Main-Chain Cholesteric Liquid Crystalline Polyesters with Chiral Pendant Groups. 1. Model Compounds and Polyesters Containing a Chiral Substituted Hydroquinone

Koichi Fujishiro[†] **and Robert W. Lenz***

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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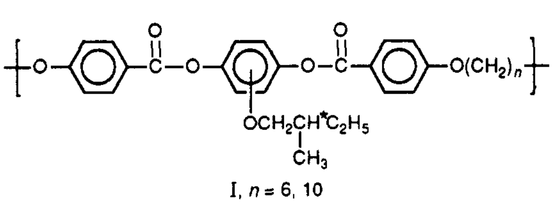
ABSTRACT: For the design and preparation of new cholesteric liquid crystalline polyesters (ChLCPs) from 2-[(*S*)-(+)-2-methyl-1-butoxy]hydroquinone as the chiral monomer, an appropriate model compound and the two LCPs containing triad ester mesogenic units and flexible spacers were prepared and characterized by wide-angle X-ray diffraction (WAXD), thermal, and optical methods. The model compound exhibited a monotropic cholesteric liquid crystalline mesophase, while the polymers had enantiotropic liquid crystalline mesophases, but the liquid crystalline temperature ranges were relatively narrow. In addition, the annealing process enhanced the degree of crystallinity and T_m of the crystalline phase; then the enantiotropic mesophase of the polymers was converted into the monotropic mesophase. The textures of both polymers in the liquid crystalline state did not develop to those expected for a cholesteric phase. WAXD indicated that the patterns for both crystalline polymers could be indexed in an orthorhombic unit cell.

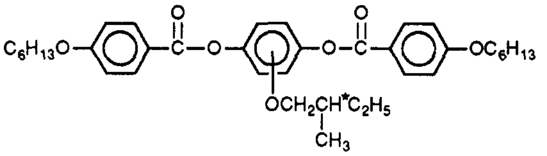
Introduction

A wide variety of thermotropic cholesteric liquid crystalline polymers (ChLCPs) have been prepared and then characterized for their unique optical properties, including selective reflection of light, thermochromism, and circular dichroism, for a variety of applications.[1] ChLCPs can be classified according to their molecular structures, that is, principally as either main-chain ChLCPs or side-chain ChLCPs,[2] but some combined types of main- and side-chain polymers have been prepared,[3] and mixtures of achiral nematic LCPs with optically active low molar mass liquid crystals have also been studied extensively.[4] Of these various types, the main-chain ChLCPs in which the backbone contains the mesogenic units have been studied to a lesser extent than the others because only a limited number of difunctional chiral monomers, such as (*R*)-3-methyladipic acid, have been available,[5] and the synthesis of such monomers can be quite difficult.[6-8] In this study, we have investigated a new type of main-chain ChLCP, in which the backbone contained the mesogenic group unit, which had a chiral substituent as shown below:



I, *n* = 6, 10

A low molar mass triad ester based on the same chiral substituted hydroquinone, II, was also prepared and characterized as a model compound for comparison with the liquid crystalline behavior of the polymers of the same type of mesogenic molecular structure to evaluate the cholesteric properties of the latter as they are influenced by the rigidity of the polymer backbones.



II

Experimental Section

Syntheses. 2-[(*S*)-(+)-Methyl-1-butoxy]hydroquinone (III), the chiral monomer, was synthesized in three steps according to the reactions shown in Scheme I.[9] Because (*S*)-(−)-2-methyl-1-butanol (IV), which was purchased from Aldrich Chemical Co. and contained 5 mol % of 3-methyl-1-butanol as an impurity, was used without purification, all of the chiral intermediates contained 3-methyl-1-butoxy-substituted compounds as impurities. The amounts of these impurities were estimated by ^{1}H NMR spectroscopy based on the integrated value of the α-methylene protons of the 2-methyl-1-butoxy and 3-methyl-1-butoxy groups.

(*S*)-(+)-2-Methylbutyl *p*-Toluenesulfonate (V).[10] In the first step, a mixture of 241 g of pyridine and 68.2 g of IV was placed in a 500-mL flask, which was cooled below 20 °C in an ice bath. To this solution was added 147.5 g of *p*-toluenesulfonyl chloride in small portions with stirring, and the reaction mixture was stirred for 3 h below 20 °C after the addition was completed. A large excess of cold dilute hydrochloric acid and ice was added after completion of the reaction, and the mixture was extracted three times with dichloromethane. The dichloromethane solution was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to afford 157 g of colorless liquid (yield 84%, purity 92 mol %). ^{1}H NMR ($CDCl_3$) δ = 0.82 (3 H, t, J = 7.0 Hz), 0.88 (3 H, d, J = 6.6 Hz), 1.2–1.8 (3 H, m), 2.45 (3 H, s), 3.8–4.0 (2 H, m), 7.35 (2 H, d, J = 8.0 Hz), 7.79 (2 H, d, J = 7.3 Hz). $[\alpha]^{20}_{D}$ = +5.7° (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49; S, 13.23. Found: C, 59.50; H, 7.38; S, 13.08.

