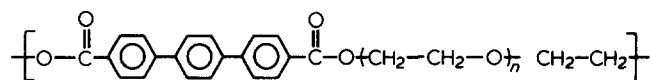# Thermotropic liquid crystalline polyesters with terphenyl moieties and flexible 'ether' spacers in the main chain

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Polyesters with the general formula:

($n=1$ (TO 5), 3 (TO 11), 9 (TO 29)) were characterized by differential scanning calorimetry, optical microscopy, miscibility tests and X-ray investigations. In polyesters TO 5 and TO 11 a smectic phase type C occurs. X-ray studies of oriented samples have suggested that the smectic C configuration is azimuthally disordered with the layers orientationally ordered. By contrast, above its melting point the polyester TO 29 shows distinct phases of liquid crystal and isotropic liquid. This is probably due to the polydispersity of the low molecular weight fraction of PEO used in preparing this polyester. A structural model is proposed to illustrate how the polyesters under investigation can adopt organizations compatible with all data known so far.

(Keywords: liquid crystalline polymers; thermotropic polyesters; glass transition; X-ray diffraction; structure determination; smectic 'C' mesophase)

INTRODUCTION

Recently some of the present authors undertook to synthesize and characterize a polymer system with thermotropic liquid crystal properties associated with the presence of mesogenic moieties in the main chain[1-3]. The system chosen was one based on a repeating unit consisting of an extended mesogenic unit followed by a flexible spacer. The general formula is:
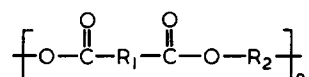
where R_1 = biphenyl, terphenyl or stilbene and R_2 = methylene groups $(CH_2)_x$, where x takes values from 2 to 10; branched alkyl segments ($X = -CH_3$, $-C_2H_5$, $-CH_2C_6H_5$); $(CH_2-CH_2-O)_y$ CH_2-CH_2- where $y = 1, 2, 3, 9$. A common feature of many polymers of this class is the exhibition of nematic and/or smectic mesophases. Identification of the type of mesophase is thus an important step in the characterization of these materials. The more definitive procedures used for classification of low molecular weight liquid crystals are:

(a) Differential scanning calorimetry (d.s.c.) which can be used to distinguish between thermotropic nematic and smectic phases by the magnitude of the enthalpy change accompanying the transition to the isotropic phase.

(b) Optical pattern or texture observations with a polarizing microscope. There are, however, limitations

with this technique and a complete classification of smectic phases by texture alone is not always possible. Similar textures may be observed with two liquid crystal states separated by a phase transition.

(c) Miscibility studies with known liquid crystals. Isomorphous mesophases are considered as equivalent and characterized by the same symbol.

(d) The possibility of inducing significant molecular orientations by magnetic or electric fields.

(e) X-ray investigations. In addition to the structural data obtained in the usual way, the diffraction diagrams recorded at low angles provide further information about the type of the mesophase.

Owing to high viscosity, broad molecular weight distribution, polycrystalline and amorphous material coexistence, the liquid crystalline nature of thermotropic polymers is usually established through a combination of these methods. In this paper we restrict our attention to the thermotropic mesomorphic behaviour of three polyesters of general structure:
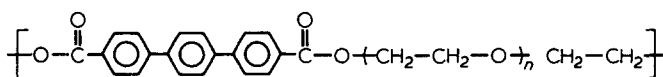
where $n=1$ (TO 5), 3(TO 11) or 9(TO 29).

EXPERIMENTAL

Polyesters were prepared in the Centre de Recherches des Carrières de Rhône-Poulenc, Saint-Fons, France, by reaction of di-n-propyl-p-terphenyl-4,4″ carboxylate with appropriate diol as described elsewhere[1].

Inherent viscosities were measured at 25°C in dich-

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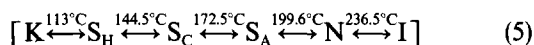loroacetic acid at a polymer concentration of 0.6 g/100 ml.

Light scattering measurements were performed on a Fica 50 photometer; the wavelength of the vertically polarized incident light was 5460 Å. Optical purification of solutions and solvent was carried out by centrifugation at 14 000 rpm for 2 h. Refractive index increments were determined with a Brice–Phoenix differential refractometer. At 23°C, the refractive-index increment, dn/dc, for green light 5460 Å was 0.188 cm³ g⁻¹ for polyester in chloroform. The familiar Zimm plot was used to analyse light scattering data. The ratios of excess scattered intensity ΔI to polymer concentration C obtained at various scattering angles θ and concentrations were plotted on a suitable grid against the concentration and as a function of scattering angle.

High resolution ¹³C n.m.r. spectra were measured on CDCl₃ solutions of polyesters at 62.9 MHz with a Brüker WP-250 spectrometer. Cross polarization, magic angle spinning ¹³C n.m.r. spectra were collected at 12.07 MHz on a home built spectrometer as described previously[2].

D.s.c. measurements were carried out on a differential thermal analyser Du Pont 990. All samples were under 10 mg and were heated at 10°C/min under a flow of dry nitrogen. Peak maximum positions were taken as the transition temperatures.

Dynamic mechanical spectra were obtained on a torsional braid analyser of nominal frequency 1 Hz. The heating rate was maintained at about 1.2 K/min.

The transition characteristics were surveyed with a polarizing microscope (Olympus BHA-P) equipped with either a Mettler FP 5 or a Reichert hot-stage. Binary mixtures were prepared by the contact procedure[4] and phase diagram was constructed by polarized light microscopy using a hot-stage. The reference compound used was the terephthalidene-bis-(4-n-butyl aniline).

$$[K \overset{113°C}{\longleftrightarrow} S_H \overset{144.5°C}{\longleftrightarrow} S_C \overset{172.5°C}{\longleftrightarrow} S_A \overset{199.6°C}{\longleftrightarrow} N \overset{236.5°C}{\longleftrightarrow} I] \qquad (5)$$

For the X-ray measurements, the samples were contained in 0.7 mm diameter Lindemann glass tubes. Low-angle diffraction patterns were recorded either on flat films with pinhole collimation or on a diffractometer operating in the transmission mode. The sealed capillary tubes were mounted in an electrically heated oven, the temperature of which was controlled with a precision of 0.2 K using a platinum resistor as sensing element. The sample holder might be contained inside a tank evacuated or filled with helium to reduce air scattering. For experiments requiring wide-angle diffraction data, X-ray studies were done at room temperature in a standard cylindrical camera. Both CrKα or CuKα radiation were used.

