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Properties of a liquid crystalline polyester with a mesogen containing the bicyclooctylene ring

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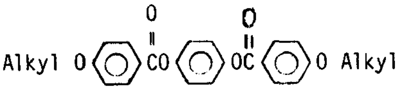
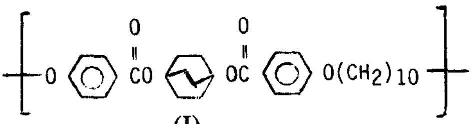
A liquid crystalline polyester with a decamethyene flexible spacer and a mesogenic unit containing a central 1,4-bicyclo(2,2,2)octylene ring was prepared for comparison with the equivalent polymer containing a central *p*-phenylene ring in the mesogen. Both polymers formed a nematic phase on melting, and as expected, the former had a much lower isotropization temperature than the latter. The polymer containing the bicyclooctylene ring, however, showed a batonnet texture, indicative of a smectic phase, at a temperature above that of the nematic state, especially on cooling from the isotropic melt.

1. Introduction

It has been reported that the replacement of one, two or all of the *p*-phenylene rings by 1,4-bicyclo(2,2,2)octylene rings in liquid-crystalline compounds of the following structure substantially lowers the isotropization temperatures of these nematogens [1, 2]:



It is of interest, therefore, to evaluate the effect of such rigid, linear units on the liquid-crystalline properties of thermotropic polyesters as part of a program in these laboratories on the evaluation of the contributions of both mesogenic units and flexible spacers to such properties [3, 4, 5]. For this purpose, a homopolymer, (I) was prepared in which the mesogenic unit was an ester triad with a central bicyclooctylene ring and which also contained a decamethylene flexible spacer, as follows:



(I)

This polyester was prepared by the reaction of bicyclo(2 : 2 : 2)octane-1,4-diol, (II) [3], and the acid chloride of 1,10-*bis*(4-carboxyphenoxy)decane, (III), which is a monomer often used in one of our laboratories to prepare thermotropic polyesters [4], so comparative data are available for evaluating the effect of the bicyclooctylene group on the LC properties of such polymers. One sample of polymer I was also prepared by the reaction of the diphenyl ester of (III) with (II).

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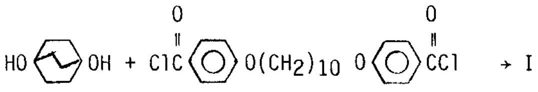


(II) (III)

2. Results

Four different procedures were applied to the preparation of polymer (I) including: (A) the melt polymerization of (II) and (III) at 190°C under a constant stream of nitrogen to remove the HCl by-product; (B) the solution polymerization of (II) and (III) dissolved in a mixture of tetrachloroethane and pyridine as the reaction solvent; (C) the interfacial polycondensation of (II) dissolved in an aqueous phase with sodium carbonate and (III) dissolved in methylene chloride; and (D) the melt polymerization of (II) with the diphenyl ester of (III) at 260°C with antimony trioxide as a catalyst. The data for the polymer samples obtained by these four methods are collected in the table. As can be seen from these data, the different methods yielded polymers with significantly different solution viscosities and transition temperatures.

Preparation and properties of polymer I.

Polymerization method†	Polymer yield, %	Elem. anal. of (I)‡		η_{inh}§ dl/g	Transitions, °C‖	
		%C	%H		T_m	T_i
(A)	71	75·02	7·96	0·18	97	217
(B)	62	74·92	7·17	0·16	93	215
(C)	42	75·67	7·87	0·24	97	240
(D)	64	75·16	7·97	0·20	90	221

† See text for description of method.

‡ Calculated analysis for I: 73·82 per cent C, 7·74 per cent.

§ Inherent viscosity at 0·5 g/dl in *p*-chlorophenol at 45°C.

‖ Melting temperature, T_m, and isotropization temperature, T_i, taken from peaks in D.S.C. thermogram of second heating cycle.

