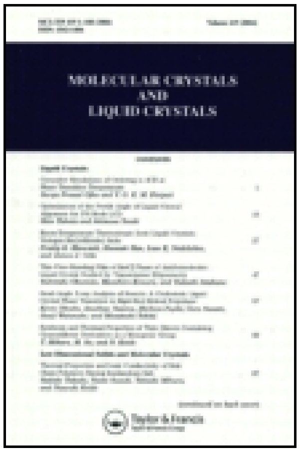

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Studies on Biphase Behaviour of Certain Thermotropic Liquid Crystalline Copolyesters

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To cite this article: R. Nanthini, R. Balakrishnan, V. Kannappan, I. K. Varma & Neeraj Gupta (1998): Studies on Biphase Behaviour of Certain Thermotropic Liquid Crystalline Copolyesters, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 319:1, 39-49

To link to this article: http://dx.doi.org/10.1080/10587259808045646

Mol. Cryst. Liq. Cryst., Vol. 319, pp. 39–49
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Studies on Biphase Behaviour of Certain Thermotropic Liquid Crystalline Copolyesters

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(Received 24 July 1997; In final form 22 December 1997)

Four Thermotropic Liquid Crystalline (TLC) random copolyesters were prepared by direct polycondensation of two diols and oxaloyl chloride in *o*-dichlorobenzene solution. The structures of the repeating units of the synthesised polyesters were examined by FT-IR and PMR spectral data. The thermal transition temperatures were determined by differential scanning calorimetry. The LC behaviour of these polymers were studied by optical polarising microscopy in conjunction with WAXD studies. Three of these polyesters exhibited interesting biphase behaviour. The polyester containing 2,5-ditertiarybutylphenylene rings in the main chain exhibited discotic behaviour.

Keywords: LC random copolyesters/biphase; discotic behaviour

1. INTRODUCTION

In recent years, there has been considerable interest in Thermotropic Liquid Crystalline polymers containing linear mesogenic units such as phenylene rings in the main chain. Their molecular self-orientation ability is responsible for a wide range of applications of these polymers as high performance materials [1–3]. Lenz and co-workers have extensively investigated the effect

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*Corresponding author.

of length of flexible spacers in the main chain polyesters and found that the thermal stability and nature of the mesophase depend on a combination of both the structure and the length of flexible spacer unit [4, 5].

Structural modifications in polymer backbone and copolymer technology can be used to depress the melting and transition temperatures which is necessary for easy processing of these polymers [6]. With this view, four random copolyesters containing oxaloyl group in the main chain were synthesised and characterised. Three of these polymers exhibited interesting biphase behaviour while the polyester containing 2,5-ditertiarybutyl phenylene rings in the polymer chain displayed discotic mesophase.

2. EXPERIMENTAL

2.1. Monomers and Solvents

Fluka sample of oxaloyl chloride was used as such. 1,8-dihydroxyanthraquinone (m.p. 193°C) was crystallised from ethanol. BDH samples of quinol, resorcinol, 1,5-dihydroxynaphthalene and 2,5-ditertiarybutylquinol were recrystallised from hot water and dried in vacuum.

o-Dichlorobenzene was dried over anhydrous calcium chloride and distilled (b.p. 181°C).

2.2. Preparation and Characterisation of Copolyesters

The random copolyesters were synthesised by the condensation of diols with oxaloyl chloride in *o*-dichlorobenzene solution in the mole ratio 1:1:2. Two diols and oxaloyl chloride were used in the synthesis of each random copolyester. The detailed procedure has been described elsewhere [7].

The $\eta_{\text{inh.}}$ values of all the polyesters were determined using Ubbelohde viscometer at 30°C on polymer solutions of 0.25 g/dL in *o*-chlorophenol. These polyesters were soluble in acetone, DMSO, DMF and *o*-chlorophenol; sparingly soluble in ethanol, methanol, CCl_4 and $CHCl_3$. As these polyesters are more soluble than wholly aromatic polyesters, these polymers can be easily processed.

