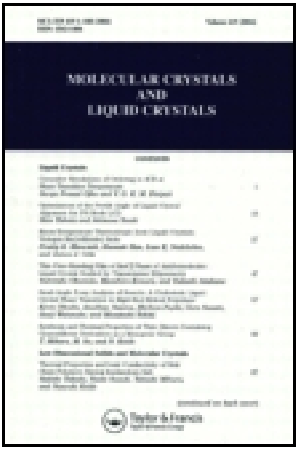

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Structural Effects on the Mesophase Formation of Certain Thermotropic Liquid Crystalline Random Copolyesters

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Structural Effects on the Mesophase Formation of Certain Thermotropic Liquid Crystalline Random Copolyesters[#]

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Thermotropic random copolyesters containing 2,2'-biphenylene rings, disclike mesogens in the polymer chain, were synthesised by the polycondensation method and characterised by viscosity measurements, and spectral analysis. Thermal properties of these polymers were investigated by DTA and DSC studies. The LC behaviour of these polymers were studied by optical polarising microscopy in conjunction with WAXD studies. Structural modifications introduced along the main chian changed the type of mesophase probably due to polar and interlocking effects.

Keywords: LC random co-polyesters, structural effects, mesophase behavior, discotic

1. INTRODUCTION

Mesomorphic behaviour is mainly attributed to the molecule shape. Anisotropic orientation-dependent polar and steric interactions contribute to the stability of the mesophase. Lenz co-workers have extensively investigated the effect of substituents in extended linear chain polyesters and suggested that the substituents as well as flexible spacers can be used to modify the structure of the main chain[1-3]. The substituents and spacers may destabilise the mesophase through dipolar interactions or stabilise by interlocking effects[4].

Random copolyesters reported in this paper contain 2,2'-biphenylene, 9,10-diketoanthracene, 2,5-ditertiarybutyl-1,4-phenylene and tetrachloro-1,4-phenylene moieties besides triethyleneoxy spacer group in the polymer chain. The polyesters containing disc-like mesogens tetrachloro-1,4-phenylene and 2,5-ditertiarybutyl-1,4-phenylene rings were expected to display discotic mesophase[5,6]. The presence of

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[#] Dedicated to the late Mr. E. Padmanaba Naidu.

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ditertiarybutyl groups in the main chain can bring about interlocking effects, which is evident from the thermal stability of the mesophase[4] in polyesters containing these mesogens.

2. EXPERIMENTAL

2.1. Monomers

An Aldrich sample of isophthaloyl chloride was recrystallised from n-hexane and dried in vacuum before use. 2,2'-Biphenol (Aldrich) was purified by crystallisation from n-butanol and BDH samples of quinol, resorcinol, tetrachloroquinol and 2,5-ditertiarybutylquinol were recrystallised from hot water and dried in vacuum. 1,8-dihydroxyanthraquinone was crystallised from ethanol and triethyleneglycol was distilled (b.p.: 285°C) and used.

2.2. Preparation and Characterization of copolyesters

The detailed procedure for the synthesis of this type of random copolyesters is described elsewhere[7]. The η_{inh} values of all polyesters were determined using Ubbelohde viscometer at 30°C on polymer solutions of 0.3 g/dL in *o*-chlorophenol. These polyesters were soluble in acetone, DMSO, DMF, *o*-chlorophenol; sparingly soluble in ethanol, methanol, CCl_4, *o*-cresol and $CHCl_3$.

The infrared spectra of the copolyesters were recorded using Perkin-Elmer X98 in KBr pellet. The spectra contained excepted absorption bands; aromatic C–C stretching at 1615 cm^{-1} and ester carbonyl stretching at 1740 cm^{-1}. The polyesters containing ethyleneoxy groups showed absorptions at 3050, 920, 820 cm^{-1} which are due to $-CH_2-$ stretching and bending vibrations. The C–Cl stretching vibrations were observed at 600–800 cm^{-1} for the polymers containing 2-chloro-1,3-phenylene and tetrachloro-1,4-phenylene rings.

