This means that there are two environments of the methyl protons influenced by a cationic charge in the molecule. (a) Smallcombe, S. H.; Casero, M. C. *J. Am. Chem. Soc.* **1971**, *3*, 5826. (b) Kice, J. L.; Favstritsky, N. A. *J. Am. Chem. Soc.* **1969**, *91*, 1751. (c) Perker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583.

(26) This hypothesis is also consistent with the previously reported mechanism for acid-catalyzed exchange reactions of asymmetric disulfides.

(27) Diphenyl disulfide. ^{13}C NMR ($CDCl_3$, ppm): 128.9, 129.0, 130.7, 138.4. Diphenyl sulfide. ^{13}C NMR ($CDCl_3$, ppm): 126.9, 129.1, 131.1, 136.0. Thianthrene. ^{13}C NMR ($CDCl_3$, ppm): 127.5, 128.6, 135.5. Thiophenol. ^{13}C NMR ($CDCl_3$, ppm): 125.4, 128.9, 129.3, 130.7.

(28) The ^{13}C NMR data of the reaction mixture coincided with the previously reported data for phenylbis(phenylthio)sulfonium cation (X). The formation of even bis[(2,6-dimethylphenyl)thio]sulfonium cation, which is a sterically hindered cation in conparison with the phenyl one. Additionally, other sulfides have been reported to form the corresponding sulfonium cations. Gybin, A. S.; Smit, W. A.; Bogdanov, V. S. *Tetrahedron Lett.* **1980**, *21*, 383.

(29) We could isolate the mixture of the cation and diphenyl disulfide, from which $SbCl_5$ was completely removed through the selective extraction $SbCl_5$ with cool ether (this procedure should be carried out at low temperature). The NMR spectrum on the isolated mixture redissolved in dichloromethane indicated the existence of phenylbis(phenylthio)sulfonium cation.

(30) MS: m/e 217, 325. IR (KBr, cm^{-1}): 3075, 3090 (ν_{C-H}); 1445, 1480, 1580 ($\nu_{C=C}$); 825 (δ_{C-H}); 695, 745, 905, 1000, 1030, 1080, 1100, 1305, 1400.

Chiral Liquid Crystal Polymers. 10. Thermotropic Mesomorphism in Chiral Isomeric Polyesters

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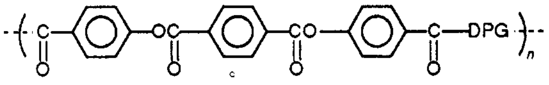
ABSTRACT: A series of four samples of chiral thermotropic polyesters 1–4 based on smectogenic 4,4′-(terephthaloyldioxy)dibenzoic (HTH) acid and the three optically active isomers of dipropylene glycol (DPG) and a commercially available mixture of the three racemic isomers was prepared. The thermotropic mesomorphism of the polymer samples was investigated with reference to the isomeric structure of the chiral spacer segment incorporated into the polyester backbone. The four polyesters display strikingly different thermal responses. The relative topology of the two methyl substituents, and hence of the two chiral centers, within the flexible segments, is effective in defining the onset, stability, and nature of the mesophases. The evolutions of the structures of the mesophases were followed as a function of temperature, and the occurrence of polymorphic sequences is proposed, which involve ordered smectic, disordered smectic, and nematic (or cholesteric) mesophases.

Introduction

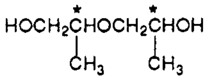
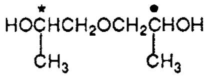
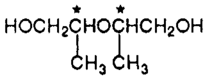
Chiral liquid-crystalline polymers are attracting ever increasing attention in respect to their potential in optical and electrooptical applications, including the design and realization of both active and passive devices.[1-14]

In connection with this interest, we have been studying for a few years the structure-property correlations in series of different thermotropic liquid-crystalline polyesters comprised of chiral semiflexible segments as derived from diols and dithiols.[15,16] Depending upon the chemical and stereochemical structural features of the flexible chiral spacer and of the rigid aromatic core, a wide variety of new polymeric materials has been prepared and analyzed for their mesomorphic behavior in the melt and chiroptical properties in dilute solutions.[15,16]

In the present contribution we highlight the effect of structural isomerism in a series of polyesters, 1–4, prepared from a powerful mesogen, such as 4,4′-(terephthaloyldioxy)dibenzoic (HTH) acid, and the various dipropylene glycol (DPG) isomers. Namely, the head-to-tail (DPGht) isomer was used for sample 1, the head-to-head (DPGhh) isomer for sample 2, and the tail-to-tail (DPGtt) isomer for sample 3, in which the two chiral centers are located in the 1,4, 1,5, and 1,3 relative positions, respectively. A mixture of the three racemic isomers (DGPrm) was also used as the precursor of sample 4.



1–4

polyester HTH–DPG	dipropylene glycol (DPG)	
1	 $\mathrm{HOCH_2\underset{CH_3}{\overset{\star}{C}}HOCH_2\underset{CH_3}{\overset{\star}{C}}HOH}$	(DPGht, **15**)
2	 $\mathrm{HO\underset{CH_3}{\overset{\star}{C}}HCH_2OCH_2\underset{CH_3}{\overset{\bullet}{C}}HOH}$	(DPGhh, **11**)
3	 $\mathrm{HOCH_2\underset{CH_3}{\overset{\star}{C}}HO\underset{CH_3}{\overset{\star}{C}}HCH_2OH}$	(DPGtt, **14**)
4	racemic mixture (DPGrm, **16**) DPGht (71%) + DPGhh (21%) + DPGtt (8%)	

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In particular, the role is stressed of subtle topological changes in the flexible dipropylene segments as responsible for effecting the overall mesomorphic behavior of the polymer samples.

