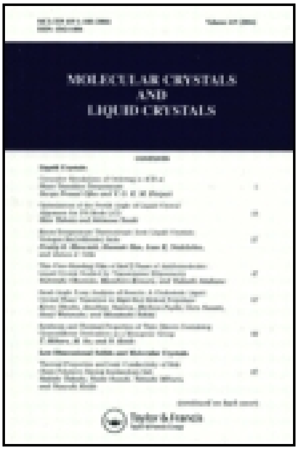


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Chiral Liquid Crystal Polymers. 5. Synthesis and Characterization of Thermotropic Polyesters of 3-O-alkylated Glycerols

Emo Chiellini [a] , Paolo Nieri [b] & Giancarlo Galli [b]
[a] Istituto di Chimica Generale (Facoltá di Ingegneria), Università di Pisa, 56100, Pisa, Italy
[b] Istituto di Chimica Organica Industriale, Università di Pisa, 56100, Pisa, Italy

Version of record first published: 17 Oct 2011.

To cite this article: Emo Chiellini , Paolo Nieri & Giancarlo Galli (1984): Chiral Liquid Crystal Polymers. 5. Synthesis and Characterization of Thermotropic Polyesters of 3-O-alkylated Glycerols, Molecular Crystals and Liquid Crystals, 113:1, 213-224

To link to this article: http://dx.doi.org/10.1080/00268948408071684

Mol. Cryst. Liq. Cryst., 1984, Vol. 113, pp. 213-224
0026-8941/84/1134-0213/$20.00/0

Printed in the United States of America

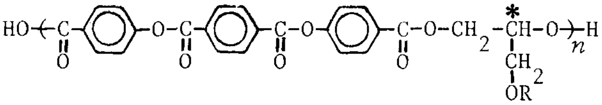
CHIRAL LIQUID CRYSTAL POLYMERS. 5.
SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC POLYESTERS OF 3-O-ALKYLATED GLYCEROLS[†]

EMO CHIELLINI, PAOLO NIERI°, and GIANCARLO GALLI°
Istituto di Chimica Generale (Facoltà di Ingegneria),
°Istituto di Chimica Organica Industriale,
Università di Pisa, 56100 Pisa, Italy

Abstract The preparation is reported of a new series of chiral polyesters based on mesogenic bis(4-carboxyphenyl) terephthalate triads and optically active or racemic 3-O-substituted glycerols. An analysis of the properties in solution and in bulk of the prepared polymers is presented. All the investigated samples exhibit a thermotropic behavior in rather accessible temperature ranges. Cholesteric structures displaying temperature dependent reflection of visible light were evidenced in all the optically active polymers.

INTRODUCTION

As a part of our continuing interest in the field of the synthesis and characterization of chiral liquid crystal (LC) polymers based on aromatic mesogenic cores and flexible segments;[1-4] attention was focused on polyesters of bis(4-carboxyphenyl) terephthalate (HTH) and 3-O-substituted chiral glycerols (GE). The general structure of the investigated polymers is represented as follows:



In a previous paper[1] it has been reported that LC bipolyesters based on the same mesogenic unit and (S)-1,2-propanediol and its head-to-tail dimer and trimer showed improved tractability with increasing length of the diol component. The samples containing longer spacers had fairly low melting temperatures, while preserving high isotropization temperatures, and better solubility in conventional organic solvents. Interesting effects on the structure of the thermotropic mesophase were also observed[1].

By working on the same line, and with the aim of producing LC polyesters possessing a somewhat enhanced hydrophilic character, it was assumed that suitable modification of the side group in the same glycol segment might play a role analogous to that exerted by the lengthening of the flexible spacer within the backbone. A desired degree of hydrophilicity could be imparted to the whole polymer system in dependence of the nature of the selected substituent.

EXPERIMENTAL PART

3-O-substituted glycerols. All the optically active and racemic glycerols were synthesized from (+)(S)-isopropylidene glycerol {b.p. 87°C/20mmHg; $[\alpha]_D^{25}$ +13.5 (methanol)} prepared from D-mannitol as the starting material[5]. The synthesis of (+)(R)-4,7,10-trioxy-1,2-undecanediol (**4**) is reported as a typical example.