The FT-IR spectra of the copolyesters were recorded using DIGILAB FTS 15/90 spectrophotometer in KBr pellets. The IR spectra of two typical polyesters are given in Figure 1. Expected absorption peaks were present in their spectra. All polyesters showed characteristic absorption at 1700–1750 cm^{-1} which is due to ester carbonyl stretching. The absorptions at

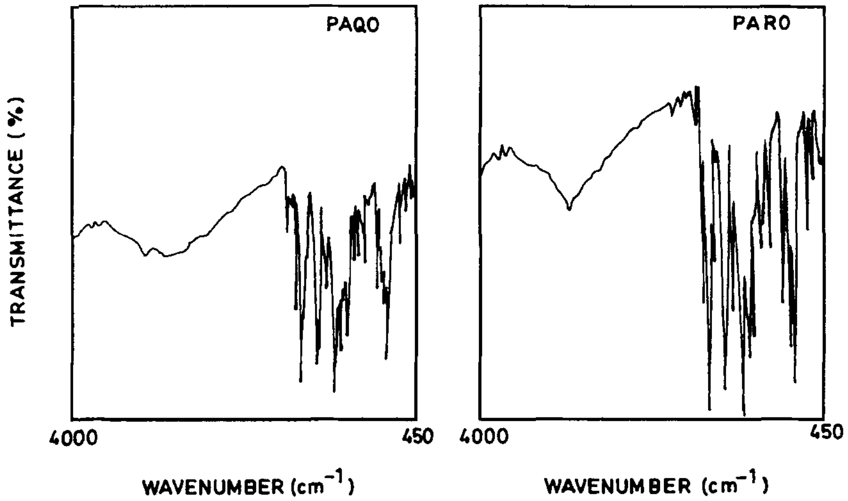

FIGURE 1 Infrared spectra of random copolyesters.

1020, 1080 and 1200 cm^{-1} are due to the ester C—O stretching vibrations. All the polyesters contain anthraquinone moiety and hence there is strong absorption at 1680 cm^{-1} which is characteristic of carbonyl stretching vibrations of anthraquinone moiety.

The PMR spectra of these polyesters were recorded with a Perkin-Elmer (model R-32) spectrometer in DMSO-d_6 solution with TMS as the internal standard. The ring protons of 9,10-anthraquinone moiety are highly deshielded and hence these polyesters have high δ values. Similarly, the protons of 1,3-phenylene and 1,4-phenylene rings present in the polymer chain also absorb at down field. In the case of polyesters containing 2,5-ditertiarybutyl-1,4-phenylene rings, there are two equivalent protons in each phenyl ring and these are indicated by the singlet at $\delta = 6.5$ ppm. the protons of tertiarybutyl groups absorb at $\delta = 1.3$ ppm.

Thermal transitions were investigated under nitrogen atmosphere using a 2910-DUPONT differential scanning calorimeter at a heating rate of 10°C/min. From endothermic peaks, glass transition (T_g), mesophase formation (T_m) and isotropisation (T_{cl}) temperatures were determined. The existence of mesophase in these random copolyesters were detected using LEITZ LABORLUX polarising microscope with a METLER hot stage and attached to a Pentax camera.

In conjunction with optical polarising microscope observations, WAXD patterns were used to identify the type of mesophase. The diffraction patterns were recorded with a SIEMENS-D-500 diffractometer with high temperature control (model HDK 2.3). A thermocouple made up of 3% tungsten and 97% rhenium was used to control the temperature. A 40 kV and 40 mA nickel filtered CuKα (λ = 1.54 Å) radiation was employed and the intensities were measured using a proportional counter.

3. RESULTS AND DISCUSSION

In the present work, we report the synthesis of four new random copolyesters and their thermotropic behaviour. Each polyester contains oxaloyl group (O) and two of the following dioxy groups in the polymer chain with the mole ratio 2:1:1.

The moieties present in these polyesters along with their yield and the inherent viscosities at 30°C in *o*-chlorophenol solution are furnished in Table I. The formula of the repeating unit in the copolyesters can be inferred from the percentage composition. All the four polyesters reported here contain carbon and hydrogen. The percentage of carbon and hydrogen were determined using a carbon, hydrogen analyser. The results obtained are given in Table I.