RESULTS AND DISCUSSION

The molecular structure of polyesters was verified by MAS CP ¹³C n.m.r. A representative spectrum is shown in *Figure 1*. The solid state ¹³C n.m.r. spectrum of polyester TO 11 consists of three lines which were identified from left to right, in order of increasing magnetic field, as a line due to the carbonyl carbons, a broad poorly-resolved line due to the aromatic carbons and a line due to the methylene carbons. The chemical shifts compare well with those deduced from the liquid state ¹³C n.m.r. spectrum and are in good agreement with data reported for
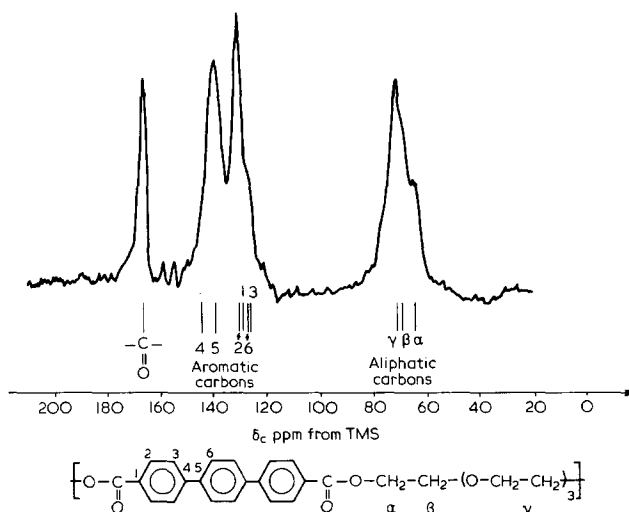

Figure 1 MAS CP ¹³C n.m.r. spectrum of polyester TO 11 at 25°C. Spectrum obtained from 10 000 accumulations with a CP contact time of 1 ms and experiment repetition time of 0.5 s

poly(tetramethylene oxy)terephthalate[6]. No signal characteristic of end groups was observed, which strongly supports relatively high molecular weights for these polyesters.

Polyester TO 5 was almost completely insoluble in virtually all common solvents at room temperature. Solubility was obtained with dichloroacetic acid, although decomposition occurred. The polyesters TO 11 and TO 29 were also soluble in chloroform.

At 25°C the inherent viscosities measured in dichloroacetic acid are 0.5, 0.6 and 0.69 dl.g⁻¹ for TO 5, TO 11 to TO 29, respectively. The existence of large aggregates of polyester TO 11 in dilute solutions of chloroform is evident from the *Figure 2*. Indeed an examination of the diagram $C/\Delta I$ vs. $\sin^2 \theta/2$ shows that a downward curvature at low scattering angles contrasts with a region of more moderate intensities at larger scattering angles. By adopting a fairly common view[7–9] (of somewhat questionable validity[10]) we interpret the slope and intercept of the high angle portion as due to the molecularly dispersed unaggregated polymer, while we consider the large molecular weight value and radius of gyration which are obtained from the low angle portion to be due to small residual amounts of aggregates. It is in this sense that we consider chloroform to be a solvent in which molecularly dispersed polymer exists although the small value of 3.5×10^{-5} ml.mole/g² obtained for the second virial coefficient A_2 implies that chloroform is a poor solvent. From high angle data, i.e. $\theta > 60°$, the value of $\bar{M}_w$ was found to be $250\,000 \pm 15\,000$ for the unaggregated material. The corresponding radius of gyration was 440 ± 30 Å.

All of the polymers exhibited thermotropic behaviour and their melting temperatures, T_m, and liquid crystal-to-isotropic transition temperatures or clearing points, T_i, could be clearly defined by either d.s.c., as seen in *Figure 3* and *Table 1*, or by the use of a hot-stage on a polarizing microscope.

The polyester TO 5 melt showed a strong stiropalescence between T_m and T_i. However, optical observations do not reveal any particular morphological feature useful in defining the type of mesophase. However, polarized light micrographs depicting the appearance of
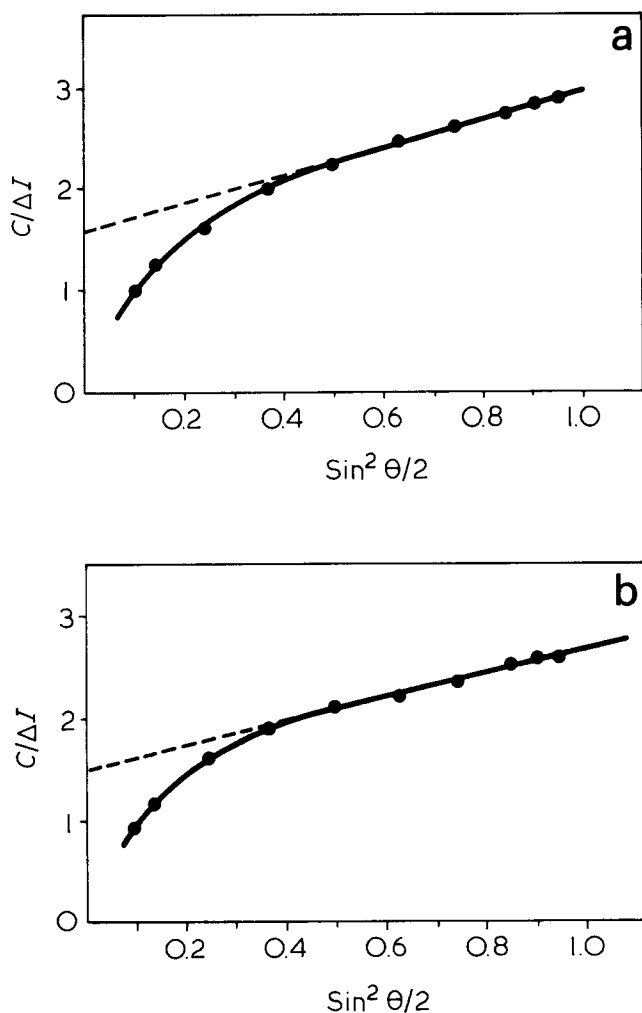
Figure 2   Reciprocal of excess scattered intensity in arbitrary units as a function of $\sin^2\theta/2$ for polyester TO 11 in chloroform at 23°C, vertically polarized incident light, $\lambda = 5460$ Å. Polymer concentration (a) $C = 13.44 \cdot 10^{-4}$ g/ml, (b) $C = 3.36 \cdot 10^{-4}$ g/ml

the mesophase of polyester TO 11 exhibit characteristic features of smectic A or smectic C mesophases as illustrated in *Figure 4*. By contrast, above its melting point ($\sim 70°$C) polyester TO 29 shows distinct phases of liquid crystal (*Figure 5*) and isotropic liquid. It should be pointed now that long flexible spacers are not usually favourable to liquid crystal formation. This reflects the decreasing thermal stability of the mesophase with decreasing polarity (dilution of the effective number of aromatic mesogenic groups) and molecular rigidity. Indeed, such long segments are capable of adopting more or less coiled conformations and favour a non-parallel arrangement of the molecules. Thus, the coexistence of a liquid crystalline phase and an isotropic phase in polyester TO 29 is probably due to the polydispersity of the low molecular weight (H 400) fraction of PEO used for preparing this polyester.

The d.s.c. curves for polyester TO 29 show complexities at about $-50°$ to $-10°$C and $20°-60°$C (*Figure 3*). Two increases in heat capacity, T_{g_L} and T_{g_U}, can be detected. There is also indication of two transitions in the temperature dependence of the dynamic mechanical properties (*Figure 6*). The position of the mechanical T_{max} are in agreement with the d.s.c. T_{g_L} and T_{g_U}. T_{g_U} is not a definite, fixed value. It can be seen from *Figure 7* that, on annealing, T_{g_L} appears always in the same temperature

range while T_{g_U} shifts slightly to a higher temperature. E.s.r.[11] and ^{13}C solid state n.m.r.[12] measurements indicated that T_{g_L}, the lower of the two glass transitions, is due to the diffusional segmental motion of the flexible 'ether' sequences located in the amorphous isotropic regions while T_{g_U} is associated with the flexible spacers located in the ordered domains restrained by crystallites.

In *Figure 8* we schematically illustrate how polyester TO 29 can adopt organization compatible with all data known so far.

