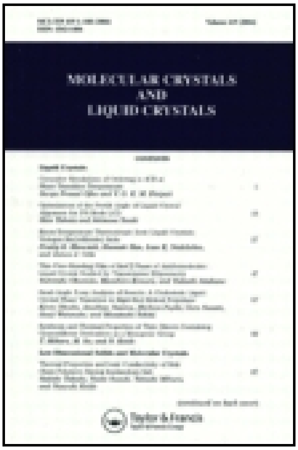

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Chiral Liquid Crystal Polymers. 7. Structural Characterization of Thermotropic Polyesters Based on 4,4'-(terephthaioyldioxy)dibenzoic Acid and 1,3-butanediol

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Chiral Liquid Crystal Polymers. 7.† Structural Characterization of Thermotropic Polyesters Based on 4,4′-(terephthaloyldioxy)dibenzoic Acid and 1,3-butanediol

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A series of five samples of poly{(R)-1-methyl-1,3-propanediyl-[4,4′-(terephthaloyldioxy)]dibenzoate} obtained by polycondensation of 1,3-butanediol (enantiomeric excess comprised between 0 and 80%) with the diacyl chloride of 4,4′-(terephthaloyldioxy)dibenzoic acid were investigated by differential calorimetry, optical microscopy and X-ray diffraction. All the samples were semicrystalline and displayed a thermotropic smectic A phase followed by a cholesteric or nematic phase. The values of the transition temperatures $T_{S\text{-}N}$ and T_i were not much affected by the enantiomeric excess of the flexible component, slight increases being detected with increasing chirality. There was evidence that the smectic A phase can assume a monolayer structure and/or an interdigitated bilayer structure.

Keywords: chiral thermotropic polyesters; poly(4,4′-terephthaloyldioxydibenzoate)s; polymorphic liquid crystalline polymers; enantiomeric excess; bilayer smectic phase; cholesteric phase.

INTRODUCTION

The synthesis and characterization of new main chain liquid crystalline (LC) polymers represent key steps to the assessment of the structure-property relationships in an expanding area at the borderline between

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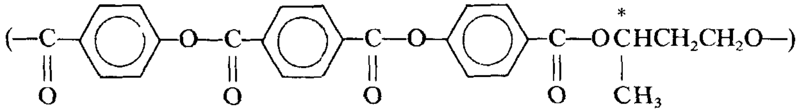
†Presented at the 11th International Liquid Crystal Conference, Berkeley, 1986. Part 6: Cf. Ref. 5

materials science and polymer organic chemistry. In that context particular interest is held by mesomorphic polymers comprising intrinsically chiral segments, for which peculiar properties strictly related to the occurrence of asymmetric perturbation in the macromolecular chain can be expected. On this line information is missing on the effects produced on the morphology and ultimate properties of LC polymeric materials by structural parameters related to the nature and enantiomeric excess of the chiral segment. In the present paper, within the scope of our continuing interest in the field of synthetic chiral polymers,[1,2] attention has been focussed on the synthesis and structural characterization by optical rotation, thermal-optical analysis and X-ray diffraction of a new series of chiral LC polyesters derived from 4,4'-(terephthaloyldioxy)dibenzoic acid (HTH mesogenic core) and chiral 1,3-butanediol (BD spacer) with different optical purity (0–80%).



EXPERIMENTAL PART

Synthesis

The commercially available (Janssen, chemical purity ≥ 98%) (R) (S)-1,3-butanediol and (R)-1,3-butanediol, $[\alpha]_D^{25}$ -24.6 (ethanol) optical purity 80%,[3] were used without further purification. (R)-1,3-butanediols with optical purity 75, 40, and 20% were obtained by mixing appropriate amounts of the two above diols. 4,4'-(terephthaloyldioxy)dibenzoic acid was prepared and converted to corresponding dichloride as previously described.[4,5]

In a typical polycondensation run 4.43 g (10 mmol) of 4,4'-(terephthaloyldioxy)dibenzoyl chloride were dissolved in 150 ml of 1,2-dichloroethane and 1.6 ml (20 mmol) of dry pyridine at 90°C. 0.90 g (10 mmol) of 1,3-butanediol were added dropwise over 40 min and the polymerization was let to proceed under stirring for 36 hrs. After cooling to room temperature, the reaction mixture was poured into a large excess of methanol and the precipitate formed was washed with 5% HCl, 5% $NaHCO_3$, water and methanol and then dried under vacuum at room temperature. Yield: 3.2 g (70%).

Physicochemical characterizations

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-2 calorimeter at a heating/cooling rate of 10°C/min. Phase transitions were taken as corresponding to the maximum in the enthalpic peaks. Indium standards were used for temperature calibration and enthalpy evaluation.

Optical polarizing microscopy observations were performed with a Reichert Polyvar microscope between glass slides without any previous treatment.

