

Chiral Liquid Crystal Polymers

3. Structurally Ordered Thermotropic Polyesters of Optically Active Propyleneglycol Ethers*

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SUMMARY

A new series of chiral, structurally ordered polyesters containing mesogenic units and optically active spacers in the main chain has been prepared. A thermotropic liquid crystal polymorphism was found to occur and quite unusual twisted smectic and/or cholesteric mesophases are believed to exist.

INTRODUCTION

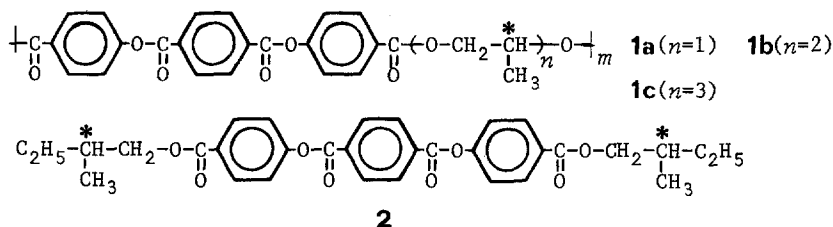
Recently great attention has been devoted to lyotropic and thermotropic mesomorphism in polymers and a wide variety of nematic, smectic and cholesteric (twisted nematic) polymers has been prepared and investigated for practical applications.

Due to their biological implications, cholesteric polymers appeared to us most interesting and suitable for potential biomedical and pharmacological applications. It is conceivable in fact that intrinsically asymmetric membranes obtained from such polymers will have, along with improved mechanical properties, enhanced selectivity to different chiral and achiral solutes by discrimination at a molecular level (CHIELLINI et al. 1982). Accordingly, we have started to synthesize thermotropic liquid crystal polymers with varying amphipatic character (GALLI et al., in press; OBER et al., in press) and potentially cholesterogenic derivatives (SCHLEIER et al. 1982). Cholesteric thermotropic addition polymers have been obtained mainly by copolymerization of mesogenic monomers with optically active comonomers, usually cholesteryl derivatives (STRZELECKI and LIEBERT 1973, FINKELMANN et al. 1978; FINKELMANN and REHAGE 1980; MOUSA et al. 1982). More recently the cholesteric behaviour of some copolypeptides has been reported (KASUYA et al. 1982). Only a few examples of main chain cholesteric polyesters are known (VAN LUYEN et al. 1980; BLUMSTEIN et al. 1982) and structure-property correlation for such systems is far from being fully elucidated.

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In this paper we describe the synthesis and the thermal-optical characterization of a new series of structurally ordered polyesters **1a-1c** incorporating mesogenic units and optically active spacers in the main chain. A low molecular weight structural model **2** was also synthesized and investigated for its liquid crystal behaviour. The circular dichroism absorption properties will be reported in a separate paper.



RESULTS AND DISCUSSION

Polymer samples were prepared by stepwise polycondensation from the diacid chloride of bis(4-carboxyphenyl)terephthalate and optically active α,ω -diols in 1,2-dichloroethane at 60°C in the presence of excess pyridine. The rigid anisotropic moiety consisting of a sequence of three aromatic rings was preformed prior to polymerization. It should be noted however that neither the diacid itself nor its precursors are liquid crystalline. The relatively flexible spacers consisting of (S)-1,2-propanediol ($n=1$) and its head-to-tail dimer ($n=2$) and trimer ($n=3$) had the same (S) absolute configuration of asymmetric carbon atoms as well as the same optical purity $\approx 95\%$. In the Table yields and some polymer properties are collected.

TABLE. Properties of thermotropic polyesters of chiral oligoethers.

Sample	Yield (%)	$\eta_{inh}^{a)}$ (dl/g)	$ \alpha _{578}^{a)}$	$T_m^{b)}$ (°C)	$T_{LC}^{b)}$ (°C)	$T_c^{b)}$ (°C)
1a	70.8	0.02	+ 9.5	334	—	360
1b	76.9	0.02	+17.2 ^{c)}	130	286	>320
1c	19.0	0.03	+20.0	275	305	321

^{a)} In fuming H_2SO_4 at 25°C. ^{b)} T_m =melting transition; T_{LC} =liquid crystal-liquid crystal transition; T_c =clearing transition. ^{c)} $|\alpha|^{25+26.6}$ in $CHCl_3$.

