Chiral Liquid Crystal Polymers. 6. Preparation and Properties in Solution and in Bulk of Optically Active Thermotropic Copolyesters

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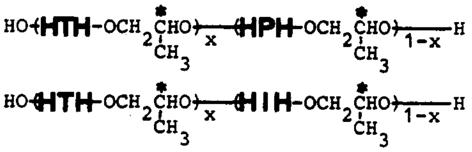
ABSTRACT: Optically active cobipolyesters based on (*S*)-1,2-propanediol and mixtures of linear, mesogenic bis(4-carboxyphenyl) terephthalate and nonlinear, nonmesogenic isomeric bis(4-carboxyphenyl) phthalate or bis(4-carboxyphenyl) isophthalate were prepared by polycondensation in solution and analyzed for their properties in solution and in bulk. Chemical composition data and solubility properties of the bipolyesters prepared are indicative of a random distribution of structurally different hard segments. Optical rotation, UV absorption, and induced circular dichroism measured in dilute solution are consistent with the existence of specific electronic interactions among the aromatic moieties embedded in a chirally homogeneous conformational environment. Thermotropic properties of the bipolyesters studied by coupled thermal analysis and optical microscopy observation allowed highlighting of the direct dependence of the onset, stability, and breadth of the temperature range of the polymer mesophase upon chemical composition. Liquid crystal behavior was observed up to as high as 70% incorporation of "nonmesogenic" aromatic units. Cholesteric mesophases with temperature-sensitive selective reflection of visible light were established at certain copolymer compositions and could be irreversibly frozen to room temperature. The great value of the copolymerization process to provide a variety of mesomorphic polyesters with modulated thermotropic behavior is stressed.

Introduction

In previous papers[1-3] of this series we have reported on the synthesis and characterization of optically active thermotropic polyesters based on bis(4-carboxyphenyl) terephthalate and chiral 1,2-propanediol and its head-to-tail dimer and trimer glycol ethers. As a major result of that investigation, the possibility was shown of preparing polymeric materials able to exhibit polymorphism in the melt phase with anisotropic structures, such as twisted smectic and twisted nematic (cholesteric), determined by the presence of flexible spacers with prevailing chirality. Lengthening of the flexible segment or introduction of stereochemical irregularities along the polymer backbone caused appreciable depression of the melting temperatures and increased the solubility properties, thus ultimately leading to polymeric products more suitable for characterization in the melt phase and in solution. Furthermore, it has been established that the use of chiral flexible segments in the side chains of bipolyesters with different lengths and different enantiomeric compositions can be of value in modulating the incidence, nature, and interval of existence of thermotropic mesophases.[4] Indeed, in mesomorphic bipolyesters of (*S*)-1,2-propanediol [(*S*)-PG] the simple replacement of a hydrogen atom in the pendant methyl group by flexible alkoxy chains leads to a marked drop (≥100 °C) of both melting and clearing temperatures, accompanied by improved solubility properties in conventional organic solvents.

In the present work we wish to report on the preparation and properties in bulk and in solution of chiral polyesters of (*S*)-1,2-propanediol coupled with different amounts of mesogenic linear aromatic triads bis(4-carboxyphenyl) terephthalate [HO(HTH)OH] and nonlinear, "nonmesogenic" bis(4-carboxyphenyl) phthalate [HO(HPH)OH] or bis(4-carboxyphenyl) isophthalate [HO(HIH)OH] isomers. The synthetic strategy based on copolymer effect has been successfully applied on an industrial scale to improve the processability of poly(ethylene terephthalate),[5] and more in general the tractability of some other conventional polycondensates.[6] That procedure, however, has not been adopted in a systematic way in the field of mesomorphic condensation polymers.[7,8] There are examples of liquid crystal polymers[9-11] in which the tendency to close packing of mesogenic residues is disrupted by the introduction of lateral substituents on the aromatic nuclei (frustated liquid crystal polymers).[8]

The general structure of the copolymers prepared, apart from the relevant distribution of aromatic moieties and orientational placements of the nonsymmetric chiral diol residues, can be represented as follows:

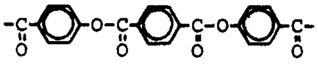


$$HO\left(HTH{-}OCH_2\underset{CH_3}{\overset{*}{C}}HO\right)_x\left(HPH{-}OCH_2\underset{CH_3}{\overset{*}{C}}HO\right)_{1-x}H$$

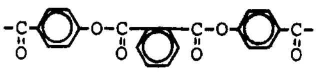
$$HO\left(HTH{-}OCH_2\underset{CH_3}{\overset{*}{C}}HO\right)_x\left(HIH{-}OCH_2\underset{CH_3}{\overset{*}{C}}HO\right)_{1-x}H$$

(x = 0-1)

HTH:



HPH:



HIH:

The present contribution stems from a project focused on the synthetic realization of new cholesteric polymers for which a stringent correlation is desired between molecular structure and morphological properties of the melt, possibly retained by either quenching or slow cooling. In fact, for such systems noteworthy applications can be interestingly anticipated in the preparation of passive devices such as polarizers, electromagnetic filters, and reflective displays. Among the procedures that are currently applied for the generation of cholesteric phases, we selected one based on the utilization of a preferentially chiral component for the formulation of a bipolycondensate. This appears indeed to be a very versatile route, in that a large

