

Combined Type Liquid Crystalline Poly(oxy-1,4-phenyleneoxyterephthaloyl)s Bearing Cholesterol Pendants Attached through Polymethylene Spacers

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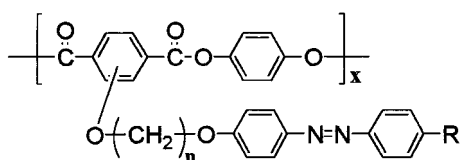
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ABSTRACT: A series of combined type thermotropic liquid crystalline (LC) poly(oxy-1,4-phenyleneoxyterephthaloyl)s bearing pendant cholesterol moieties attached to the backbone through oxyalkyleneoxy groups (hexamethylene, octamethylene, decamethylene, and dodecamethylene) of varying length, have been synthesized anew. And their LC properties and, especially, the dependence of mesophase morphology on the spacer length were studied by differential scanning calorimetry (DSC), optical microscopy, and small (SAXD)- and wide-angle X-ray diffractometry (WAXD). All the polymers were found to be amorphous, but thermotropic. And they formed layered morphologies in their mesophase when the spacer group is long. According to SAXD analysis the layered structure becomes better defined as the length of spacers increases. They exhibit two thermal transitions before isotropization. The lower temperature occurs between 34 and 56 °C, and the high-temperature ones between 94 and 156 °C, both of which decrease with increasing the length of the spacers.

Introduction

Combined type liquid crystalline polymers (LCPs)¹ have been investigated least among various types of thermotropic LCPs, although there are many structural variables one can change to control the morphology of their mesophases. The main chain in the combined type LCPs can be either of rigid nature without containing any flexible spacer^{2–6} or of nonrigid character containing flexible spacers.^{7–12} The structures of the main chain and the pendant, the presence or nonexistence and structures of spacers either in backbone or in the side group or in both, and regioregularity in the placement of the side groups are some of the more important structural variables involved in governing the LC properties of the combined type LCPs.

Especially, relative orientation of backbone and the side group pendants should profoundly depend on interactions between the two structural elements.^{9,10,13–17} Earlier we reported synthesis and LC properties of a series of combined type thermotropic LCPs consisting of the poly(*p*-phenylene terephthalate) backbone and the azobenzene mesogenic structures that are attached to the backbone through oxyoligoalkyleneoxy spacers of varying length:^{3–5}



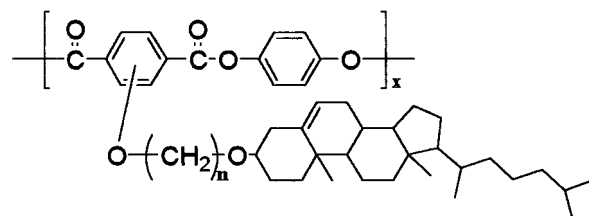
R : *n*-Bu *n*=3–6 and 10^{3,5}

: Ph *n*=5–10 and 12⁴

All the polymers formed the nematic phase in melt,

which implies that the pendant groups are most probably directed more or less parallel with the main chain. In other words, the side mesogenic groups are not oriented perpendicular to the backbone.

In the present investigation, we replaced the azobenzene side-group mesogenic unit with the nonpolar cholesterol group, which is expected to reduce the attractive interactions between the backbone and the pendant.



CHOL-*n* (*n*=6, 8, 10 and 12)

This article describes synthesis, thermal transition properties, thermotropic liquid crystallinity, and morphology in mesophase of the polymers, CHOL-*n*, with *n* being 6, 8, 10, and 12. The polymers were characterized by measurement of solution viscosity and molecular weight, differential scanning calorimetry (DSC), wide-angle (WAXD) and small-angle X-ray diffractometry (SAXD) and by observing their optical textures on a polarizing microscope.