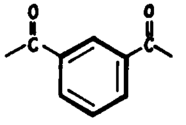
The PMR spectra of these polyesters were recorded in DMSO-d_6 solution with TMS as the internal standard. The aromatic protons of the isophthaloyl rings gave signals at $\delta = 7.8$ ppm while the protons of anthraquinone ring absorbed at $\delta = 8.3$–9 ppm. The protons of 2,2'-biphenylene and other phenylene rings of the diols absorbed at $\delta = 6.5$–9.6 ppm. The tertiarubutyl protons had absorption at $\delta = 1.4$ ppm.

Thermal transitions were investigated under nitrogen atmosphere using a Perkin-Elmer DSC 7 instrument at a heating rate of 10°C/min. From endothermic peaks mesophase formation (T_m) and isotropisation (T_i) temperatures were determined. Glass transition (T_g) decomposition (T_d) and oxidation (T_{ox}) temperatures of these polyesters were calculated from DTA thermograms. The phase transitions and LC properties were observed in the Leitz Laborlux optical polarising microscope using Mettler Hot Stage.

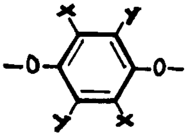
In conjunction with microscope observations WAXD spectra were used to identify the mesophase. These were recorded with a Philips vertical diffractometer PW 1850 with a microprocessor control. A 35 kV and 25 mA nickel filtered CuK_α ($\lambda = 1.54$ Å) radiation was employed and the intensities were measured using a proportional counter.

3. RESULTS AND DISCUSSION

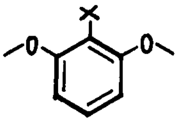
In the present work we report the synthesis of eight new random copolyesters and their thermotropic behaviour. Each of these polyesters contain isophthaloyl group (IA) and two of the following dioxy groups in the polymer chain with the mole ratio 2:1:1.



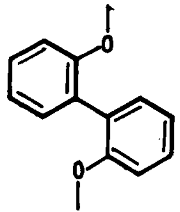
IA



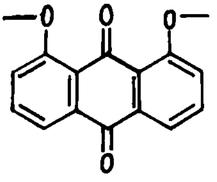
Q : X = Y = H
TB : X = H, Y = t-Bu
TC : X = Y = Cl



R : X = H
CR : X = Cl



BP



A

$\left(O - CH_2 - CH_2 - O \right)_3$

TG

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 1.

4. THERMAL CHARACTERISATION

The glass transition temperatures of these polyesters were obtained from the DTA thermograms while the mesophase formation (T_m) and isotropisation (T_i) temperatures were derived from the DSC thermograms. As the DTA thermograms were taken in air, atmosphere exotherms were obtained at temperatures above 500 °C due to oxidation of the degraded products. The thermal properties of these polyesters are summarised in Table 2.

TABLE 1
Structural units, yield and inherent viscosities of the thermotropic random copolyesters

Polymer No.	Structural Units (Mole ratio 1:1:2)			Yield(%)	η_{inh}(dL/g)
1.	BP	Q	IA	50	0.28
2.	BP	R	IA	45	0.21
3.	BP	CR	IA	55	0.18
4.	A	TG	IA	50	0.24
5.	A	R	IA	50	0.30
6.	TB	TC	IA	40	0.19
7.	TB	R	IA	45	0.23
8.	TB	Q	IA	50	0.26

TABLE 2
Thermal transition points of the thermotropic random copolyesters (°C)

Polymer No.	T_g	T_m	T_i	T_d	T_{ox}	Mesophase$^{\xi}$
1.	90	150	175	450	550	N
2.	85	140	165	380	530	N
3.	85	125	150	370	525	N
4.	105	170	220	450	560	S
5.	90	245	290	485	575	S
6.	90	140	195	340	480	D
7.	92	150	205	360	520	D
8.	96	160	220	380	535	D

ξ N = Nematic; S = Smectic; D = Discotic

It may be noted that the copolyesters containing TB moiety in the polymer backbone have lower degradation temperatures while those containing the moiety A decompose at higher temperatures.

These thermal data suggest that both T_m and T_i values of the polyesters are influenced by the mesogenic units present in the polymer backbone.