4. THERMAL CHARACTERISATION

The transition temperatures such as glass transition (T_g), mesophase formation (T_m) and isotropisation (T_{cl}) temperatures were derived from the DSC thermograms (Fig. 2). These are summarised in Table II.

Of the four polyesters reported, first three polyesters contain two sharp endotherms in their DSC thermograms. This suggests that these polyesters may exhibit two characteristic LC mesophases at different temperatures prior to the formation of isotropic melt. These thermal data indicate that both T_m and T_{cl} are influenced only slightly by the mesogenic units present in the polymer back bone. It may also be noted that T_g, T_m and T_{cl} values for these four polyesters are much less than those synthesised from aromatic acid chlorides containing similar mesogenic units [8]. The introduction of aliphatic group in the main chain reduces the transition temperatures considerably.

5. LIQUID CRYSTALLINE PROPERTIES

These random copolyesters contain anthraquinone moiety as the common mesogen. Copolyesters with anthraquinone mesogens in the polymer chain

TABLE I Structural units, molecular formula, percentage of carbon and hydrogen, yield and inherent viscosities of the thermotropic LC random copolyesters

Polymer	*Structural units* (*Mole ratio* 1:1:2)	*Molecular formula*	*Percentage composition*				*Yield* (%)	$\eta_{inh.}$ (*dL/g*)
			Carbon		*Hydrogen*			
			Cal.	*Obs.*	*Cal.*	*Obs.*		
PAQO	A Q O	$(C_{24}H_{10}O_{10})_n$	62.9	62.7	2.18	2.20	60	0.34
PARO	A R O	$(C_{24}H_{10}O_{10})_n$	62.9	63.0	2.18	2.21	55	0.29
PANO	A N O	$(C_{28}H_{12}O_{10})_n$	66.1	66.2	2.36	2.39	55	0.16
PABO	A B O	$(C_{32}H_{26}O_{10})_n$	67.3	67.1	4.56	4.55	50	0.26

TABLE II Thermal transition points of the thermotropic random copolyesters (°C)

Polymer	T_g	T_m	T_{cl}	*Temperature range of mesophase stability*
PAQO	60	S175, N180	190	10
PARO	58	S170, N175	185	10
PANO	55	S160, N175	180	5
PABO	55	150	180	30

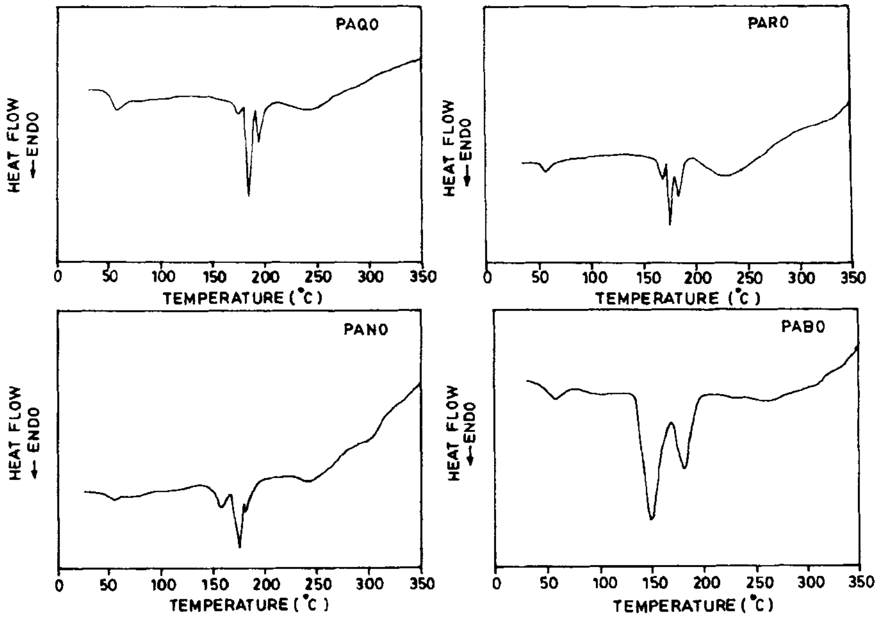

FIGURE 2 DSC thermograms of the thermotropic LC copolyesters.

are less familiar. All these four polymers exhibited thermotropic LC behaviour.