Experimental Section

Synthesis of Monomers. Ethyl (2*S*)-2-((Tetrahydropyran-2′-yl)oxy)propanoate (6). To a solution of 365.0 g (3.08 mol) of ethyl (*S*)-lactate (**5**), $[\alpha]^{25}_{D}$ −11.0 (neat), and 421.0 g (5.01 mol) of 3,4-dihydro-2*H*-pyran were slowly added 30 drops of concentrated HCl at 0 °C. The solution was stirred for 10 h while it reached room temperature. Na_2CO_3 (30 g) was added, and stirring was continued for 10 h. The reaction mixture was then filtered, concentrated to small volume, and distilled to give 519 g (yield 83%) of chemically pure (GLC) **6**: bp 74–78 °C (1.2 mm) (lit.[17] bp 66–68 °C (0.2 mm)); α^{25}_{D} −38.1° (neat).

(2*S*)-2-((Tetrahydropyran-2′-yl)oxy)-1-propanol (7). To a suspension of 120.0 g (3.16 mol) of $LiAlH_4$ in 750 mL of dry diethyl ether was added a solution of 518.7 g (2.57 mol) of **6** in 400 mL of diethyl ether at 0 °C under nitrogen atmosphere over 8 h. After 12 h at room temperature, the reaction mixture was refluxed for 5 h. Methyl acetate (25 g), 210 mL of 10% NaOH, and 830 mL of water were then added in that order to the mixture cooled at room temperature. The precipitate was filtered off, and the solution was concentrated, dried over K_2CO_3, and finally distilled to give 351.5 g (yield 86%) of chemically pure (GLC) 7: bp 76–84 °C (1.5 mm) (lit.[17] bp 64–66 °C (1 mm)); α^{25}_{D} +14.5° (neat).

(2*S*)-1-((*p*-Tolylsulfonyl)oxy)-2-((tetrahydropyran-2′-yl)oxy)propane (8). A solution of 226.8 g (1.42 mol) of **7** in 450 mL of dry pyridine was cooled in a water–ice bath under nitrogen atmosphere. *p*-Toluenesulfonyl chloride (295 g, 1.55 mol) was added in small portions over 2.5 h. After being stirred at room temperature for 18 h, the mixture was filtered and the precipitate was washed with benzene (6 × 50 mL). The filtrate and washings were concentrated and shaken twice with iced water. The aqueous phase was slowly acidified with cold 3 N HCl to pH = 4–5 and extracted with benzene (3 × 50 mL). The organic fractions were washed with 170 mL of cold 3 N HCl, and water and then dried over $MgSO_4$. After evaporation of the solvent 360.1 g (yield 81%) of clear oily **8** was obtained that was used without further purification.

(2*S*,6*S*)-2,6-Bis((tetrahydropyran-2′-yl)oxy)-4-oxaheptane (10). A solution of 14.6 g (9.1 mmol) of **7** in 50 mL of dry tetrahydrofuran was added dropwise over 3 h at room temperature under nitrogen atmosphere to a suspension of 2.4 g (0.10 mol) of NaH in 100 mL of dry tetrahydrofuran. After being refluxed for 5 h, the mixture was cooled to ambient temperature and then a solution of 28.8 g (9.2 mmol) of **8** in 100 mL of dry tetrahydrofuran was added over 2 h. After the mixture was refluxed for 12 h, 200 mL of water was added very slowly to the cooled mixture. The aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with water, dried over $MgSO_4$, and finally evaporated to dryness to obtain 30.1 g of crude **10** that was used without further purification.

(2*S*,6*S*)-2,6-Dihydroxy-4-oxaheptane (11). Crude **10** (30.1 g) was dissolved in 80 mL of methanol, and 2 mL of 12 N HCl was added. After 18 h at room temperature, triethylamine was added to pH = 7–8. The mixture was concentrated to small volume, and the suspended salts were filtered off. The filtrate was washed with pentane (2 × 30 mL) and distilled over CaH_2 to yield 9.8 g (yield 73%) of **11** with a chemical purity (GLC) of 92%; bp 81–84 °C (1.4 mm) (lit.[18] bp 52–57 °C (0.2 mm)). The reaction product (0.6 g) was further purified by flash chromatography. A 40 mm × 18 in column was filled with 6 in. of 40–60-μm silica gel (from Merck), and the benzene/acetone mixture (2:1 by volume) was used as the eluent at a flow rate of 2 in./min. Chemically pure **11** (0.15 g) was obtained; $[\alpha]^{25}_{D}$ +49.7° (chloroform, c = 3.30 g/dL). IR (liquid film): 3340, 2970–2880, 1450, 1375, 1335, 1180–1040 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ (ppm from TMS) 76.82 (CH_2), 66.25 (CH), 18.94 (CH_3). gas-MS: *m/e* (% *I*) 135 (8), 117 (10), 89 (49), 59 (73), 45 (100), 42 (58), 41 (29), 31 (60), 29 (31).

