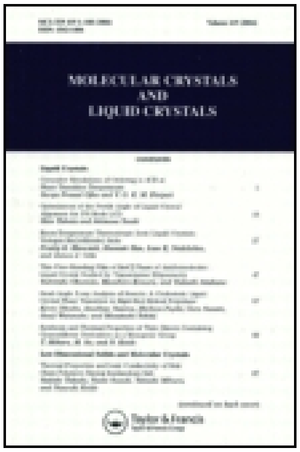

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Chiral Liquid-Crystalline Polymers. IX. The Effect of Chiral Spacer Structure in Thermotropic Polyesters

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CHIRAL LIQUID-CRYSTALLINE POLYMERS. IX. THE EFFECT OF CHIRAL SPACER STRUCTURE IN THERMOTROPIC POLYESTERS

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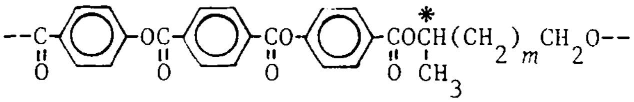
Abstract *The synthesis and characterization are reported of three new classes 1-3 of chiral thermotropic polyesters containing the 4,4'-(terephthaloyldioxy)dibenzoyl mesogen and various chiral segments. In all cases the stability of the mesophase was fairly high and its nature could be varied depending on the structure and chirality of the spacer segment. Mesomorphic polymorphism was also detected in some samples, including ordered-type smectic structures.*

INTRODUCTION

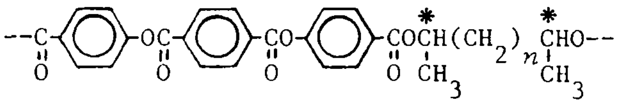
Among thermotropic liquid-crystalline polymers, those containing chiral moieties offer additional opportunities for the establishment, within definite ranges of temperature, of supermolecular structures affecting the ultimate characters of particular interest for optical and electro-optical applications[1]

In this connection we are studying since some time the structure-property correlations in series of thermotropic polyesters consisting of different mesogenic groups and chiral diols and dithiols[2,3] As a continuation of this interest, we report on three new series of polyesters derived from the strongly effective mesogen 4,4'-(terephthaloyldioxy)dibenzoic acid (HTH) and homologous series of chiral (optically active or racemic) diols of different length and substituted glycols with various substituents (structures 1-3):