Because of the much higher content of ordered structure, only one glass transition is detected between 20° and 60°C for polyester TO 11. From e.s.r.[11] and n.m.r.[12] data it seems reasonable to associate it with a motion of the $-CH_2-CH_2-O-$ units in the 'glassy' smectic phase. The spectra of the aromatic carbons are those of the rigid lattice until the melting point ($\sim 125°$C). Only the samples which have been rapidly quenched from the isotropic state (i.e. $T > 253°$C) exhibit a marked increase in heat capacity in the T_{g_L} temperature range. The polyester TO 5 is essentially crystalline in character: no glass transition is discernible.

As observed for many polymers of this class[1-3], higher transition temperatures T_m and T_i occur for the polyesters incorporating shorter flexible spacers. This is the result of
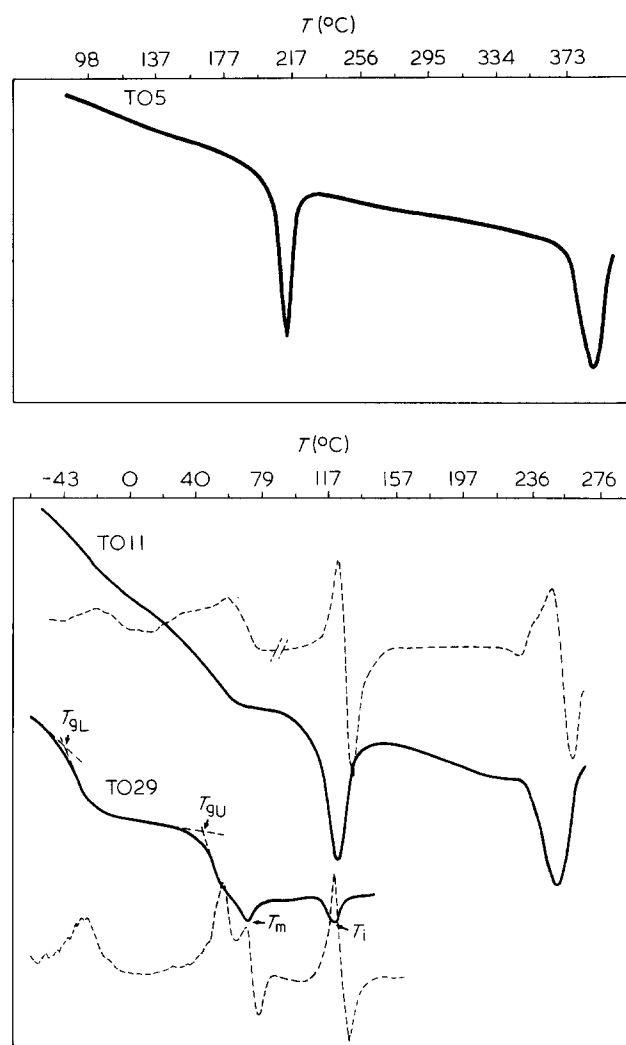

Figure 3   Differential scanning calorimetry (d.s.c.) thermograms taken during the second heating for polyesters. Virgin samples were heated above T_i, rapidly cooled and reheated.
(———) Derivatives curves

Table 1 Inherent viscosities and thermodynamic data for glass transitions, solid-mesophase and mesophase—isotropic liquid transitions

| Polyester	η_{inh} (dl.g^{-1})	Tg (°C)	T_m (°C)	ΔH_m (cal mol^{-1})	ΔS_m (cal mol^{-1} K^{-1})	T_i (°C)	ΔH_i (cal mol^{-1})	ΔS_i (cal mol^{-1} K^{-1})
TO 5	0.5	$-^a-$	213	1460	3	389	1740	2.6
TO 11	0.6	-20^b, +40	125	1257	3.15	253	754	1.43
TO 29	0.69	-40, +40	70			117	744	(1.9)

^{a} None detected
^{b} Very weak increase in heat capacity
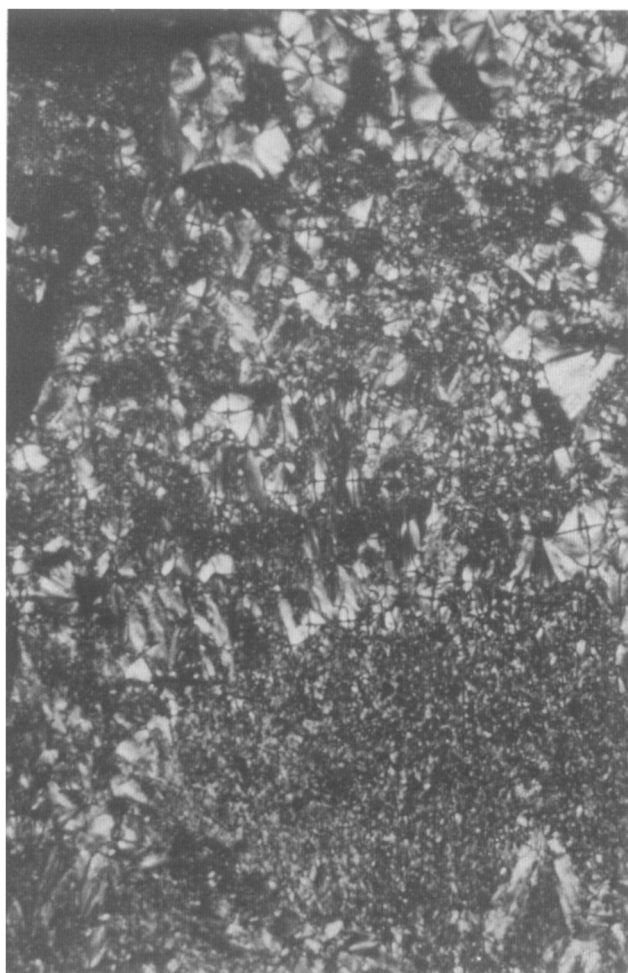
Figure 4 Micrograph of smectic mesophase from polyester TO 11 at 240°C. Focal-conic texture. Crossed polarizers (magnification ×200)

the increase in the effective number of aromatic mesogenic groups in the macromolecule and the decreased flexibility of the polymer chain. Thus, the transition temperatures, T_m and T_i, for the polyester TO 5 are higher than those determined for the polyesters TO 11 and TO 29. In particular, the clearing temperature of the former was much higher than that of the latter two. The shorter 'ether' segments in polyester TO 5 must be responsible for the much enhanced thermal stability of the mesophase and thus, the increased T_i. The corresponding higher value of ΔS_i suggests a higher degree of order in its liquid crystalline state.

Crystallographic data are summarized in *Table 2*. The three polyesters studied show some structural analogies in their crystalline modifications since the wide-angle diffraction rings bracketed in *Table 2* occur approximately at the same angle with identical relative intensities (*Figure 9*). The crystal lattices of polyesters TO 5, TO 11 and TO 29

probably differ in the length of only one unit cell parameter, say C, the value of which could be deduced from the low-angle rings, i.e., 20.8, 26.5 and 38.0 Å, respectively. Although these characteristic distances closely correspond to the length of the monomer units in their most extended *trans*-conformation (*Figure 10*) and some bonds rotated in the *gauche* position do exist and seem to agree with these identity periods. In actual fact, fully extended molecular chains with the terphenyl moieties stacked in approximately parallel arrays would imply two monomer units of one macromolecular chain per unit call and, hence, identity periods twice those determined from X-ray data.