5. LIQUID CRYSTALLINE PROPERTIES

5.1. Biphenol based copolyesters

These random copolyesters (polymers 1–3) contain 2,2′-biphenylene rings as common moiety. All the three BP based copolymers exhibited thermotropic LC behaviour. Although the mesomorphic behaviour had been observed in similar polyesters with tetrephthaloyl rings, they were not extensively investigated 7. In the temperature rnage of 127–0170 °C the crystals began to glow under the polarizer in thes polyesters. A thread-like optically birefringent texture was observed at 150 °C in the copolyester with BP and Q groups (Fig. 1). Subsequent heating of the sample showed that the thread-like texture disappeared at 175 °C and no birefringence was observed above this

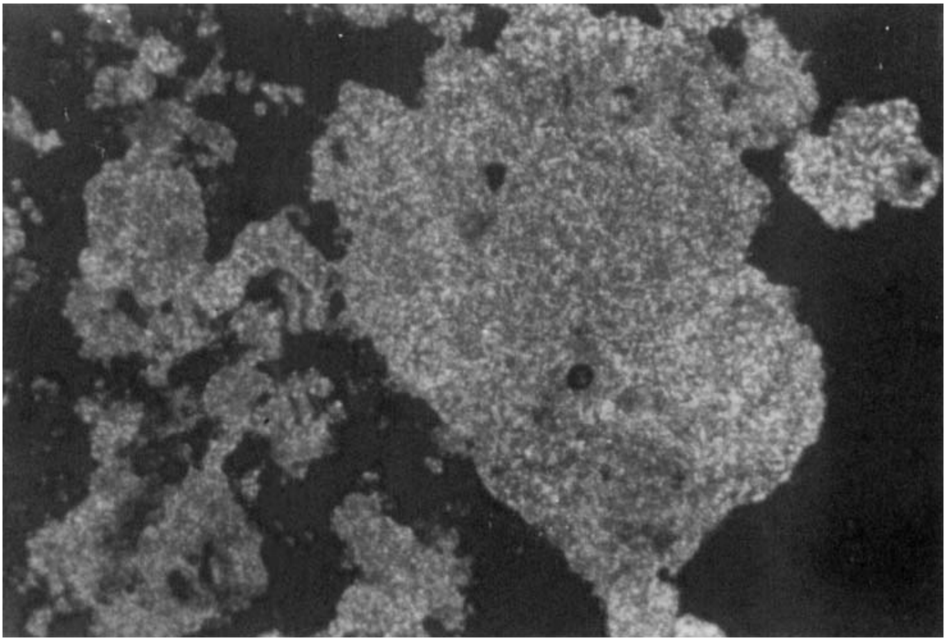


FIGURE 1 Thread-like optical texture (160 x) observed in the copolyester 1 at 150 °C on heating. See Color Plate I.

temperature. Similar observations were made on the other two BP based polyesters. It may be pointed out that copolyesters containing a 1,3-phenylene ring have a lower T_m value than that with 1,4-phenylene ring. The presence of substituents at C-2 position in the 1,3-phenylene ring also lowers the T_m. It has been raported that the polyesters prepared from HOOC-$(CH_2)_n$-COOH and 4,4′-biphenol exhibited a nematic phase for odd values of n and smectic phase for even values[8,9]. Thus the three BP based polyesters exhibited nematic behaviour and the mesophase is stable within a temperature range of of 25 °C.

5.2. Anthraquinone based copolyesters

Copolyesters with anthraquinone mesogens in the polymer chain are less familiar. Two copolyesters were prepared with this mesogen. Polymer 5 contains 1,3-phenylene and isophthaloyl groups while the polymer 4 contains TG instead of R. On heating the polymer 4, a finegrain structure (Fig. 2a) was seen at 170 °C which is indicative of a smectic mesophase. Annealing the isotropic melt of this polymer at 5 °C/min. resulted in rod-like crystallites at 150 °C (Fig. 2b). A similar texture was also seen in the case of polymer 5 but at a higher temperature. When the isotropic melt of polymer 5 was cooled slowly at 10 °C/min. a batonette optical texture (Fig. 2c) was obtained in the polarising micrograph at 100 °C. This is also indicative of a smectic phase[10].