(2*S*,4*S*)-2,4-Dicarbethoxy-3-oxapentane (13). To a suspension of 12.0 g (0.52 mol) of metallic sodium in 250 mL of dry diethyl ether was added 58 mL (0.51 mol) of ethyl (*S*)-lactate (**5**) dropwise with stirring at room temperature under nitrogen atmosphere. After the mixture was stirred for additional 18 hours, 73.9 g (0.41 mol) of ethyl (*RS*)-2-bromopropionate (**12**) was added over 2 h. The mixture was stirred for 3 h at room temperature and then it was washed with water up to neutral pH, dried over $MgSO_4$, concentrated to small volume, and distilled to give 53.2 g (yield 60%) of chemically pure (GLC) **13**: bp 118–120 °C (18 mm) (lit.[19] bp 121–123 °C (15 mm)). The ^{13}C NMR analysis of **13** showed that it was a mixture of meso and optically active diastereomers in 1:3 ratio.

(2*S*,4*S*)-1,5-Dihydroxy-2,4-dimethyl-3-oxapentane (14). A solution of 40.0 g (0.18 mol) of **13** in 50 mL of dry diethyl ether was added under nitrogen atmosphere over 2 h to a suspension of 10.0 g (0.26 mol) of $LiAlH_4$ in 400 mL of diethyl ether at 0 °C. After the mixture was stirred at reflux for 10 h, 20 mL of ethyl acetate in 50 mL of diethyl ether was added at room temperature. To the cooled mixture were added 80 mL of water and 125 mL of 12 N HCl in that order. The aqueous phase was passed on a column packed with 150 g of the cation-exchange resin Amberlite 200, in its sodium salt form. The aqueous acidic solution obtained (800 mL) was neutralized by addition of $CaCO_3$, concentrated, salted with NaCl, and extracted continuously with diethyl ether over 28 h. The combined extracts were concentrated and distilled over CaH_2 to give 17.8 g (yield 72%) of chemically pure (GLC) **14**: bp 92 °C (0.2 mm) (lit.[20] bp 116–118 °C (10 mm)); $[\alpha]^{25}_{D}$ +1.9° (chloroform, c = 3.66 g/dL). IR (liquid film): $\tilde{\nu}$ 3640–3000, 2960–2870, 1450–1375, 1335, 1140, 1045 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ (ppm from TMS) 75.72 (CH(*R*,*S*), 48), 72.27 (CH(*S*,*S*), 145), 65.69 (CH_2(*R*,*S*), 68), 65.78 (CH_2(*S*,*S*), 185), 17.17 (CH_3(*R*,*S*), 44), 15.56 (CH_3(*S*,*S*), 104). Numbers in parentheses refer to the intensity of the signals. MS: *m/e* (% *I*) 103 (23), 59 (100), 45 (49), 43 (39), 41 (29), 31 (85), 29 (18), 27 (17).

The mixture of diastereomers (1.5 g) was separated by preparative liquid chromatography on a silica gel column (215 g) (from Merck) using the benzene/methanol mixture (5:1 by volume) as the eluent at a flow rate of 26 ml/min. Fractionation yielded 0.43 g of chemically pure (GLC) **14**; $[\alpha]^{25}_{D}$ +1.8° (chloroform, c = 2.69 g/dL). ^{13}C NMR analysis indicated the isolated product to be a mixture of 98% of the optically active isomer and 2% of the meso isomer.

(2*S*,5*S*)-1,5-Dihydroxy-2-methyl-3-oxahexane (**15**) (bp 96 °C (0.5 mm); $[\alpha]^{25}_{D}$ +67.4° (chloroform, c = 2.08 g/dL); ee 94%) was prepared as previously reported.[21]

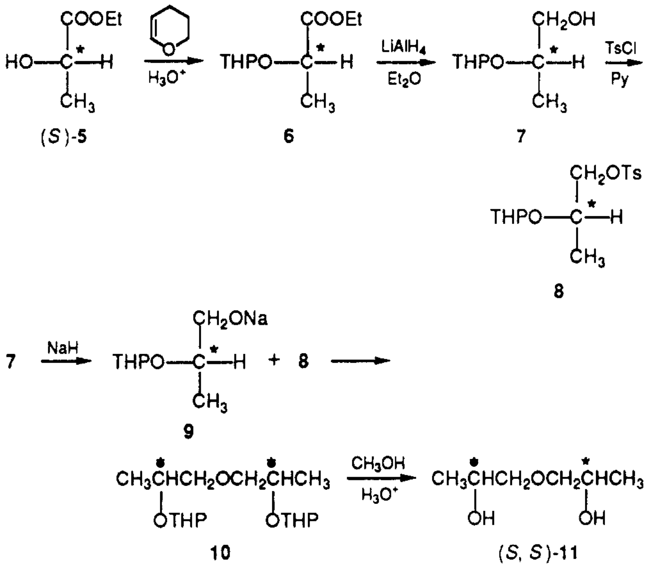
The commercially available (Aldrich) racemic mixture **16** of dipropylene glycols consisted of 71% head-to-tail, 21% head-to-head, and 8% tail-to-tail isomers, according to GLC analysis. It was azeotropically distilled with benzene prior to use.

4,4′-(Terephthaloyldioxy)dibenzoyl chloride (**17**) was prepared and purified as previously described.[22,23]

Preparation of Polymers. In a typical polymerization experiment 4.80 g (10.8 mmol) of **17** was dissolved in 120 mL of 1,2-dichloroethane at 90 °C, and then a solution of 1.45 g (10.8 mmol) of **14** and 1.75 mL (21.6 mmol) of dry pyridine in 30 mL of 1,2-dichloroethane was added dropwise. After the solution was refluxed for 8 h, 0.2 g of tetrabutylammonium bromide was added and reflux was continued for additional 8 h. The reaction mixture was poured into a large volume of methanol, and the coagulated polymeric product was suspended in 5% HCl, 5% $NaHCO_3$, water, and methanol in that order and finally precipitated from trifluoroacetic acid solution into methanol. The product was thoroughly washed with methanol, filtered, and dried under vacuum at 50 °C till constant weight. Yield: 3.0 g (55%).