3-[(*S*)-(+)-2-Methyl-1-butoxy]-4-hydroxybenzaldehyde (VI). In the second step, a solution of 15.2 g of 3,4-dihydroxybenzaldehyde in 180 mL of ethanol was added to 90 mL of 10% sodium hydroxide solution. After the solution was heated at 50 °C, 26.65 g of V was added dropwise to the solution. The mixture was stirred at 50 °C for 70 h, after which the solvent was removed by evaporation in vacuo, and the residue was dissolved in 200 mL of water and extracted with diethyl ether. The remaining aqueous solution was acidified with dilute hydrochloric acid and extracted with diethyl ether. The ether solution was washed with a saturated sodium bicarbonate solution and with water, successively, and then dried over anhydrous sodium sulfate. After the

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[†] Present address: Chemicals Research Laboratory, R&D Laboratories—1, Nippon Steel Corp., 1618 Ida, Nakahara-ku, Kawasaki 211, Japan.

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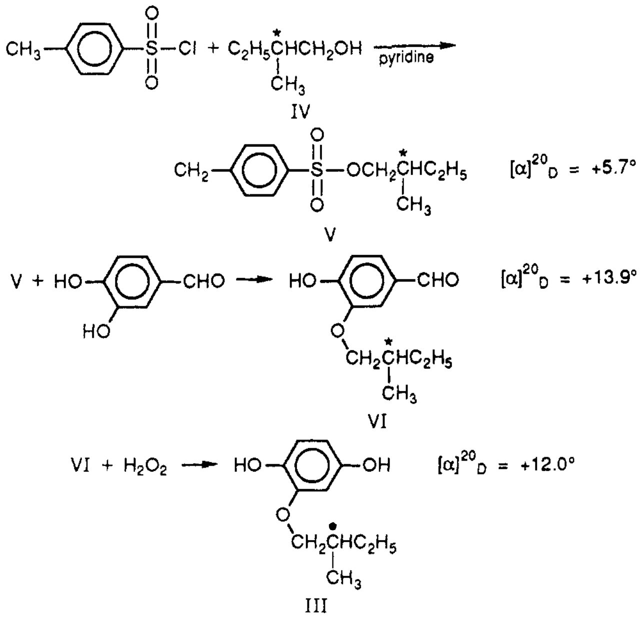
Scheme I



ether solution was evaporated in vacuo, 60 mL of a mixture of chloroform and petroleum ether (1:1 volume ratio) was added to the residue, the precipitate was removed by filtration, and the filtrate was concentrated and purified by column chromatography (silica gel, chloroform) to yield 5.5 g of yellow crystals (yield 24%, purity 96 mol %). Mp 51–53 °C. $[\alpha]^{20}{}_D$ = +13.9° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ = 0.97 (3 H, t, *J* = 7.4 Hz), 1.06 (3 H, d, *J* = 6.7 Hz), 1.2–2.0 (3 H, m), 3.8–4.0 (2 H, m), 6.24 (1 H, s), 7.05 (1 H, d, *J* = 8.1 Hz), 7.4–7.5 (2 H, m), 9.82 (1 H, s). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.25; H, 7.69. Found: C, 69.27; H, 7.62.

2-[(*S*)-(+)-2-Methyl-1-butoxy]hydroquinone (III). In the third step, 4.1 g of VI was dissolved in 27 mL of 1.5 N sodium hydroxide solution, and to this solution was added dropwise 2.30 g of a 30% hydrogen peroxide solution with stirring. The solution was stirred for 2 h, and the temperature of the solution was kept at less than 30 °C during the reaction. The reaction mixture was acidified with dilute hydrochloric acid and extracted three times with diethyl ether. The ether solution was washed with sodium metabisulfite solution and water, successively, and then dried over anhydrous sodium sulfate. After evaporation in vacuo, the residue was purified by column chromatography (silica gel, dichloromethane). After the eluent was evaporated, the residual solid was recrystallized with a mixture of hexane and chloroform (65:35 volume ratio) to afford 2.40 g of colorless crystals (yield 63%, purity 95 mol %). Mp 70–71 °C; $[a]^{20}{}_D$ = +12.0° (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 0.945 (3 H, t, *J* = 7.3 Hz), 1.01 (3 H, d, *J* = 6.7 Hz), 1.2–2.0 (3 H, m), 3.7–3.9 (2 H, m), 4.78 (1 H, s), 5.26 (1 H, s), 6.30 (1 H, dd, *J* = 8.6, 2.6 Hz), 6.43 (1 H, d, *J* = 2.6 Hz), 6.77 (1 H, d, *J* = 8.6 Hz). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.37; H, 8.16. Found: C, 67.34; H, 8.22.

The 4,4′-dichloroformyl-α,ω-diphenoxyalkane monomers were prepared according to a method previously described.[11]

Measurement of Optical Purity. ^1H NMR and ^{13}C NMR spectra were obtained for III in the presence of chiral shift reagents to attempt to determine its optical purity. Two shift reagents were used in this work: tris[(3-heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) (Eu(hfc)$_3$) (Aldrich Chemical Co.) and tris(*d,d*-dicamphorylmethanato)europium(III) (Eu(dcm)$_3$) (Alfa Products).[12] The racemic monomer, 2-[(±)-2-methyl-1-butoxy]hydroquinone (III′), was prepared as previously described. Both the optically active and the racemic mixtures were converted to the diacetate, IIIA and IIIA′, and to the trimethylsilyl ether, IIIB and IIIB′, by modification of the procedures previously described.[13,14]

1,4-Diacetoxy-2-[(±)-2-methyl-1-butoxy]benzene (IIIA′): ^1H NMR (C_6D_6/CCl_4 = 10/90 volume ratio) δ = 0.92 (3 H, t, *J* = 7.3 Hz), 0.97 (3 H, d, *J* = 6.8 Hz), 1.1–1.9 (3 H, m), 2.15 (6 H, s), 3.6–3.8 (2 H, m), 6.58 (1 H, dd, *J* = 2.3, 8.5 Hz), 6.62 (1 H, d, *J* = 2.3 Hz), 6.88 (1 H, dd, *J* = 2.1, 8.5 Hz). ^{13}C NMR (C_6D_6/CCl_4 = 10/90 volume ratio) δ = 11.7, 16.8, 20.5, 21.1, 26.3, 35.0, 73.2, 107.4, 113.1, 122.8, 137.9, 149.2, 151.3, 167.2, 167.7.