Table I
Physicochemical Properties of Bipolyesters Based on Linear HTH and Nonlinear HPH (Runs TP) or HIH (Runs TI) Aromatic Triads and (*S*)-1,2-Propanediol[a]

run	comp[b] % HTH	sol[c]	[η],[d] dL/g	$[\Phi]^{25}_{D}$[e]	thermal prop[f] T_m, °C	T_i, °C
T	100	A	0.02[g]	+42[g]	334	360
TP1	90	B	0.14	+337	208	290
TP2	70	[B]	0.15	+283	182	271
TP3	50	C, [D]	0.16[h]	+259	130[i]	277
P	0	B, C, D, E	0.18[h]	+123	115[i]	*j*
TI1	90	B	0.22	+409	222	325
TI2	70	[B]	0.18	+364	145	285[i]
TI3	50	[B], C, D	0.25[h]	+367	139	220
TI4	30	B, C, D, E	0.18[h]	+297	112[i]	115[i]
I	0	B, C, D, E	0.20[h]	+297	130[i]	*j*

[a] Enantiomeric purity ≥95%. [b] Coincident with that of the starting diacid chloride mixture by NMR. [c] Apparent solubility in (A) fuming sulfuric acid, (B) trifluoroacetic acid, (C) chloroform, (D) tetrahydrofuran, and (E) dioxane. Letters in brackets refer to the hot solvent. [d] In trifluoroacetic acid at 30 °C. [e] In trifluoroacetic acid. [f] By DSC, if not otherwise indicated. [g] In fuming sulfuric acid. [h] $\overline{DP}_n$ = 8–15 and $\bar{M}_w/\bar{M}_n$ = 1.5–1.6 by gel permeation chromatography. [i] By optical microscopy. [j] Not liquid crystalline.

Chart I
Limit Conformations of Aromatic HTH (a), HIH (b), and HPH (c) Triads

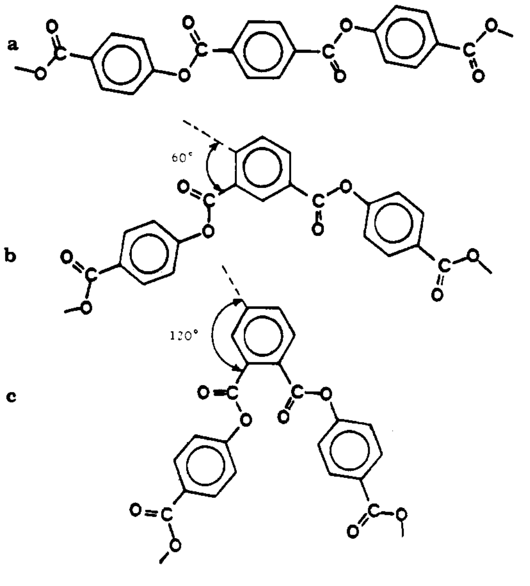
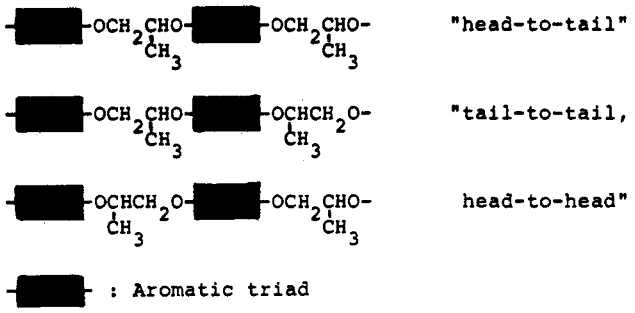


Chart II
Orientational Placements of Two Adjacent Nonsymmetric Diol Residues



variety of mesomorphic polymers can be prepared by subtle chemical or stereochemical variations in both polymer precursors.

Results and Discussion

Synthesis and Properties in Solution. The preparation of the two series of cobipolyesters (series TP and TI) was carried out by reacting (*S*)-1,2-propanediol [(*S*)-PG] with stoichiometric amounts of different diacid chloride mixtures derived from bis(4-carboxyphenyl) terephthalate [HO(HTH)OH] and bis(4-carboxyphenyl) phthalate [HO(HPH)OH] or bis(4-carboxyphenyl) isophthalate [HO(HIH)OH]. These last two intermediates were formed prior to polycondensation according to a general procedure described for the linear diacid isomer.[11,12]

A 2:1 (v/v) 1,2-dichloroethane/pyridine mixture was used as the solvent and hydrochloric acid acceptor for the condensation reaction, which was performed by heating (5–20 h) at 60–70 °C with vigorous stirring. Yields between 25% and 75% were usually obtained.