Samples **1a** and **1c** were virtually insoluble in all solvents, except fuming H_2SO_4 and hot CF_3COOH , whereas **1b** could be dissolved in $CHCl_3$ and dioxane. The polymeric products were characterized by a medium-

low molecular weight, as reflected by the values of the inherent viscosity in fuming H_2SO_4 at room temperature. However, the occurrence of some polymer degradation in such solvent cannot be here excluded. Indeed, measurements of intrinsic viscosity in CHCl_3 at 25°C gave for **1b** values of 0.2 dl/g.

All the samples obtained were optically active and the sign of the optical rotation at 578nm was consistently positive as that of the starting optically active oligoethers.

The thermotropic liquid crystal behaviour of the polymers and of the model was investigated by DSC and by qualitative observation of stiro-palescence and of optical textures (DEMUS and RICHTER 1978) on the hot stage of a polarizing microscope. The polymer samples gave rise to birefringent melts whose onset (T_m), despite the identical stereochemical order of the ether spacer, was very markedly affected by the number of atoms within the flexible segment, in accordance to what has been reported for analogous series of liquid crystal polyesters (ANTOUN et al. 1981; ROVIELLO and SIRIGU 1982). A very sharp drop in the melting temperature was observed in the case of sample **1b** with an odd number of atoms in the ether segment. On the contrary, the isotropization (clearing) temperature (T_C) appears not to be very influenced by the length of the spacer.

On heating, the DSC curves of **1a** exhibit an intense endotherm ($\Delta H_m=0.7$ cal/g) with a maximum at 334°C and an additional broad endotherm ($\Delta H_m=0.3$ cal/g) centred at about 360°C , that are attributed to crystal melting and to mesophase clearing respectively. Both transitions have a high degree of supercooling ($\approx 50^\circ\text{C}$) and this is rather unusual for mesophase transitions, that are generally known to be characterized by relatively small degrees of supercooling. It is worth noting that the corresponding polymer obtained from racemic 1,2-propanediol has a much lower melting temperature at 262°C , with a nematic mesophase existing over a much broader range (GALLI et al., in press). Apparently, the configurational regularity of the chiral spacer has a pronounced effect in enhancing the crystallinity of the polymer, with a consequent diminishing of its propensity to mesophase formation.

The DSC thermograms of **1b** display a very structured melting transition between 95 and 135°C , with a pre-melt crystallization exotherm at about 90°C . Consequently, a melting temperature of 130°C was estimated by the appearance of flow and stiro-palescence. Another first order transition ($\Delta H_{LC}=0.5$ cal/g) is present at 286°C , that displays on cooling only a moderate degree of supercooling ($\approx 10^\circ\text{C}$). When observed on a polarizing microscope, **1b** gave after melting at 130°C a highly birefringent viscous fluid exhibiting a homogeneous texture, that in the range 240 – 290°C developed more irregularities resembling typical bundles of oily streaks (Fig. 1A). It is also of interest to note that in the interval 190 – 240°C the sample shows a distinct red-orange reflection of light. Furthermore, in regions of