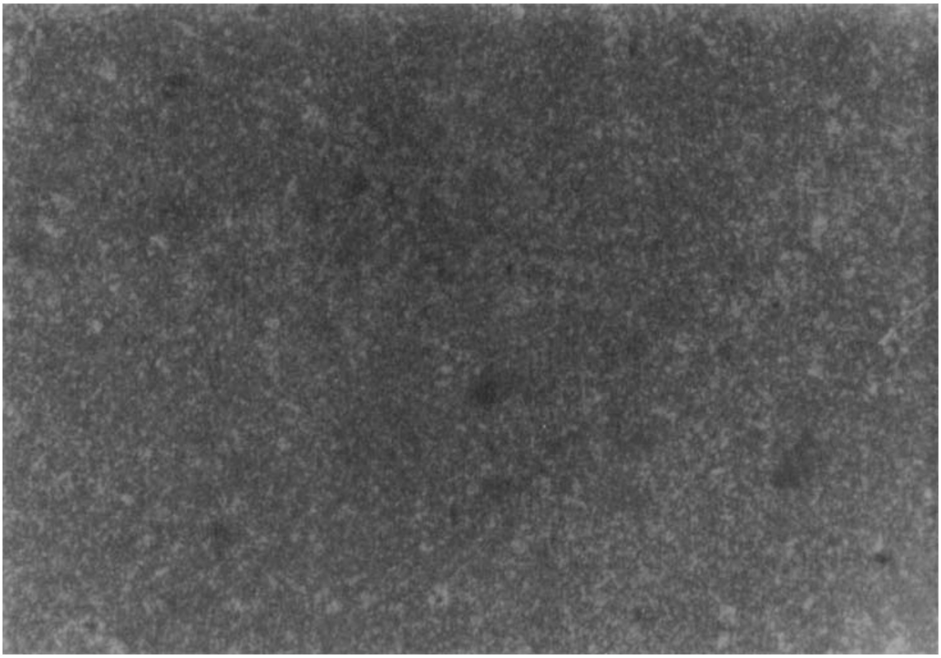


FIGURE 2a Finegrain structure obtained in the optical micrograph (160x) of copolyester 4 at 170°C (heating). See Color Plate II.

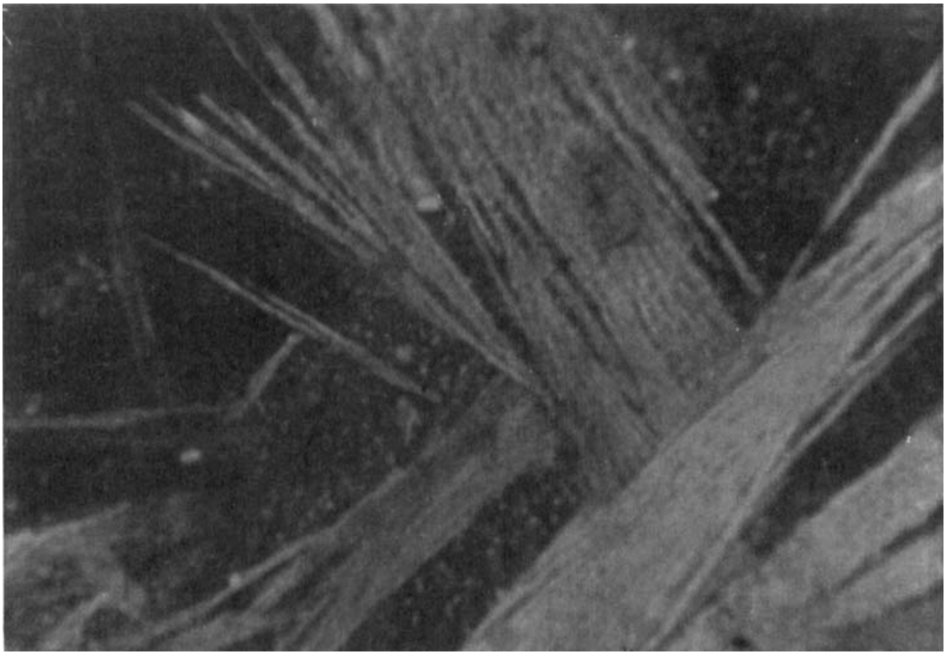


FIGURE 2b Rod-like crystallites (160x) observed at 150°C on cooling the melt of polyester 4. See Color Plate III.