X-ray diffraction measurements were carried out in a transmission geometry by means of a conventional X-ray powder diffractometer. Ni filtered CuKα radiation ($\lambda = 1.54$ Å) was used. Heating was achieved by a hot stage whose temperature was controlled to ±0.1°C by an electronic device. The degrees of crystallinity of polymers were determined by the ratio of the areas of crystalline peaks over the total diffracted area in the angular region $2\theta = 15-30°$.

RESULTS AND DISCUSSION

The results relevant to the synthesis and structural characterization of the investigated chiral polyesters will be presented in three separate sections dealing with i) the synthesis, ii) characterization by thermal analysis (DSC) and polarizing microscopy, and iii) X-ray diffraction.

Synthesis

The preparation of the series of HTH/BD polyesters was realized by reacting in 1,2-dichloroethane/pyridine solution stoichiometric amounts of either racemic or enriched in R enantiomer (e.e. 20, 40, 75, and 80%) 1,3-butanediol and 4,4′-(terephthaloyldioxy)dibenzoyl chloride at 80–90°C for 24–36 hours. Details relevant to a typical run are reported in the experimental section.

The polymers, obtained with yields comprised between 50 and 70%, were soluble in trifluoroacetic acid and *p*-chlorophenol/sym-dichloroethane mixture (1:1 by weight), whereas showed partial solubility in the other most common organic solvents. The samples were characterized by intrinsic viscosities $[\eta] = 0.1-0.2$ dl/g in *p*-chlorophenol/sym-dichloroethane at 30°C. From these values average degrees of polymerization $\overline{DP}_n \approx 10-15$ were extrapolated[5] and assumed to guarantee for a practical molecular weight-independence of the properties,[5,6] in both bulk and dilute solution. No precise information can be provided on the molecular weight distribution of the prepared samples, but a rather wide degree of polydispersity can be anticipated on the basis of the bulk property responses.

The polyesters from prevailing chiral diols were optically active (Table I) and the molar optical rotation had the same sign, but was one order of magnitude higher than those of the parent diol and low molar mass model compound.[5] The trend of molar optical rotation of the polymers as against the enantiomeric excess in the diol, and consistently in the polymer, was found to be linear, thus indicating that no specific cooperative effects dependent upon the optical purity are operating. It is however worth remarking that, in comparison with an analogous series of polymers based on the inferior homolog (S)-1,2-propanediol,[7] the introduction of a methylene group in the flexible segment favors the population of molecular conformations characterized by high values of optical rotation.

DSC and polarizing microscopy

The DSC heating curves of the polymers, a typical profile of which is reported in Figure 1, are rather complex and consist of a melting endotherm (ΔH_m = 5–8 cal/g) and at least two other endotherms of lower intensity (ΔH = 0.4–2.3 cal/g) at higher temperatures due to mesophase transitions (Table II). The former is attributed to a smectic A-(twisted) nematic transition ($T_{S\text{-}N}$), and the latter corresponds to the isotropization process (T_i). The stability of the mesophase was in any case very high ($T_i \geqslant 250°C$) and the LC behavior extended over a broad interval ($T_i - T_m$ = 80–110°C). It should be noted that the

TABLE I

Synthesis and optical rotation properties of poly-{(R)-l-methyl-1,3-propanediyl-[4,4'-(terephthaloyldioxy)]dibenzoate}s (HTH/BD) of different enantiomeric excess (e.e.).

	Parent diol		Polyester	
Sample	e.e. (%)	$[\Phi]_D^{25\,a}$	yield (%)	$[\Phi]_D^{25\,a}$
HTH/BD80	80	−37	70	−370
HTH/BD75	75	−35	73	−342
HTH/BD40	40	−18	70	−198
HTH/BD20	20	− 9	56	−107
HTH/BDrac	0	—	48	—

[a] Molar optical rotation, in trifluoroacetic acid.

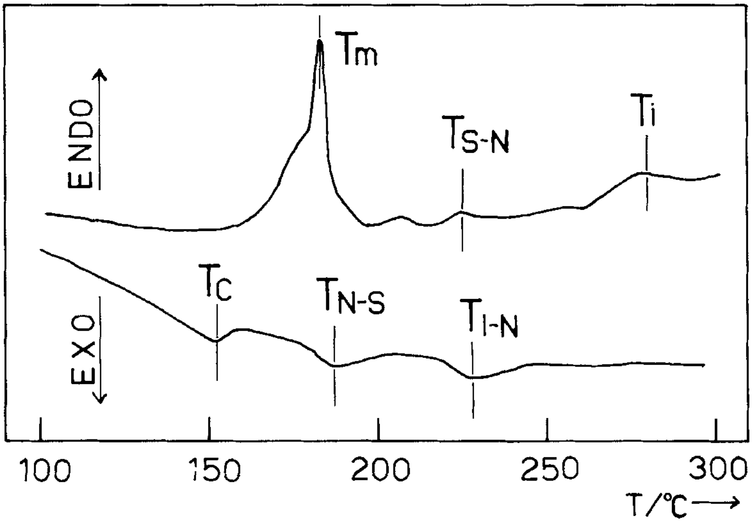


FIGURE 1 DSC heating and cooling curves with transition temperatures of polyester HTH/BD75 (scanning rate 10°C/min).

