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Chiral liquid-crystalline polymers

XII. New chiral polyesters by chemical modification of a nonmesophasic polymer

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SUMMARY

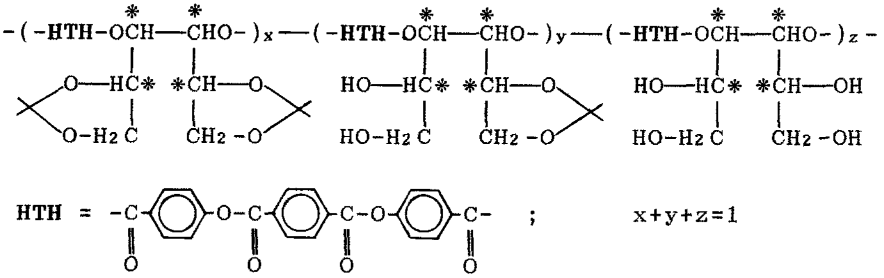
The preparation is described of a new class of chiral liquid-crystalline polyesters by means of an acidic hydrolysis of the polyester based on 4,4'-(terephthaloyldioxy)dibenzoic acid and (+)-1,2:5,6-di-O-isopropylidene-D-mannitol. Whilst the parent polymer is not mesogenic, the deprotected hydroxyl-containing polyesters give rise to anisotropic melts extending over a broad range of temperatures with a clearing point above 300°C.

INTRODUCTION

Among thermotropic liquid-crystalline polymers, those containing chiral moieties offer additional opportunities for the assessment of dissymmetric supermolecular structures. Chirality affects the macroscopic character of these mesophasic states and renders them inherently suitable to novel potential electrical and optical applications (1). In that respect, we are involved since some time in setting up the synthesis of thermotropic polyesters based on different mesogenic groups and chiral diols or dithiols and in studying their properties in bulk and dilute solutions (2-4).

In the present contribution we report on the synthesis and characterization of a new series of functional polyesters consisting of the 4,4'-(terephthaloyldioxy)dibenzoyl (**HTH**) mesogenic group and chiral hydroxyl-containing spacer segments.

The polymer samples with variable contents of hydroxyl groups [deprotection 50-90%; $0.5 \le (y/2+z) \le 0.9$] were obtained by smooth acid-promoted hydrolysis of the same polymeric



precursor constituted by monomeric units containing 100% protecting acetonide groups (x=1). Interestingly, deprotection of the acetonide groups generates cholesteric mesomorphism in a polymer matrix which originally was nonmesomorphic.

EXPERIMENTAL

Synthesis

(+)-1,2:5,6-di-O-isopropylidene-D-mannitol (DIPM, 1) was prepared by slightly modifying a procedure previously described (5). A mixture of 1300 ml of acetone, 250 g of powdered zinc chloride and 92 g of molecular sieves (beads, 3 Å) was stirred at room temperature for 2 days. 158 g (0.69 mol) of D-(+)-mannitol were then added and the mixture was stirred for 6 hours at room temperature. After filtration, the solution was poured into 700 g of 50% Na_2CO_3 aqueous solution and 1 l of diethyl ether. The precipitate was filtered and washed with 400 ml of acetone/diethyl ether 1:1 (vol:vol). The organic phases were combined and evaporated to dryness. The solid residue obtained was suspended in the minimum amount of boiling water, and the aqueous phase was separated. The organic phase was extracted with hot water (2x250 ml) and the aqueous phases were combined and evaporated to dryness. The pale yellow solid obtained was crystallized from water giving 39.0 g (yield 17%) of 1 as white needles: m.p. 120-121°C, $[\alpha]_D^{25}=+4.0$ ($c=0.75$ g·dl^{-1} in methanol). A small amount of the product was also crystallized from cyclohexane and employed in the polymerization reaction (m.p. 122°C).
^1H-NMR (CD_3COCD_3): δ=1.2-1.5 (m,12H,CH_3), 2.7-3.0 (m,2H,OH), 3.6-4.3 (m,8H,CH+CH_2) (p.p.m. from TMS).

4,4'-(terephthaloyldioxy)dibenzoyl dichloride (Cl-HTH-Cl, 2) was synthesized and purified as previously described (6).

Polycondensation of 1 with 2 (**HTH/DIPM100**). To a solution of 4.98 g (11.2 mmol) of 2 in 90 ml of anhydrous 1,2-dichloroethane, a solution of 2.95 g (11.2 mmol) of 1 in 10 ml of anhydrous 1,2-dichloroethane and 10 ml of anhydrous pyridine was added dropwise under nitrogen atmosphere. After reacting for 50 hours at 85°C, the mixture was cooled to room temperature and poured into 300 ml of methanol. The solid obtained was filtered and washed with water and methanol and finally precipitated from chloroform into methanol. Yield: 5.5 g (77%).