FIGURE 2c Batonette optical texture (160x) observed at 100 °C on cooling the polyester 5. See Color Plate IV.

5.3. TB based copolyesters

The optical properties of TB-based random copolyesters are quite interesting. It has been suggested that polyesters containing tetrasubstituted 1,4-phenylene rings are dis-like mesogens and a discotic mesophase has been identified in such polymers[11-13]. Probably 1,4-phenylene rings with atleast two tertiarybutyl groups may be disc-like and polymers with this mesogen can exhibit a discotic structure. Three random copolyesters with TB moiety in the polymer chain are found to be thermotropic. The polyarized optical micrograph of the polyester 6 at 140 °C is given in Figure 3a. Small crystallites in hexagonal arrangements could be seen and the size of the crystallites decreased with temperature and at 195 °C an isotropic liquid resulted. The clear melt was cooled at 10 °C/min. The magnified optical micrograph taken at 120 °C had a feather-like structure (Fig. 3b) indicating discotic mesophase. It has been reported that polymers exhibiting disc-like columnar structures with hexagnoal packing of the columns give a fan-like structure 6. When the melt of polymer 7 was cooled to 100 °C a broken fan-like structure was observed at 100 °C (Fig. 3c). Polyester 7, therefore exhibited a discotic mesophase. Similar observations were made on polyester 8 and their transition temperatures were higher than those of polymer 7. It may be seen from the thermal properties of these polymers that the discotic mesophase is stable in the temperature range of 50–60 °C. The higher mesophase stability of these polyesters may probably be due to the interlocking of the tertiarybutyl groups present in the polymer chain.

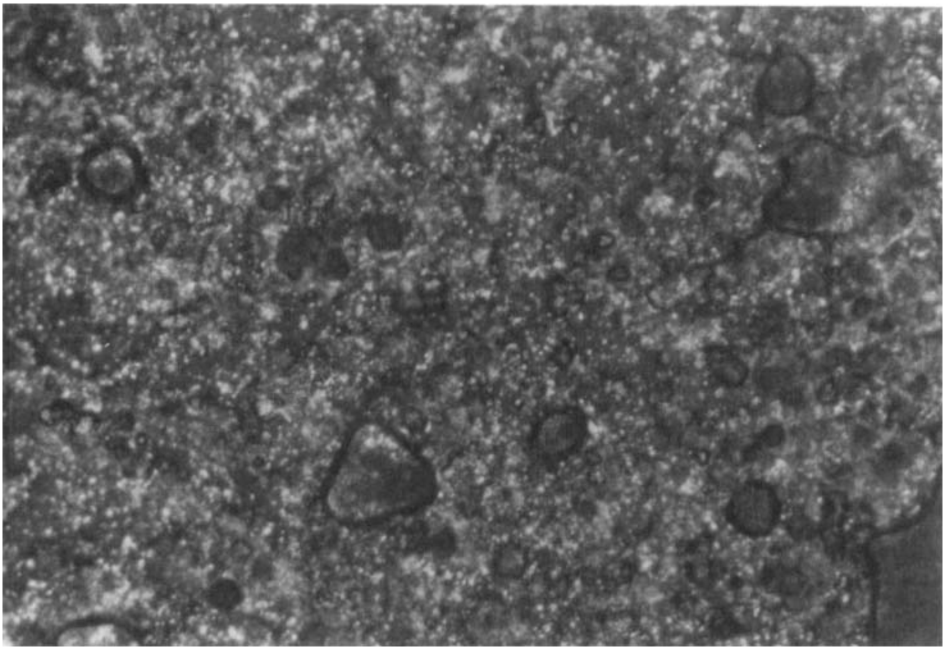


FIGURE 3a The polarised optical micrograph (160x) of polyester 6 at 140°C on heating. See Color Plate V.