A mixture of 12.0g (91mmol) of isopropylidene glycerol, 25.0 g (180mmol) of 1-chloro-3,6-dioxy-heptane, 50ml (940mmol) of 50% NaOH, and 1.2g (3.7mmol) of $(n\text{-}C_4H_9)_4\overset{+}{N}\overset{-}{Br}$ was let to react with vigorous stirring at 110-120°C for two days.

After cooling, the organic phase was washed with water and then refluxed with 43ml of 0.75M H_2SO_4 for 4 hours. The aqueous phase was neutralized with Na_2CO_3 and extracted with chloroform. The combined organic phases were dried over Na_2SO_4 and distilled to give 3.3g (yield 19%) of pure **4** {b.p. 140-145°C/0.1mmHg; $[\alpha]_D^{25}$ +0.3 (neat)}.

The other glycerol derivatives prepared are reported below, with their boiling point and optical rotation.

(-)(R)-4-oxy-1,2-pentanediol (**1**): b.p. 72-74°C/0.1mmHg; $[\alpha]_D^{25}$ -5.7 (methanol). (+)(R)-4-oxy-5-phenyl-1,2-pentanediol (**2**): b.p. 138°C/0.3mmHg; $[\alpha]_D^{25}$ +4.5 (neat). (R)(S)-4,7-dioxy-1,2-octanediol (**3**): b.p. 169°C. (R)(S)-4,7,10,13-tetraoxy-1,2-tetradecanediol (**5**): b.p. 150-160°C/0.1mmHg.

Bis(4-carboxyphenyl) terephthalate and the corresponding diacid chloride were prepared as previously reported[6].

Polymerizations. All the polycondensation reactions were carried out with equimolar mixtures of glycerol and diacid chloride in pyridine at 60-70°C for 5-10 hours. The reaction products were precipitated several times from dioxane solution into isopropanol and washed with 5% HCl, 5% $NaHCO_3$, water, and methanol (yields 50-75%).

Polymer characterizations. DSC analysis was performed by a Perkin-Elmer DSC2 apparatus under dry nitrogen flow at a heating/cooling rate of 10°C/min. Transition temperatures were taken in correspondence of the maximum of the enthalpic peaks. Optical observations were carried out with transmitted or incident light using a Reichert polarizing microscope on thin polymer films between glass slides without previous treatments.

UV and CD spectra were recorded of dilute polymer solutions in dioxane ($c \simeq 10^{-4}$ mole repeat unit/l) using Varian DMS80 and Jasco J500C spectrophotometers, respectively (path length 0.1-1cm).