In Table I data are reported relevant to the chemical composition, solubility, intrinsic viscosity, molar optical rotation, and thermal properties of the cobipolyesters prepared. The bipolyesters of the three aromatic diacids (runs T, P, and I) have been included for comparison with the corresponding cobipolyesters. Within the limits of experimental accuracy inherent in NMR spectroscopy, the copolymer samples are characterized, even at low degrees of conversion (20–25%), by the same chemical composition as the starting comonomer mixtures. This is indicative of a practically identical reactivity of the three different diacid chlorides,[45] and therefore it may be reasonably assumed that linear and nonlinear aromatic residues are randomly distributed along the polymer backbone. As a limiting case, a deviation from overall chain linearity of 60° and 120° can be produced (Chart I). No clear indication has been yet gained on the relative orientation placements of the 1,2-propanediol residues, which in principle may assume, with respect to adjacent positioning within the main chain, either a "head-to-head, tail-to-tail" or a "head-to-tail" structural topology (Chart II). Structural isomerism in polycondensates derived from a nonsymmetric precursor has been described and theoretically discussed,[14] and the term bipolyester is used here accordingly. However, taking into account that the reactivity in the esterification with the same acid chloride of a primary alcohol is greater than that of the respective secondary isomer,[13] it is plausible that a nonrandom distribution of the possible placements is realized along the polymer backbone. Considering the fairly high chemical and thermal stability possessed by the reported homo- and cobipolyesters, the incidence of any structural rearrangement during the preparation stage and successive handling of the polymer has to be excluded. Any consideration of the structural features related to the distribution of the absolute configuration of the chiral propanediol units can be neglected, in that the enantiomeric excess in the starting diol is higher than 95%[15,16] and is not diminished during the polymerization process, which involves smooth reaction conditions suitable to allow a total retention of configuration. It may be observed that structural regularity in bipolycondensates may ultimately affect the liquid crystalline properties of the polymer[17] and also in this respect would deserve further investigation.

All the polymeric products are more or less soluble in organic solvents such as chloroform, dioxane, and trifluoroacetic acid (TFA). Bipolyester based on HTH units (run T) is soluble practically only in fuming sulfuric acid, in which some degradation process may occur. The solubility in both copolymer systems increases with increasing content of distorted aromatic triad residues, as expected. The values of the intrinsic viscosity measured at 30 °C in

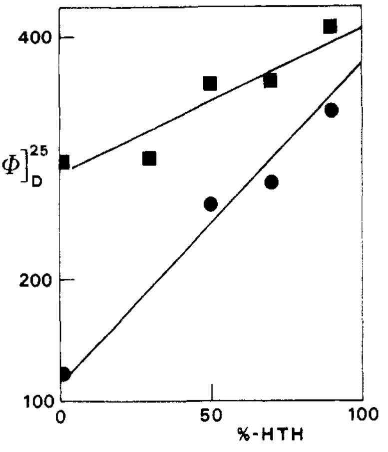
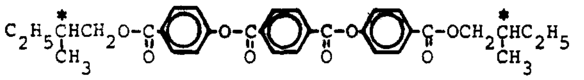


Figure 1. Variation of the molar optical rotation ($[\Phi]^{25}_{D}$) with chemical composition in HTH/HPH–(*S*)-PG (●) and HTH/HIH–(*S*)-PG (■) cobipolyesters.

trifluoroacetic acid, with the exception of the sample of run T (measured in sulfuric acid), are in the range 0.14–0.25 dL/g. Average molecular weights, as measured by GPC on samples soluble in tetrahydrofuran, are in the range 4000–7500 ($\bar{M}_w/\bar{M}_n$ = 1.5–1.6), to which values average degrees of polymerization ($\overline{DP}_n$) included between 8 and 15 correspond (Table I). According to previous results on the molecular weight dependence of the liquid crystalline behavior in polyesters,[18] we assume that no peculiar influence on the thermotropic properties of the investigated polymer samples is effective.

All the polymer samples are optically active and the molar optical rotation measured in TFA at the sodium D line decreases with increasing content of HPH or HIH units in a nearly linear fashion (Figure 1) to indicate that no marked changes in the local conformational features are generated by the proximity of either identical or different aromatic residues. Incidentally, a value of molar optical rotation in TFA of +390 ± 15° can be extrapolated for bipolyester HTH–(*S*)-PG (run T). It may be observed that the molar optical rotations are of the same sign as the starting optically active diol component and the low molecular weight model compounds bis[4-(((*S*)-2-methylbutoxy)carbonyl)phenyl] terephthalate (1)[1] and bis[4-



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(((*S*)-2-methylbutoxy)carbonyl)phenyl] isophthalate (2)[19] ($[\Phi]^{25}_{D}$ +21.3° and +24.0° for 1 and 2, respectively). However, the values of molar optical rotation of all the bipolyesters reported are by far higher than those of the corresponding low molar mass models, and this fact substantiates the persistence, even in dilute solution, of a conformational situation for the polymer backbone characterized by a high homogeneity, which is not much affected by randomness of the different aromatic triads and relative orientation of asymmetric diol residues.