Physicochemical Characterization. ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer operating at 25.2 MHz. In all cases the chemical shifts were referenced to TMS. The enantiomeric excess (ee) of the prepared diols was evaluated on $CDCl_3$ solutions of the diol containing 0–50% molar concentrations of chiral shift reagents, such as the tris(3-((trifluoromethyl)hydroxymethylene)-(+)-camphorato)praseodymium ($Pr(tfc)_3$) and -ytterbium ($Yb(tfc)_3$) derivatives. The average integrated areas of the signals were used for calculations,

Scheme I
Synthesis of the Head-to-Head Dipropylene Glycol Isomer 11



Scheme II
Synthesis of the Tail-to-Tail Dipropylene Glycol Isomer 14

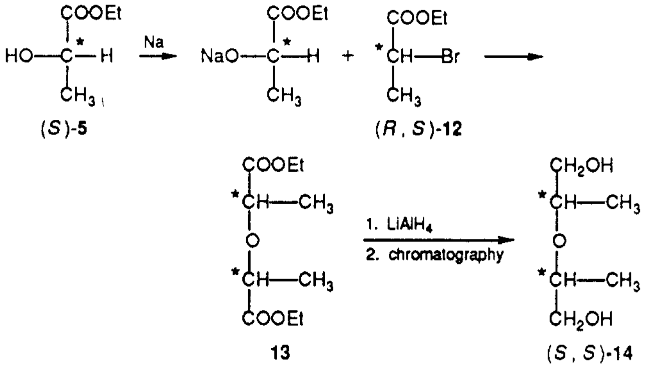


Table I
Preparation and Physicochemical Characteristics of Polyesters 1–4 Containing Different Isomeric Dipropylene Glycols

	dipropylene glycol				polyester	
sample	isomer[a]	$[\Phi]^{25}_{D}$,[b] deg	ee, %	yield, %	η_{inh},[c] dL/g	$[\Phi]^{25}_{D}$,[b] deg
1	head-to-tail	+84[d]	94	77	0.20	+143[d]
2	heat-to-head	+49	≥98	55	0.19	+360
3	tail-to-tail	+2	8	56	0.16	+7
4	racemic mixture			66	0.14	

[a] (S,S) absolute configuration, unless otherwise specified. [b] Molar optical rotation in trifluoroacetic acid, unless otherwise specified. [c] Inherent viscosity in *p*-chlorophenol/1,2-dichloroethane (1:1 by weight) at 30 °C; $c = 0.6$ g/dL. [d] In chloroform.

assuming the same NOE for each set of carbon atoms (primary, secondary, and tertiary) in the (*R,S*), (*R,R*), and (*S,S*) forms.

Optical rotatory power measurements were performed with a Perkin-Elmer 141 spectropolarimeter (path length 1 dm). Molar optical rotation was calculated from the relation $[\Phi] = [\alpha]M/100$, in which M is the molecular weight of the repeating unit (ru).

Differential scanning calorimetry analyses were performed under dry nitrogen flow on polymer samples (5–10 mg) with Perkin-Elmer DSC2 apparatus. The transition temperatures were taken as corresponding to the maximum in the enthalpic peaks obtained with a heating/cooling rate of 10 °C/min. Indium and tin standards were employed for temperature calibration, while indium samples were used for enthalpy evaluation.

Texture observations were carried out on polymer films between glass slides, without any previous treatment, by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage. Photomicrographs were taken at the original magnification of 240×. X-ray diffraction diagrams were recorded on unoriented samples under vacuum with a Guinier-type focusing camera equipped with a bent quartz monochromator giving a linear collimation of strictly monochromatic X-rays and a device allowing the study of the samples between 20 and 200 °C with an accuracy of ±1 °C. The degree of crystallinity of the polymer samples was evaluated by the ratio of the areas of the crystalline peaks over the total area of diffraction in the X-ray patterns recorded with a Siemens D-501 diffractometer connected with a Kristalloflex Siemens generator. Cu $K\alpha_1$ ($\lambda = 1.54$ Å) radiation was used in all cases.

Results and Discussion

Synthesis. The head-to-head and tail-to-tail dipropylene glycol isomers **11** and **14** were prepared from ethyl (*S*)-lactate (**5**), as the chiral precursor, according to the synthetic routes in Schemes I and II, respectively.

The enantiomeric excess of the two optically active diols was evaluated by ^{13}C NMR using the chiral shift reagents Yb(tfc)$_3$ and Pr(tfc)$_3$. While (*S,S*)-**11** is nearly enantiomerically pure (ee ⩾ 98%), (*S,S*)-**14** exhibits an enantiomeric excess of 8%, as obtained by chromatographic separation of the diastereomeric mixture consisting of 27% of the erythro form and 73% of the threo form. We cannot explain the occurrence of the marked racemization process under the adopted conditions, but this might have taken place during the preparation of the sodium alcoholate of **5** through the formation of a carbonyl intermediate in the oxidizing medium[24,25] or the replacement of the α-hydrogen by enolization of the ester moiety.