polyester based on the same HTH mesogenic core and linear trimethylene spacer showed a less persistent mesophase ($T_i - T_m = 75°C$), although characterized by a higher thermal stability ($T_i \simeq 350°C$).[8,9]

The transition ranges, as revealed by DSC, were rather broad and the biphasic gap width at isotropization was 20–30°C. This made it somewhat difficult to locate precisely the transition temperature and

TABLE II

Phase transition temperatures and thermodynamic data[a] for poly{(R)-1-methyl-1,3-propanediyl-[4,4′-terephthaloyldioxy)]dibenzoate}s (HTH/BD) of different enantiomeric excess

Sample	T_m °C	ΔH_m °C	$\Delta H_{S\text{-}N}$ cal/g	$T_{S\text{-}N}$ °C	T_i °C	ΔH_i cal/g
HTH/BD80	176	7.6	245	0.4	277	2.3
HTH/BD75	182	6.6	222	0.3	276	2.3
HTH/BD40	161	5.7	234	0.6	265	0.7
HTH/BD20	150	4.8	216	0.4	266	0.6
HTH/BDrac	185	4.9	227	0.4	250	2.3

[a] By differential scanning calorimetry, heating rate 10°C/min: T_m, melting temperature; $T_{S\text{-}N}$, smectic-nematic (or cholesteric) transition temperature; T_i, isotropization temperature.

to evaluate the corresponding enthalpy with accuracy.[10] The trends of the transition temperatures of HTH/BD polyesters against the enantiomeric excess of the starting diol are reported in Figure 2 as normalized to the transition temperatures of the racemic sample HTH/BDrac. Within the range of optical purity examined, the temperatures appear not to be affected in a significant way, the smectic-nematic and isotropization temperatures following a very slightly increasing trend, while a certain depression of the melting temperature occurs at intermediate values of the optical purity. The enthalpies measured for individual polymers are of the same order of magnitude as those observed in other thermotropic polyesters[11] and consistent with the proposed phase transitions.[12] Moreover, they are found to be independent of the enantiomeric excess of the diol (Table II) and suggest that the nature of the occurring mesophases is the same throughout the interval examined. The surprisingly low values of the isotropization enthalpies of polyesters HTH/BD20 and HTH/BD40 (ΔH_i = 0.6–0.7 cal/g) can be attributed in a first instance to lower molecular

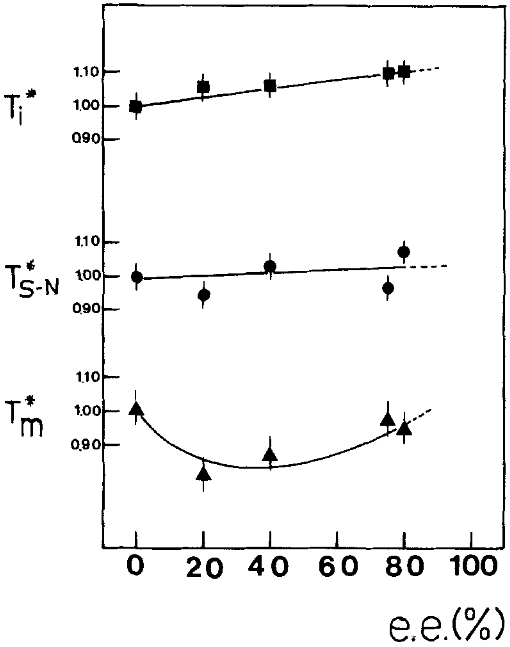


FIGURE 2 Trends of transition temperatures vs. enantiomeric excess (e.e.) of HTH/BD polyesters as normalized to transition temperatures of the racemic sample (T*): melting (▲); smectic-(twisted)nematic (●); isotropization (■).

weights accompanied by a higher polydispersity, as also detected by X-ray analysis.

On cooling, the polymers exhibited weak crystallization exotherms (T_c) with a limited degree of supercooling (~20°C), whereas the isotropic-nematic and nematic-smectic transitions were highly supercooled (30–40°C), the former process being more affected. This behavior is unusual and resulted in a mesophasic range wider on heating than on cooling (60–80°C).

