units) which provide the linear alignment and commonly reported mesogenic groups include at least two aromatic or cycloaliphatic rings connected in the para-position through a rigid linkage. Recent reviews have shown that the use of cycloaliphatic rings has been restricted to cyclohexyl units (DE GENNES 1975 and LENZ 1984). We have synthesised a new main chain LC polymer containing cyclooctyl units with the following structure.



EXPERIMENTAL

Phase transitions in the polymer were identified using two techniques. A Reichert Thermovar hot-stage polarising microscope was used to follow the changes optically while a Perkin Elmer DSC-2 differential scanning calorimeter was used for more accurate location of the temperature ranges of the transitions.

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Synthesis of Monomer

p-Ethoxycarbonyloxybenzoic Acid (I)

Ethylchloroformate (50ml) was added to a chilled (0°C) solution of p-hydroxybenzoic acid (60g, 0.434mol) and sodium hydroxide (38g, 0.955mol) in 900ml of water. The reaction mixture was then acidified with 2M HCl and the precipitate was filtered, washed with excess water, and recrystallised from water/acetone mixture. Yield: 90%, mp: 158°C. (OBER et al. 1982).

p-Ethoxycarbonyloxybenzoyl Chloride (II)

Compound I (20g, 0.095mol) was refluxed with thionyl chloride (15g, 0.126mol) and two drops of dimethylformamide. The excess thionyl chloride was distilled off, and the crude product was recrystallised from hexane. Yield: 80%.

Cis-1,5-Cyclooctane bis(p-Ethoxycarbonyloxybenzoate) (III)

Cis-1,5-Cyclooctanediol (ALDRICH) (6.3g, 0.028mol) was added to a solution of compound II (2.0g, 0.014mol) in 20ml of 1,2-dichloroethane. The mixture was refluxed overnight under a nitrogen atmosphere, then cooled and poured into 50ml cold 0.5M NaOH solution. The product was extracted into toluene and dried with anhydrous $MgSO_4$. The solvent was distilled off and the product was recrystallised in ethanol. Yield: 70%, mp: 90°C. H nmr: ($CDCl_3$ & TMS) 1.50 (t;$-CH_3$), 1.95 (m; cyclic-CH_2-), 4.25 (q;$-CH_2-$), 5.10 (s;-CH-), and 7.05, 7.85 (d;-Ar-) ppm.

Cis-1,5-Cyclooctane bis(p-Hydroxybenzoate) (IV)

Compound III (6.0g, 0.011mol) was dissolved in 20ml ethanol and treated with 12ml of 2M NaOH solution on a steam bath for 30 minutes. The excess ethanol was evaporated. The residue was adjusted to pH 7 with 10% acetic acid, filtered, dried and recrystallised from water/ethanol (1:1) mixture. Yield: 46%, mp: 197°C. H nmr: (d-acetone & TMS) 1.90 (m;cyclic-CH_2-), 5.10 (s;$-CH_2-$) and 6.75, 7.75 (d;-Ar-) ppm.

Synthesis of Polymer

Monomer IV (3.127g, 8.13mmol) was dissolved in 2ml of anhydrous pyridine, and to this was added a solution of adipoyl chloride (1.417g, 8.13 mmol) in 30ml of tetrachloroethane. The mixture was stirred at room temperature under a nitrogen atmosphere for 24 hours and then poured into 200ml of methanol. The precipitated polymer was washed with methanol and digested in 20% Na_2CO_3 solution for 4 hours, filtered, washed with dilute HCl and then water, and finally dried under vacuum at 60°C. Yield: 87%.

RESULTS AND DISCUSSION

Fig. 1 shows the DSC curves of the polymer under study which has a tetramethylene spacer. On the first heating scan (curve 1), a small and broad melting transition appeared at about 393K followed by a much larger endothermic transition in the temperature range of 400K to 430K for the mesophase to isotropic phase transition. The second heating did not display any changes compared with the first scan. On cooling (curve 3), the isotropic to mesomorphic transition appeared at 388K and there was no indication of a crystallization transition. The clearing transition (T_i) obtained from cooling is 36K lower than the heating which was possibly due to supercooling effects (GRIFFIN and HAVENS, 1981; and MARET and BLUMSTEIN, 1984). However, after annealing the sample at 400K for 4 hours, an enhanced melting transition and a better resolved mesophase to isotropic phase transition was detected (curve 2), which clearly shows two distinct transitions at 405K and 417K.

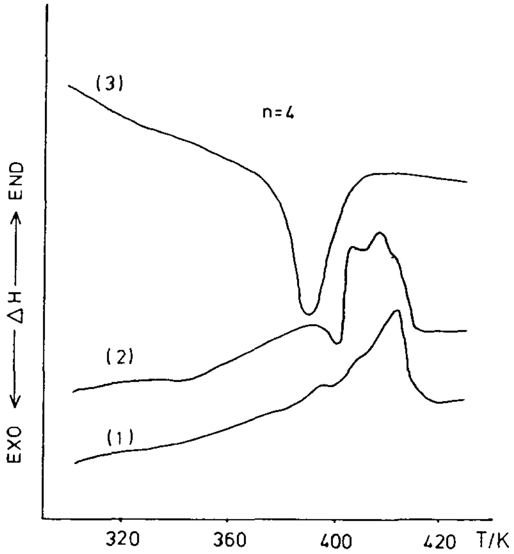

Fig. 1: DSC thermogram, scanning rate 20K/min, curve 1: heating, curve 2: annealed at 400K for 4 hours, curve 3: cooling.

Microscopic observation showed the existence of two different mesophases. When the isotropic melt was cooled to 405K, a batonnet like texture started to appear first, and then the homeotropic background gradually changes to a mosaic texture. Fig. 3 shows the phase transition. We tentatively assign the peaks at 417K and 405K as smetic A and smetic B respectively (GRAY and GOODBY, 1984). Thus the sequence of transitions is

$$C \xrightarrow[393K]{} S_B \xrightarrow[405K]{} S_A \xrightarrow[417K]{} I$$

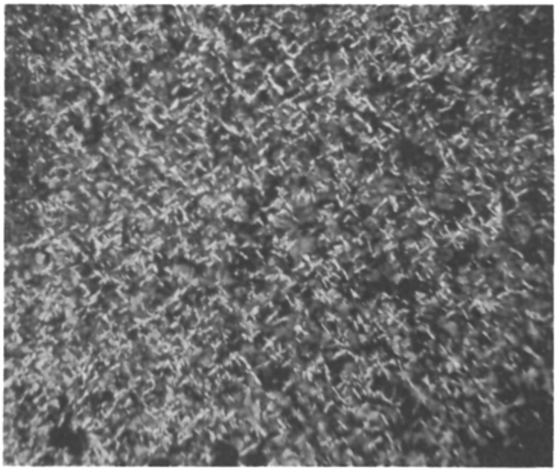

Fig. 2: Photomicrograph shows batonnet and mosaic textures. Magnification 100x, crossed polarisers.

A more detailed report with X-ray diffraction, optical and thermal studies of this series of polymer with different spacers is in preparation.

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