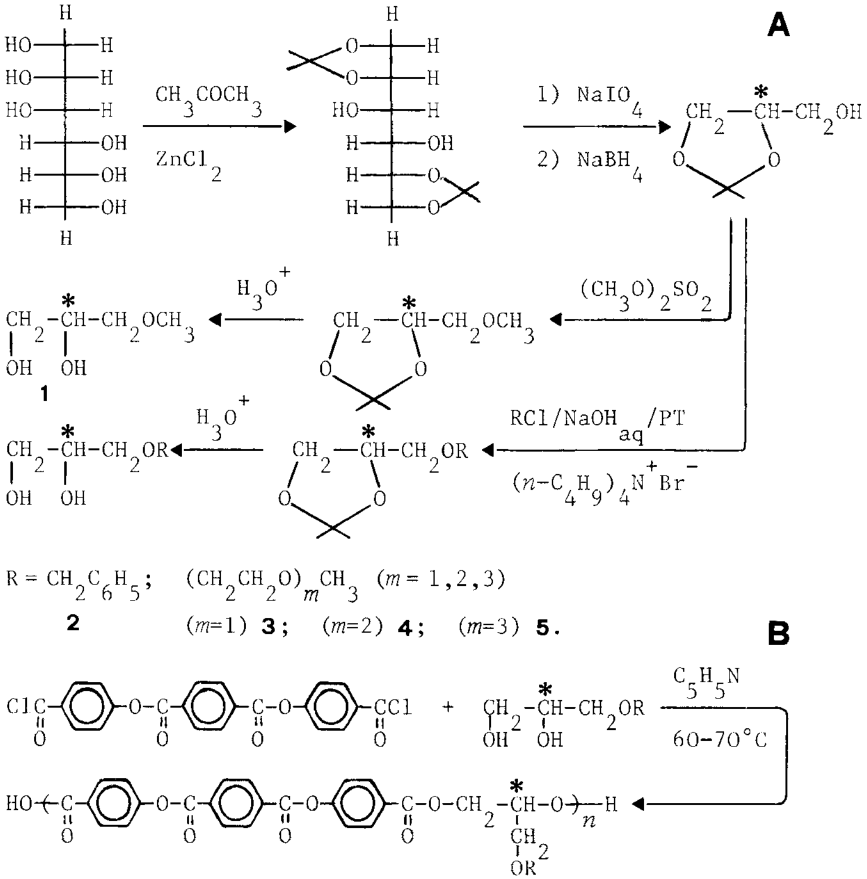
RESULTS AND DISCUSSION

Bipolycondensate samples were prepared in pyridine solution at 60-70°C by a stepwise polymerization of the diacid chloride of the preformed mesogenic bis(4-carboxyphenyl) terephthalate and different 3-O-alkylated glycerols (**1-5**) obtained from D-mannitol as the commercially available chiral precursor (Scheme 1).

The molar optical rotation properties of the starting glycerols and corresponding bipolyesters, together with polymer melting (T_m) and isotropization (T_i) temperatures are reported in Table 1.

Three out of five glycerol derivatives were optically active (samples **1**, **2**, and **4**), whereas samples **3** and **5** were racemic. For the first glycerols, however, we do not yet know the optical purity. The sequence of reactions involving the oxidative cleavage of D-mannitol diacetonide, reduction of isopropylidene glyceraldehyde, and alkylation of isopropylidene glycerol with the alkyl (or arylalkyl) chloride of choice under alkaline phase-transfer catalysis conditions occurs

SCHEME 1. Synthesis of: A) chiral 3-O-substituted glycerols (GE); B) bipolyesters of GE with the diacid chloride of bis(4-carboxyphenyl) terephthalate (ClHTHCl)



without any appreciable racemization. The acid removal of the blocking isopropylidene group represents a severely critical step in affecting the final enantiomeric purity of the 3-O-alkyl glycerol. The optimization of the deblocking reaction conditions in respect of the acid concentration and temperature and duration of reaction is currently investigated.

TABLE 1. Structural characteristics and properties of HTH/GE bipolyesters

3-O-Alkyl glycerol[a)]			Bipolyester[b)]			
type	substituent	$[\Phi]_D^{25}$ [c)]	sample	$[\Phi]_D^{25}$ [d)]	T_m (°C)	T_i (°C)
1	CH_3	-6.0[e)]	**P1**	+174.2	135[f)]	287
2	$CH_2C_6H_5$	+8.2	**P2**	+127.5	145	202
3[g)]	$CH_2CH_2OCH_3$	-	**P3**	-	151	270
4	$(CH_2CH_2O)_2CH_3$	+0.6	**P4**	+195.7	103	205
5[g)]	$(CH_2CH_2O)_3CH_3$	-	**P5**	-	115	160

a) (R) absolute configuration, if not otherwise indicated. *b)* $[\eta]$ = 0.1-0.2 dl/g in dioxane at 30°C. *c)* Neat, if not otherwise indicated. *d)* In dioxane, referred to a structural repeat unit. *e)* In methanol. *f)* Smectic-cholesteric transition at 143°C. *g)* Racemic.

The bipolymer samples (**P1**-**P5**) obtained in variable yields (50-75%) were soluble in common organic solvents (chloroform, dioxane) and characterized by intrinsic viscosity values in the range 0.1-0.2dl/g. These data are indicative of fairly high molecular weights[7] in keeping with the typical macromolecular behavior exhibited by bipolyesters in both solution and melt phase. No clear indication is yet available on the structural isomerism[8] connected with the relative orientation placements of non-symmetric GE residues. Analogously, no information is known of the sequencing of enantiomeric units in bipolycondensates of racemic or not optically active pure GE diols.