The head-to-tail dipropylene glycol isomer (*S,S*)-**15** (ee = 94%) had been previously synthesized starting from the same chiral building block **5**.[21] The racemic mixture of dipropylene glycols **16** was comprised of 71% head-to-tail, 21% head-to-head, and 8% tail-to-tail isomers.

Polyesters 1–4 were prepared by a polycondensation reaction of 4,4′-(terephthaloyldioxy)dibenzoyl chloride (**17**) with structurally different dipropylene glycols in 1,2-dichloroethane solution in the presence of pyridine, as a promoter and acid acceptor. Some relevant features of the synthesis and physicochemical characteristics of the polymers are summarized in Table I. The values of inherent viscosity in *p*-chlorophenol/1,2-dichloroethane (1:1 by weight) are rather low and may indicate relatively low molecular weights for the polymers ($\overline{DP}_n \simeq 8$–10), according to previous findings on analogous polyesters.[23,26] While the effects of molecular weight were not studied, these values should guarantee that the liquid-crystalline properties of the samples are not affected to a significant extent.[27,28] In fact, according also to recent results with similar semiflexible polyesters, provided with an even higher degree of chain flexibility, saturation values for the thermodynamic parameters were reached at $\overline{DP}_n \simeq 5$–8, corresponding to intrinsic viscosity values of 0.20–0.25 dL/g.[29]

All polymer samples, except 4, which is derived from the racemic mixture of diols, are optically active, and the molar optical rotation in trifluoroacetic acid or chloroform solution is of the same sign but much higher than that of the corresponding optically active precursor. These data indicate that asymmetric conformations with a fairly high rotatory strength are populated by the repeating units in solution. We have previously shown[30] by mea-

Table II
Phase Transitions and Their Thermodynamic Parameters for Polyesters 1–4 Containing Isomeric Dipropylene Glycols[a]

sample	T_m, °C	T_{S-S}, °C	ΔH_{S-S}, kJ/mol	T_{S-N}, °C	ΔH_{S-N}, kJ/mol	T_i, °C	ΔH_i, kJ/mol	ΔS_i, J/(mol·K)
1	105	192	0.7	235	nd	290	0.7	1.2
2	108	155[b]	nd	191[c]	0.5	213	2.0	4.2
3	203					280	0.8	1.4
4	112	170[d]	0.6	238	1.7	260	0.6	1.2

[a] By DSC, at a heating rate of 10 °C/min. Abbreviations: m, melting; S–S, ordered smectic–disordered smectic; S–N, disordered smectic–nematic (or cholesteric); i, nematic (or cholesteric)–isotropic liquid transitions, unless otherwise indicated. Enthalpies and entropies refer to 1 mol of repeating unit (ru). [b] Ordered smectic–ordered smectic transition, no detectable enthalpy. [c] Ordered smectic–cholesteric transition. [d] Disordered smectic–disordered smectic transition at 195 °C, no detectable enthalpy.

surements of circular dichroism absorption in dilute solution the possibility of adoption for polyester **1** at the molecular level of chirally homogeneous conformations with the intramolecular order of aromatic units embedded in a local helical-like array.

Thermal Analysis. The phase transition behavior of the polymers is rather complex and includes extended polymorphism in the liquid-crystalline state. The major phase transitions and their thermodynamic parameters, as revealed by DSC, are summarized in Table II. The melting temperatures are centered around 110 °C, except for polymer **3** for which T_m = 203 °C. The mesophase is very stable, the isotropization temperature being in any case higher than 210 °C and the highest for polymer **1** (T_i = 290 °C). Accordingly, the mesophasic range is broad ($T_i - T_m > 75$ °C), the largest persistence being 185 °C in polymer **1**.

Intermediate transitions (see Table II) are observed for polymer **1** at 192 °C, for **2** at 191 °C, and for **4** at 170 °C. The relevant enthalpies are comparable with each other (ΔH_{S-S} = 0.5–0.7 kJ/mol ru) and consistent with an ordered smectic–disordered smectic transition.[26] Additionally, a smectic–nematic transition appears to occur at 238 °C (ΔH_{S-N} = 1.7 kJ/mol ru) in polymer **4**. The isotropization enthalpies (ΔH_i = 0.6–2.0 kJ/mol ru) and entropies (ΔS_i = 1.2–4.2 J/(mol ru K)) are low and indicate that the high-temperature mesophase is nematic (or cholesteric, N*) in character.[22,26] The above transitions are reversibly observed on cooling from the isotropic melt with a limited degree of supercooling (5–15 °C), which is greater for the onset of the ordered smectic phases. Such transitions extend over rather broad ranges of temperature, which results in biphasic regions of 10–30 °C. The mesophase–crystal transition is very supercooled in sample **4** (T_c = 65 °C), but crystallization does not take place in the other polymers and the mesophase can be frozen-in in the solid state. This behavior is common with side chain liquid-crystalline polymers, which, on cooling, yield glassy mesophases,[31,32] but is more unusual with main chain systems[33-37] in which crystallization partially prevents quenching of the mesophase.[37] While optical microscopy or X-ray diffraction analyses point to the existence of other liquid-crystalline polymorphs in polymers **1**, **2**, and **4** (see below), differential calorimetry does not allow us to detect additional phase transitions probably because of their low enthalpy changes over broad ranges of temperature.