The polyesters, PAQO, PARO and PANO exhibited smectic phase at characteristic temperatures which transformed into nematic phase at higher temperatures before they formed isotropic melt. Rigid rod-like optically birefringent texture could be seen in the micrograph of the copolyester PANO (Fig. 3a) taken at 160°C which is typical of smectic phase. On heating further, it transformed into nematic phase at 175°C as evidenced from the threaded texture (Fig. 3b). Subsequent heating of the sample showed that the thread-like texture disappeared at 180°C and birefringence was absent above this temperature.

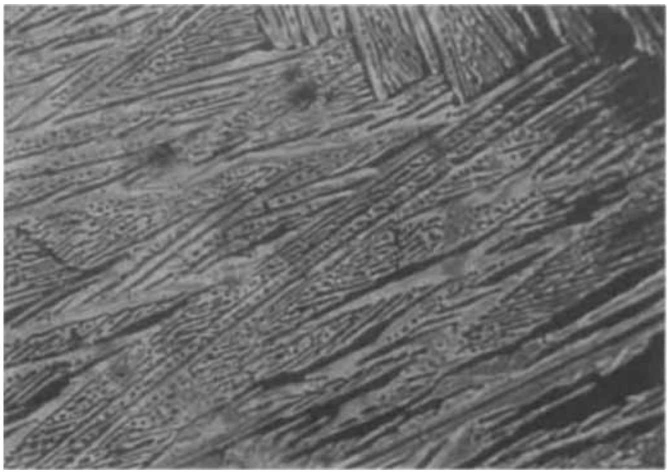

FIGURE 3a Rigid rod-like structure obtained in the optical micrograph (160 x) of copolyester PANO at 160°C on heating. (See Color Plate II).

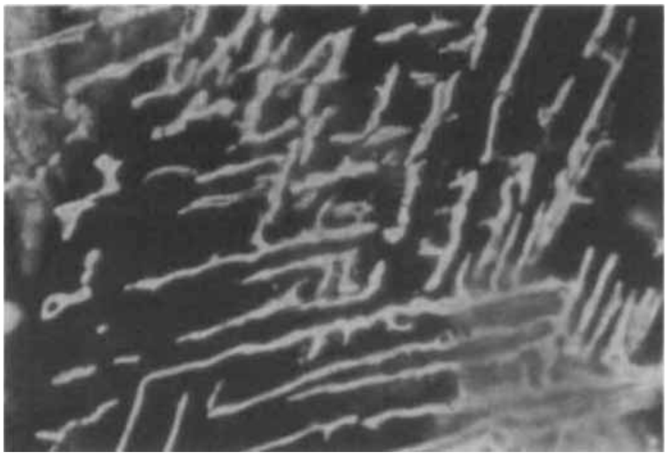

FIGURE 3b Thread like optical texture (160 x) observed in the copolyester PANO at 175°C on heating. (See Color Plate III).

The magnified polarised optical micrograph (Fig. 4) of the polyester PAQO at 175°C suggests that this polyester shows batonnete texture which is indicative of smectic phase [9]. Upon heating, it transformed into nematic phase at higher temperature (180°C). Similar observations were made in the

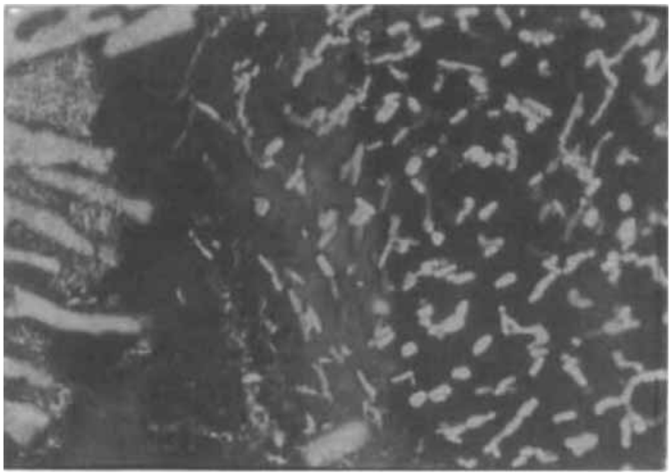

FIGURE 4 Batonnete texture (160x) observed at 175°C on heating the polyester PAQO. (See Color Plate IV).

case of polyester PARO (Fig. 5). It may be pointed out that copolyesters containing 1,3-phenylene ring have a lower T_m value than that with 1,4-phenylene ring.