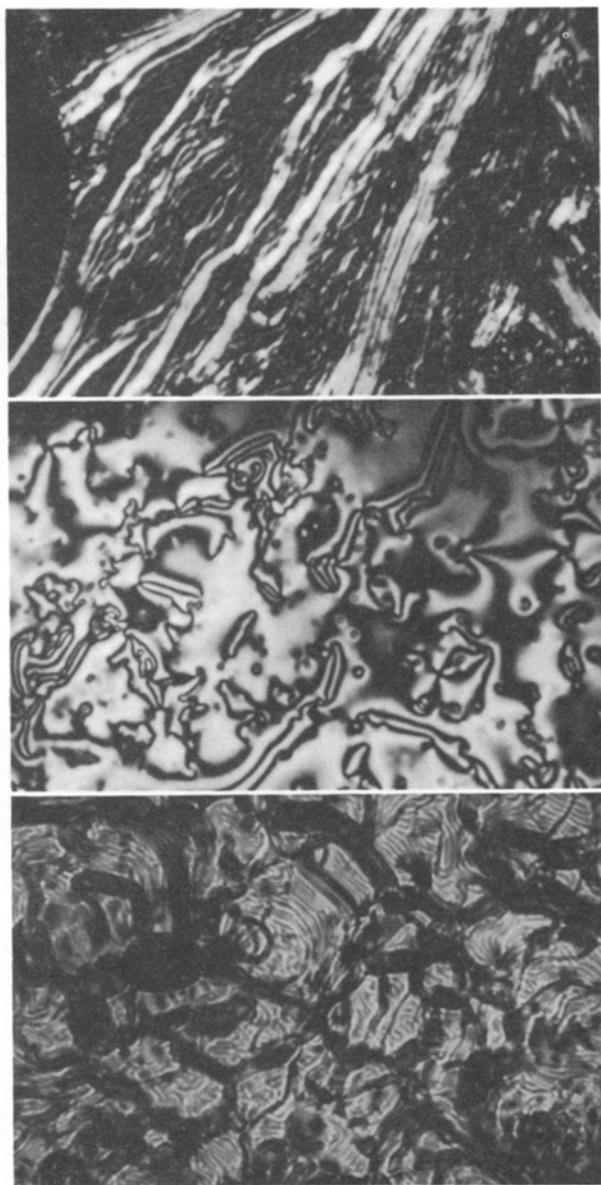


Fig. 1. Optical textures between crossed polarizers of liquid crystal polyester **1b**: (A) oily streaks at 250°C (heating); (B) schlieren texture at 298°C (heating); (C) chevron-like texture at 280°C (cooling).

thinner preparation, typical schlieren textures were observed and maintained up to 290°C. At that temperature large homeotropic regions appeared and the light was almost completely extinguished. At higher temperatures birefringence and stiropalescence increased and the sample displayed a blurred schlieren texture (Fig. 1B). No visual clearing was observed below 320°C. Interestingly, on cooling from the anisotropic melt, the schlieren texture was preserved down to room temperature, with only partial crystallization in the solid state, whereas on cooling from the homeotropic state at 290°C, a mesophase nucleated in spheres that afterwards coalesced in larger domains with a striated pattern resembling a chevron or myelinic texture (Fig. 1C).

At present this complex liquid crystal behaviour cannot be completely accounted for, but it appears from thermal and textural features that several mesophases are present within the broad temperature range of existence. In particular, at low temperatures a twisted smectic, possibly C, phase seems to establish, that on further heating can give rise to another modification with high tendency to become homeotropic. The two mesophases may coexist up to approximately 290°C and beyond that limit the onset of a cholesteric mesophase is thought to occur.

Polymorphism in the liquid crystal state appears to occur also in the case of **1c**. In fact, the DSC heating curves exhibit after a broad melting peak ($\Delta H_m=1.5$ cal/g) two additional endotherms below the beginning of decomposition at about 340°C (Fig. 2). While the latter is tentatively attributed to the isotropization transition, the former must be due to the transition from a highly ordered liquid crystal phase ($\Delta H_{LC}=4.0$ cal/g) to a less ordered mesophase.

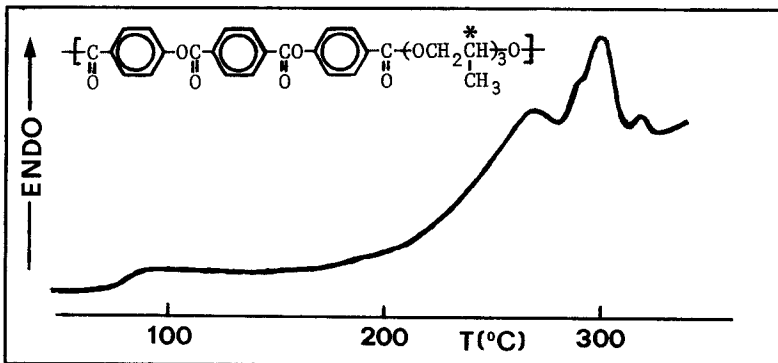


Fig. 2. DSC heating curve of liquid crystal polyester **1c**.

Optical observations seem to support these suggestions, in that typical phenomena such as birefringence and stiro-palescence were detected at $\approx 270^\circ\text{C}$ and an unspecific schlieren texture was maintained up to 300°C . Furthermore, in the same temperature range a weak green-blue reflection of circularly polarized light was observed, thus indicating even in the case of **1c** the existence of a twisted smectic structure.

We are unaware of previous reports on the existence of both twisted smectic and cholesteric mesophases in thermotropic liquid crystal polymers. Twisted smectic mesophases have been previously obtained in polymers only by addition of chiral compounds to smectic thermotropic polymers (FAYOLLE et al. 1979). However, the existence of such polymorphism does not seem unlikely in the present series of optically active polyesters, as the onset of smectic and/or nematic mesophases has been already observed for related polymers having the same mesogenic unit and achiral polymethylene (OBER et al. 1982) or polyoxyethylene (GALLI et al., in press) flexible spacers in the main chain. Furthermore, the model compound clearly displays enantiotropic smectic A and cholesteric mesophases (Fig. 3). Additional X-ray studies now in progress should provide more definitive information to fully characterize the liquid crystal structures involved.