All the samples gave above melting a rather viscous fluid with a very fine schlieren textures. The racemic sample underwent a sharp change to a mosaic-like nematic pattern at 210°C, while the four optically active polymers HTH/BD80-HTH/BD20 displayed cholesteric textures with oily streaks typically above 235, 215, 225, and 215°C respectively. In particular, the cholesteric phase of HTH/BD40 had a blue iridescence at 230°C, while polyester HTH/BD20 showed blue and violet reflections at 230 and 245°C, respectively. It is well established[13] that cholesterics can reflect the light and such a reflection is maximum when the wavelength of the incident light is comparable with the cholesteric helical pitch. For perpendicularly incident light, the reflected wavelength is $\lambda = \bar{n}p$[14], where $\bar{n}$ is the average refractive index and p is the length of the pitch. Assuming the refractive index to be independent of temperature within the narrow ranges of reflection observed, it is concluded that the length of the cholesteric pitch in HTH/BD polyesters can vary with the temperature and extent of chirality of the spacer segment.[5,15,16] In all cases, the isotropization process was centred around 260°C and clearing was completed at $T \leqslant 290$°C, indicating the existence of rather broad biphasic gaps (15–30°). On cooling of the isotropic liquid, the mesophase reappeared in small spheres, that afterwards coalesced to give focal conic textures with fans or polygons. In all cases the nucleation and growth of the mesophase were slow and the transition range was broad (20–30°C) in agreement with DSC results.

X-ray diffraction

The prepared samples, with exception of HTH/BD75, were analyzed by X-ray diffraction between room temperature and a maximum temperature of 250°C, at which however the melt never became isotropic, to avoid decomposition phenomena caused by the long permanence times required. The diffraction patterns for sample HTH/BD20 during the first heating cycle from 25 to 220°C are reported in Figure 3. At room temperature the polymer presented a relatively high degree

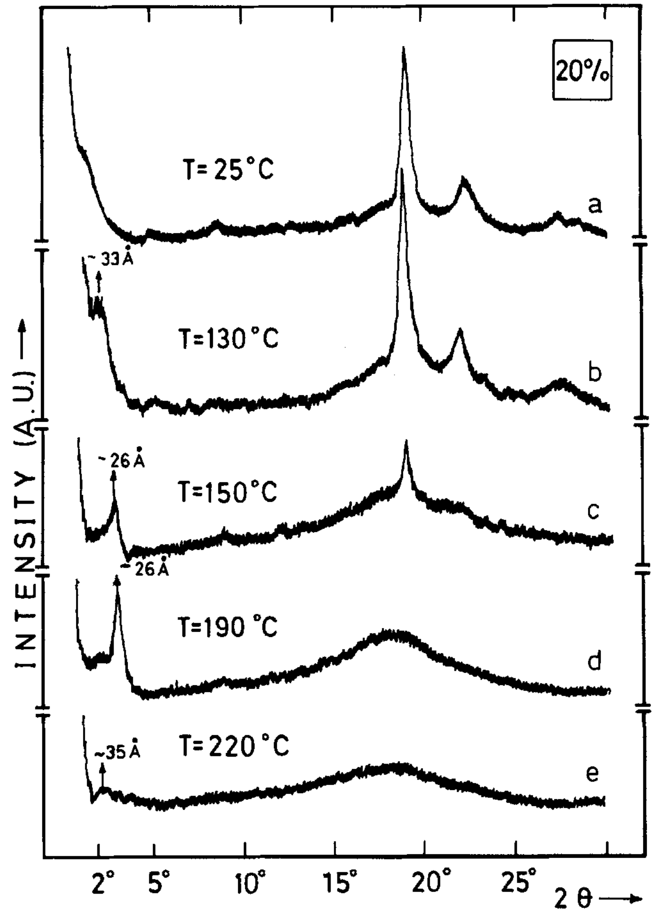


FIGURE 3 X-ray diffraction patterns of polyester HTH/BD20 at different temperatures on heating from 25°C.

of crystallinity ($X_c \approx 50\%$), and the Bragg peak in the low angle region appeared as a shoulder of the large scattering probably due to a high concentration of defects generated during the isolation of the polymer by non-solvent precipitation. Above the glass transition temperature ($T_g \simeq 120°C$, by DSC) the low angle reflection became better resolved probably as a consequence of the disappearance of lattice defects by annealing, and the intense Bragg peaks indicated an increased degree of crystallinity (Figure 3b). A layer periodicity $d \simeq 33$ Å was detected for this crystalline form. In the approximate temperature range 140–180°C a solid-smectic A transition took place

(Figure 3c) and two phases coexisted as suggested by the layer periodicity $d \simeq 26$ Å strictly related to the length of the repeat unit ($L \simeq 25$ Å), and the superposition of sharp Bragg peaks on a diffuse halo associated with the short range positional order within the S_A layers. Figure 3d shows a diffraction profile typical of the S_A phase ($D \simeq 4.7$ Å). On further heating to about 195°C, a progressive attenuation of the intensity of the low angle Bragg peak began indicating a transition to a cholesteric phase that was completed at 208°C. Figure 4 reproduces the diffraction patterns relevant to polyester HTH/BD20 either slowly cooled with regular scanning of spectra (Figures 4a and 4b), or rapidly quenched to room temperature from the solid/smectic