Lenz has found that in a series of random copolyesters with flexible spacers such as ethyleneoxy groups, the polymers with shorter spacer units formed smectic as well as nematic phases while the polymer with longer spacer units exhibited single mesophase or did not exhibit LC behaviour. In the present investigation, the oxaloyl group is the shortest spacer group. The present investigations are in agreement with those made by Lenz and coworkers [10].

The optical properties of TB based random copolyester is quite interesting. On heating the polymer PABO to 150°C, dendritic finger like contours typical of discotic mesophase was observed (Fig. 6). This mesophase gave clear melt at 180°C. It has been suggested by the earlier workers that polyesters containing tetra substituted 1,4-phenylene rings are disc-like mesogens and a discotic mesophase has been identified in such polymers [11 – 13]. Recently, Kannappan *et al.*, have reported that 1,4-phenylene rings with two bulky tertiary butyl groups at 2 and 5 positions of the phenylene rings may be disc-like and polymers with this mesogen can exhibit a discotic mesophase [6]. They found that polyesters exhibiting discotic mesophase have greater temperature range of mesophase stability than the smectic and nematic type of polyesters.

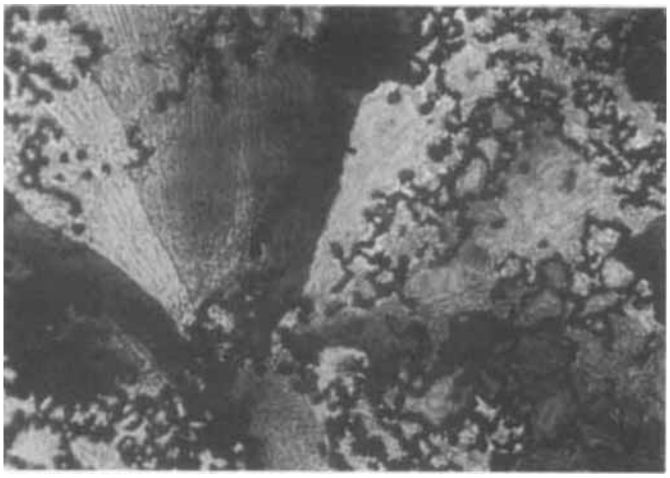

FIGURE 5 Polarised optical micrograph (160x) obtained for polyester PARO at 170°C on heating. (See Color Plate V).

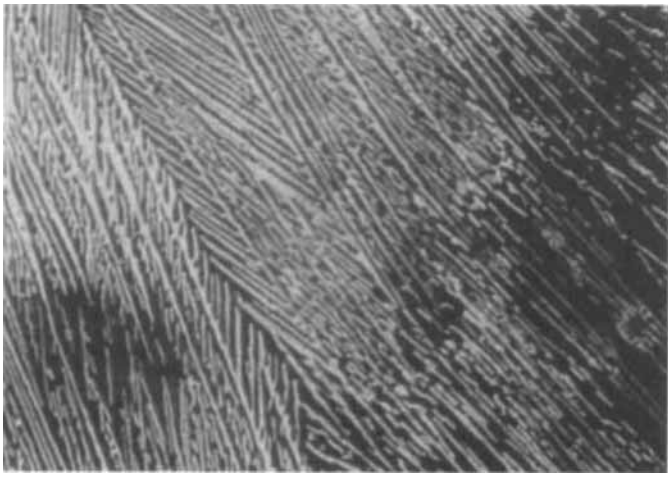

FIGURE 6 Dendritic finger like contours obtained for polyester PABO at 150°C on heating. (See Color Plate VI).