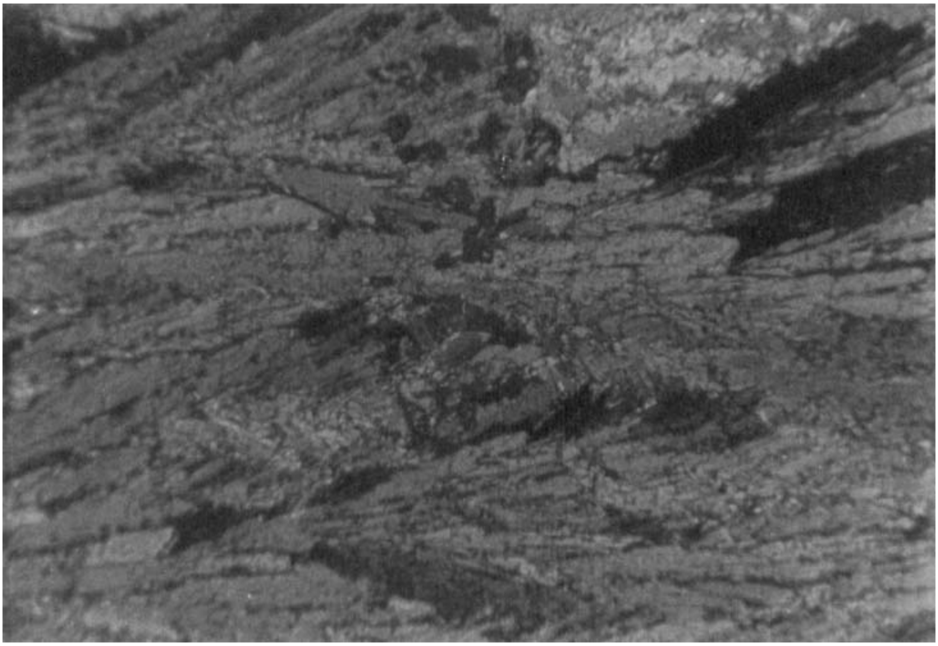


FIGURE 3b Feather-like texture (160x) in the copolyester 6 at 120°C (cooling). See Color Plate VI.

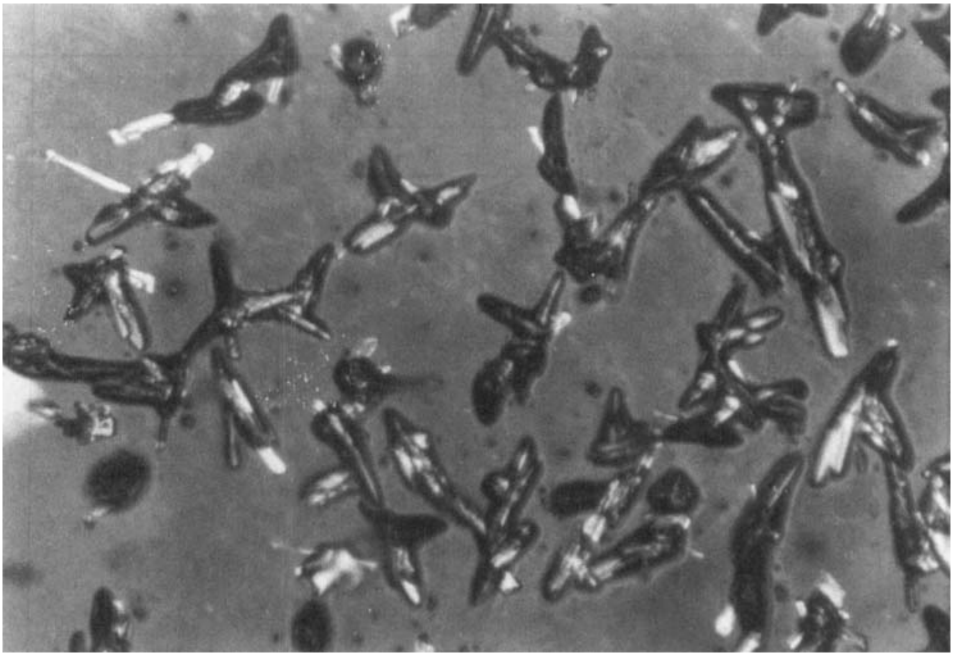


FIGURE 3c Polarised optical micrograph (160x) obtained from polyester 7 at 100°C (cooling). See Color Plate VII.