In addition to the main transitions, the D.S.C. thermograms contained several other small and broad endotherms in the heating cycle. The melting transitions in the D.S.C. thermograms were assigned from observations of samples heated on a polarizing microscope stage. For Polymer (C), the polymer with the highest solution viscosity, the isotropization temperature was found to be much higher than those for Polymers (A), (B) and (D). For all of the polymers, except Polymer (C), a small and broad endotherm was observed immediately following a much larger endotherm. The peak of the smaller endotherm approximately corresponded to the peak temperature for the isotropization endotherm for Polymer (C). It is likely that the second, much smaller endotherm is for isotropization too, and this suggestion could account for the higher value of the endothermic isotropization peak maxima for Polymer (C).

In the cooling cycle, three exotherms were observed for all of the polymers. The exotherm at approximately 215°C is attributed to deisotropization, while the exotherm with a peak maxima at about 70°C is assigned to a nematic-solid transition. These two transitions were confirmed by optical microscopy. The third exotherm, occurring at about 140°C could not be properly assigned. No significant change in the samples at this temperature during the cooling cycle could be observed by polarized light microscopy. The deisotropization exotherm for Polymer (C) contains

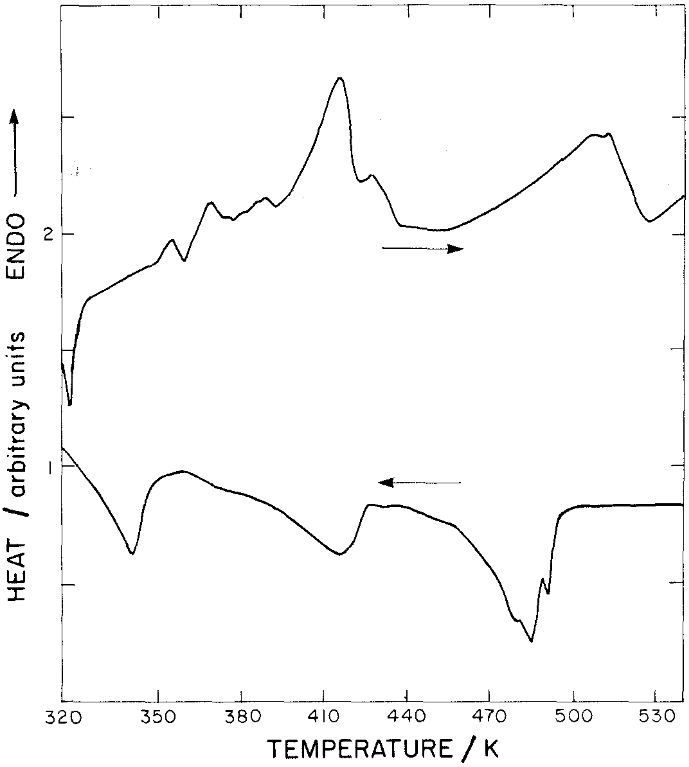


Figure 1. DSC thermograms of polymer (C) in the heating and cooling cycles at 20°C/min.

a sharp shoulder at about 220°C, which is 8°C higher than the corresponding peak maxima. Figure 1 shows the D.S.C. thermograms for Polymer (C) in the second heating and cooling cycles.

All four polymer samples formed nematic melts above their melting temperature as indicated by a threaded Schlieren texture consisting of singularities with four as well as two associated brushes ($S = \pm 1$ and $\pm \frac{1}{2}$). A typical nematic texture, that for Polymer (C) at 120°C, is shown in figure 2.

When a sample of Polymer (C) was heated, an unusual change in texture occurred at about 230°C. The nematic Schlieren texture disappeared, and the formation of a batonnets occurred with decreasing intensity up to 257°C, after which complete isotropization was observed. On cooling, the batonnets first reappeared at about 220°C, and at approximately 215°C the nematic Schlieren texture began to reappear. At 205°C only the Schlieren texture was observed. The temperature of reappearance of the batonnets from the isotropic melt in the cooling cycle corresponded to the temperature of the sharp shoulder in the deisotropization exotherm in the DSC thermogram of the cooling cycle.