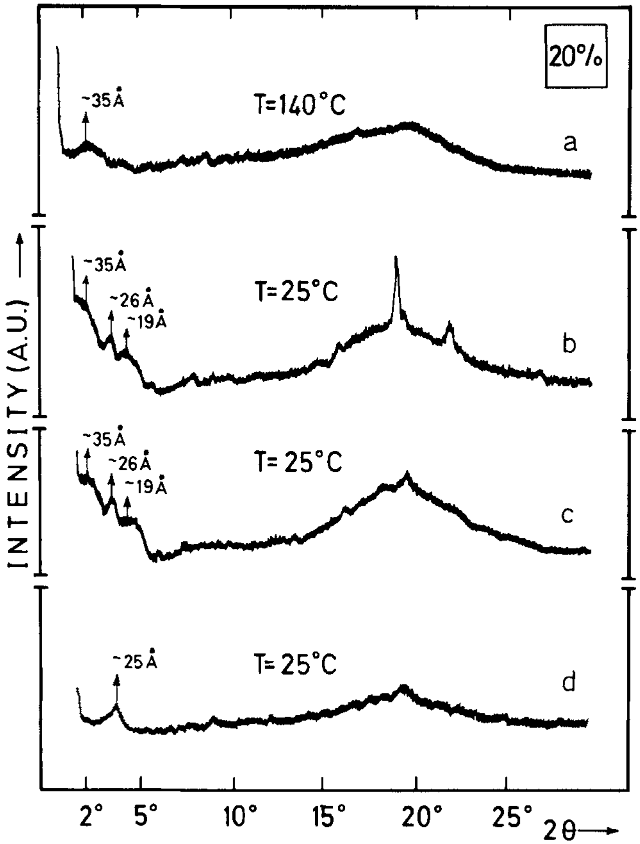


FIGURE 4 X-ray diffraction patterns of polyester HTH/BD20 at different temperatures: cooled from 220°C to 140°C (a) and to 25°C (b); quenched from the solid/smectic biphase at 150°C (c); quenched from the cholesteric phase at 220°C (d).

biphasic region at 150°C (Figure 4c) and from the cholesteric phase at 220°C (Figure 4d). No significant variations occur in the cholesteric-type profile from 220°C down to 135°C (Figure 4a), at which temperature wide angle reflections due to incipient crystallization appear, without any evidence of the onset of intermediate smectic phases. Apparently, this sample exhibits smectic and cholesteric phases on heating, but the smectic phase can be restored with difficulty on cooling. This behavior is rather unusual but similar results were reported for a polyester based on 4,4′-dihydroxy-biphenyl and azelaic acid, for which crystal-smectic and smectic-isotropic transitions were observed on heating and isotropic-nematic and nematic-crystal transitions on cooling.[17] The room temperature diffraction spectra of the samples slowly cooled from the cholesteric phase and quenched from the solid/smectic biphasic region are characterized by signals in the low angle region associated with three different periodicities, namely 35 Å, 26 Å (about the repeat unit length), and 19 Å (about the HTH moiety length),[18] whereas in the profile of the diffractogram of the sample quenched from the cholesteric phase at 230°C only the regularity corresponding to a 24 Å periodicity is present. These results demonstrate that the solid form obtained on cooling from the melt depends on the thermal history of the polymer, although is invariably characterized by a very low degree of crystallinity, and that it is possible to produce cholesteric mesophases persisting at room temperature by quenching from the corresponding state stable under thermodynamic conditions.[5]

The diffraction patterns obtained for the HTH/BD40 sample during the first heating cycle are rather similar to those shown by the HTH/BD20 sample. A higher degree of crystallinity ($X_c \simeq 55\%$) was however observable together with a better resolution of the low angle Bragg peak, that corresponded to a layer thickness $d \simeq 30$ Å. A smectic A phase ($d \simeq 26$ Å, $D \simeq 4.7$ Å) was fully evidenced above 195°C and evolved to a cholesteric phase around 220°C.

Figure 5 reports the diffraction profiles obtained during the first cooling of polymer HTH/BD40 once heated up to 225°C. A S_A phase is clearly detected below 170°C (Figure 5a) with a periodicity of 26.7 Å and a more diffuse one at 19 Å as previously noted in the case of polyester HTH/BD20. The onset of crystallization was detected at 140°C (Figure 5b). In Figure 6 are reported the diffraction patterns obtained for sample HTH/BD80 during the first heating. This sample showed a high degree of crystallinity ($X_c \simeq 70\%$), as demonstrated by the very sharp peaks in the wide angle region (Figure 6a). At the same time the low angle region is characterized by the presence of a