6. X-RAY DIFFRACTION STUDIES

WAXD patterns were recorded for three typical polyesters, as synthesised, annealed and quenched samples. These spectra suggest that there is some degree of crystallinity in these polymers at room temperature. There are differences in the WAXD spectra of these polymers indicating that these polyesters exhibit different types of mesophases. The *d*-spacings obtained from the WAXD spectra of these polyesters are shown in Table 3. The diffraction patterns in polymer 1 showed spacing of about 3-7Å. The annealed sample of this polymer gave a similar diffraction pattern except with fewer peaks. But the quenched sample contained spacings less than 3 ÅA also. This type of scattering pattern may be indicative of a material possessing a lower degree of order and consistent with the presence of a quenched LC solid, and the polyester 1 may thus exhibit a nematic mesophase 14. The diffraction pattern of polymer 4 had both smaller (3–Å) and large spacings of the order of 14 Å. In the annealed sample of this polymer, spacings less than 3 Å were observed while the quenched sample had a diffraction pattern almost similar to that of the synthesised sample. This polyester exhibited a smectic behaviour 15. The x-ray diffraction pattern of polymer 6 contained only small spacings of the order of 2–5 Å and similar diffraction patterns were obtained for the annealed and quenched samples. This polyester may thus exhibit a discotic mesophase. Further work on the XRD studies of a number of thermotropic polyesters is under progress.

TABLE 3
WAXD pattern of copolyesters

Polymer No.	Sample, as synthesised		Sample annealed from the T_i; 2hrs.		Sample quenched from the the T_i	
	d-spacing Å	Intensity	d-spacing Å	Intensity	d-spacing Å	Intensity
1.	7.63	vs			7.52	s
	5.50	vw	5.44	vw	5.14	vw
	4.94	vw	4.82	w		
	4.55	s	4.40	s	4.42	s
	4.19	vw	4.00	vw	4.08	vw
	3.87	w	3.78	w	3.82	w
	3.73	w	3.68	w	3.66	w
	3.56	w	3.42	s	3.34	s
	3.36	s			2.96	w
					2.68	vw
4.	13.73	vw	13.40	vw	13.61	vw
	10.62	vw	10.50	vw	10.56	vw
	4.50	vs	4.45	vs	4.48	vs
	3.95	w	3.84	vw	3.88	s
	3.69	w	3.45	vw	3.52	vw
	3.53	vs	3.38	vs	3.46	vs
	3.15	s	3.10	s	3.12	s
			2.72	vw		
			2.28	vw		
			2.10	vw		
6.	4.98	vs	4.84	vs	4.78	vs
	3.93	w	3.86	w	3.88	w
	3.47	w	3.38	w	3.36	w
	3.32	vw	3.10	vw	3.18	vw
	3.15	vs	2.98	vs	2.86	vs
	2.97	vw	2.64	vw	2.62	vw
	2.80	vw	2.13	vw	2.11	vw
	2.25	vw			2.04	vw
	2.17	vw				

7. CONCLUSION

It has been shown that thermotropic LC behaviour can be achieved in random copolyesters. Copolymers baded on 2,2′-biphenol and aromatic mesogens exhibited a nematic phase. Anthraquinon-based random copolyesters containing either aromatic mesogens or flexible spacers in the main chain had a rigid rod-like structure and exhibited a smectic mesophase. Bulky tetiarybutyl groups as side chain in the mesogen made them disc-like and polyesters with such groups exhibited a stable discotic mesophase, probably due to the interlocking of the side chains.

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