Thermotropic liquid crystalline mainchain polyesters containing cyclooctyl units: 5. Effect of the cyclooctyl ring as a semi-flexible spacer

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(Received 20 November 1987; accepted 22 December 1987)

Several mesogenic units comprising two phenyl rings linked by azo, azoxy and carbon–carbon double bonds were polymerized with cyclooctane diol to form a new series of liquid crystalline polymers. Each polymer exhibited a nematic phase but only in the case of the polymer with the stilbene structure was a smectic phase identified. The influence of the cyclooctyl ring was assessed.

(Keywords: polymer liquid crystals; cyclooctane; azo mesogen; azoxy mesogen; stillbene mesogen)

INTRODUCTION

The pioneering work on mainchain liquid crystalline polymers began by incorporating bifunctional mesogenic monomers into a polymer backbone[1]. The majority of these mesogens contained two aromatic rings connected by a short rigid link such as azo, azoxy and stilbene, which are probably the most extensively studied examples despite the fact that these unsaturated groups are very susceptible to heat and irradiation.

We have already reported on the dual role of the cyclooctyl ring which acts as (a) part of a mesogen and (b) a semi-flexible spacer[2]. Here a new series of polyesters based on conventional mesogenic monomers with a common spacing unit, viz. the cyclooctyl ring, is described. Polymers incorporating similar mesogens but linear flexible spacers have been studied before by others[3,4] and it is of interest to compare their behaviour with this series to determine if the cyclooctyl ring imparts properties which are significantly different.

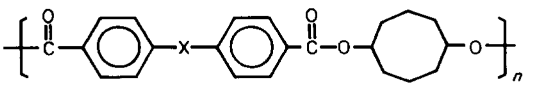
EXPERIMENTAL

Monomers and polymers were synthesized as described elsewhere[2,5].

Thermal transitions were recorded using a Perkin–Elmer DSC-2, while mesomorphic changes were observed on a Reichert Thermovar polarizing microscope fitted with a hot stage (magnification 100 ×). These techniques allowed identification of the glass transition temperature T_g, the melting temperature T_m and the clearing temperature T_i.

RESULTS AND DISCUSSION

The schematic structure of the polymers under study is illustrated below:



where X = N=N, N=NO or CH=CH.

These polymers are designated with the codes: AZO–CO, AZOXY–CO and STIL–CO, where CO stands for the cyclooctyl ring.

Polymer AZO–CO

A preliminary study using the hot-stage microscope revealed that this polymer began to decompose at about 550 K. In order to obtain more reproducible results, the sample was only heated to 383 K in the first heating scan and held at this temperature for 2 min to ensure there was no solvent residue. After cooling to room temperature at 20 K min^{-1}, the sample was then scanned at a rate of 40 K min^{-1} until just prior to decomposition which started to occur, i.e. 542 K. The cooling scan was obtained by setting the instrument to the auto-cooling mode at the same rate in order to avoid excessive decomposition and the d.s.c. thermograms of this polymer, which are reproducible, are shown in *Figure 1*. According to curve A, T_g, T_m and T_i were 478, 509 and 540 K, respectively. Three exotherms were also obtained from the cooling scan at 538, 488 and 460 K. The obscurity of the fusion transition was attributed to the high cooling rate.

The poor thermal stability of this polymer made it very difficult to study on a hot-stage, hence, the hot-stage was preheated to 540 K before the sample was loaded. The sample was observed to melt and become transparent. On switching off the thermostat and blowing nitrogen over the sample, the temperature was rapidly decreased to 513 K when a nematic texture started to appear at the expense of the homeotropic background. The mesomorphic order of polymer AZO–CO is proposed to be:

$$k \xrightarrow{509\,\mathrm{K}} n \xrightarrow{540\,\mathrm{K}} i$$

where *k* represents the crystalline state and *i* the isotropic state.