Samples **P1**, **P2**, and **P4** containing the optically active glycerols exhibited a molar optical rotation two orders of magnitude higher than that of the corresponding diols. This finding indicates that a fairly high contribution to the polymer optical rotation derives from the mesogenic units assembled in a dissymmetric environment. Correspondingly, the circular dichroism spectra show in connection with the $\pi \rightarrow \pi^*$ electronic transition of the aromatic moiety[9,10] an intense dichroic absorption with a positive band at about 260nm and a negative band at about 230nm of comparable rotatory strength (Figure 1). The reported bands closely resemble the typical exciton splitting profile,[11] similar to that already reported for analogous bipolyesters of (S)-1,2-propanediol dimer and trimer.[2] On the contrary, no appreciable signal was detected in the CD spectra of the low molecular weight model compound bis[4-(2-methylbutoxycarbonylphenyl)] terephthalate.[2] It may be assumed, therefore, that the mesogenic aromatic units retain even in dilute solution a prevailing chiral conformation which allows for significant intramolecular interactions.

All the samples are solid at room temperature and semicrystalline at the X-ray analysis with well defined enthalpy of melting ($\Delta H_m = 0.2-1.1 cal/g$). The melting temperature values were rather low (100-150°C) in comparison to the values observed for the bipolyester obtained from the same mesogenic unit and (S)-1,2-propanediol ($T_m = 334°C$).[1] In all cases, broad endothermic peaks were observed 50-100°C above T_m and attributed to the mesophase isotropization. Within the limits of

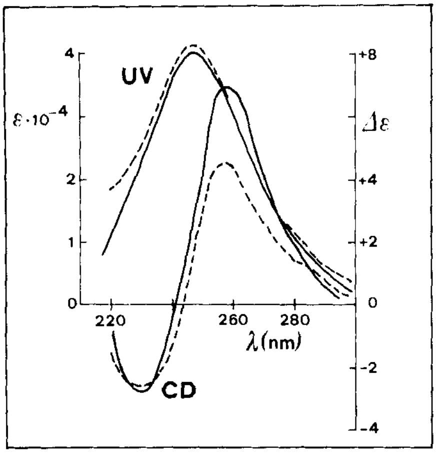


FIGURE 1. UV and CD spectra in dioxane of: (——) sample **P1**; (---) sample **P2**.

of the relatively low number of runs and of the dishomogeneity of the stereochemical properties of the bipolycondensates prepared, one may point out the odd-even trend of T_m and T_i with increasing length of the side substituents. This behavior is frequently observed in LC polyesters constituted of flexible spacers of different length[12-14] and interestingly seems to apply even to LC polymers containing flexible side groups[15] able to assume local zig-zag planar conformations with different symmetry parameters.

Above T_m, each polymer gave rise to melts which retained optical anisotropy at the polarizing microscope obervation, within more or less broad ranges of temperature (50-100°C), depending on the chemical structure of the GE residue. It must be stressed that, in spite of the size and complexity of the pendant group in the repeat unit, a surprisingly wide persistence of the mesomorphic state occurs in all cases.

The maximum value of T_i is detected in sample **P1** and is by far lower than the value reported for analogous bipolycondensates of HTH mesogenic core with 1,2-propanediol either racemic or of high optical purity.[1] The replacement of a hydrogen atom of the methyl group in HTH/(S)-1,2-propanediol by long, flexible substituents affects in a very significant way the onset, stability, and nature of the mesophase. All the optically active bipolyesters were, in fact, characterized by a common feature of giving rise to twisted nematic phases. In sample **P1** a smectic A phase was additionally evidenced between 135° and 143°C. A detailed investigation of all the samples by X-ray analysis is in progress. In samples **P1** and **P2** containing the methylated and benzylated glycerol residue, respectively, the cholesteric mesophase spontaneously assumed typical planar textures with oily streaks (Figure 2) that gave rise to selective reflection of visible light.[16] In particular, sample **P1**, when observed with incident polarized light, was orange at 190°C, yellow at 200°C, green at 210°C, blue at 220°C, and violet at 230°C. This variation of color with increasing temperature denotes a shrinkage of the cholesteric pitch analogous to what is commonly reported in low molecular mass cholesterogens.[17] A similar thermochromic behavior has been described for cholesteric polysiloxanes containing mesogenic side groups.[18] Sample **P4** showed a strong tendency to develop a non-planar rexture with a sort of focal-conics (Figure 3). However, on cooling the mesophase displayed a light blue reflection at 95-100°C which by mechanical

FIGURE 2. Cholesteric planar texture with oily streaks of sample **P1** at 220°C. (See Color Plate VII)