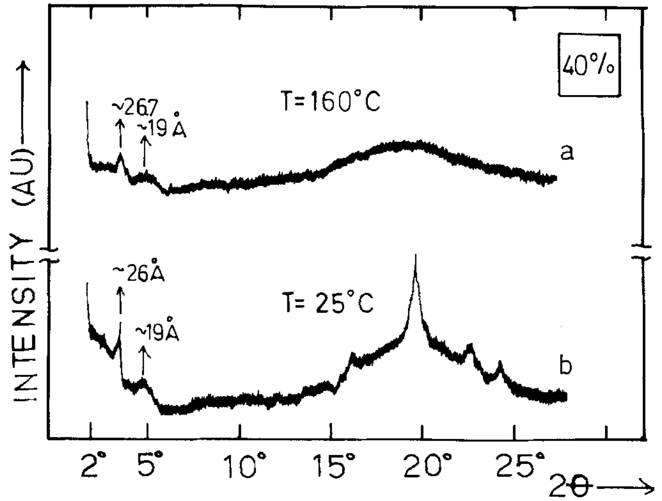


FIGURE 5 X-ray diffraction patterns of polyester HTH/BD40 at different temperatures on cooling from 225°C.

rather sharp peak corresponding to a layer thickness of 28.4 Å with second and third order reflections as a further support to the existence of a high degree of regularity in the crystalline sample. The recorded pattern remained practically unaltered up to 175°C at which temperature the diffractogram started to evolve toward that of a disordered smectic phase (Figure 6c), that was fully established at 235°C ($D \simeq$ 4.7 Å). The low angle peak corresponded to a periodicity of 23 Å which suggests that the repeat unit may not be in its all-trans fully extended conformation. However, the existence of a (chiral) smectic phase, to which a tilt angle of approximately 27° would be associated, cannot be completely ruled out. By increasing the temperature, the low angle peak gradually diminished in intensity and eventually disappeared between 244 and 249°C, indicating the transformation to a nematic-like (cholesteric) phase (Figure 6d). During the cooling, the above cholesteric diffraction curve did not change till about 210°C (Figure 7a), with only the progressive formation of a diffuse signal corresponding to a periodicity of 23 Å. This peak is broader than the corresponding peak occurring on heating at the same angular position (Figure 6c) and suggests that a short range positional order exists along the main molecular axis. At about 180°C a Bragg peak corresponding to a layer thickness of 44 Å started to appear (Figure 7b). This periodicity is considerably longer than the length of the repeat unit in its fully extended conformation and implies the existence of

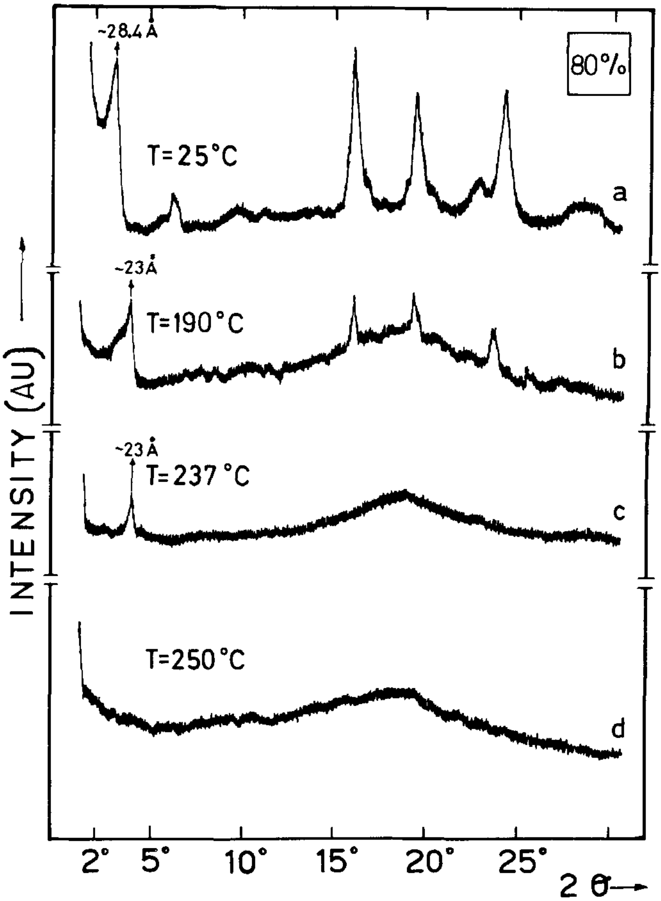


FIGURE 6 X-ray diffraction patterns of polyester HTH/BD80 at different temperatures on heating from 25°C.

some form of bilayer organization. Examples of smectic A bilayer structures with interdigitation of the molecules in an anti-parallel arrangement are well known in low molar mass liquid crystals[19,20] and have also been observed in side chain LC polymers.[21] Moreover, the persistence of the 23 Å periodicity along with the 44–40 Å layer thickness may be related to an incommensurate organization in the smectic phase of bilayer structure regions with monolayer structure regions.[22] On the other hand, it has been recently proposed that interdigitated smectics exist as a new, distinct family of smectic liquid crystals.[23] At 165°C solidification took place with a consequent re-