Optical Microscopy. Preliminary observations of the texture behavior of polymer **1** have been reported,[38] even though a somewhat higher isotropization temperature was found in that case. It should be mentioned here that above 240 °C the cholesteric phase of **1** exhibits typical bundles of oily streaks and a smectic–cholesteric transition may be located at 230–235 °C. The clearing range spans from 280 to 300 °C. Polymer **2** does not show any particular pattern on heating to isotropization which occurs in the 205–215 °C range. On cooling, the mesophase reappears at 210 °C as batonnets that afterward develop a focal-conic texture with fans. These elements are in keeping with a layered structure, such as the cholesteric phase,[39,40] in agreement with X-ray results (see below). On further cooling, the fans show striations, and below 155 °C the fine broken-fan texture is established of a tilted smectic phase.[39,40] The mesophase of polymer **3** only shows textures with thin threads and homeotropic regions in the vicinity of the isotropic transition that occurs in the 275–290 °C range. On cooling from the isotropic melt, we observe familiar schlieren textures with numerous disclination points, either isolated or combined in pairs[39] (Figure 1). These observations suggest the presence of a nematic phase, while no microscopic indications have been obtained of the occurrence of a cholesteric phase. Similarly, sample **4** displays a nematic phase with a mosaiclike texture above 240 °C, and the biphasic gap extends from 250 to 265 °C. On cooling from the isotropic phase, the nematic phase develops a homeotropic texture from which the smectic phase appears in focal-conic domains with fans or polygons below 220 °C (Figure 2). In the 215–185 °C range the smectic fans become more and more broken, due to the transition to a tilted smectic phase[40] (Figure 3). The broken-fan textures of polymers **2** and **4** remain as paramorphotic modifications of the ordered smectic phase at low temperatures.

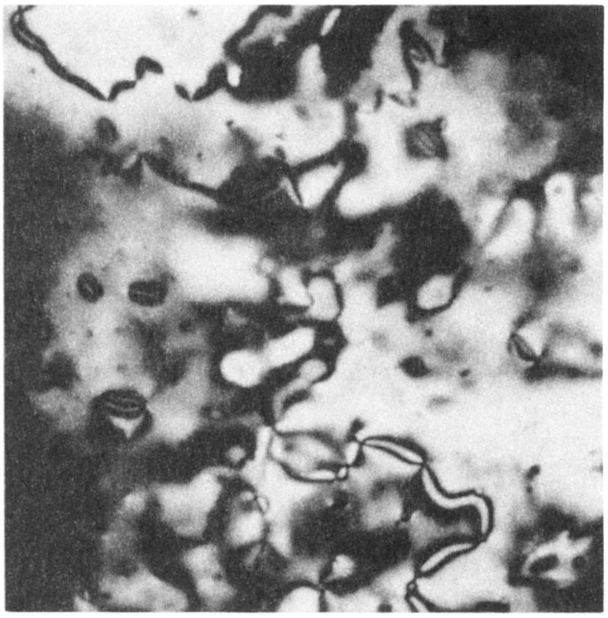


Figure 1. Optical texture of the nematic mesophase of polyester **3** with schlieren at 220 °C.

X-ray Diffraction. Polymers **1**, **2**, and **4** were analyzed by X-ray diffraction between room temperature and 200 °C, while for polymer **3** the investigation was extended to 250 °C. Four types of X-ray diagrams were recorded corresponding to different structures, namely, the lamellar crystalline, ordered smectic, disordered smectic, and nematic structures.[41] The length L of the repeating unit in its fully extended all-trans conformation, as calculated from known bond angles and distances,[42] is 28.2 Å. When the thickness d of the crystalline lamellae or of the smectic layers is equal to L, the polymer chains must be orthogonal to the plane of the lamellae or layers. When

Figure 2. Focal-conic texture of the smectic mesophase of polyester **4** at 212 °C.

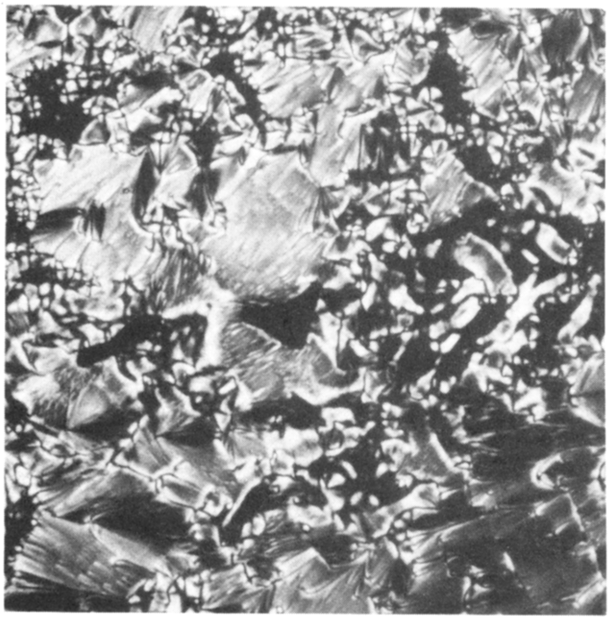


Figure 3. Broken-fan texture of the smectic mesophase of polyester **4** at 188 °C.