For polyester TO 29, the crystalline structure does not change with increasing temperatures up to a temperature close to the melting point (~70°C). A further slight increase in temperature results in the disappearance of the small-angle lines. Simultaneously, the wide-angle lines vanished in a diffuse halo at $q = 1.37$–1.4 Å^{-1} within a narrow temperature range, covering about 5°C (*Figure*
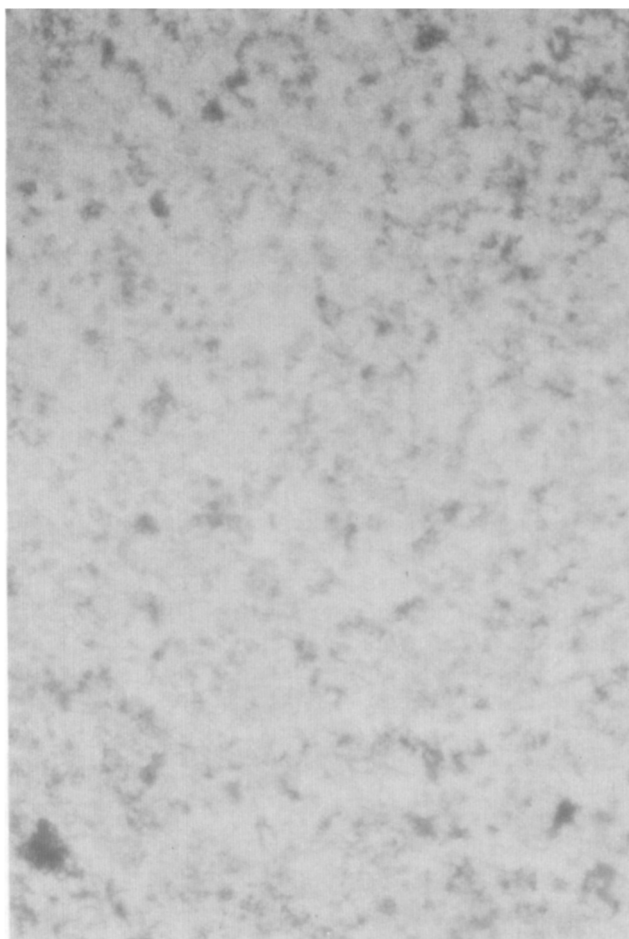
Figure 5 Liquid crystalline phase of polyester TO 29 at 90°C. Crossed polarizers (magnification ×300)
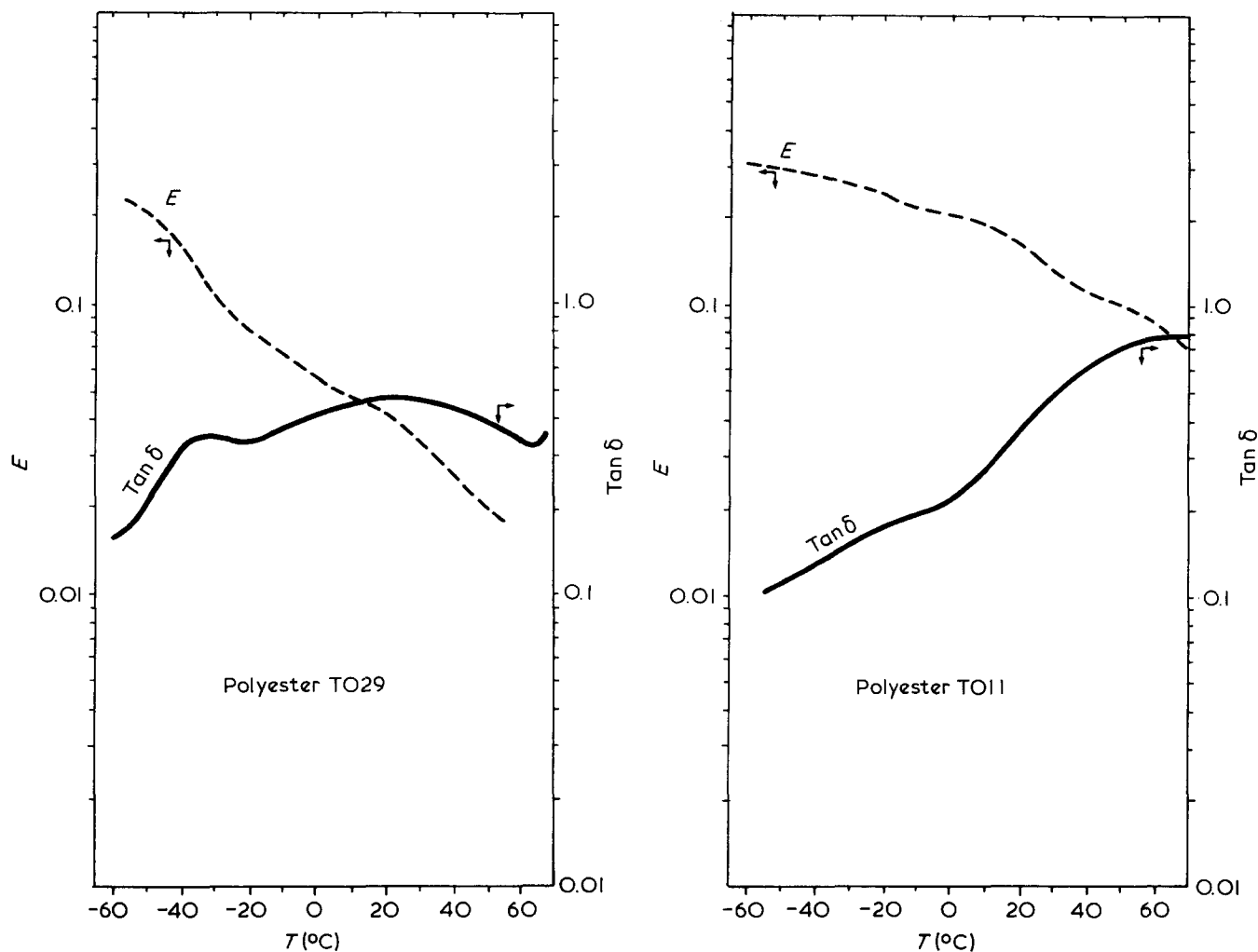
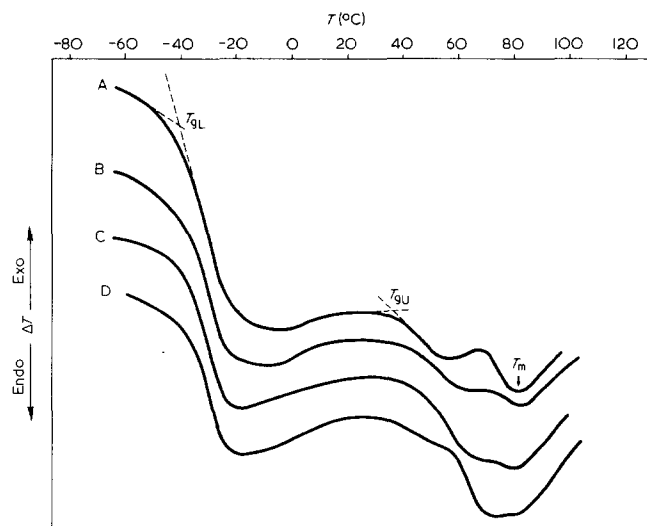**Figure 6** Temperature dependence of the dynamic mechanical properties of polyesters TO 29 and TO 11

Figure 7 Effect of the annealing temperature on T_{g_L} and T_{g_U} for polyester TO 29. With the exception of the unannealed sample (A), the samples used were annealed for one hour at 40°C (B), 45°C (C) and 50°C (D)

11). It is clear that the three dimensionally ordered regions are destroyed at the first order phase transition. The structure of the mesophase is characterized by the existence of only a short range order. We thus have to conclude that the structure of this state resembles that of a

nematic phase. The diffraction diagram does not change at the transition from the liquid crystalline state to the isotropic melt.