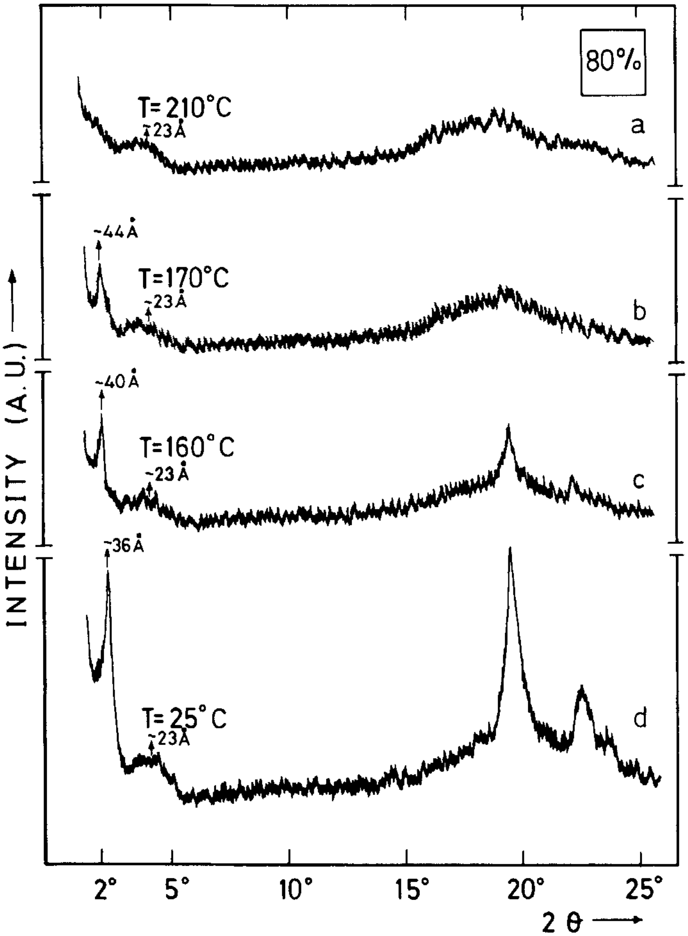


FIGURE 7 X-ray diffraction patterns of polyester HTH/BD80 at different temperatures on cooling from 255°C.

duction of the bilayer periodicity (Figure 7c) indicating a greater overlap or compenetration of the units within the bilayer as forced by crystallization, whereas the short range periodicity at 23 Å is not appreciably influenced by the crystallization ordering.

The diffraction curves of polyester HTH/BDrac during the first heating cycle are reported in Figure 8. The overall profile at room temperature (Figure 8a) appears very similar ($X_c \simeq 75\%$) to that of polyester HTH/BD80 and is maintained unaffected on heating up to 170°C. Between 170 and 180°C an additional peak corresponding to

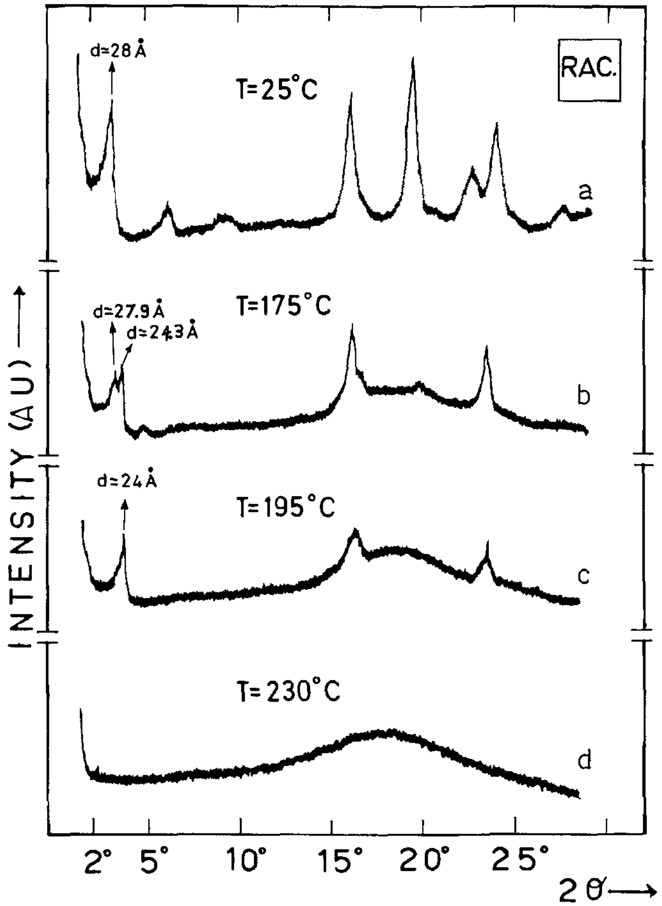


FIGURE 8 X-ray diffraction patterns of polyester HTH/BDrac at different temperatures on heating from 25°C.