Further support for this suggestion is provided by UV and circular dichroism (CD) measurements performed in dilute solution. In Figure 2 are reported, as typical examples, the UV and CD spectra of homobipolyester HIH–(*S*)-PG (run I) and two cobipolyester samples having the same molar content (10%) of nonlinear units (runs TP1 and TI1). In Table II are collected the values of molar

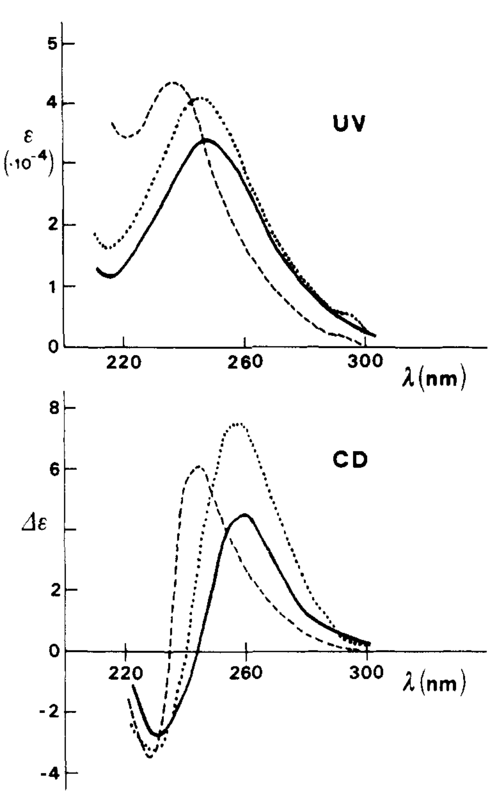

Figure 2. Ultraviolet (UV) and circular dichroism (CD) spectra in dioxane solution of HIH bipolyester (- - -), and cobipolyesters containing 10% HPH units (—) or HIH units (···).

Table II
UV Absorption Data[a] of Bipolyesters Based on Linear HTH and Nonlinear HPH or HIH Aromatic Triads and (*S*)-1,2-Propanediol

		HIH cobipolyesters				HPH cobipolyesters		
comp % HTH		λ_{max}, nm		ϵ_{max}, M^{-1} cm^{-1}		λ_{max}, nm		ϵ_{max}, M^{-1} cm^{-1}
100	hypsochromism ↓	250	hypochromism ↓↑	53 000	hypsochromism ↓	250	hypochromism ↓↑	53 000
90		246		40 500		246.5		34 000
70		244		38 500		245		33 500[b]
50		241.5		40 500		243.5		32 500
30		239.5		41 500				
0		237		43 000		236		34 000

[a] In dioxane solution ($c \approx 10^{-4}$ (mol of repeating unit)/L. [b] Interpolated value.

extinction coefficient (ϵ_{max}) and wavelength (λ_{max}) of the UV absorption band vs. cobipolyester composition for the TP and TI series. The position of the UV maximum connected with the $\pi \rightarrow \pi^*$ electronic transition undergoes an unequivocal blue shift with increasing content of distorted HPH or HIH units. The introduction of isomeric aromatic triads is accompanied in all cases by a more or less marked hypochromic effect. Such a behavior is known for a variety of vinyl aromatic polymers[20,21] and is indicative of the presence of electronically interacting chromophores.[22] The CD spectra of all cobipolyesters and of bipolyesters HPH–(*S*)-PG and HIH–(*S*)-PG exhibit a well-pronounced dichroic absorption with a positive (ca. 260 nm) and a negative (ca. 230 nm) maximum of comparable rotatory strength, whereas no signals of appreciable intensity were observed in the CD spectra of homobipolyester HTH–(*S*)-PG. The dichroic bands are located in close correspondence with the UV absorption band connected with the $\pi \rightarrow \pi^*$ electronic transitions of the aromatic chromophore.[23] It is of interest to note that the intensity of the dichroic absorption is comparable to those

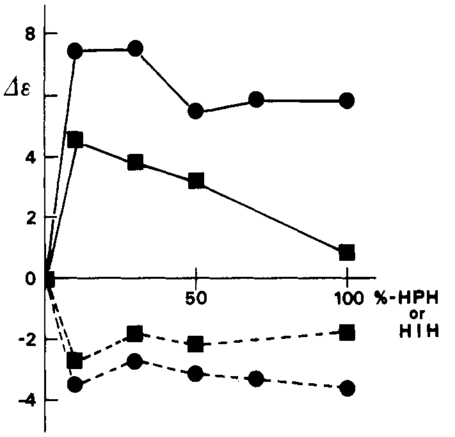

Figure 3. Variation of the dichroic absorption coefficient ($\Delta\epsilon$) at ca. 260 nm (—) and at ca. 230 nm (- - -) with chemical composition in cobipolyesters HTH/HPH-(*S*)-PG (■) and HTH/HIH-(*S*)-PG (●).

observed for poly(α-amino acids)[24] and synthetic optically active polyamides[25] that are known to adopt in dilute solution a helical conformation with a prevailing screw sense. By contrast, the low molar mass model compounds show only positive dichroic bands of comparatively low ($\Delta\epsilon$ = +0.4 at 260 nm and $\Delta\epsilon$ = +0.2 at 292 nm) or extremely low ($\Delta\epsilon$ = 0) intensity for models 2 and 1, respectively. The shape and location of the two CD maxima in the polymers with symmetrical position with respect to the crossover zero point centered at a wavelength in correspondence with the maximum in the UV absorption strongly support the occurrence of an intramolecular exciton splitting band. That should arise from interacting aromatic chomophores, either linear or nonlinear, which are assembled in a conformationally homogeneous environment.[20,26,27] It may be observed that maximum effects in induced CD occur at cobipolyester compositions of 15–25% HPH or HIH units (Figure 3), at which a maximum hypochromic effect is detected (Table II). In that range of compositions an optimized conformational situation is apparently established allowing rather high interactions among aromatic triads.