For the polyester TO 5, the mesophase is characterized by three well defined inner rings corresponding to a spacing of 20.2 Å and a diffuse halo at $q \simeq 1.35 \text{ Å}^{-1}$. Above the clearing point ($\sim 389°C$), the inner rings disappear. Simultaneously the halo broadens and its intensity decreases (*Figure 12*). Similar behaviour is observed for the polyester TO 11 (*Figure 13*). We thus have to conclude that the one dimensional long range positional order, which is characteristic of the smectic C and A phases is present in the liquid crystalline state. It is worth noting that the X-ray patterns obtained from polyesters TO 5 and TO 11 resemble those of S_A and S_C phases[13]. This result is in agreement with the data obtained from optical studies (*Figure 4*).

The 'as-received' polyester TO 11 is fibrous in form and thus ideally suited to X-ray studies on oriented material. Above the crystal-mesophase temperature ($\sim 125°C$), the two sharp small-angle reflections on meridian have to be attributed to regular smectic layer distance while the diffuse arcs observed along the equator are due to the short range positional order of the chains within the smectic layers (*Figure 14*). The relative position of the small angle reflections with respect to the diffuse crescents, yields X-ray patterns similar to those of the class S_A[13]. However, the S_C nature of the mesophase has been
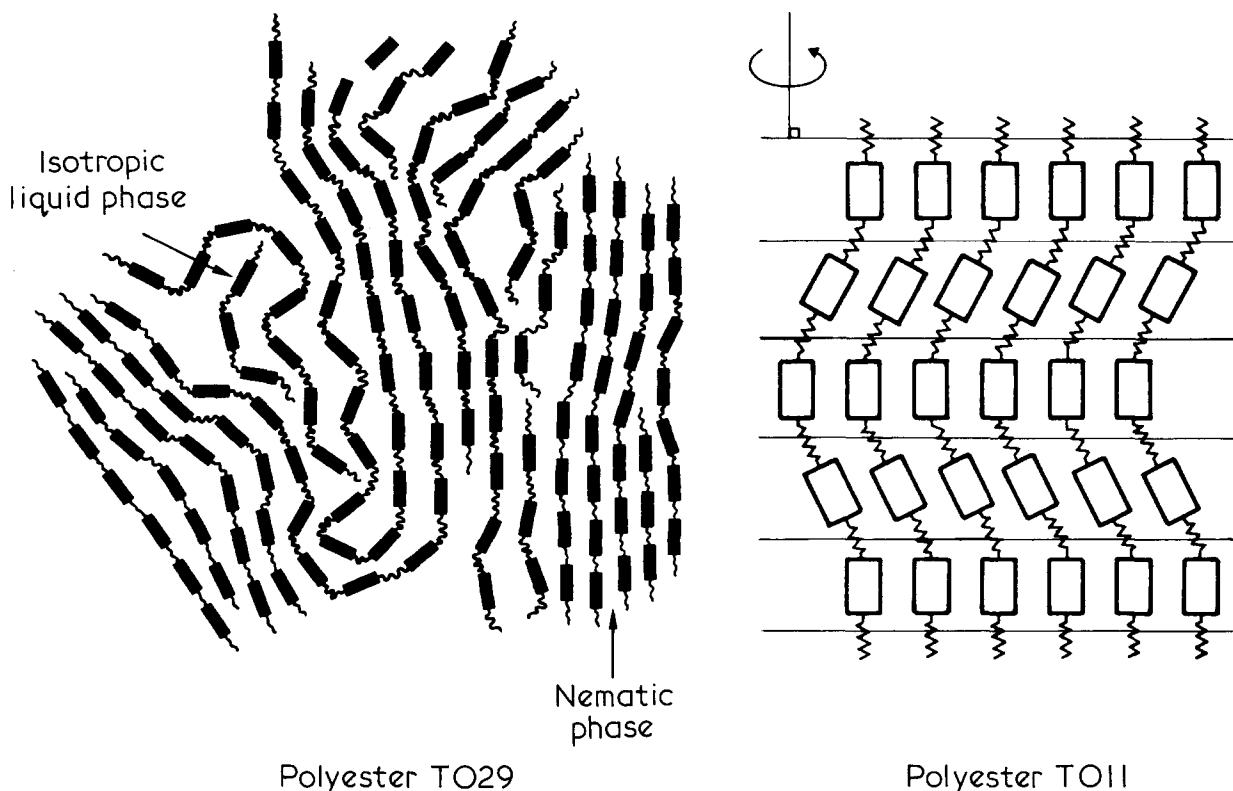
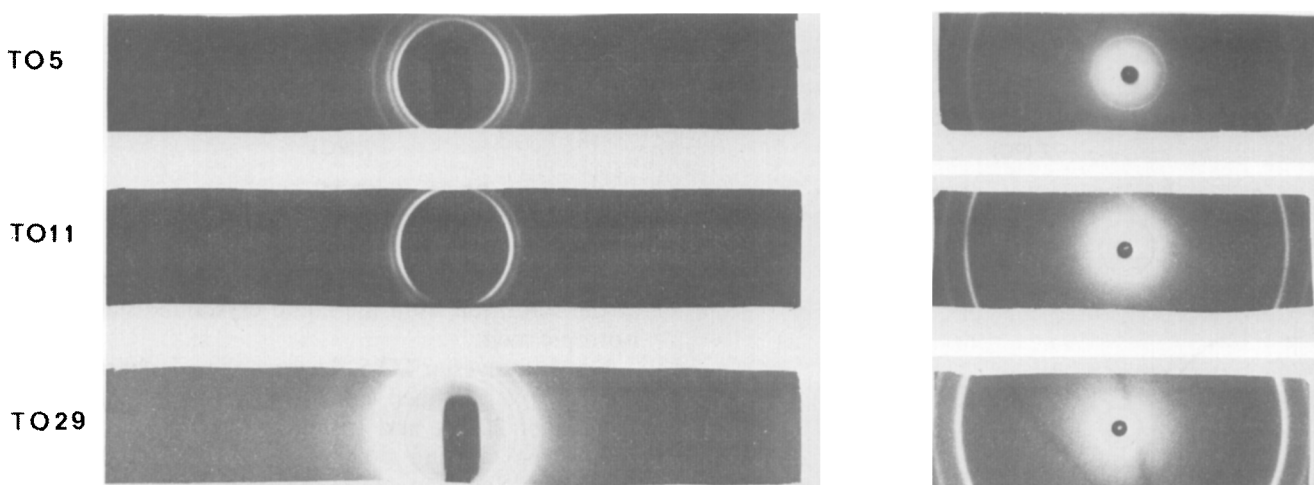**Figure 8** Distribution of macromolecular chains in polyesters TO 11 and TO 29
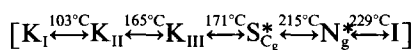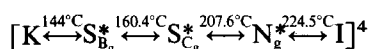