Deprotection with Amberlyst-15 resin at room temperature (**HTH/DIPM50**). A solution of 0.62 g of polymer **HTH/DIPM100** in 280 ml of tetrahydrofuran/methanol 1:1 (vol:vol) was stirred with 0.6 g of Amberlyst-15 resin for 6 days at room temperature. The catalyst was filtered off and the solution was evaporated under vacuum to give 0.56 g of white solid, that showed a degree of deprotection of 50%.

Deprotection with Amberlyst-15 resin at 50°C (**HTH/DIPM30**). A solution of 0.33 g of polymer **HTH/DIPM100** in 180 ml of 1,2-dichloroethane/methanol 1:1 (vol:vol) was stirred with 0.5 g of Amberlyst-15 resin for 24 hours at 50°C. The catalyst was removed by filtration and the solution was evaporated to dryness. The white solid residue showed a degree of deprotection of 70%.

Deprotection with hydrochloric acid (**HTH/DIPM10**). To a solution of 0.30 g of polymer **HTH/DIPM100** in 180 ml of 1,2-dichloroethane/methanol 1:1 (vol:vol), three drops of concentrated hydrochloric acid were added. The reaction mixture was stirred for 5 days at room temperature, and then ten drops of triethylamine were added. The solution was evaporated under vacuum and the polymer was purified by dialysis: the residue was dissolved in a mixture of water/tetrahydrofuran 1:1 (vol:vol) using as the dialyzing mixture water, water/tetrahydrofuran 1:2 (vol:vol) in that order. Dialysis tubings of 4-22/32' size (Medicell International Ltd.) were used. The dialyzed mixture was evaporated under vacuum, giving a white solid showing a degree of deprotection of 90%.

Physicochemical characterization

NMR spectra were recorded on a Varian VXR-300 spectrometer; the percentage of deprotection was evaluated from the ratios of integrated areas of the aromatic proton peaks and methyl proton peaks, and the error on the determined values was ± 5%. Differential scanning calorimetry was performed with a Perkin-Elmer DSC 7 calorimeter. Texture observations were carried out using a Reichert-Jung Polyvar microscope equipped with a Mettler FP52 hot stage. Optical rotatory power measurements were performed with a Perkin-Elmer 141 spectropolarimeter (path length 1 dm) using polymer solutions ($c=0.3-1.0\ g\cdot dl^{-1}$) in dioxane or trifluoroacetic acid. Ultraviolet and circular dichroism absorption spectra were recorded with a Jasco Uvidec 710 spectrophotometer and a Jasco J500C dicrograph respectively, using polymer solutions ($c \approx 10^{-4}$ mol repeating unit$\cdot l^{-1}$) in dioxane (path length 0.1 cm).

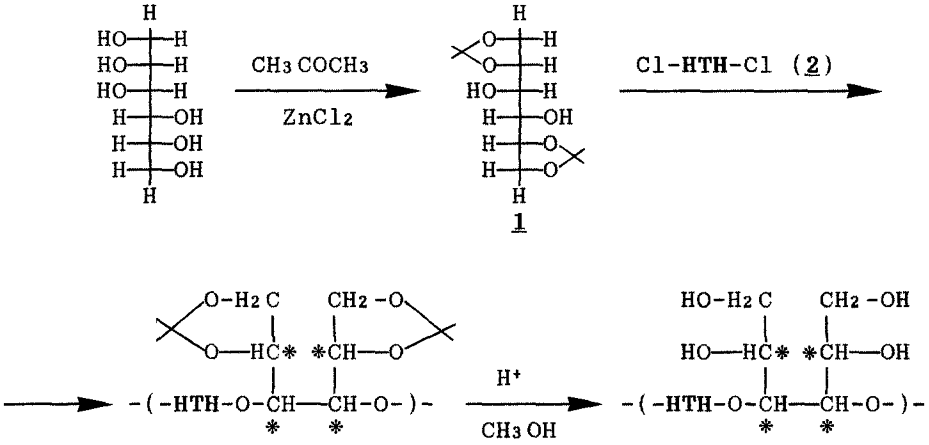
RESULTS AND DISCUSSION

In previous papers (4,7,8) we reported on the utilization of (+)-1,2:5,6-di-O-isopropylidene-D-mannitol (**DIPM**) as a versatile precursor for the preparation of optically active 3-O-alkyl substituted glycerols, glyceric acid derivatives and glycidyl ethers. Standing the fairly high chemical and stereochemical stability of **DIPM** under alkaline conditions and even weak acid conditions at room temperature, it appeared an interesting diol to be used in the synthesis of chiral potentially reactive liquid-crystalline polyesters (Scheme 1).

The presence of the two acetonide groups in the repeating unit of such polyester, could offer the opportunity for the preparation of a wide series of new polyesters by means of a facile acidic removal of the acetonide groups to an extent tunable on the basis of the experimental conditions adopted for the cleavage reactions.

The basic polymer (x=1) was prepared by the polycondensation reaction of stoichiometric amounts of Cl-**HTH**-Cl and **DIPM** in 1,2-dichloroethane solution in the presence of pyridine as a hydrochloric acid acceptor. Three samples of

Scheme 1



the basic polymer were submitted to an acidic cleavage of the isopropylidene protecting groups by using an Amberlyst resin or hydrochloric acid as a catalyst at various temperatures (see Experimental). The deprotection degree could be adjusted in the range of 50-90 mol%, higher degrees being achievable with also partial polymer backbone hydrolysis.