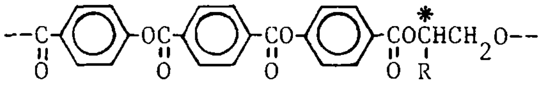
series 1

1	a	b	c	d
m	0	1	2	3



series 2

2	a(I-III)	b	c
n	0	1	2



series 3

3	a	b	c	d	e
R	CH_3	C_2H_5	$n.C_4H_9$	$n.C_6H_{13}$	$CH_2OCH_2CH_2OCH_3$

3	f	g
R	$CH_2O(CH_2CH_2O)_{6.4}CH_3$	C_6H_5

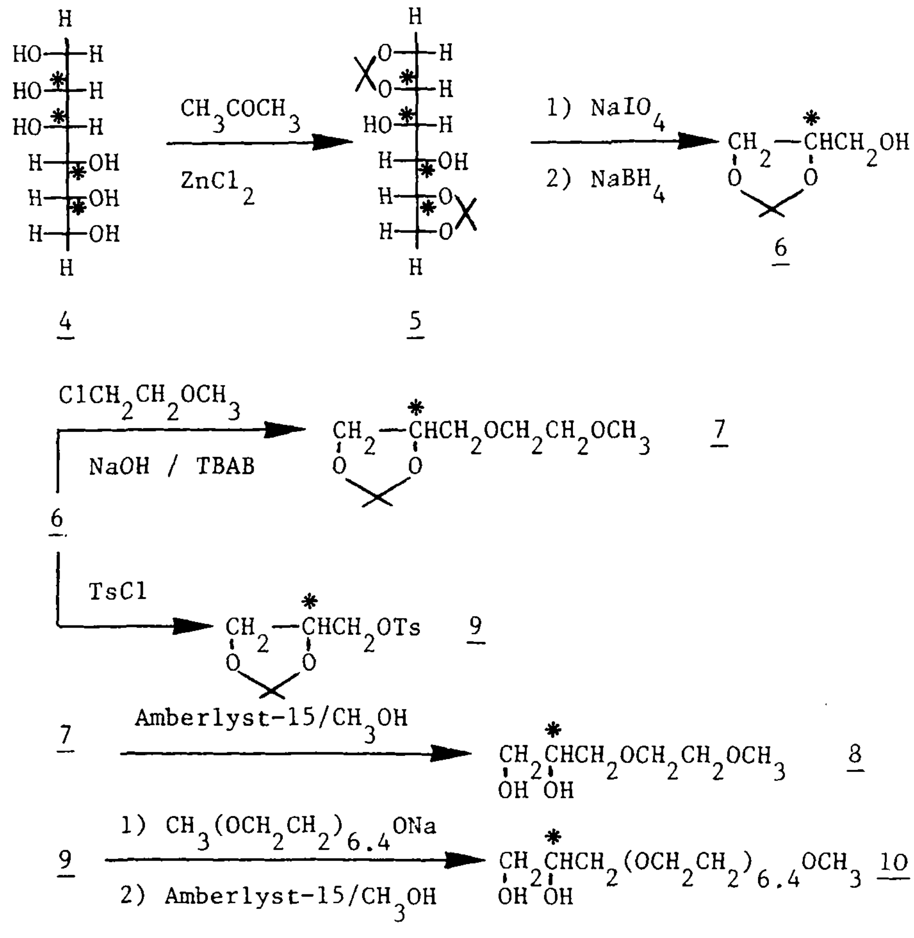
These series of polymers are characterized by the common feature of possessing the chiral center(s) directly connected to the ester function. Polymer samples 1a (or 3a) and 1b had been already described in previous work[4,5] and are here reconsidered for the sake of comparison and completeness of the homologous series.

EXPERIMENTAL PART

MONOMERIC PRECURSORS

Optically active diols 8 and 10 were synthesized (Scheme 1) from D-mannitol, as the chiral precursor, via formation of the diacetonide 5[6] followed by its oxidative cleavage and reduction to (S)-(+)-4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (6)[7] 6 was converted to the different protected diols

SCHEME 1 Synthetic route for the preparation of optically active diols 8 and 10



either directly under phase transfer catalysis conditions (diol 8) or through the intermediate tosylate 9[8] (diol 10). The synthesis of (R)-(+)-3-(2-methoxyethoxy)propane-1,2-diol (8) is reported in detail.

A mixture of 13.6g (0.10mol) of 6, 20.2g (0.21mol) of 1-chloro-3-oxabutane, 50ml of 50% aqueous NaOH and 1.4g of tetrabutylammonium bromide (TBAB) was heated at reflux for 16 hours under vigorous stirring. After cooling, the mixture was extracted with diethyl ether (3 x 50ml) and the combined organic phases were washed with NaCl-saturated water and dried over anhydrous Na_2SO_4. After removal of the solvent, 20.1g of 7 as an oily residue were obtained, which were dissolved in 300ml of methanol in the presence of 7g of the Amberlyst-15 resin (strong acid form, from Fluka). After stirring at room temperature for 24 hours, the solution was filtered, concentrated to small volume and then distilled giving 10.6g (yield 69%) of pure 8: b.p. 99-103°C/0.1mmHg, α_D^{25} +0.05° (neat).

Commercially available (R)(S)-butane-2,3-diol (11) and (R,R)-butane-2,3-diol (12), α_D^{25} -13.0° (neat) optical purity ≥99%[9], were used without further purification. The sample with intermediate optical purity was prepared by appropriate mixing of the above diols. All the other commercially available diols were dried by azeotropic distillation with benzene prior to use.

4,4'-(terephthaloyldioxy)dibenzoic acid (HTH, 13) and its dichloride (14) were prepared and purified as previously reported[4, 10]

POLYMERS

Polymerization experiments were carried out by reacting stoichiometric amounts of the diol and diacid chloride, in 1,2-dichloroethane or 1,1,2,2-tetrachloroethane (TCE) solutions at reflux, in the presence of pyridine as a promoter and proton acceptor. In a typical polycondensation reaction, a solution of 1.96g (13.0mmol) of diol 8 in 7ml (0.09mol) of pyridine and 30ml of TCE was added to a solution of 5.77g (13.0mmol) of diacid chloride 14 in 80ml of TCE. The solution was maintained at 120°C for 48 hours and then, after cooling, was poured into a large excess of methanol. The polymeric product was filtered and thoroughly washed with 5% HCl, 5% $NaHCO_3$, water and methanol and finally precipitated from TCE solution into methanol to give 3.6g (yield 55%) of polymer 3e as a white powder.