Figure 9 X-ray low- and wide-angle diffraction patterns obtained from polyesters

determined by establishing its isomorphy with the S_C phase of the standard material: terephthalidene-bis-(4-n-butylaniline)[4]. Besides, the smectic phase of the polyester was found to be miscible with the left handed twisted S_C phase of either the chiral compound 4'-(2 methyl-hexyloxy)biphenyl-4-carboxylic acid

$$[K_I \overset{103°C}{\longleftrightarrow} K_{II} \overset{165°C}{\longleftrightarrow} K_{III} \overset{171°C}{\longleftrightarrow} S_{C_g}^* \overset{215°C}{\longleftrightarrow} N_g^* \overset{229°C}{\longleftrightarrow} I]$$

or the optically active substance terephthalylidene-bis-4-((+)-4'-methylhexyloxy) aniline

$$[K \overset{144°C}{\longleftrightarrow} S_{B_g}^* \overset{160.4°C}{\longleftrightarrow} S_{C_g}^* \overset{207.6°C}{\longleftrightarrow} N_g^* \overset{224.5°C}{\longleftrightarrow} I]^4$$

These compounds in addition to the polyester mesophase cause the formation of the typical twisted S_C textures. Taking into account these results, we have to admit that

the polyester exhibits in the liquid crystalline state an S_C configuration which is azimuthally disordered with the layers orientationally ordered (*Figures 8* and *15b*)[14].

In *Figure 16* the layer spacing, L, is given as a function of temperature T. Sets of experiments were performed and the reproducibility of the phenomena was found to be good. The most important observation is that L increases significantly and monotonically with T in the temperature range 125°–210°C and then decreases as T reaches 210°C, the beginning of the smectic–isotropic phase transition. Two explanations could be offered for this variation, possibly in combination:

(i) One possibility is that the long 'ether' chains of polyester TO 11 might depart from the all-*trans* conformation. Indeed, configuration-dependent properties of polyoxide chains such as $[(CH_2)_yO]_x$ have been widely investigated[15-16]. The most characteristic feature of such polymeric chains is a decisive preference for the *gauche*
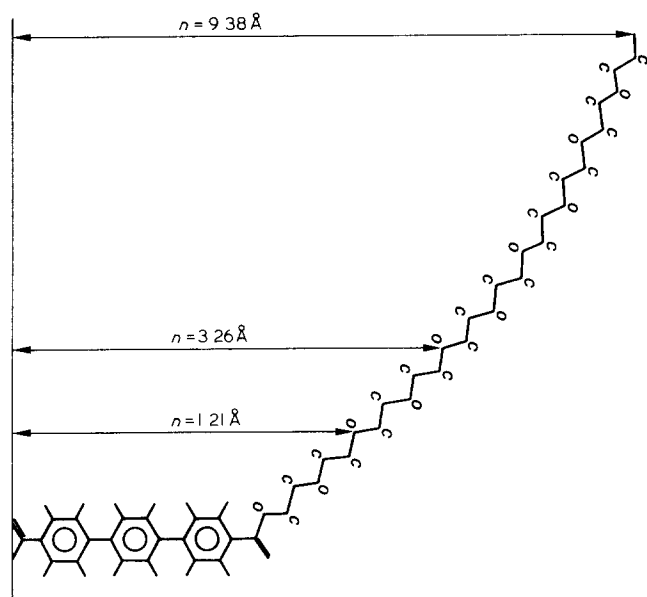
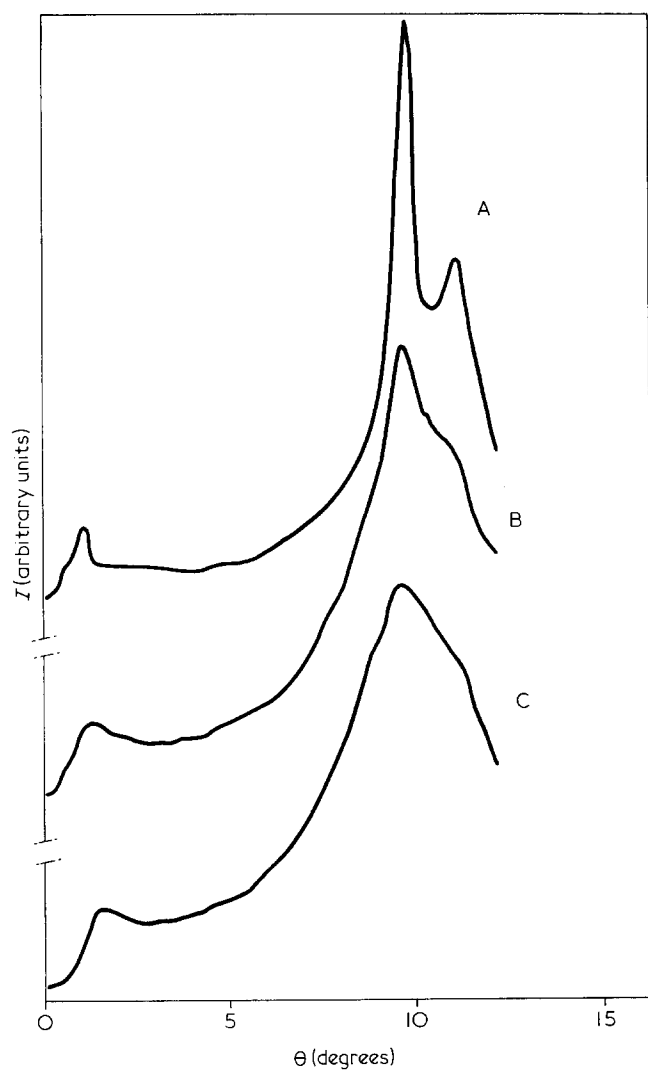**Figure 10** Proposed model of packing within layers in crystalline polyesters