Liquid Crystal Properties. The two series of cobipolyesters prepared were analyzed by combined differential scanning calorimetry (DSC) and hot-stage optical microscopy. Data gained by the two analytical techniques are collected in Table I.

In both series of polymeric samples, the melting, or softening, temperature (T_m), the onset of mesomorphic behavior, and the isotropization temperature (T_i) are strongly dependent upon chemical composition. The reported values of T_m and T_i were taken in correspondence of the maximum of the relevant DSC endotherms, if not otherwise indicated.

The DSC curves of both series of cobipolyesters are characterized by the presence of relatively weak endotherms of melting (ΔH_m = 2–4.5 cal/g) for samples with a content of nonlinear HIH residues up to 50% or HPH residues up to 30%, whereas no melting peaks were revealed in samples with higher contents, even after prolonged annealing. In such cases, the softening temperature was evaluated by optical microscopy when the sample started to flow and could be easily sheared by touching the glass cover slip. Interestingly, in samples containing ≥50% HIH units, more or less pronounced glass transition inflections were observed at rather high temperatures (90–100 °C), practically independent of chemical composition. Such high values of glass transition temperatures are interpreted by assuming the persistence of a certain degree of molecular order typical of the mesophasic state even in the amorphous phase.[32-34] The isotropization transitions were in every case broad and resulted in wide biphasic regions (30–40 °C). The corresponding endotherms were rather weak and clearing enthalpies could not be measured with accuracy (ΔH_i = 0.5–1 cal/g). No isotropization peaks were observed in the DSC curves of cobipolyesters TI2 and TI4, and the transition temperatures were taken by optical microscopy at the complete disappearance of melt birefringence. These values may be, therefore, 10–15 °C higher than those virtually determined by DSC. Polydispersity of the polymers and low degrees of order of the liquid crystal phase, inputable to copolymer effects, can be claimed to be responsible for the observed behavior.

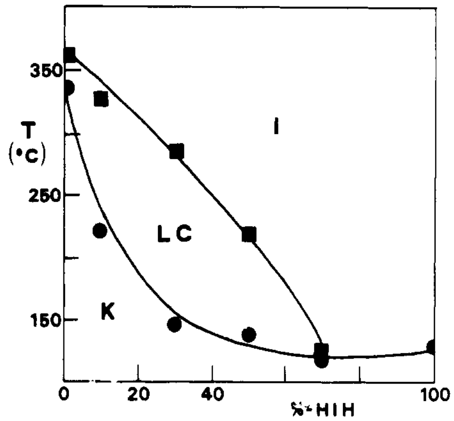

Figure 4. Thermal phase diagram of HTH/HIH-(*S*)-PG cobipolyesters: (●) melting or softening temperature; (■) isotropization temperature.

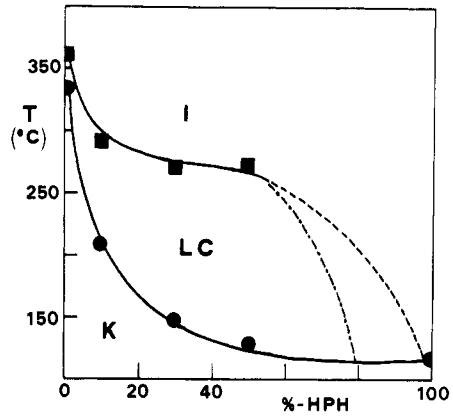

Figure 5. Thermal phase diagram of HTH/HPH-(*S*)-PG cobipolyesters: (●) melting or softening temperature; (■) isotropization temperature with maximum expected trend (- - -) and minimum expected trend (- · · -).