The texture of Polymer (C) in the heating cycle is shown in figure 3. On isotropization from the batonnet texture in the heating cycle, Polymer C was found not to form droplets, indicating that isotropization did not occur from a nematic state. Polymer (D) also showed a batonnet texture near the isotropization temperature in the heating cycle, and on deisotropization batonets reappeared. This texture was rapidly followed by the formation of a nematic Schlieren texture on further cooling.

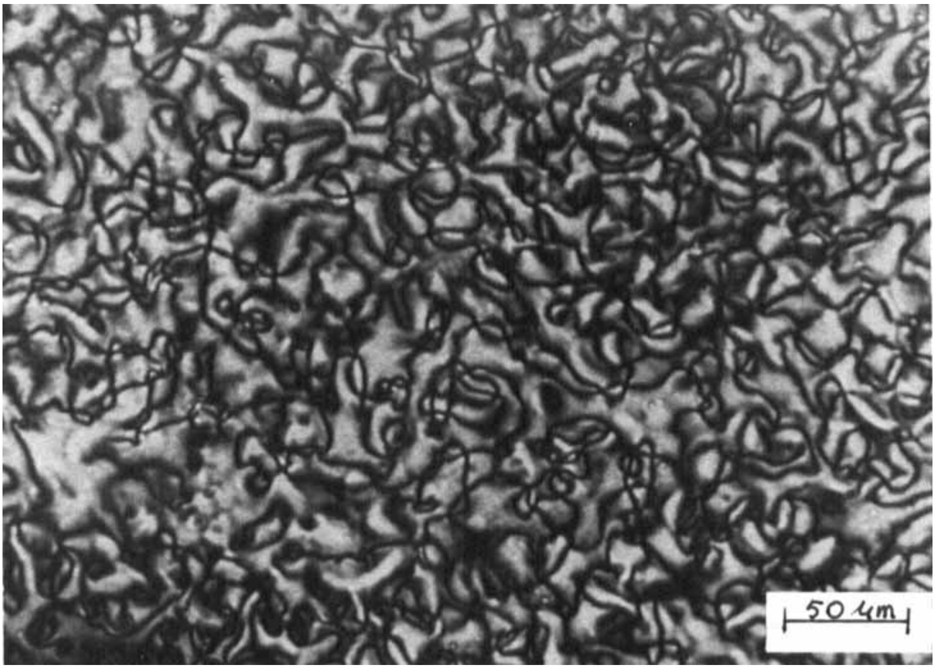


Figure 2. Nematic schlieren texture of polymer (C) at 120°C.

In the case of Polymer (B), no batonnet texture was observed in the heating cycle. However, on cooling from the isotropic melt, the batonnets appeared at about 220°C. At approximately 205°C a nematic Schlieren texture appeared, and below 200°C only the later was observed. The texture changes for Polymer (B) during the cooling cycle are shown in figure 4 at four different temperatures.

Batonnet textures are generally associated with the smectic liquid crystalline state, more specifically with the smectic A and C states [6]. The non-planar structures of both the smectic A and C states exhibit batonnet textures which can be differentiated in that the smectic C state also exhibits tilt inversion walls, but the smectic A state does not. No tilt inversion wall was observed for the present samples precluding the possibility of the existence of a smectic C state.

The batonnet texture is never associated with the nematic state to our knowledge. Moreover, the Schlieren texture, which was observed for all the bicyclooctylene polymers in their mesophases at lower temperatures, was clearly that of a nematic phase as evident by the presence of singularities with both two and four associated brushes. Hence, it appears that these samples first formed a nematic state at lower temperature then formed a smectic A phase at higher temperatures. This type of behaviour is most unusual for polymers but can occur for small molecule liquid crystals.