1,4-Bis(trimethylsiloxy)-2-[(±)-2-methyl-1-butoxy]benzene (III′): ^1H NMR (C_6D_6/CCl_4 = 10/90 volume ratio) δ = 0.20 (9 H, s), 0.24 (9 H, s), 0.95 (3 H, t, *J* = 7.4 Hz), 1.03 (3 H, d, *J* = 6.7 Hz), 1.2–1.9 (3 H, m), 3.6–3.8 (2 H, m), 6.18 (1 H, dd, *J* = 2.9, 8.5 Hz), 6.29 (1 H, d, *J* = 2.8 Hz), 6.56 (1 H, d, *J* = 8.4 Hz).

Model Compound: 1,4-Bis[(4-(hexyloxy)benzoyl)oxy]-2-[(*S*)-2-methyl-1-butoxy]benzene (II). To a solution of 0.060 g of 2-[(*S*)-2-methyl-1-butoxy]hydroquinone (III) in 2 mL of dry dichloromethane was added 0.12 g of triethylamine, after which a solution of 0.148 g of 4-(hexyloxy)benzoyl chloride in 3 mL of dry dichloromethane was added dropwise with stirring. The combined solution was heated at 40 °C for 3 h, after which the reaction mixture was purified by column chromatography (silica gel, dichloromethane). The fractions containing the desired product were collected and evaporated in vacuo to yield 0.058 g of colorless crystals of II (yield 32%). Mp 78–80 °C. $[\alpha]^{25}{}_D$ = +3.0° (*c* 3.7, $CHCl_3$). ^1H NMR ($CDCl_3$) δ = 0.7–1.0 (12 H, m), 1.0–1.6 (14 H, m), 1.8–2.0 (5 H, m), 3.7–3.9 (2 H, m), 4.05 (4 H, t, *J* = 6.4 Hz), 6.8–6.9 (2 H, m), 6.97 (4 H, d, *J* = 8.6 Hz), 7.18 (1 H, dd, *J* = 8.4, 2.0 Hz), 8.15 (4 H, d, *J* = 8.3 Hz). Anal. Calcd for $C_{37}H_{48}O_7$: C, 73.49; H, 7.94. Found: C, 73.65; H, 7.86.

Polymer Synthesis. Both polymers were prepared by the solution polymerization of III with the respective 4,4′-dichloroformyl-α,ω-diphenoxyalkane monomer. In 10 mL of dry dichloromethane (distilled over phosphorus pentoxide) was dissolved 0.50 g of III with 0.7 mL of triethylamine (distilled over potassium hydroxide), and a solution of an equimolar amount of 4,4′-dichloroformyl-α,ω-diphenoxyalkane in 20 mL of dry dichloromethane was added dropwise. The reaction mixture was stirred at room temperture for 24 h and at reflux temperature for 24 h. The reaction mixture remained homogeneous throughout the entire polymerization. The polymer solution was poured into 120 mL of methanol, and the precipitated polymer was washed three times with methanol and dried at 70 °C in vacuo. The yield and the characterization data for the two polymers are collected in Table I.

Characterization of Monomer, Model Compound, and Polymers. ^1H NMR spectra were obtained with a Varian XL-200 spectrometer on solutions in deuterated chloroform ($CDCl_3$). The specific rotations of the optically active compounds in chloroform were measured with an Autopol polarimeter (Rudolph Research Co.). The inherent viscosities of the polymer solutions were measured in *p*-chlorophenyl at 45.3 °C at a concentration of 0.5 g/dL using a Ubbelohde 150 type capillary viscometer. The molecular weights of the polymers were also determined on a Waters GPC instrument with a refractive index detector and "Ultrastyragel Linear" and "Ultrastyragel 500 Å" columns using chloroform as the eluent and polystyrene standards for calibration. Liquid crystalline transitions were characterized by differential scanning calorimetry (DSC), by use of a polarized light microscope, and by WAXD. Thermal analyses of the model compound and the polymers were obtained on a Perkin-Elmer DSC-2 at a scanning rate of 10 and 20 °C/min, respectively. The peak maxima of the phase transitions were recorded from the second heating and cooling cycles for each sample. After the third cycles the thermograms did not change. Textures were observed with a Leitz Orthous optical microscope equipped with a Mettler FP-2 hot stage. X-ray diffraction patterns were obtained with a Laue camera using Ni-filtered Cu radiation on both oriented and unoriented samples on a hot stage. Patterns were obtained for the unoriented samples at different temperatures after annealing for 3 h at the same temperature on the second heating cycle. Oriented fibers were drawn at 5–10 °C above the isotropic temperature (T_i) and annealed between the melting temperature (T_m) and T_i for 3 days under an argon atmosphere.