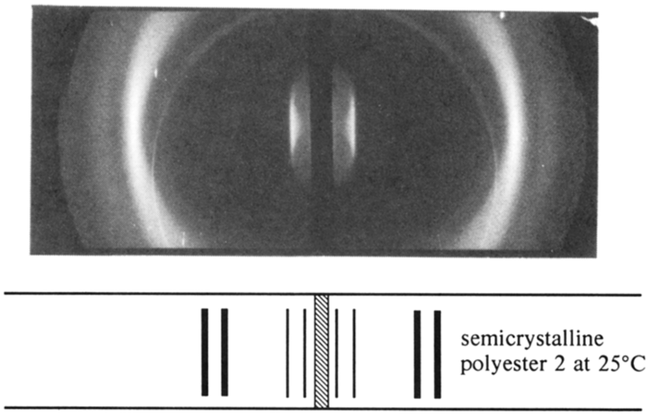


Figure 4. X-ray diffraction pattern of the crystalline structure of polyester **2** at 25 °C.

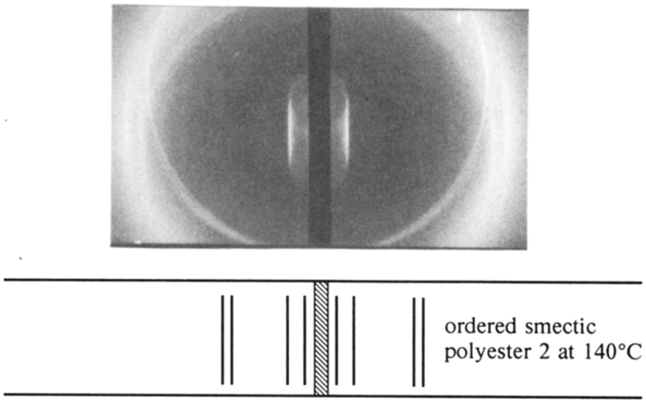


Figure 5. X-ray diffraction pattern of the ordered smectic mesophase of polyester **2** at 140 °C.

d is shorter than *L*, the polymer chains are believed to be tilted by an angle, *θ*, to the normal to the lamellae or layers.

Lamellar Crystalline Structures. The X-ray diagrams corresponding to the lamellar crystalline structures are characterized by the presence in the small-angle region of one or two sharp reflections with Bragg spacings in the 1:2 ratio and by the presence in the wide-angle region of at least two reflections (Figure 4) that were not indexed. The four virgin samples display degrees of crystallinity in the 45–55% range. Tilted crystalline structures are found for polymers **2** and **3**. Polymer **2** has a lamellar thickness of 26.4 Å and a tilt angle of $\simeq 21°$, while polymer **3** has a lamellar thickness of 27.7 Å and a tilt angle of $\simeq 11°$. Both lamellar thickness and tilt angle are unaffected by temperature up to melting. On the contrary, polymer **4** exhibits between 20 and 105 °C an orthogonal lamellar crystalline structure with a layer thickness of 28.2 Å. For polymer **1** no definite lamellar structure was detected, according to previous results.[43]

Ordered Smectic Structures. The X-ray diffraction patterns of the ordered smectic structures detected in samples **1**, **2**, and **4** are characterized by the presence in their low-angle region of one or two sharp reflections with Bragg spacings in the 1:2 ratio and the presence in the wide-angle region of two sharp reflections related to the lateral organization of the polymer chains on a centered rectangular lattice (Figure 5). These findings suggest the existence of a smectic E phase or of a tilted smectic H variant and eliminate the possibility of other smectic phases with hexagonal lattices, such as B and others.[40,41] Polymer **2** exhibits a S_H structure between 108 and 155 °C. The parameters of the centered rectangular lattice in a plane perpendicular to the polymer chains, $a' = 8.0$ Å and $b' = 4.8$ Å, are not affected by temperature, whereas *d* increases in a progressive way from 27.2 to 28.5 Å (Figure 6), with the tilt angle therefore decreasing from $\theta = 15.3°$ to $\theta = 0°$. A S_E-type phase occurs at about 160 °C for polymer **2** with the polymer chains orthogonal to the smectic layers. The parameters *d*, *a*, and *b* of the S_E structure remain constant till the appearance of a cholesteric phase at about 190 °C (Figure 6). A S_H structure is also observed for polymer **1** between 105 and 185 °C. The parameters of the centered rectangular lattice, $a' = 7.9$ Å and $b' = 4.6$ Å, are independent of temperature, whereas the interlayer distance *d* increases from 25.9 to 28.0 Å, corresponding to a decrease of the tilt angle from $\theta = 23°$ to $\theta = 7°$ with increasing temperature.[43] On the contrary, the S_H structure of polymer **4** is unaffected by temperature in the 110–160 °C range and all the parameters remain constant, so $d = 26.2$ Å, $\theta_H = 22°$, $a' = 8.0$ Å, and $b' = 4.8$

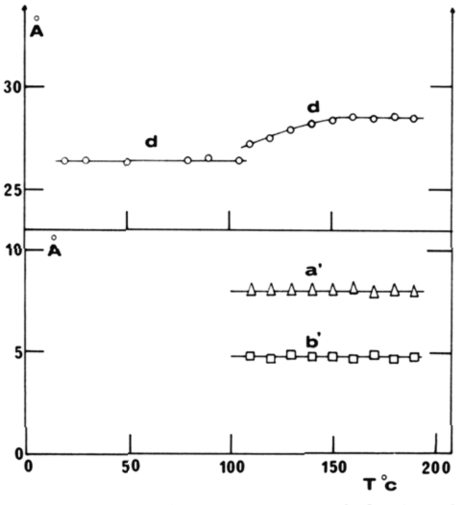


Figure 6. Variation with temperature of the interlayer distance (d) and rectangular lattice parameters (a' and b') of the ordered smectic mesophases of polyester 2.