a periodicity of 24.3 Å is observed (Figure 8b), which increases in intensity till 180°C and persists up to 210°C. At the same time the 28 Å periodicity peak decreases and completely vanishes at 190°C, which temperature can be taken as the end of a multiple melting process, in agreement with DSC results. Above 210°C the smectic A phase ($D \simeq 4.8$ Å) transforms into a nematic phase (Figure 8d). On cooling (Figure 9), the nematic phase persists till 170°C, at which temperature a narrow peak of low intensity is observed corresponding to a 45 Å layer thickness. This can be associated with the presence of a bilayer smectic A phase, that is preserved substantially unaffected down to

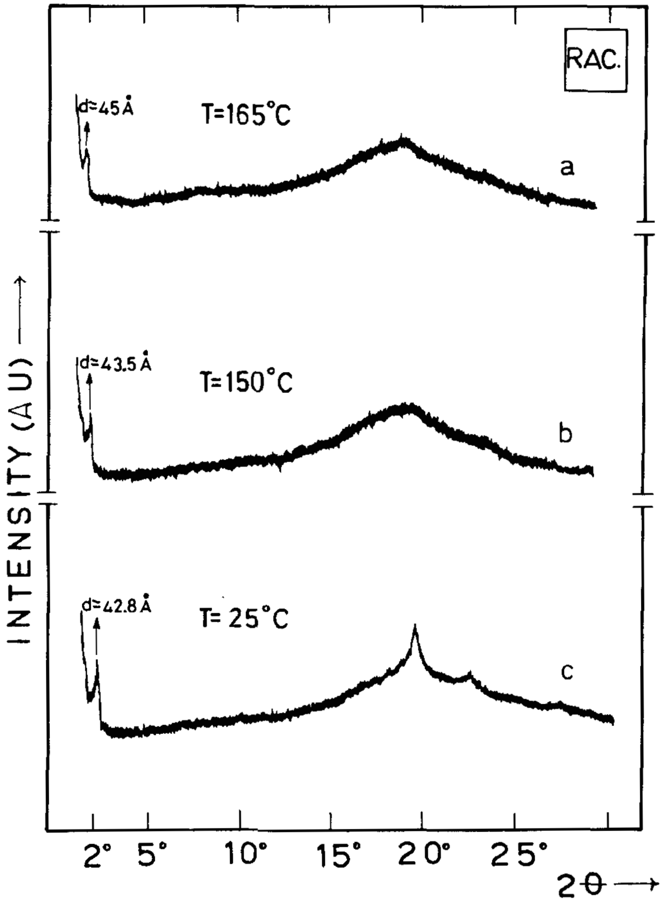


FIGURE 9 X-ray diffraction patterns of polyester HTH/BDrac at different temperatures on cooling from 240°C.

room temperature (Figure 9c), despite the onset of crystallization at 125°C.

CONCLUDING REMARKS

The thermotropic liquid crystalline behavior of a new set of samples of chiral polyesters based on 4,4′-(terephthaloyldioxy)dibenzoic acid and 1,3-butanediol was established by thermal analysis and optical microscopy. The X-ray diffraction analysis performed at different temperatures allowed to elucidate in part the liquid crystal polymorphism of the polymers and to derive some structural information. All the polymers are semicrystalline and exhibit, above a more or less broad melting transition, a smectic A phase, which is followed by a nematic phase in the case of the racemic polymer (e.e. 0%), or cholesteric in all the optically active ones (e.e. 20–80%). The structural data are consistent with the occurrence of a 'normal' smectic A monolayer organization. On cooling from the cholesteric phase of polymer HTH/BD80 (nematic for polymer HTH/BDrac), the smectic A phase appears to have a bilayer structure, possibly of incommensurate type including interdigitated layers with anti-parallel organization. It is interesting to speculate whether even fairly short sequences of repeat units with one single absolute configuration or placement of orientationally asymmetric diol residues can couple adjacently to sequences of units with opposite configuration building up a bilayer structure. Uncoupled units, on the contrary, can be packed in a different, monolayer structure with a high degree of translational disorder. Therefore, while the thermodynamic characteristics (transition temperatures and enthalpies) of this class of chiral thermotropic polyesters do not vary significantly with the optical purity in the range 0–80%, specific details of the smectic and cholesteric phases may be affected in an uneven way by the intrinsic chirality of the polymer. Furthermore, the mesophase behavior depended in a marked way on the thermal history and treatments in successive heating/cooling cycles, in analogy with other HTH based polyesters.[8,24] Such a behavior appears of rather special interest and will be the object of further investigation.

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