Results and Discussion

Attempts were made to determine the optical purity of monomer III by use of shift reagents in a mixture of deuterated benzene and carbon tetrachloride (10/90 volume ratio) based on 300-MHz ^1H NMR spectra recorded at

Table I
Yields and Properties of Polymers I

polymer	yield, %	$[\eta]$, dL/g	mol wt $\bar{M}_n$	mol wt $\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$[\alpha]^{20}_D$, deg (c = 0.1, $CHCl_3$)	^1H NMR ($CDCl_3$, 200 MHz)
I-10	80	0.51	11 000	34 000	3.1	+4.1	0.7–0.9 (6 H, m), 1.3–2.0 (19 H, m), 3.7–3.9 (2 H, m), 4.05 (4 H, t, J = 6.3 Hz), 6.80 (1 H, d, J = 8.5 Hz), 6.86 (1 H, s), 6.98 (4 H, d, J = 8.6 Hz), 7.19 (1 H, d, J = 8.5 Hz), 8.14 (1 H, d, J = 8.5 Hz)
I-6	94	0.58	18 000	48 000	2.7	+4.3	0.7–0.9 (6 H, m), 1.0–1.8 (11 H, m), 3.7–3.9 (2 H, m), 4.08 (4 H, t, J = 6.3 Hz), 6.81 (1 H, d, J = 8.5 Hz), 6.87 (1 H, s), 6.98 (4 H, d, J = 7.6 Hz), 7.17 (1 H, d, J = 8.5 Hz), 8.15 (4 H, d, J = 8.5 Hz)

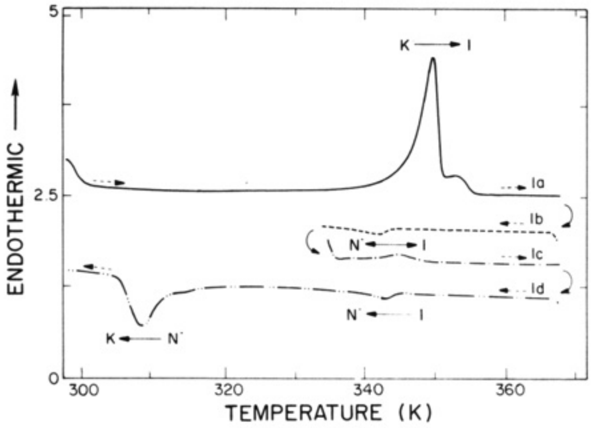


Figure 1. DSC thermograms of model compound II (scanning rate, 10 °C/min): (a) the second heating; (b) the second cooling up to 62 °C; (c) reheating over the isotropization transition; (d) cooling up to 25 °C.

room temperature. The following combinations were evaluated for the racemic monomer and its diacetate (IIIA′) and bis(trimethylsilyl) (IIIB′) derivatives using several different ratios of IIIA′ and IIIB′ to the shift reagent: (1) IIIA′ + Eu(hfc)$_3$, (2) IIIA′ + Eu(dcm)$_3$, (3) IIIB′ + Eu(hfc)$_3$, (4) IIIB′ + Eu(dcm)$_3$. Both the methyl proton peaks of the acetoxy groups for IIIA′ and the methyl proton peaks of the methylbutoxy groups for IIIA′ and IIIB′ were shifted and split into distinct peaks in the presence of the shift reagent, but no combination of the two gave an observable separation of the resonance peaks of the optical isomers, although a broadening of the peaks occurred at combinations up to equal molar amounts for both IIIA′ and IIIB′. Similarly, ^{13}C NMR spectra of IIIA′ + Eu(hfc)$_3$ combinations up to a ratio of 0.82 mol/mol did not show separate peaks for the optical isomers. Although the NMR spectra could not be used to determine the optical purity of the monomer III, the specific rotation $[\alpha]^{20}_D$ of III of +12.0° (c 1.0) indicated that the optical purity of the starting chiral alcohol, IV, was retained through the synthesis of III.

Model Compound. The model compound, II, was characterized, and its properties were compared to those of the polymers. The DSC thermograms and polarized light photomicrographs of II are shown in Figures 1 and 2, respectively. The heating cycle thermogram (1a) contained two endotherms as seen in Figure 1, and the enthalpy ratio of these two endotherms changed with thermal history. The cooling cycle thermogram (1d) contained both a small exotherm (ΔH = 0.4 kcal/mol) and a broad exotherm. When the sample was reheated before the second exotherm appeared (1b), a new endotherm was observed (1c).

A sample on the hot stage of the polarizing microscope, when heated above the melting temperature of the needle-like crystals (Figure 2a), did not show any birefringence. On cooling to 76 °C from the isotropic state, birefringent droplets appeared in the isotropic phase and formed a planar texture as shown in Figure 2b. On continued cooling to 50 °C, a spherulitic morphology formed (Figure 2c), which finally changed again to the texture shown in Figure 2a. The transition between the planar texture and the isotropic melt was reversible if the sample was reheated before spherulite formation was observed.