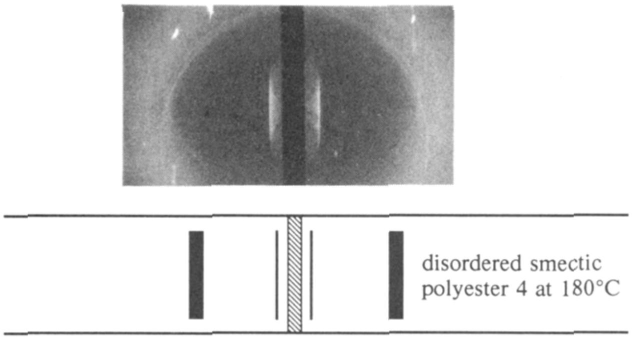


Figure 7. X-ray diffraction pattern of the disordered smectic mesophase of polyester 4 at 180 °C.

Å[43]. The occurrence of an angle slightly different from 90° between a' and b' cannot be completely ruled out, as two reflections could only be detected at wide angles for the ordered smectic phases encountered. On the other hand, the presence of two sole reflections is generally observed for smectic H and E phases. The comparison of the relative intensities and positions of the signals revealed for polymers **1**, **2**, and **4** and mesomorphic ribbon structures of potassium and rubidium soaps[44,45] provides further argument in favor of a rectangular lattice for these smectic phases. A better definition of the reported structural assignments would imply X-ray diffraction studies on fibers drawn and analyzed at the temperature of the mesophases. However, we failed to draw fibers from the smectic phases of the polymers,[53] nor was it possible to identify these polymorphs by miscibility studies with reference to low molar smectogens, e.g., TBBA.[46] Such drawbacks appear to be a common feature for highly ordered mesophases of main chain polyesters[43,47,48] and can render unambiguous assignments difficult.

Disordered Smectic Structures. The X-ray diagrams corresponding to the disordered smectic phases encountered typically exhibit one or two sharp signals with Bragg spacings in the 1:2 ratio in the low-angle region and a diffuse band in the wide-angle region. This broad band is correlated with the liquidlike arrangement in the smectic layers and is compatible with the existence of disordered S_C or S_A phases. A S_C structure is observed for polymer **4** (Figure 7) between 165 and 195 °C. When the temperature increases, d increases from 27.1 to 28.2 Å and accordingly θ decreases from 16° to 0°, indicating the transformation of the tilted smectic C phase into the orthogonal smectic A phase, with an average intermolecular distance, D, of $\simeq$5.4 Å. A S_A mesophase is also formed in polymer **1** above 195 °C, with the same interlayer spacing, $d = 28.2$ Å, and an interchain distance, $D \simeq 5.5$ Å.[43]

Nematic Structures. The X-ray diffraction patterns of polymer **3** above the melting temperature only display a broad halo at wide angles consistent with the liquidlike order of the nematic phase. The high-temperature mesophase of samples **1** and **2** could not be studied by X-ray analysis, due to some thermal degradation, and the onset of a cholesteric phase was only inferred by polarization microscopy and thermal analyses (Table I).

Concluding Remarks

Four chiral thermotropic polyesters have been prepared, in which the isomeric chemical structure is varied systematically. On the basis of the results obtained with the three complementary techniques employed, we propose the occurrence of complex phase sequences as follows: K–S_{H*}–S_A–N*–I for **1**, K–S_{H*}–S_E–N*–I for **2**, K–N–I for **3**, and K–S_H–S_C–S_A–N–I for **4**.

The smectogenic effectiveness of the long, lathlike 4,4'-(terephthaloyldioxy)dibenzoyl core is also recognized in the corresponding low molar mass bis(alkyl esters)[49] and polyesters with linear alkylene spacers.[50,51] This ability is even reinforced in the present isomeric polymers, including copolymer **4**, in spite of the presence of two methyl substituents per repeating unit. The location of the two alkyl groups in the proximity of the mesogenic core in **2** greatly destabilizes the nematic phase, while preserving a high stability of the ordered smectic phase, in analogy to the trend observed in low molar mass mesogens.[52] On the other hand, the presence of two methyl substituents in 1,3-positions may impose specific constraints to the repeating unit of polymer **3**, which result in a comparatively very high melting temperature, such as to inhibit the formation of smectic phases. We also note the striking differences in the evolutions with temperature of the smectic properties of **1**, **2**, and **4**. All these polymers give rise to a smectic H phase practically at the same melting temperature. Nevertheless, the tilt angle for **2** is smaller than for the other ones, and an orthogonal smectic phase is attained at relatively low temperature, that is, still characterized by short-range positional order (S_E). The tilt angle of **1** follows a nearly parallel descending trend with increasing temperature, and an orthogonal smectic phase is formed with the concomitant disruption of the lateral organization within the layers (S_A). On the contrary, when the temperature is raised, the layer thickness of the smectic H phase of **4** remains unaffected and this behavior would perhaps be explained by the incorporation into the copolyester of an appreciable amount of the tail-to-tail isomer. Within this temperature range, the ordered arrangement of different structural units is easily destroyed, the net result being the onset of a disordered tilted mesophase (S_C).

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(53) We wish to remark that, even by following the detailed guidelines suggested by a reviewer, we have been unable to obtain coherent fibers with a preferential orientation. Techniques used by other laboratories are under current trials for future studies.