PHYSICOCHEMICAL CHARACTERIZATIONS

Optical rotatory power measurements were performed with a Perkin-Elmer 141 spectropolarimeter (path length 1dm). Ultraviolet and circular dichroism absorption spectra were recorded with a Jasco Uvidec 710 and a Jasco J500C spectrophotometer (path length 0.1cm), respectively. Molar absorption coefficients (ε and Δε) were referred to one repeat unit. Differential scanning calorimetry (DSC) measurements were performed by using a Perkin-Elmer DSC2 calorimeter at a heating/cooling rate of 10 K/min. Phase transitions were taken as corresponding to the maximum in the enthalpic peaks. Indium standards were used for temperature calibration and enthalpy evaluation. The phase transition enthalpies were referred to one mole of repeat unit. Optical polarizing microscopy observations were carried out with a Reichert Polyvar microscope and the optical textures were compared with those typical of low molar mass mesogens. X-ray diffraction patterns 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 (CuK_α), at various temperatures between 20 and 200°C.

RESULTS AND DISCUSSION

SYNTHESIS

Optically active 3-O-substituted glycerols 8 and 10 were synthesized starting from the natural product D-mannitol (4), following the route outlined in Scheme 1, as a partial modification of literature procedures.[7,8] The deblocking reaction of the isopropylidene-protected glycols was carried out in methanol solution at room temperature in the presence of the Amberlyst-15 resin in its acid form, such as to minimize racemization processes as previously discussed.[11] However, the optical purity of the optically active diols employed was not known, except for (R,R)-butane-2,3-diol for which it was varied from 99% to 50% to 0%.

All of the polyesters were prepared by a polycondensation reaction of stoichiometric amounts of 4,4'-(terephthaloyldioxy)dibenzoyl chloride and the appropriate diol in solution of chlorinated solvents (yields 50-80%). The intrinsic viscosity values are relatively low. The effect of molecular weight on the thermal properties of the polymers was not studied, but it should not be a limiting factor here, analogous to other HTH polyesters[4] or different classes of thermotropic polyesters.[12,13]

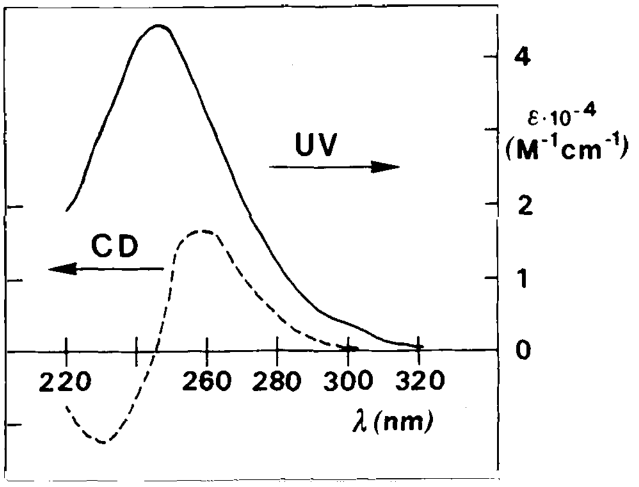
The polymers derived from optically active diols are optically active and typically show molar optical rotations much greater than those of respective chiral precursors (Table 1).

TABLE 1 Optical rotation properties of chiral diols and derived liquid-crystalline polyesters

polymer sample	starting diol		polyester
	$\|\Phi\|_D^{25a)}$	absolute configuration	$\|\Phi\|_D^{25a)}$
1a	$+22.3^{b)}$	(S)	$+42^{b)}$
2a-II	$-7.1^{c)}$	(R,R)	$-119^{d)}$
2a-III	$-15.0^{c)}$	(R,R)	$-230^{d)}$
3e	$+0.1^{e)}$	(R)	$+16^{c)}$
3f	$-2.3^{e)}$	(R)	$+140^{c)}$
3g	$-92.3^{e)}$	(R)	$+6^{c)}$

a) Molar optical rotation, in various solvents. b) In fuming sulfuric acid (possible polymer degradation). c) In trifluoroacetic acid. d) In p-chlorophenol/1,2-dichloroethane (1:2 by weight). e) In chloroform.