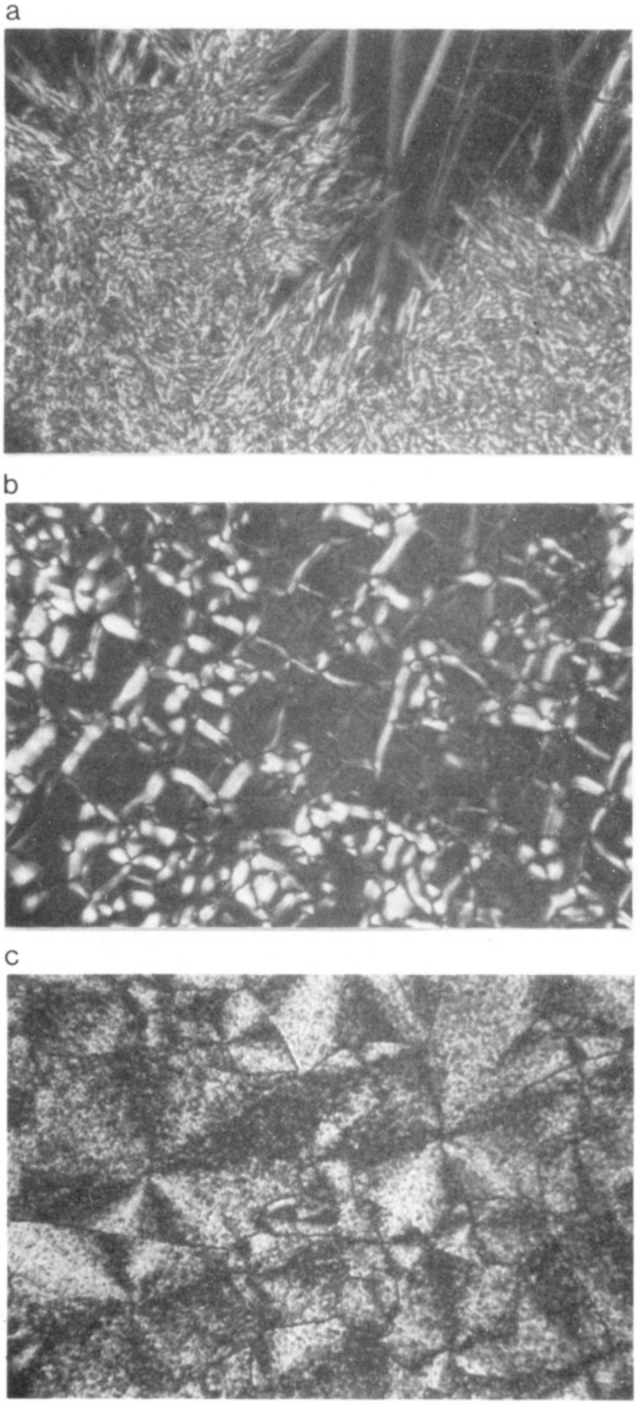


Figure 2. Photomicrographs of model compound II: (a) 77 °C on heating; (b) 76 °C on cooling; (c) 50 °C on cooling.

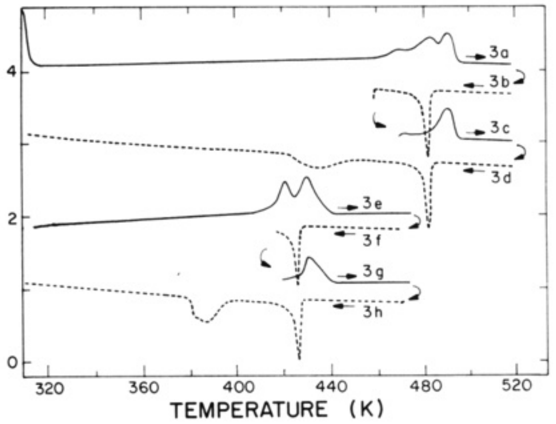


Figure 3. DSC thermograms of polymers I-6 (a–d) and I-10 (e–h) (scanning rate, 20 °C/min).

Table II
Thermal Transitions[a] and Thermodynamic Properties[b] of Polymers I

poly-mer	heating cycle T_m	T_i	cooling cycle[c] T_c	T_d	ΔH_m, kcal/mru	ΔH_i, kcal/mru	ΔS_i, cal/(mru·K)
I-10	148	158	112	151	1.6	1.3	3.1
I-6	196, 211	219	161	209	1.3	1.4	3.0

[a] T_m = crystalline to liquid crystalline transition; T_i = isotropization transition; T_c = recrystallization transition; T_d = liquid crystalline to isotropic transition. [b] Determined from the second cooling cycle. [c] The scanning rate was 20 °C/min.