The introduction of either one of the two nonlinear aromatic triads causes a significant depression of T_m and T_i with respect to homobipolyester containing linear HTH units (Figures 4 and 5). The trend of this decrease with increasing HPH or HIH units is consistent with larger effects on T_m, which reaches a shallow minimum at about 70–80% of nonlinear units and eventually increases very slightly tending to the value of corresponding not-liquid crystalline bipolyester HPH-(*S*)-PG (run P) or HIH-(*S*)-PG (run I). Incorporation of as little as 10% of nonlinear units produces a sharp drop of 100–150 °C in T_m. A linear trend in T_i with a rather smooth slope (about 30% of the drop in T_m) is recorded for the second series of cobipolyesters, the existence of a mesophase still being proved at 70% of HIH units with a distortion angle of 60° (Figure 4). A more complex trend, even within the smaller number of data available, appears to hold in the first series of cobipolyesters. The sharp depression of T_i, which is detected at low contents of HPH residues with a distortion angle of 120°, levels off at higher percentages of HPH (up to 50–60%), and then a more or less marked drop (broken line in Figure 5) is expected, in analogy to what is found in the former series. Accordingly, mesophases extending over exceptionally wide ranges of temperatures (>100–140 °C) are obtained at intermediate copolymer compositions. This demonstrates the possibility of producing stable mesophases in copolymers even derived from rigid, "nonmesogenic" precursors.[28] It is surprising that the mesomorphic behavior is retained up to chemical compositions corresponding to a statistical sequencing of two nonlinear units per linear mesogenic unit. An analogous behavior has been observed in fully aromatic copolyesters based on mesogenic *p*-phenylene terephthalate units and nonlinear *m*-phenylene terephthalate units[29] but is very rare even in low molar mass compounds.[30,31]

The optical microscopy investigation performed on the samples at different temperatures up to the instrumental maximum limit of 300 °C with transmitted and/or reflected polarized light confirmed and complemented the DSC findings, as anticipated. In particular, in both series, planar textures with oily streaks typical of cholesteric structures were observed in copolymers incorporating up to 30% of nonlinear residues. In Figure 6, there are reported the photomicrographs between crossed polarizers of the cholesteric phase of samples TP1 and TI1 containing 10% of HPH and HIH units, respectively. On further heating, the texture of the former sample developed more and more defects in the form of "schlieren" with disclinations of integer and half-integer strength (Figure 7). Cobipolyesters TP3 and TI3, both containing 50% of HTH residues, exhibited a texture with very broad extinction bands and a marked tendency to homeotropism, particularly evident in the latter sample. The melt phase of sample TI4 having a content of 70% of HIH units still showed a faint birefringence, but, due to the very narrow range of temperatures involved, observation of textures was difficult and the reported transition temperatures may be affected by some error. No birefringence was developed by the solid, amorphous phase or by the melt, isotropic phase of homobipolyesters P and I. A detailed investigation of mesophase nature by X-ray diffraction studies is reported elsewhere.[35]

It is interesting to note that the planar texture of copolymers TP1 and TI1 selectively reflected the visible light in appropriate ranges of temperature. Thus, sample TI1, when observed with perpendicularly reflected light, showed a violet iridescence at 230 °C, blue at 240 °C, green at 255 °C, green-yellow at 260 °C, orange at 265 °C, and red at 270 °C. When the samples were cooled, usually we observed hysteresis phenomena,[36] and the cholesteric textures could be quenched to room temperature, providing variously colored, solid films. The observed variations of reflected light with increasing temperature are associated with the lengthening of the cholesteric pitch,[37] which might be influenced by molecular weight polydispersity of the samples. The unwinding of the helical array is in contrast to the trend commonly recorded with low molar mass cholesterics[38] and with analogous homobipolyesters of HTH residue and optically active alkyl glycerol spacers.[4] An extension of the helical pitch with increasing temperature has been observed in thermotropic (hydroxypropyl)cellulose acetate[39] and copolypeptides[40] and lyo-