The chiroptical properties of polymers 3f and 3g were also investigated in dilute dioxane solutions by circular dichroism (CD) absorption measurements. While the CD spectrum of polymer 3g does not show any appreciable signals, the spectrum of 3f is characterized by strong dichroic absorptions ($\Delta\varepsilon$ +3 $M^{-1}cm^{-1}$ at 260nm and -2.5 $M^{-1}cm^{-1}$ at 230nm) corresponding to the $\pi\rightarrow\pi^*$ electronic transitions of the aromatic chromophore[14,15] (Figure 1). It is noteworthy that the intensity of the induced circular dichroism is comparable with that reported for some poly(α-aminoacids)[16] and synthetic optically active polyamides[17,18] that are known to adopt in solution a helical conformation with a prevalent screw sense. By contrast, no signal had been detected in the CD spectra of bis|(S)-2-methylbutyl| 4,4'-(terephthaloyldioxy)dibenzoate, that was chosen as the simplest model compound[4]. Our results suggest that the aromatic units are embedded in a polymer backbone with preferential chirality[19,20] whose conformational homogeneity must depend on the structure of the repeat unit.



MESOMORPHIC BEHAVIOR

The liquid-crystalline properties of polymers 1 are summarized in Table 2. All polymers exhibit a very stable mesophase (Ti > 500 K) and the isotropization temperature decreases in an alternating fashion on increasing the length of the chiral spacer. However, the melting temperature is depressed more dramatically, and consistently the mesophasic range extends over a broad range of temperatures, which is maximum for 1c ($m = 2$; Ti - Tm = 146 K). In polymer 1a ($m = 0$) there exists only one mesophase of limited persistence, supposedly nematic or cholesteric. The higher homologues investigated ($m = 1 \div 3$) show two mesophases. In all cases, the high temperature mesophase is nematic, according to polarizing microscopy and X-ray diffraction analyses. Previous X-ray investigations[5] of 1b samples had shown that the low temperature mesophase is a disordered mesophase of orthogonal type (S_A). The smectic phase of polymers 1c and 1d occurs at progressively lower temperatures. The X-ray diagrams (Figure 2) present in the low angle region a sharp reflection corresponding to an interlayer distance of 26.0 Å and 27.2 Å for 1c and 1d , respectively. The observed thickness lengths practically

TABLE 2 Liquid-crystalline properties of polyesters 1 containing homologous chiral spacers with one chiral center

sample	m	η_{inh} [a] (dl/g)	Tm (K)	Tsn (K)	ΔHsn (kJ/mol)	Ti (K)	ΔHi (kJ/mol)
1a	0	0.02[b]	607	-	-	633[c]	nd[c]
1b	1	0.14	458	500	0.8	523	4.4
1c	2	0.15	404	482[c]	0.2[c]	550[c]	3.2[c]
1d	3	0.14	393	419	2.6	503	3.9

[a] Inherent viscosity in p-chlorophenol/1,2-dichloroethane (1:1 by weight) at 30°C (c = 0.6 g/dl). [b] In fuming sulfuric acid (possible polymer degradation). [c] With partial decomposition.

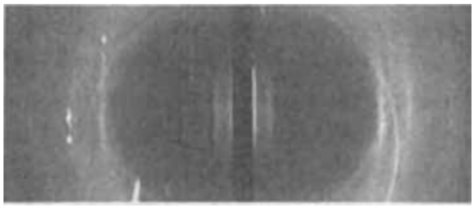


FIGURE 2 X-ray diffraction pattern of polyester 1c: ordered smectic structure at 423 K

coincide with the lengths (25.8 Å and 27.1 Å) of the fully extended monomeric units in trans conformations as evaluated according to known bond angles and distances.[21] In both cases, the wide angle spectral region exhibits three sharp signals that can be indexed as (100), (010) and (110) reflections of a rectangular lattice with parameters a = 5.2 Å and b = 4.4 Å. These data suggest the presence of an ordered smectic E phase. Its structural parameters are practically independent of temperature both on heating and on cooling within the whole range of existence (Figure 3). The density values computed