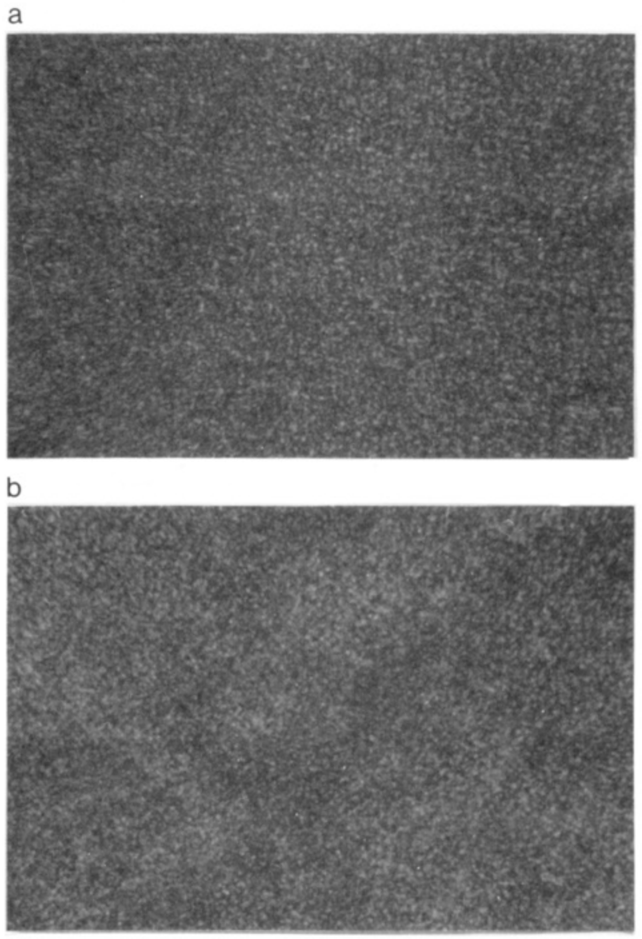


Figure 4. Photomicrographs of (a) polymer I-10 at 155 °C and (b) polymer I-6 at 215 °C without annealing.

These observations indicate the model compound, II, showed a monotropic cholesteric liquid crystal behavior and exhibited the cholesteric liquid crystalline phase only during the cooling cycle before crystallization occurred.

Polymers. The two polymers prepared were similar in solubility characteristics to those of an earlier series prepared in this laboratory, which contained alkoxy substituents on the mesogens and which were soluble in many common organic solvents. For this reason it was possible to characterize their properties in solution, including optical rotation, NMR spectra, and molecular weight. The data obtained are collected in Table I.

Both polymers had relatively high molecular weights with inherent viscosities greater than 0.5 dL/g and M_n values greater than 10 000, which were generally higher than those of previously reported[6–8] main-chain ChLCPs ($[\eta] < 0.25$ dL/g) presumably because of their solubilities in the reaction solvent. Both polymers were optically active with specific rotations, $[\alpha]^{20}{}_D$, of from +4 to +5° (c 0.1), which are generally lower than those of previously reported ChLCPs with chiral centers in the backbones but similar to those of side-chain ChLCPs in which the chiral centers are present as terminal groups in the side-chain mesogens.[3]

DSC thermograms and transition temperature data for the two polymers with different spacer lengths (I, $n = 6$, 10) are shown in Figure 3 and Table II, respectively. Polymer I-10 with $n = 10$ showed two endotherms and two exotherms in the second heating and cooling cycles, respectively (Figure 3e,d). When the sample was reheated before the second exotherm appeared in the cooling cycle, an endotherm was observed at the same temperature as the last one in the second heating cycle as shown in Figure 3e–g. However, for polymer I-6 with $n = 6$, three endotherms and two exotherms are seen in heating and cooling cycles, respectively, as shown in Figure 3a,d. This polymer also exhibited the same endotherm as in the heating cycle when it was reheated before the second exotherm appeared on the cooling cycle, as shown in Figure 3c.

Visual examination of the polymers on the hot stage of a polarizing microscope verified that the highest temperature endotherms corresponded to the clearing or isotropization temperatures (T_i) and lower temperature transitions to melting transitions (T_m). Figure 4 shows the photomicrographs of polymers obtained between T_m and T_i without annealing on a polarizing microscope. Both polymers showed the same fine schlieren texture, which did not develop during 48 h of annealing. Besides, no texture change was observed between those endotherms. The two lower temperature endotherms of polymer I-6 in Figure 3a must likely represent melting followed by recrystallizing and remelting. Only one exotherm corresponding to recrystallization appeared on cooling, so the polymers in this series exhibited enantiotropic liquid crystalline behavior in both the heating and cooling cycles.

Thermal transition behaviors of both polymers were influenced dramatically by annealing conditions as shown in Figure 5 for polymer I-6 and Figure 6 for polymer I-10. All of the thermograms were taken after the polymers were cooled below their isotropization temperatures at a cooling rate of 20 °C/min, then reheated to a given temperature, annealed at that temperature for 3 h, and cooled to 47 °C at a cooling rate of 20 °C/min. The melting temperatures and the enthalpies of melting after the annealing were significantly increased so that the thermogram for polymer I-6 in Figure 5c indicated a T_m of 220 °C, which was almost the same as the T_i of the nonannealed sample (Figure 5a), while the thermogram of polymer I-10 (Figure 6c) showed a T_m of 165 °C, which is above the T_i of the

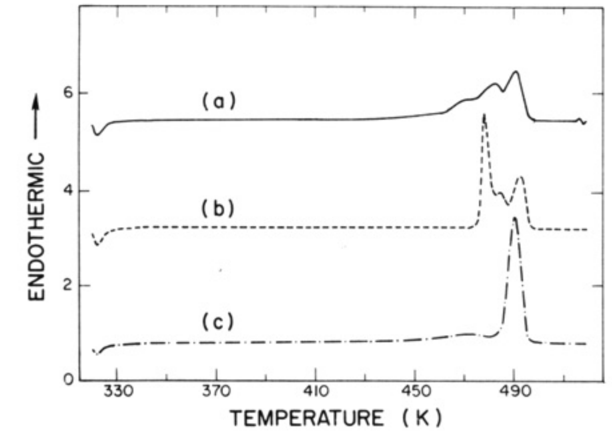


Figure 5. DSC thermograms of polymer I-6 annealed at different temperatures: (a) without annealing; (b) at 190 °C; (c) at 205 °C (scanning rate, 20 °C/min.).