Figure 11 Diffractograms of polyester TO 29: (A) crystalline state at 22°C; (B) liquid crystalline state at 90°C; (C) isotropic melt at 130°C
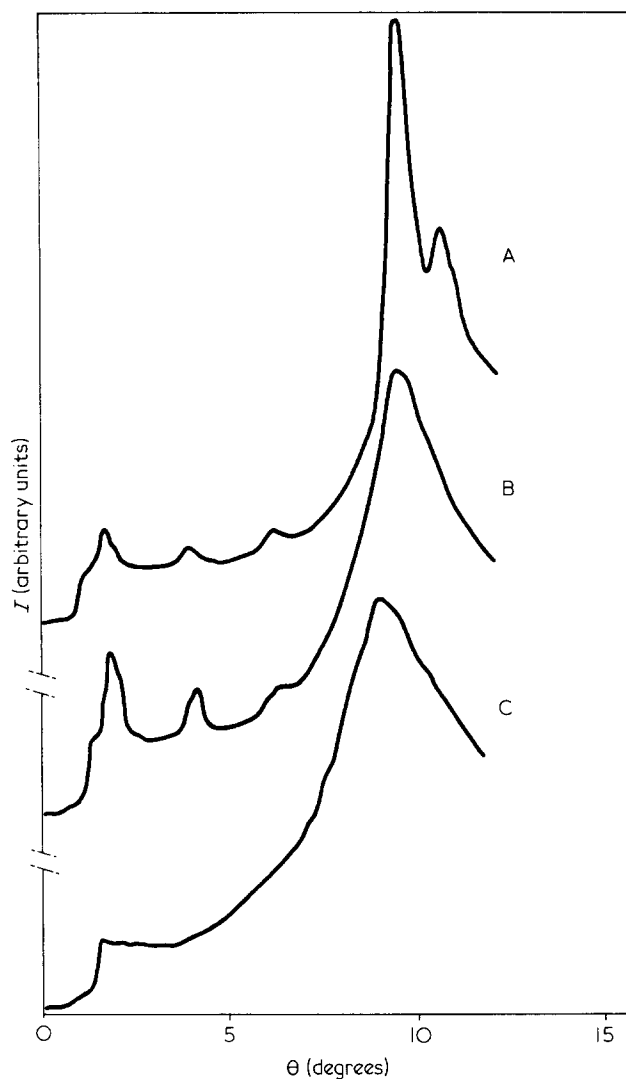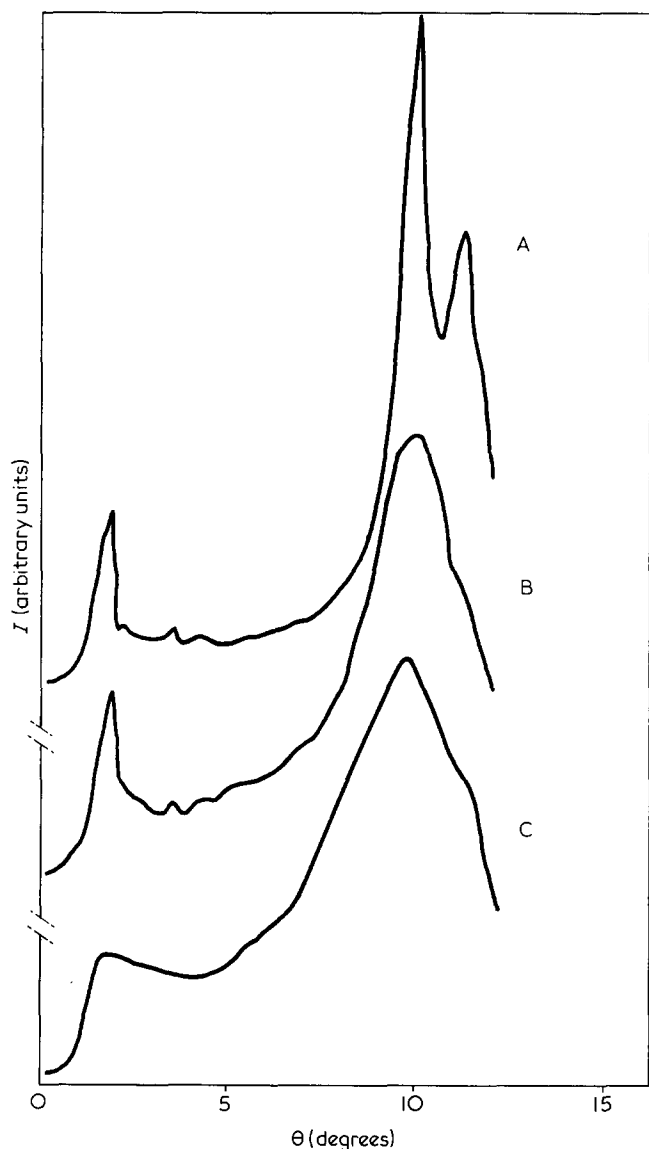

Figure 12 Diffractograms of polyester TO 5: (A) crystalline state at 22°C; (B) liquid crystalline state at 250°C; (C) isotropic melt at 390°C

Table 2 Structure characteristics obtained by X-ray diffraction for polyesters ($q = 4\pi \sin \Theta/\lambda$ is approximately equal to $2\pi/d$ if a reticular distance d can be defined)

Polyester	Crystalline phase		Liquid crystalline phase	
	d (Å)	hkl	d (Å)	q (Å^{-1})
TO 5	20.8	(001)	20.2	
	10.29	(002)	10.2	
	6.40	(003)		
	4.59)			
	4.04)		Diffuse halo: 1.35	
	3.28)			
TO 11	26.5	(001)	25.2	
	13.21	(002)	12.8	
	4.53)			
	4.00)			
	3.21)			
	2.57		Diffuse halo: 1.41	
	2.37			
	1.88			
	1.60			
TO 29	38.0	(001)		
	4.53)			
	3.98)		Diffuse halo: 1.37—1.4	
	3.20)			

bonds of poly(diethylene glycol terephthalate) (PDET) are *ca.* $0.5 \, \text{Kcal mol}^{-1}$ below those of POE. Although very surprising, it seems that the presence of two planar *trans* ester groups in the repeat unit of the chains confers freedom of rotation on adjoining groups.

The length of monomer units in which bonds are rotated into the *gauche* position is clearly inferior to that obtained with the all-stretched conformer. Hence, our data cannot preclude the possibility that there is noticeable kinking of the 'ether' chains at the crystal–smectic phase transition, that is to say between 110° and 130°C.

The increase in the interlayer spacing L with temperature might arise from decreasing kinking since for POE and PDET the fraction of *trans* states about CH_2–CH_2 bonds increases with temperature[23,28]. The contribution of the conformations of the other bonds to the changes on molecular dimensions with temperature is rather small in comparison. However, it is worth noting that no noticeable broadening of the diffraction peaks has been found between 110° and 210°C, which suggests that the coexistence of several conformers is rather questionable in this temperature range. Work is continuing by careful *FT*i.r. experiments in order to establish, whether or not, polyester TO 11 exhibits such conformational changes.

(ii) Alternatively, changes in the molecular arrangement, such as a decreasing tilt angle θ with increasing temperature might offer an equally plausible explanation of the increase in L observed from 130°C up to 220°C. Such an explanation would imply that in the temperature
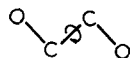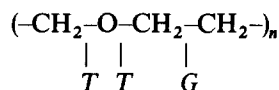
Figure 13 Diffractograms of polyester TO 11: (A) crystalline state at 22°C; (B) liquid crystalline state at 185°C; (C) isotropic melt at 280°C
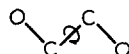
conformation over the *trans* around certain skeletal bonds. Thus, in poly(oxyethylene) (POE; $y=2$), *gauche* states about an internal

bond are found to be $0.4 \, \text{Kcal mol}^{-1}$ lower in energy than the alternative *trans* states[17-21]. A similar conclusion is obtained from the vibrational spectra of dimethoxyethane, $CH_3OCH_2CH_2OCH_3$, a model compound for POE[22]. The preferred conformation of the POE chains is known to be[23-26]:

$$(-CH_2-O-CH_2-CH_2-)_n$$
$$\underset{T \quad T \quad \quad G}{| \quad | \quad \quad |}$$