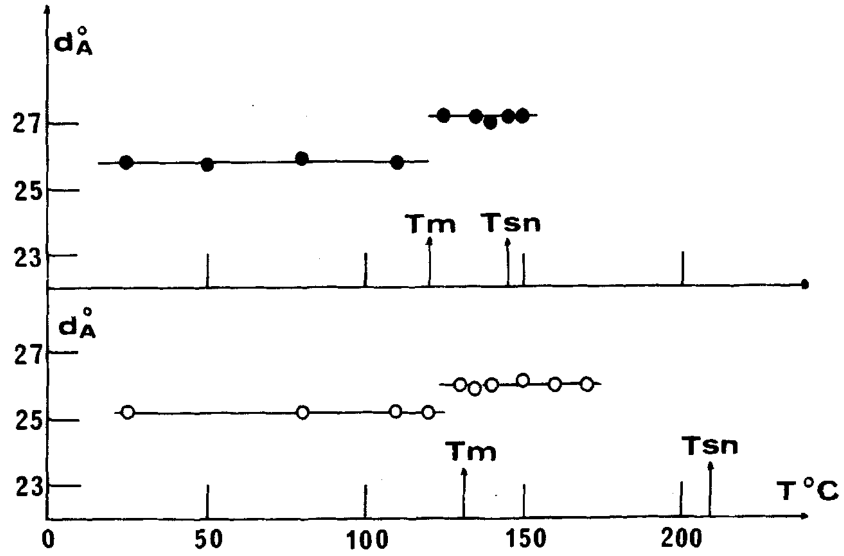


FIGURE 3 Variation with temperature of the inter-layer thickness d of polyesters 1c (○) and 1d (●) (arrows indicate transition temperatures by DSC)

for the two polymers in the smectic phase from the unit cell parameters result 1.35 g/cm^3 (polymer 1c) and 1.33 g/cm^3 (polymer 1d), which values are comparable with those reported for analogous ordered smectic polymers.[22,23] It should be mentioned that the two samples below the melting temperature are semi-crystalline with a lamellar crystalline structure of thickness d = 25.2 Å and 25.8 Å, respectively (Figure 3), to which tilt angles of ≃12° and ≃18° should be associated. In contrast, sample 1b had been found to exhibit crystalline polymorphism, the high temperature phase having an orthogonal lamellar structure (d = 24.3 Å).[5] 1d shows a S_E-N transition at 423 K, whereas in the case of sample 1c some decomposition starts to take place at temperatures higher than 443 K and the evolution of the smectic phase could not be fully investigated above this temperature. However, the DSC curves display for 1c a transition at 482 K, that we assign to the S_E-N transition (Table 2). This phase sequence is rather rare in thermotropic polymers, but seems to be more common in low molar mass mesogens (see for instance ref.[24]). The isotropization enthalpies and entropies are on the order of ΔHi≃3-4 kJ/mol and ΔSi≃6-8

J/mol·K, in agreement with a N-I transition.[10] On the contrary, the ΔH values observed for the S-N transitions are comparatively low, in analogy to what is found in structurally similar mesomorphic polyesters.[10] In the case of sample 1c, thermal decomposition might be at least partially responsible for the unexpectedly low values of enthalpies determined. Analogous polymers 2 containing two asymmetric carbon atoms in the spacer segment display mesomorphism in the melt and the relevant thermal features are summarized in Table 3. In all cases a nematic phase is established in a fairly broad range of temperatures with corresponding isotropization above 460 K. The lower and upper limit temperatures are dependent on the structure of the aliphatic spacer, the minimum values being detected for sample 2b characterized by an odd number of skeletal carbon atoms. We note that the introduction of a second methyl group in the diol segment of polyesters 2 depresses the isotropization temperature at least by 50 K, and prevents the formation of any smectic-type structure. Polymers 3 are characterized by the same number of carbon atoms but different substituents R on the chiral center, including linear alkyl chains, oxyethylene oligomers and the

TABLE 3 Liquid-crystalline properties of polyesters 2 containing homologous chiral spacers with two chiral centers

sample	n	η_{inh} a) (dl/g)	Tm (K)	Ti (K)	ΔHi (kJ/mol)
2a-I	0	0.13	493	≈573 b)	nd b)
2b	1	0.22	404	468	1.0
2c	2	0.24	439	500	2.3

a) Inherent viscosity in p-chlorophenol/1,2-dichloroethane (1:1 by weight) at 30°C (c = 0.6 g/dl). b) With partial polymer decomposition