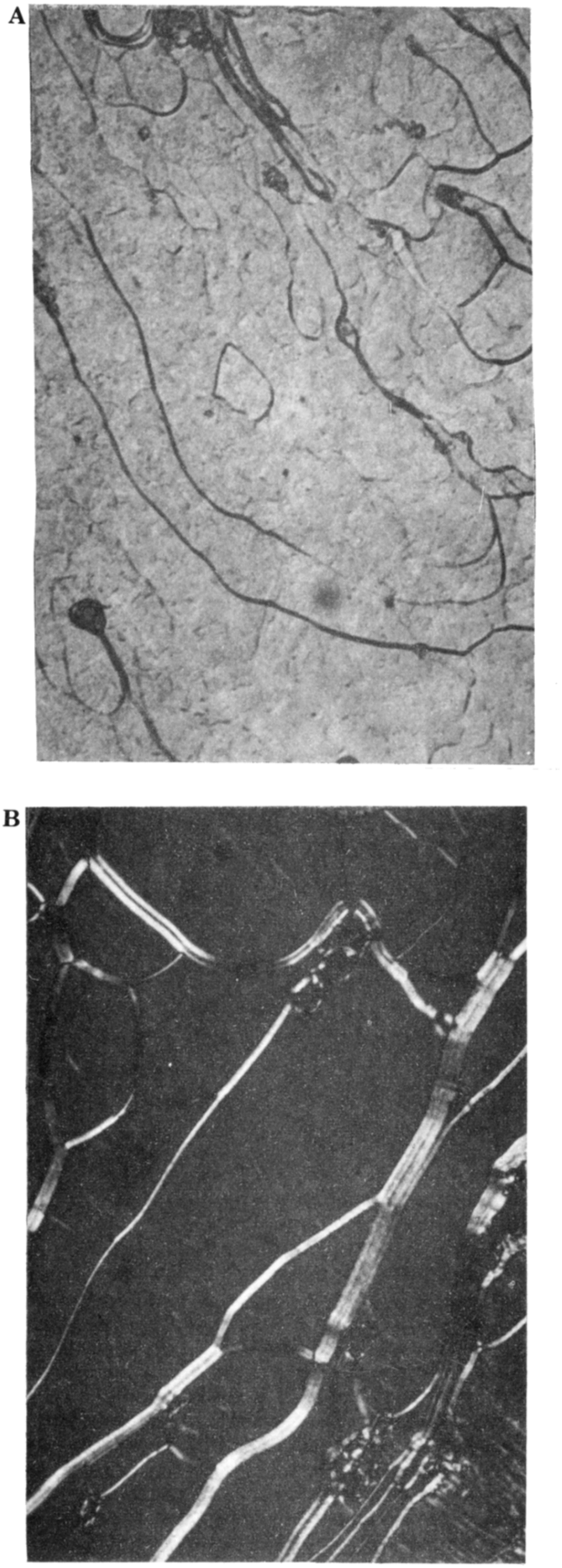

Figure 6. Cholesteric textures with oily streaks of cobipolyesters containing 10% HPH units (T = 248 °C, transmitted light, yellow background) (A) or HIH units (T = 278 °C, transmitted light, blue background) (B).

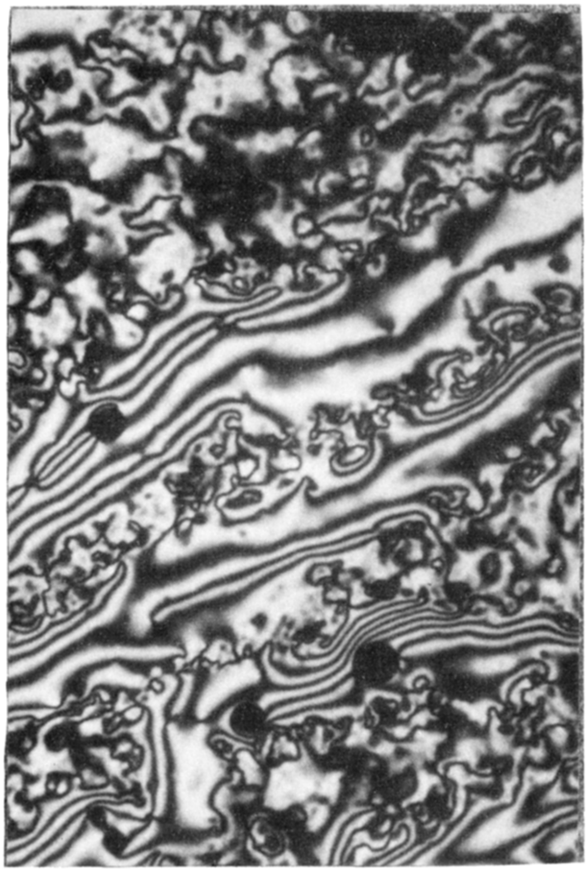

Figure 7. "Schlieren" texture at 295 °C of HTH/HPH-(*S*)-PG cobipolyester containing 10% HPH units.

tropic poly(γ-benzyl L-glutamate).[41,42] Such an anomalous behavior may be explained by assuming the occurrence of conformers originated by free rotation along the polymer backbone axis, as sufficiently enhanced by the introduction of small amounts of nonlinear units, which in turn would be able to reduce the anisotropy in the intermolecular potential.[43]

Conclusions

As a general conclusion of the first part of this work dealing with the synthesis and properties in solution of the cobipolyesters prepared, we can stress the high value of the copolymerization procedure to produce polyesters based on a short spacer, such as that derived from 1,2-propanediol and linear and nonlinear aromatic triads that show improved solubility properties as controlled on the basis of the ratio linear/nonlinear aromatic residues. The adopted procedure is comparable in efficiency to that involving the use of long-side-chain substituents,[4] and even better suited than that based on the lengthening of the flexible main-chain segment.[1]

Optical rotatory power measurements along with ultraviolet and circular dichroism absorption data offer simple and clear indication of the capability of the polymers investigated to adopt in dilute solution chiral conformations characterized by a high local homogeneity. Strong electronic interactions occur between mesogenic and nonmesogenic aromatic units independent of the intrinsic nature of the structural units and their average sequencing.

From the second part of the present work dealing with the thermal-optical characterization of the thermotropic properties of the cobipolyesters investigated, we can further emphasize the importance of the copolymerization procedure to provide polymeric materials with liquid crystalline behavior. The onset, stability, and persistence of the polymer mesophase can be modulated on the basis of balanced chemical compositions of the feed mixture. In the present systems, the anisotropic properties of the melts were maintained up to levels of 60–70% of inherently nonmesogenic aromatic units. This result offers valuable hints for potential applications of liquid crystalline polymers in the field of composites. In particular, the most appropriate copolymer composition could be selected when fairly restricted conditions of melting temperature would be requested for an optimization of the blending process without appreciably depressing the anisotropic properties of the melt.

Finally, the capability of a number of the reported cobipolyesters to give cholesteric planar textures retaining selective reflection of visible light at room temperature may open ways to optical devices based on thermoplastic materials and suited to store information by thermal input hysteresis.