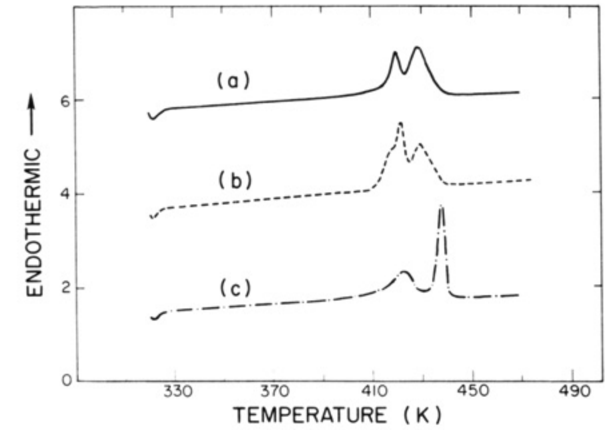


Figure 6. DSC thermograms of polymer I-10 annealed at different temperatures: (a) without annealing; (b) at 127 °C; (c) at 152 °C (scanning rate, 20 °C).

nonannealed specimen in Figure 6a. That is, the liquid crystalline properties of both polymers were converted from the enantiotropic to the monotropic mesophases by annealing.

The model compound and the polymers with the chiral substituent, the 2-methyl-1-butoxy group, all had narrow liquid crystalline temperature ranges and showed monotropic mesophases, while an earlier series of similar polymers prepared in this laboratory which contained alkoxy substituents exhibited very wide temperature ranges and enantiotropic liquid crystalline phases.[15] In addition, the present polymer series showed a large dependency of thermal behavior on the annealing process. That is, the crystallization is kinetically controlled, and the higher T_m is observed for the larger crystals which form during annealing, while the mesophase is mostly thermodynamically controlled; then the bulky chiral group provides a slow kinetic process. These properties of the present series may result from the steric requirements of the branched alkyl group in the 2-methyl-1-butoxy substituent. Weissflog and Demus reported that a compound similar to II based on 2,4-dihydroxybenzoate also formed a monotropic cholesteric liquid crystal phase.[16]

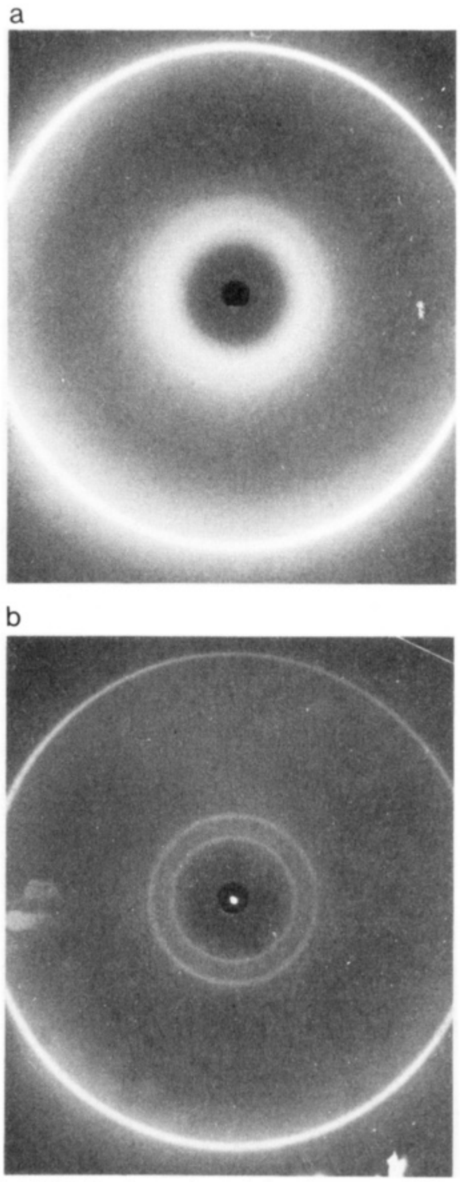


Figure 7. WAXD of unoriented specimens at different temperatures: (a) polymer I-10 at 155 °C; (b) polymer I-6 at 215 °C.

Table III
WAXD Data (Å) for Polymers I[a]

polymer I-10			polymer I-6		
unoriented		oriented annealed at 155 °C measd at 25 °C	unoriented		oriented annealed at 205 °C measd at 25 °C
measd at 80 °C	measd at 155 °C		measd at 80 °C	measd at 215 °C	
4.40	4.48	4.38 (E)	4.43	4.53	4.39 (E)
			6.10	6.30	6.13 (E)
			6.75	6.93	6.70 (E)
11.5	11.4	11.6 (E)	12.6	13.3	12.3 (E)
14.8	14.8	14.8 (E)	16.9	17.3	16.9 (E)
		17.9 (E)			
		10.1 (M)			8.11 (M)
		7.53 (M)			6.13 (M)
		6.09 (M)			4.88 (M)
		5.04 (M)			4.06 (M)

[a] M = meridian; E = equator.