TABLE 4 Liquid-crystalline properties of polyesters 3 containing chiral spacers with different substituents R

sample	R	η_{inh} (dl/g)	Tm (K)	Ti (K)	ΔHi (kJ/mol)
3a	CH_3	0.02[c)]	607	633[c)]	nd[d)]
3b	C_2H_5	0.15	435	538	2.7
3c	$n.C_4H_9$	0.20	440	518	1.5
3d	$n.C_6H_{13}$	0.21	385	449	0.3
3e	$CH_2OCH_2CH_2OCH_3$	0.25	405	481	1.3
3f	$CH_2O(CH_2CH_2O)_{6.4}CH_3$	0.15	407	473	0.2
3g	C_6H_5	0.15	425	485	1.4

a) Inherent viscosity in p-chlorophenol/1,2-dichloroethane (1:1 by weight) at 30°C (c = 0.6 g/dl). b) Coincident with sample 1a. c) In fuming sulfuric acid (with possible polymer degradation). d) With partial decomposition.

phenyl ring. The liquid-crystalline properties of the prepared samples 3 are collected in Table 4. One mesophase is present, which is nematic for racemic samples and cholesteric for optically active 3e and 3f, according to optical microscopy and X-ray analyses. On lengthening the alkyl substituent from a methyl group (3a, Ti = 633 K) to a n.hexyl group (3d, Ti = 449 K), the isotropization temperature is lowered by about 180 K. The introduction of oxyethylene segments apparently results in a low depression of the mesophase stability relative to the alkyl substituents (cf. 3d and 3e). This may be due to smaller disturbing effects of the flexible side substituents even at oxyethylene chains comprising as much as 21 atoms in a sequence (3f). It is also interesting to stress that polymer 3g containing the bulky phenyl ring displays a mesophase expanding over 60 K up to 485 K. No clear evidence of a cholesteric phase was obtained for this sample, possibly due to the low dissymmetry of the repeat unit as also indicated by CD absorption measurements.

TABLE 5 Phase transition temperatures for polyesters 2a containing (R,R)-2,3-butanediyl residues of varying optical purity

sample	η_{inh}[a) (dl/g)	o.p. (%)	Tm (K)	Ti[b) (K)
2a-I	0.13	0	493	≈573
2a-II	0.16	50	495	≈580
2a-III	0.14	99	490	≈580

[a)] Inherent viscosity in p-chlorophenol/1,2-dichloroethane (1:1 by weight) at 30°C (c = 0.6 g/dl).
[b)] With partial decomposition.

In order to evaluate the influence of stereochemical dishomogeneities as originated by the variable optical purity of the diols used, three polymer samples were considered in series 2, in which the optical purity of the (R,R)-butane-2,3-diol precursor was varied from 99% in 2a-III to 0% in 2a-I. The phase transition temperatures observed are reported in Table 5. Some decomposition takes place at the isotropization transition and there is some uncertainty on the exact values of this transition temperature and relevant enthalpy. Nonetheless, it is possible to note that the phase transition temperatures of the polymers are unaffected over the entire range of optical purities of the precursors. No copolymer effect can be appreciated, as due to different sequences of chiral centers of opposite absolute configurations along the polymer backbone analogous to previous results[5]. The optically active samples 2a-II and 2a-III exhibit a cholesteric phase, which is nematic for racemic 2a-I, according to optical microscopy observations.

CONCLUSIONS

In semiflexible polyesters based on the HTH mesogen and chiral diols of different structures, the introduction of two methyl substituents adjacent to the mesogen inhibits the great smectogenic effectiveness of the HTH unit, and purely nematic (or cholesteric) polymers are obtained. At the same time, an appreciable depression in the isotropization temperature is produced by the conformational restrictions of the flexible spacer. On the other hand, the use of long and bulky groups, such as the oxyethylene oligomers or phenyl ring, on the chiral center of short spacers does not depress significantly the stability of the mesophase. Consistently, nematic or cholesteric phases can spread over broad ranges of temperatures for these polymers.

From the comparison of the three sets of polymers investigated we conclude that smectic mesophases, even with high degree of order, will be originated in chiral HTH polyesters incorporating long alkylene spacers bearing only one methyl substituent adjacent to the ester moiety. This tendency is not altered in polymers with quite different optical purities of chiral units. Odd-even alternations of phase transition temperatures are possible in chiral thermotropic polyesters.

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