Thus, the polyesters PABO with TB moiety in the main chain exhibits discotic mesophase and has a greater mesophase stability than the other three polyesters containing unsubstituted phenylene and napthalene rings in the polymer chain. The higher mesophase stability of these polyesters was due to the interlocking of the tertiarybutyl groups present in the polymer chain.

TABLE III *d*-Spacings and intensities obtained from WAXD pattern of random copolyesters

Polymer	*Sample as synthesised*		*Sample annealed*		*Sample quenched*	
	d-Spacing (*Å*)	*Intensity*	*d-Spacing* (*Å*)	*Intensity*	*d-Spacing* (*Å*)	*Intensity*
PARO	7.9	VS	5.8	VW	13.6	VW
	5.7	VW	5.6	W	9.4	VW
	5.0	VW	5.0	W	8.6	VW
	4.6	W	4.8	VW	7.9	VS
	3.9	VW	4.6	VS	7.4	W
	3.8	VW	4.1	VW	6.8	W
	3.6	VW	4.2	VW	6.5	VW
	3.4	VW	4.0	VW	5.8	VW
	3.0	VW	3.9	VW	5.6	VW
	2.8	VW	3.8	W	5.0	VW
	2.6	VW	3.7	VW	4.8	VW
	2.5	VW	3.6	VS	4.6	S
	2.4	VW	3.5	S	4.5	VW
	2.3	VW	3.4	S	4.6	VW
			3.4	S	4.4	VW
			3.3	S	4.3	VW
			3.2	S	4.0	VW
			3.1	W	3.9	VW
			3.0	VW	3.8	S
			2.8	VW	3.6	S
			2.6	VW	3.5	W
			2.5	VW	3.4	W
			2.3	VS	3.3	S
			2.2	VW	3.2	VW
			2.1	VW	3.0	VW
			2.0	VW	2.8	VW
			1.8	VW	2.7	VW
					2.6	VW
					2.6	VW
					2.5	VW
					2.4	VW
					2.3	VW
					2.2	VW
					2.0	VW
					1.8	VW
					1.8	VW
					1.7	VW
PABO	4.1	VS	4.1	VS	4.1	VS
	3.9	W	3.8	W	4.8	W
	3.6	VW	3.6	VW	3.5	W
	3.5	W	3.4	W	3.4	VW
	3.3	W	3.3	W	3.3	W
	3.1	W	3.1	W	3.0	W
	2.9	VS	2.9	VS	2.9	VS
	2.9	W	2.8	W	2.7	W
	2.7	VW	2.7	W	2.6	W
	2.6	W	2.5	W	2.5	W
	2.4	W	2.3	W	2.3	VW
	2.3	W	2.3	VW	2.3	VW
	2.3	VW	2.1	VW	2.0	VW
	2.3	VW	2.0	VW	1.9	W
	2.2	VW			1.9	W

VS: Very strong; S: Strong; W: Weak; VW: Very Weak.

6. X-RAY DIFFRACTION STUDIES

WAXD patterns were recorded for two typical polyesters (PARO and PABO) as synthesised, annealed and quenched samples. These diffractograms suggest that there is some degree of crystallinity in these polymers at room temperature.

There are differences in the WAXD pattern of the polyesters PARO and PABO indicating that these polyesters exhibit different types of mesophases. The *d*-spacings obtained from the WAXD patterns of these polyesters are shown in Table III.

It is seen that the XRD pattern of annealed and quenched samples of the polyester PARO contain larger number of smaller spacings than those of the synthesised sample. Further, the XRD pattern of the synthesised sample of this polymer contains spacings of 2–8 Å. This may probably be an indication of the smectic phase in this polyester.

The XRD pattern of the copolyester PABO contains only small spacings of 2–4 Å and similar diffraction patterns were obtained for the annealed and quenched samples. Further, the XRD pattern for annealed and quenched samples are almost similar to that of synthesised samples. This suggested that the polyester PABO may exhibit a discotic phase. Similar observations were made by earlier workers in wholly aromatic polyesters which displayed discotic mesophase [6]. Further work on the XRD studies of the number of thermotropic polyesters at different temperatures is under progress.

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