Wide-angle X-ray diffraction (WAXD) studies were carried out for the two polymers at different temperatures. The WAXD patterns of unoriented specimens of both polymers indicated that some crystals still remained up to T_i as shown in Figure 7 and Table III. That is, the patterns of I-10 showed one sharp outer ring at 4.40 Å and two somewhat diffuse inner rings at 11.5 and 14.8 Å at 80 °C, and the two inner rings became more diffuse at 155 °C as seen in Figure 7a. In contrast, the patterns of polymer I-6 exhibited one sharp outer ring at 4.43 Å, two sharp inner rings at 12.6 and 16.9 Å, and two weak middle inner rings at 6.10 and 6.75 Å at 80 °C, but all of the diffraction rings were still sharp at 215 °C as shown in Figure 7b. These WAXD data indicate that the multiple

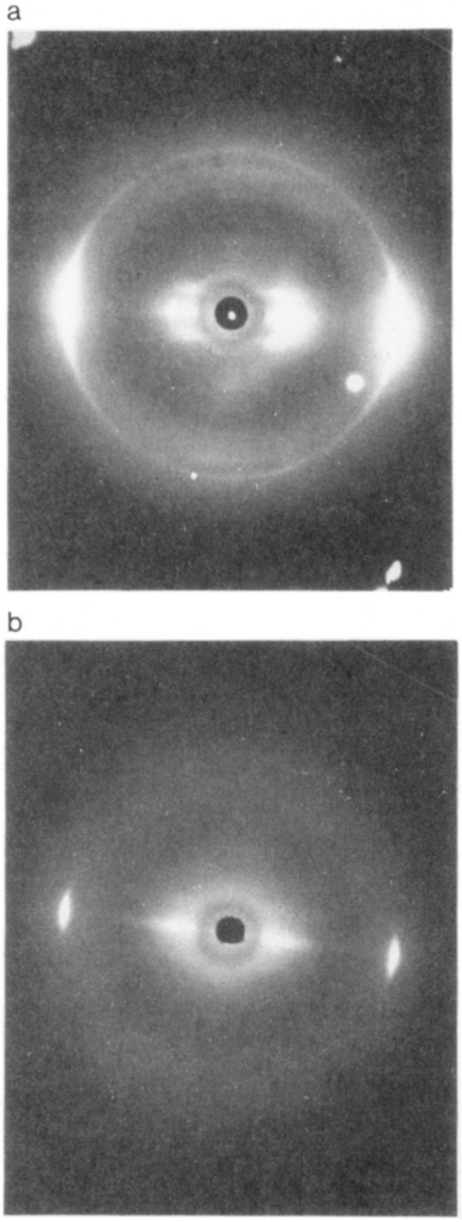


Figure 8. WAXD of oriented speciments in the crystalline state: (a) polymer I-10; (b) polymer I-6.

melting endotherms in the DSC thermograms shown in Figure 3 came from the same crystalline form and that the annealing process enhanced the degree of crystallinity and T_m of the crystalline phase as expected.

To obtain detailed information on molecular packing of the polymers in the solid state, oriented samples were prepared for WAXD studies, but it was not possible to prepare highly oriented fibers between T_m and T_i because the polymer melts were two viscous for drawing into fibers. However, fibers could be drawn at 5–10 °C above T_i, and these were annealed between T_m and T_i for 3 days before the WAXD patterns were obtained. The results of this study are shown in Figure 8 and Table III. All of the spacings for both polymers which had been observed in the unoriented samples appeared on the equator, and, additionally, weak discrete layer lines appeared on the meridian.

On the basis of the spacings of the meridian, the effective lengths of the repeating unit parallel to the polymer main chain were calculated to be 30.3 and 24.3 for polymer I-10 and polymer I-6, respectively, as determined from the 003 to 006 spacings. These first-order spacings compared well to the calculated values of 29.6 Å of polymer I-10 and 24.6 Å of polymer I-6 for the extended molecules, while the outer diffraction spacings of 4.4–4.5 Å on the equator presumably corresponded to the packing of mesogenic groups. The other spacings on the equator, which were not influenced as much by the presence of the flexible spacer, may come from crystallization of the mesogenic units with the chiral substituents in the direction perpendicular to the chain axis.

The crystalline patterns of both polymers can be indexed as orthorhombic crystals. In contrast, Atkins and coworkers reported that a similar series of polymers with long alkyl substituents could be indexed on a triclinic unit cell.[17–18] In addition, other thermotropic polyesters with azoxybenzene mesogenic units and flexible spacers were also considered to have triclinic crystals.[5,19] These polymers had wider temperature ranges for the liquid crystalline phases than the present chiral polymers. In the present polymer the chiral substituents are presumably fully extended and enhance the formn of orthorhombic crystals, which exhibited narrow liquid crystalline temperature ranges because of the steric requirements of the branched alkyl groups.

Conclusion

The model compound exhibited a monotropic cholesteric liquid crystalline mesophase, while the polymers had enantiotropic liquid crystalline mesophases, but the liquid crystalline temperature ranges were relatively narrow. In addition, the annealing process enhanced the degree of crystallinity and T_m of the crystalline phase; then the enantiotropic mesophase was converted into the monotropic mesophase. The textures of both polymers in the liquid crystalline state did not develop to those expected for a cholesteric phase. WAXD indicated that the patterns for both crystalline polymers could be indexed in an orthorhombic unit cell.

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Registry No. I (n = 6) (copolymer), 137175-30-5; I (n = 6) (SRU), 137393-10-3; I (n = 10) (copolymer), 137175-31-6; I (n = 10) (SRU), 137393-11-4; III, 137175-23-6; IV, 1565-80-6; V, 38261-81-3; VI, 137203-85-1; TsCl, 98-59-9; H_2O_2, 7722-84-1; $H_3C(CH_2)_5OC_6H_4$-p-C(O)Cl, 39649-71-3; 3,4-dihydroxybenzaldehyde, 139-85-5.