Moreover, a recent conformational analysis using ^{1}H n.m.r. spectroscopy[27] suggests that *gauche* states for the
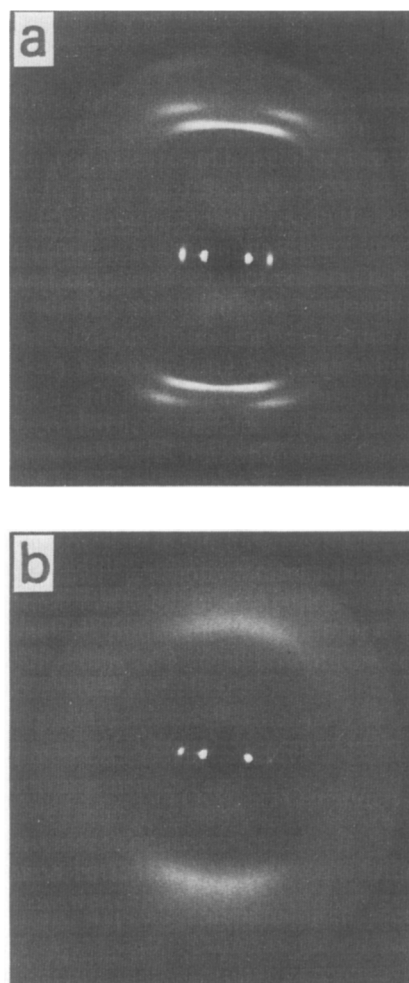

Figure 14 X-ray diffraction photographs obtained from oriented samples TO 11 (a) at room temperature, (b) at 145°C
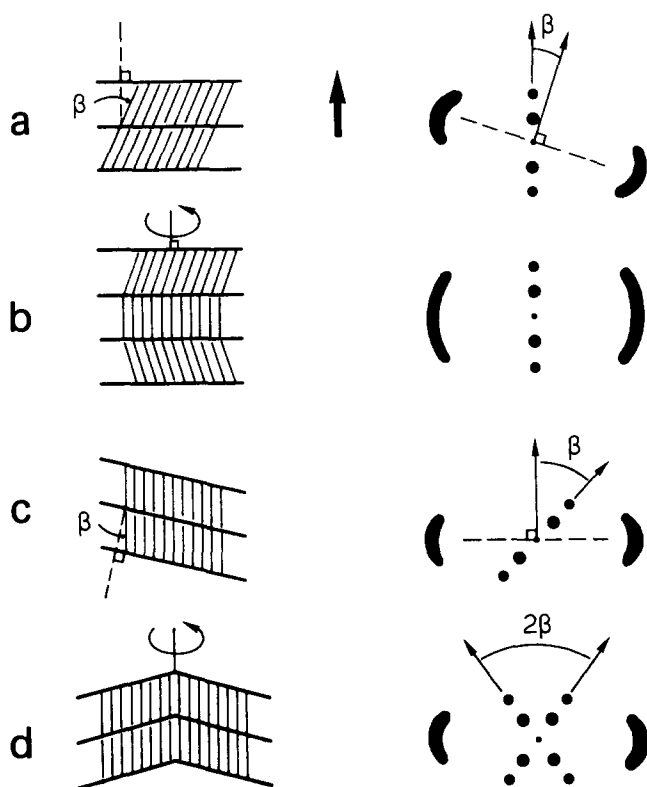
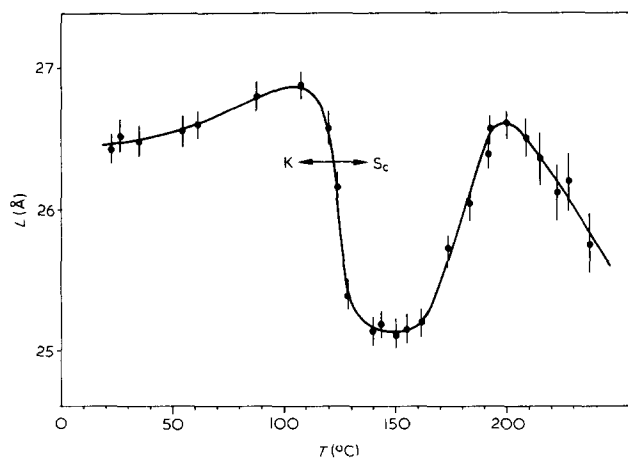**Figure 15** Different S_C configurations from ref. 14

Figure 16 Layer spacing, L, as a function of temperature for polyester TO 11

range 190°–210°C the molecules tend to stand perpendicular to the layers, which closely resembles the currently accepted description of smectic A phases. Indeed, the commonly held view concerning the distinction between smectic A and C phases is that the molecules are perpendicular to the layers in the former and tilted in the latter. Some evidence for a $S_C \leftrightarrow S_A$ transition is found in the small endotherm which can be detected at about 200°–220°C in the d.s.c. curves (*Figure 3*). Conventional liquid crystals also show an exceptionally small S_C/S_A transition heat[29–31] which indicates a close structural relationship between the S_C and S_A phases. However, the existence of S_C and S_A phases is in contradiction to our initial study by optical microscopy[4]. Polyester TO 11 was found to exhibit only a smectic C phase as judged by miscibility criteria. While conventional liquid crystals have well defined transition temperatures, in the polyesters under investigation, because of the polydispersity of the samples,

the transitions occupy a range of temperatures within which there is an equilibrium two phase microstructure. The appearance of the isotropic phase could have prevented or screened a subtle change in the texture such as could be expected for a S_C/S_A transition. A wider range of carefully selected miscibility experiments must of course be carried out to establish, whether or not, polyester TO 11 exhibits a S_A phase in the temperature range 190°–210°C.

SUMMARY AND CONCLUSIONS

In this paper we have investigated polyesters prepared from di-n-propyl-p-terphenyl 4,4″ carboxylate and HO–$(CH_2-CH_2-O-)_mH$. The inherent viscosities in dichloroacetic acid are 0.5, 0.6 and 0.69 dl g^{-1} for TO 5 ($m=2$), TO 11 ($m=4$) and TO 29 ($m=10$). The polyester TO 11 was characterized by light scattering in dilute solutions of chloroform. The existence of large aggregates was proved. However, from high scattering angle data the value of $\bar{M}_w$ was found to be 250000 ± 15000 for the unaggregated material. The crystal lattices of polyesters under investigation probably differ in the length of only one unit cell parameter, say C, the value of which closely corresponds to the length of the monomer unit in its most extended *trans* conformation. Both polyesters TO 5 and TO 11 exhibit a '2D-liquid' smectic phase.

For polyester TO 11, the smectic C nature of the mesophase was easily established from the broken focal conic texture and miscibility tests with standard materials. Besides, X-ray studies of oriented samples suggested that the smectic C configuration is azimuthally disordered with the layers orientationally ordered. The interlayer spacing L sharply decreases at the crystal–smectic C transition (110°C–130°C) and then increases significantly as the temperature is progressively raised up to 210°C. Two explanations can be offered for this behaviour. Above the melting point the flexible spacers might depart from the all-*trans* conformation. Indeed the most characteristic features of macromolecular chains such as $\{(CH_2-)_yO\}$ and poly(diethylene glycol terephthalate) are (i) a decisive preference for the *gauche* conformation over the *trans* around certain skeletal bonds and (ii) an increase in the fraction of *trans* states with temperature. Alternatively, changes in the molecular arrangement such as a decreasing tilt angle with increasing temperature might offer an equally plausible explanation of the increase in L observed in the temperature range 130°–210°C.

The polyester TO 29 shows distinct phases of liquid crystal and isotropic liquid above the melting point. This is probably due to the polydispersity of the low molecular weight fraction of PEO used for preparing this polyester. Indeed short spacers are usually favourable to liquid crystal formation whereas long flexible spacers are capable of adopting more or less coiled conformations and favour non-parallel arrangement of the molecules.

Structural models are proposed to illustrate how polyesters TO 11 and TO 29 can adopt organizations compatible with all data known so far.

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