Iimura *et al.*[4] used the same mesogen and copolymerized it with different linear alkane diols

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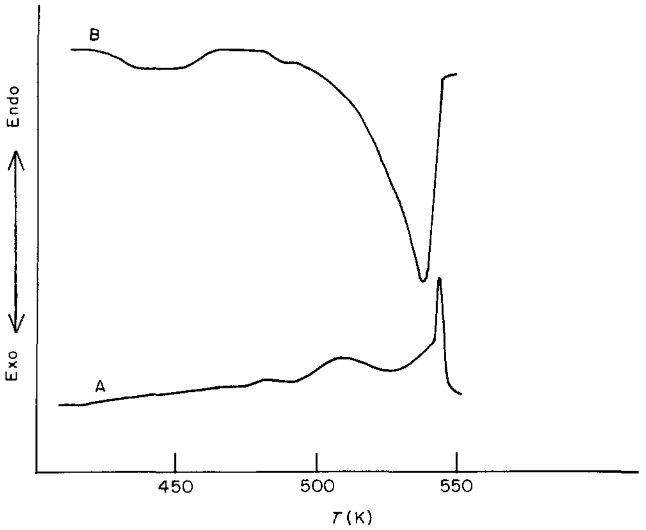

Figure 1 D.s.c. thermograms of polymer AZO–CO: A, heating; B, cooling

containing 6 to 12 carbon atoms but they reported that these polymers did not show any liquid crystalline behaviour. Thus introduction of the cyclooctyl ring leads to the formation of a nematic phase which is absent if the linear analogues are incorporated as spacers in the polymer.

Polymer AZOXY–CO

Polymer AZOXY–CO was treated the same way as polymer AZO–CO. *Figure 2* shows the d.s.c. thermograms with the values of T_g, T_m and T_i at 393, 510 and 548 K, respectively. The cooling scan displayed a large exotherm at 493 K which is believed to be the supercooled fusion transition. Observation under the microscope at 505 K illustrated a thread-like texture characteristic of a nematic phase, hence, the mesomorphic order of this polymer is:

$$k \xrightarrow{510\,\mathrm{K}} n \xrightarrow{548\,\mathrm{K}} i$$

When the cyclooctyl ring was replaced by 1,5-pentanediol in the investigation by Iimura *et al.*[4] a smectic texture was observed, so the cyclooctyl ring apparently produces a more disordered phase than the alkane spacer.

Polymer STIL–CO

The d.s.c. thermograms for the polymer STIL–CO are shown in *Figure 3*. Thermal treatment was similar to that for the previous sample despite the fact that this polymer is more thermally stable. From the heating curve, T_g and T_m were assigned at 447 and 495 K, respectively, while T_i was found at 563 K accompanied by a small shoulder about 23 K lower. The cooling scan revealed that the shoulder exerted a much larger supercooling effect when compared with the other two transitions. The sequence of appearance of these exotherms was 553, 503 and 491 K.

Microscopic observation showed that when the sample was cooled from the isotropic state to 543 K, the typical thread-like texture of a nematic phase was observed. On further cooling to 533 K, a bead-like texture was observed which probably corresponds to the broad shoulder detected by d.s.c. at 540 K. A similar texture was observed for poly(hexamethylene-*p*-biphenyl-4,4′-carboxylate)[3] and some other sidechain LC polymers[6]. This texture is generally recognized as either a smectic A or C modification[3], therefore the mesomorphic order of polymer STIL–CO is tentatively assigned as:

$$k \xrightarrow{495\,\mathrm{K}} S_A \xrightarrow{540\,\mathrm{K}} n \xrightarrow{563\,\mathrm{K}} i$$

A polymer with an equivalent linear spacer, $-(CH_2)_5-$, was studied by Meurisse *et al.*[3] and they concluded that this polymer is liquid crystalline but no particular ordered phase was identified. Consequently, no comparison can be drawn in this case.

CONCLUSION

The proportion of *cis/trans* isomers in the system is not known, although the synthetic methods which were followed claimed to give exclusively *trans* isomers. The discussion is based on the assumption that the rigid linkages are in the *trans* state.

Figure 4 shows the mesomorphic temperature ranges (ΔT) versus different mesogens, and the order of thermal