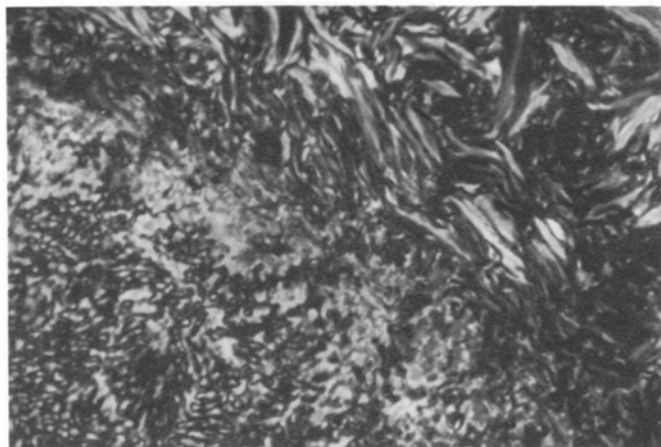


Fig. 3. Optical texture between crossed polarizers of liquid crystal model compound **2**: cholesteric \rightarrow smectic transition at 146°C (cooling).

EXPERIMENTAL PART

Bis(4-carboxyphenyl)terephthalate was prepared as previously reported (GALLI et al., in press).

(S)-1,2-propanediol $\{(n=1), |\alpha|_D^{25} +26.5 \text{ (CHCl}_3)\}$ and its head-to-tail dimer $\{(n=2), |\alpha|_D^{25} +67.4 \text{ (CHCl}_3)\}$ and trimer $\{(n=3), |\alpha|_D^{25} +66.3 \text{ (CHCl}_3)\}$ were synthesized according to the general procedure described in Part 2.

Bis{4-(S)-2'-methylbutoxycarbonylphenyl}terephthalate **2**. A mixture of 13.8g (0.3mol) of 4-hydroxybenzoic acid, 26.4g (0.3mol) of (S)-2-methyl-1-butanol $\{|\alpha|_D^{25} -5.72 \text{ (neat), optical purity 98\%}\}$, 30ml of benzene was heated at reflux in a Dean-Stark apparatus for 3hr. After cooling, the mixture was washed with 5% NaHCO₃ and water, dried over Na₂SO₄ and then distilled in vacuo to give 12.5 g (yield 60%) of 2-methylbutyl-4-hydroxybenzoate **3**, as a colourless oil: b.p. 158°C/1mmHg; $|\alpha|_D^{25} +6.3 \text{ (acetone)}$. A solution of 2.45g (12mmol) of terephthaloyl chloride in 30ml of anhydrous dioxane was added in 1hr to a solution of 5.0g (24mmol) of **3** in 35 ml of dioxane and 2ml of pyridine. The reaction mixture was stirred overnight at room temperature, then poured into 200ml of cold 5% HCl. The precipitate formed was washed with 5% NaHCO₃, water and twice crystallized from DMSO/water 6/1 (vol/vol) to give 3.1g (yield 47%) of **2**: $|\alpha|_D^{25} +3.9 \text{ (CHCl}_3)$; K \rightarrow S 135°; S \rightarrow Ch 146°; Ch \rightarrow I 160°C.

¹H-NMR (d₆-DMSO): δ (from TMS) = 8.5 (s, 2H, terephthalate), 8.2 and 7.6 (two d, 4H, oxybenzoate) 4.1 (d, 2H, COOCH₂) and 2.1-0.8ppm (m, 9H, aliphatic).

IR (KBr) = 1735, 1720, 1705, 1605, 1270, 1020, 880, 765, 720 and 690cm⁻¹.

Polymers **1a-1c** were prepared and purified according to a previous procedure (GALLI et al., in press).

Viscosity measurements were performed at 25°C with 10ml of polymer solution of 0.6 g/dl concentration in fuming sulphuric acid by an Ostwald viscometer. Differential scanning calorimetry analyses were carried out by a Perkin-Elmer DSC-2 apparatus at heating-cooling rate of 20°C/min under dry nitrogen flow. ΔH values were determined on unannealed samples by means of indium standards and are indicative since the degrees of crystallinity were not known.

Texture observations were performed between crossed polarizers on a Reichert Polyvar microscope equipped with a programmable Mettler FP52 hot stage. Thin layers of polymer were analyzed between slide and cover slips without any further treatment. Original magnification of all photomicrographs was 250 \times .

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