All of the polymer samples are optically active (Table 1). The molar optical rotation of the polyesters is positive consistent with that of the polyester precursor. No significant racemization takes place during the deprotection step. The circular dichroism spectra in dilute solutions are

TABLE 1. Characteristics of 4,4'-(terephthaloyldioxy)dibenzoic acid/(+)-1,2:5,6-di-O-isopropylidene-D-mannitol polyester and partially deprotected samples.

Polymer sample	Deprotection	$[\eta]$ a)	$[\Phi]_D^{25}$ b)	T_m	T_i
	mol %	$dl \cdot g^{-1}$	deg	°C	°C
HTH/DIPM100	0	0.25	+228	140	not LC
HTH/DIPM50	50	0.25	+236	160	≈310 d)
HTH/DIPM30	70	n.d.	n.d.	200 d)	≈310 d)
HTH/DIPM10	90	0.20	+258 c)	210 d)	≈310 d)

a) Intrinsic viscosity in *p*-chlorophenol/1,2-dichloroethane 1:1 by weight; b) Molar optical rotation in dioxane unless otherwise indicated; c) In trifluoroacetic acid; d) By optical microscopy.

characterized by a strong optically active band ($\Delta\varepsilon$=5-6 $M^{-1}\cdot cm^{-1}$) at around 240 nm in correspondence of the $\pi\rightarrow\pi^*$ electronic transitions of the aromatic chromophore (9) (Figure 1). The mesogenic units experience, therefore, a homogeneous dissymmetric environment originating from the chiral centers in the main chain and in the side chains of both **HTH/DIPM100** and derived homologues, with the latter possessing a greater anisotropy factor. This is in agreement with previous circular dichroism findings with other chiral **HTH** polyesters based on a variety of spacer segments (4,10), in which however an electronic couplet was also evidenced as due to intermolecular interactions among aromatic units.

The polyester samples exhibit very low degrees of crystallinity or are essentially amorphous, and the softening temperature was evaluated by optical microscopy (Table 1). Polyester **HTH/DIPM100** does not show any mesophase, even on supercooling of the isotropic melt. In complete contrast,

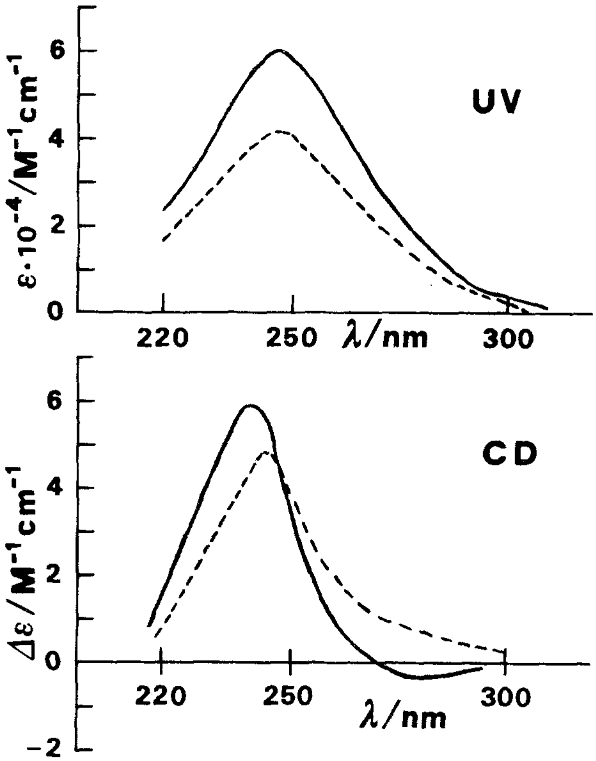


Figure 1. Ultraviolet (UV) and circular dichroism (CD) absorption spectra in dilute dioxane solution of polymers HTH/DIPM100 (——) and HTH/DIPM50 (----).

the partially deprotected samples show a very broad mesophasic range, extending for at least 100°C (polymer **HTH/DIPM10**). The cholesteric phase does not display any chiroptical effect in the visible range. The transition to the isotropic melt spreads on the range 290-320°C, and the exact location of the isotropization temperature is difficult. The occurrence of such a biphasic region must be primarily associated with the chemical heterogeneity of the copolyester samples, but concomitant transesterification reactions may well take place at the elevated temperatures. The even partial cleavage of the acetonide protecting groups decreases the steric hindrance and can enhance the conformational freedom of the chiral spacer segment, thus favouring the onset of a very persistent and stable mesophase.

CONCLUSION

The preparation of chiral liquid-crystalline polymers by the chemical modification of nonmesophasic polymers may be a new synthetic approach to otherwise unfeasible molecular architectures (11). This procedure complements that recently reported (12) for the preparation of cholesteric polymers by the asymmetric chemical modification of nematic polymeric precursors.

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