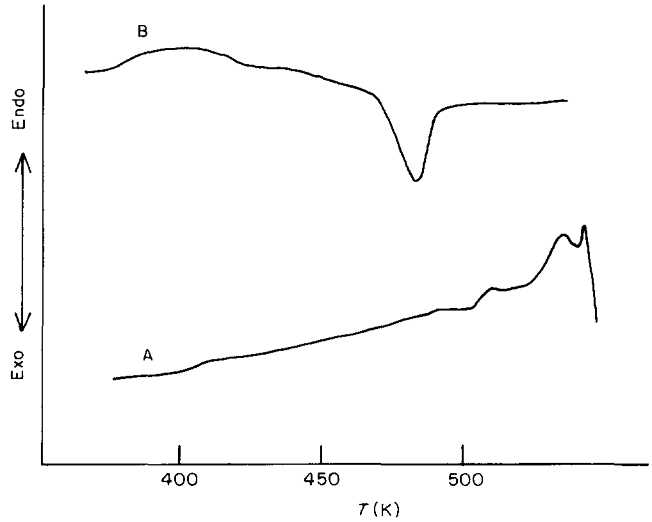

Figure 2 D.s.c. thermograms of polymer AZOXY–CO: A, heating; B, cooling

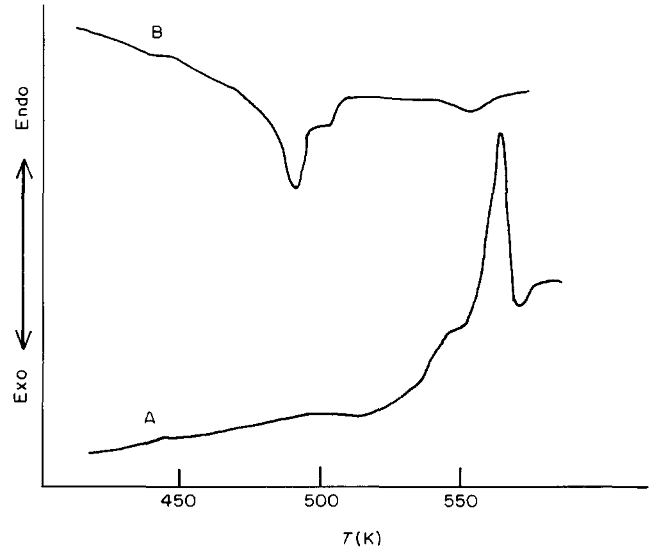

Figure 3 D.s.c. thermograms of polymer STIL–CO: A, heating; B, cooling

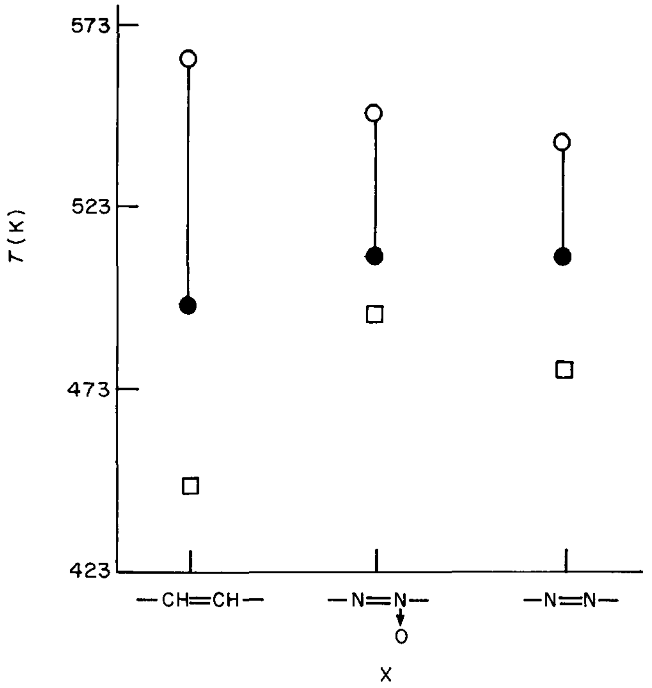

Figure 4 Plot of mesophase stability ($\Delta T = T_i - T_m$) against linking groups. T_g (□), T_m (●) and T_i (○) from d.s.c.

stability of each mesomorphic region is accordingly:

-CH=CH- > N-NO- > -N=N-

The AZO and AZOXY polymers which have mesogenic units of the same length as the stilbene unit (13.5 Å) possess higher melting temperatures. The AZOXY polymer ($\Delta T = 38$ K) has a wider range of mesophase stability than the AZO polymer ($\Delta T = 31$ K), whereas the much broader liquid crystalline range of the stilbene polymer ($\Delta T = 68$ K) actually encompasses both a smectic and a nematic phase. The former is absent in the other two polymers but they all exhibited a nematic mesophase as a common feature.

The inclusion of the cyclooctyl ring does appear to have a significant effect on the liquid crystalline properties. In one series (AZO) it actually promotes a liquid crystalline phase and in another (AZOXY) it increases the disorder. Unfortunately, no comparison can be made with the STIL series but here two phases could be identified.

ACKNOWLEDGEMENT

We wish to thank SERC for a grant supporting this work.

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