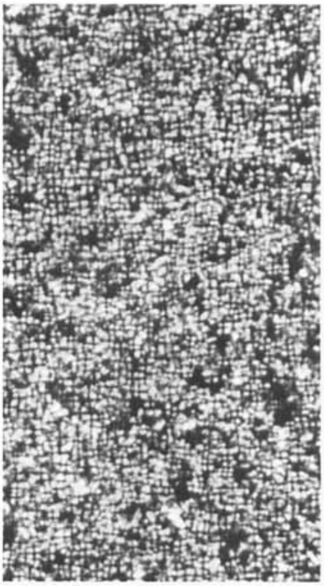


FIGURE 3. Cholesteric non-planar texture with focal conics of sample **P4** at 110°C . (See Color Plate VIII)

shearing of the cover slip turned to blue-violet. We must also notice that in sample **P2** the iridescent behavior was enantiotropic in heating-cooling cycles, whereas in sample **P1** the reversibility with temperature of the reflective properties was inhibited by hysteresis phenomena.[19] Bipolyesters **P3** and **P5** containing racemic glycerol residues gave nematic phases, as expected. Threaded textures with homeotropic regions typically appeared.

CONCLUDING REMARKS

The results reported are to be considered for the breakthrough in the synthetic approach to polymeric liquid crystals with peculiar optical responses in the melt phase. The great potential of the synthetic procedure involving simple and multiform chemical variations realizable on optically active isopropylidene glycerol opens routes to possible exploitations of structurally tailored chiral liquid crystal polyesters.

Substitution in the side chain of a chiral glycol unit produces marked effects on the thermotropic properties of bipolycondensates. Cholesteric structures can be obtained at reasonably low temperatures and are characterized by enantiotropism of selective reflection of visible light in rather narrow temperature ranges.

The chiroptical properties in dilute solution of the optically active bipolycondensates suggest the persistence of a conformational environment of high homogeneity and able to originate dipolar intramolecular interactions among mesogenic segments.

ACKNOWLEDGMENT

This work was carried out with the financial support of Ministero Pubblica Istruzione of Italy (Fondi 40%).

REFERENCES

1. E.Chiellini, G.Galli, C.Malanga, and N.Spassky, Polym.Bull., 9, 336 (1983).
2. E.Chiellini and G.Galli, Makromol.Chem., Rapid Commun., 4, 285 (1983).

3. E.Chiellini, G.Galli, R.W.Lenz, and C.K.Ober, in Polymer Blends, edited by M.Kryszewski and E.Martuscelli (Plenum Press, New York, in press).
4. E.Chiellini and G.Galli, in Recent Advances in Liquid Crystal Polymers, edited by L.L.Chapoy (Applied Science Publisher, London, in press).
5. J.LeCocq and C.E.Ballou, Biochemistry, 3, 976 (1964).
6. G.Galli, E.Chiellini, C.K.Ober, and R.W.Lenz, Makromol. Chem., 183, 2693 (1982).
7. C.Noel, J.Billard, L.Bosio, C.Friedrich, F.Laupetre, and C.Strazielle, Polymer, 25, 263 (1984).
8. U.W.Suter and P.Pino, Macromolecules, in press.
9. G.Cilento, J.Am.Chem.Soc., 74, 3748 (1953).
10. R.Martin and G.Coton, Bull.Soc.Chim.Fr., 1442 (1973).
11. W.Hug, F.Ciardelli, and I.Tinoco, Jr., J.Am.Chem.Soc., 86, 80 (1974).
12. A.C.Griffin and S.J.Havens, J.Polym.Sci., Polym.Phys.Ed., 19, 951 (1981).
13. A.Roviello and A.Sirigu, Makromol.Chem., 183, 895 (1982).
14. A.Blumstein and O.Thomas, Macromolecules, 15, 1264 (1982).
15. Q.F.Zhou and R.W.Lenz, J.Polym.Sci., Polym.Chem.Ed., 21, 3313 (1983).
16. H.L.DeVries, Acta Crystall., 4, 219 (1951).
17. P.N.Keating, Mol.Cryst.Liq.Cryst., 8, 315 (1969).
18. H.Finkelmann and G.Rehage, Makroml.Chem., Rapid Commun., 1, 733 (1980).
19. G.D.Dixon and L.C.Scala, Mol.Cryst.Liq.Cryst., 10, 317 (1970).

[†] Paper presented at the 4th European Winter Conference on Liquid Crystals of Low Dimensional Order, Bovec (Yugoslavia), March 26-30, 1984.