Experimental Section

Materials. (+)-(*S*)-1,2-Propanediol [(*S*)-PG] $\{[\alpha]^{25}_{D}$ +15.4° (neat)$\}$ was synthesized from (*S*)-ethyl lactate $\{[\alpha]^{25}_{D}$ −11.6° (neat), optical purity ≥95%$\}$ as the chiral precursor according to a literature procedure.[15,44]

Bis(4-carboxyphenyl) terephthalate [HO(HTH)OH], bis(4-carboxyphenyl) phthalate [HO(HPH)OH], and bis(4-carboxyphenyl) isophthalate [HO(HIH)OH] diacids were prepared by the same general procedure[11] starting from benzyl hydroxybenzoate and terephthaloyl, phthaloyl, and isophthaloyl chloride, respectively. HO(HTH)OH, HO(HPH)OH, and HO(HIH)OH diacids were converted to the corresponding diacid chlorides by action of thionyl chloride in the presence of catalytic amounts of DMF and then purified by crystallization from 1,2-dichloroethane under a nitrogen atmosphere.

Polymerization, or copolymerization, runs were carried out by reacting stoichiometric amounts of (*S*)-1,2-propanediol and the diacid chloride, or appropriate mixture of diacid chlorides, of choice in 2:1 (v/v) 1,2-dichloroethane/pyridine at 60–70 °C. The polymeric products were purified by pouring the reaction mixture into a large excess of methanol and thoroughly washed with 5% HCl, 5% $NaHCO_3$, water, and methanol. Chloroform soluble samples were additionally precipitated several times from chloroform solution into methanol. Finally, all the products were dried at room temperature till constant weight.

Model compound 1 $\{[\alpha]^{25}_{D}$ +3.9° (chloroform)$\}$ and model compound 2 $\{[\alpha]^{25}_{D}$ +4.4° (chloroform)$\}$ were synthesized as previously described.[1]

Physicochemical Characterizations. Intrinsic viscosity measurements were carried out at 30 °C in trifluoroacetic acid solution by using a Desreux–Bischoff dilution viscometer. Copolymer compositions were evaluated from ^{1}H NMR spectra recorded by a Varian XL-100 spectrometer.

Average molecular weights of the polymers were measured by gel permeation chromatography (GPC), using tetrahydrofuran as the eluent, a Perkin–Elmer 2/2 liquid chromatograph equipped with Shodex A802/S and A803/S columns, and a Perkin–Elmer LC75 spectrophotometric detector (detection wavelength $\lambda = 280$ nm). Monodisperse polystyrene standard samples ($\bar{M}_v$ = 500, 2100, 4000, 9000, and 83000) were used for calibration.

Optical rotatory power measurements were performed by a Perkin–Elmer 141 spectropolarimeter with a sensitivity of ±0.001° (path length 1 dm) on polymer solutions (c = 0.1–0.3 g/dL) in trifluoroacetic acid. The reported values for HTH-(*S*)-PG bipolyester (run T) are indicative, since some polymer degradation may well occur during the measurements performed in fuming sulfuric acid. Molar optical rotation was calculated from the relation $[\Phi] = [\alpha]M/100$, in which M is the molecular weight of the repeating unit.

Ultraviolet (UV) and circular dichroism (CD) spectra were recorded in the region 350–210 nm on solutions ($c \approx 10^{-4}$ (mol of repeating unit)/L) of spectral grade dioxane (path length 0.1 cm) by a Varian DMS-80 and a Jasco J500C spectrophotometer, respectively. Molar differential absorption coefficients ($\Delta\epsilon$) referred to a monomeric unit were calculated from the equation $[\theta] = 3300\Delta\epsilon$, where $[\theta]$ is the molar ellipticity.

Differential scanning calorimetry (DSC) analyses were performed under nitrogen flow on polymer samples (7–12 mg) by a Perkin–Elmer DSC-2 calorimeter equipped with a scanning autozero. A heating/cooling rate of 10 °C/min was used, and the transition temperatures were taken in correspondence of the maximum in the enthalpic peaks. Indium and tin standards were employed for temperature calibration. Enthalpy changes were evaluated on unannealed samples by means of indium reference samples.

Texture observations were performed on polymer films between glass slides without any previous treatment by means of a Reichert Polyvar polarizing microscope equipped with a programmable Mettler FP52 hot stage. Photomicrographs were taken between crossed polarizers at the original magnification 300×. Light reflections from cholesteric textures were qualitatively determined with perpendicular incidence and perpendicular observation at a scanning rate of 10 °C/min.

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Registry No. (HTH)·((*S*)-1,2-propanediol) (-copolymer), 97592-39-7; (HTH)·((*S*)-1,2-propanediol) (SRU), 97643-60-2; (HTH)·(HIH)·((*S*)-1,2-propanediol) (copolymer), 97592-41-1; (HTH)·(HIH)·((*S*)-1,2-propanediol) (SRU), 97654-66-5; (HTH)·(HPH)·((*S*)-1,2-propanediol) (copolymer), 97592-43-3.

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