In comparison to the behaviour of these polyesters containing the bicyclooctylene group, a polyester previously prepared in our laboratory, which had a structure closely analogous to (I) but contained a central *p*-phenylene ring in the triad ester mesogen, formed only a nematic melt. The latter polyester had a T_m of 243°C and a T_i of 295°C while the former had T_m and T_i transitions at 97°C and 240°C, respectively, at a comparable inherent viscosity of 0·26 dl/g [7]. Hence, replacement of the *p*-phenylene group with the linear bicyclooctylene group destabilized the nematic phase, but the T_m was lowered by a much greater extent than

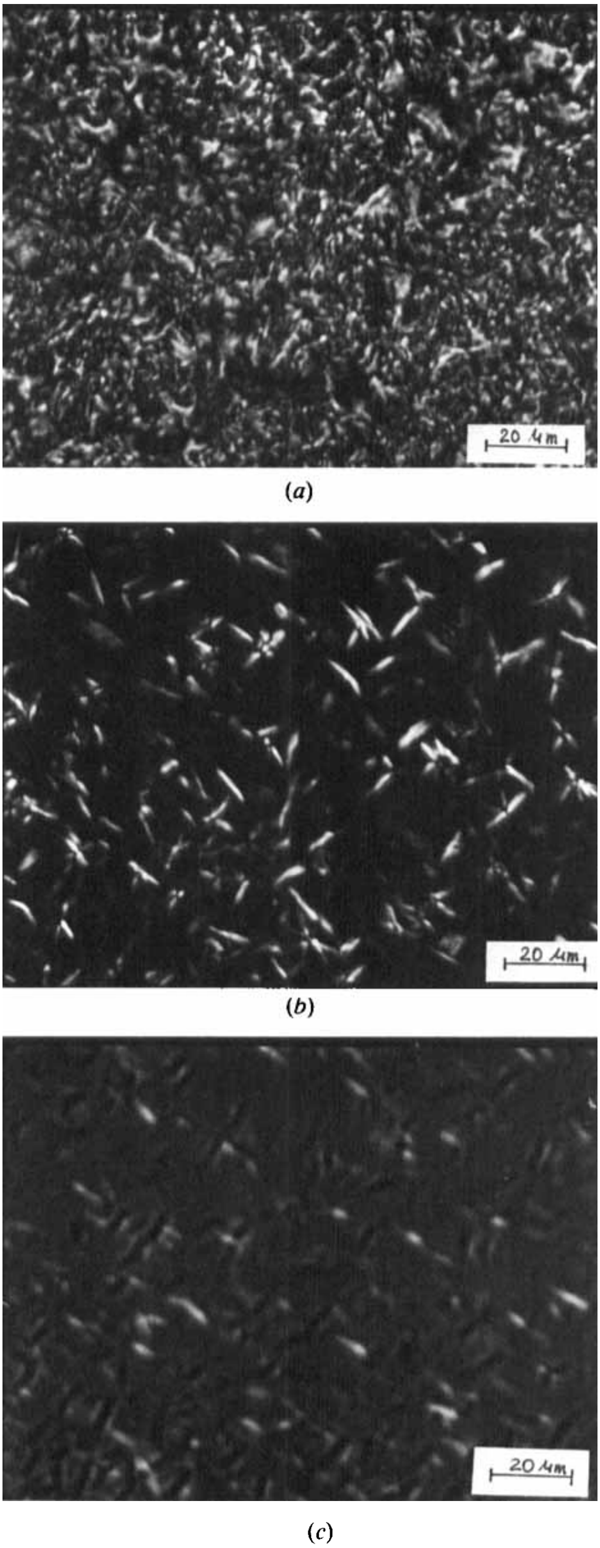
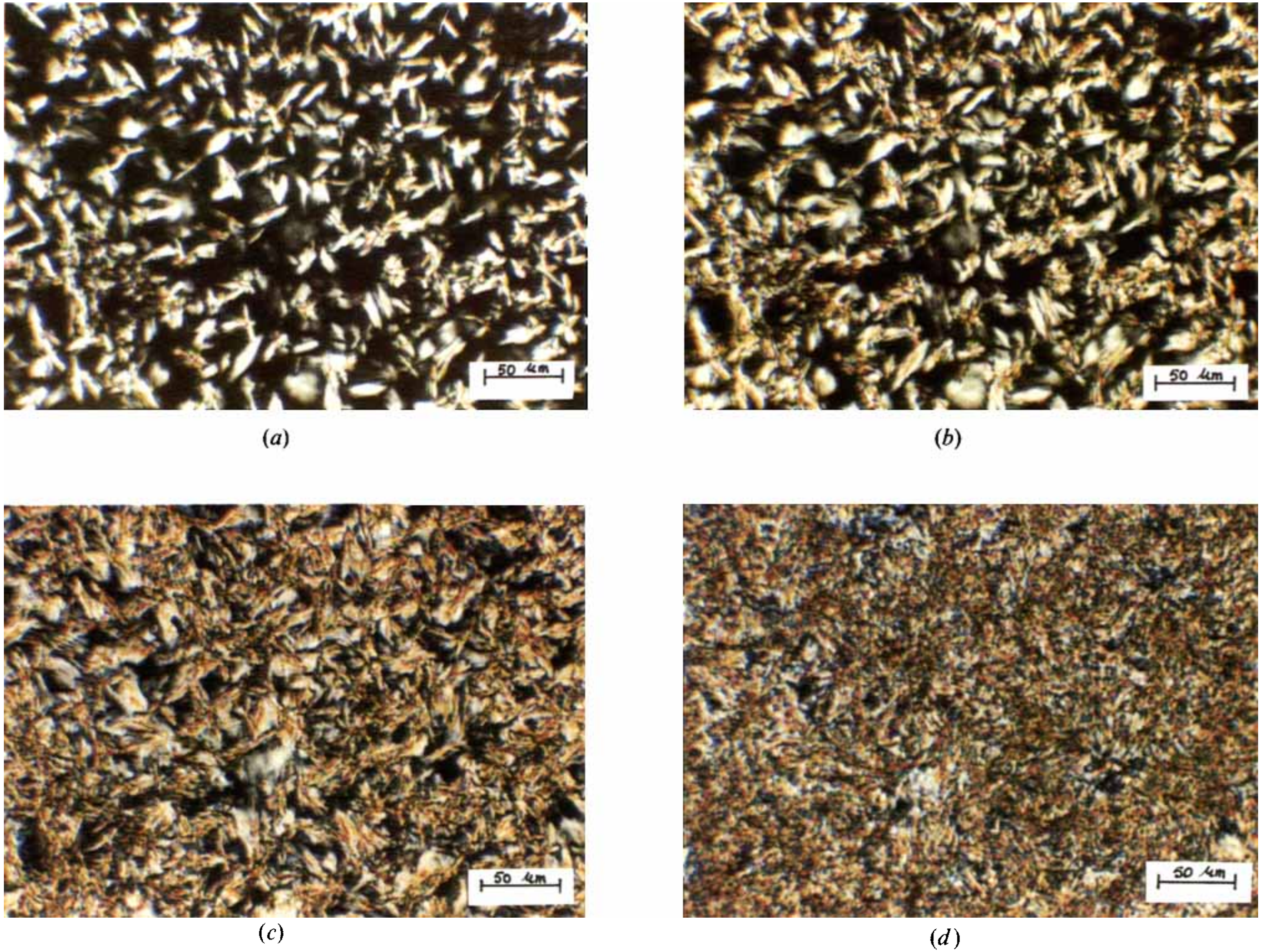


Figure 3. Optical textures of polymer (C) at (*a*) 140°C, (*b*) 235°C, and (*c*) 254°C, in the heating cycle.



(*a*) (*b*) (*c*) (*d*)

Figure 4. Optical textures of polymer (B) at (*a*) 220°C. (*b*) 210°C, (*c*) 200°C, and (*d*) 180°C, in the cooling cycle.

the T_i, so a much broader temperature range of nematic phase formation was obtained.

The reduction in T_i resulting from replacement of a *p*-phenylene ring with the equally linear and rigid bicyclooctylene ring in model compounds, as mentioned in the Introduction, is generally taken as an indication that phenylene rings can participate in intermolecular interactions, which help to stabilize the LC state, and are not thermotropic only as a result of their geometrical contribution [1].

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