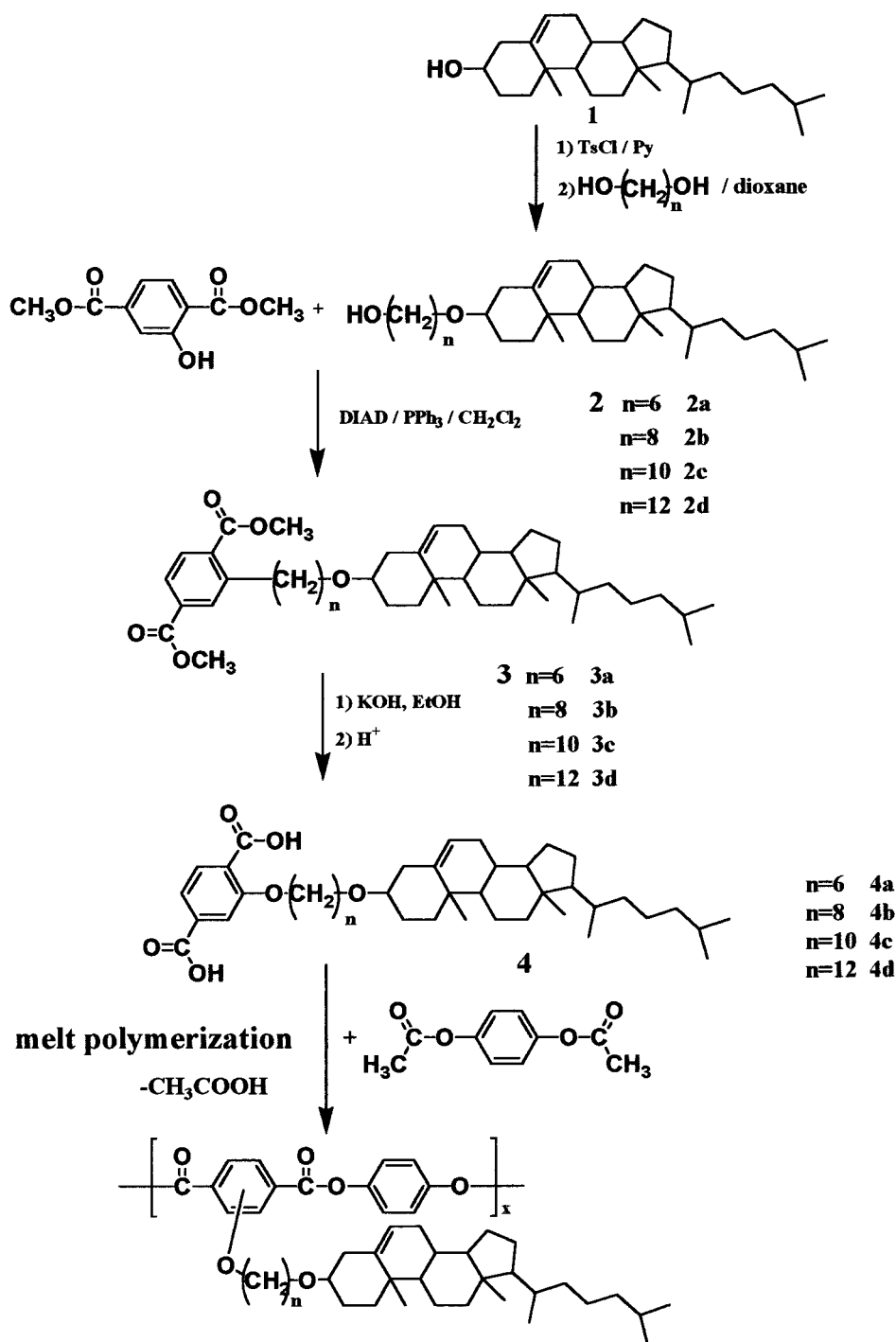
Experimental Section

The synthetic routes to the monomers and polymers are summarized in Scheme 1. Detailed synthetic procedures are described below. The numbers given to the compounds are same as those depicted in Scheme 1. Since the synthetic method is the same for the series, detailed synthetic descriptions are given only for the compound with the dodecamethylene (*n* = 12) spacer.

Synthesis of Monomers. 12-Cholesteryloxydodecanol, 2d. Cholesteryl tosylate (20.8 g, 38.5 mmol) prepared from

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Scheme 1. Synthetic Route to Polymers CHOL-*n*'sCHOL-*n* (*n*=6, 8, 10 and 12)

cholesterol (**1**) and tosyl chloride was refluxed for 24 h with 1,12-dodecanediol (39.0 g, 192.8 mmol) in 300 mL of dry dioxane.¹⁸ The insolubles were removed by filtration. The residue obtained after removing the dioxane solvent from the filtrate using a rotavap was redissolved in dichloromethane. The insoluble precipitate, mostly 1,12-dodecanediol, was removed by filtration. The dichloromethane solvent was removed by distillation, and the solid product was purified by recrystallization from acetone. The yield was 13.6 g (62%); mp 81 °C. ¹H NMR (CDCl₃, δ ppm): 0.67–2.40 (m, 63H, –CH₃, –CH(CH₃)–, –CH–, –CH₂–), 3.12 (m, 1H, –CHO–), 3.42–3.46 (t, 2H, –CH₂–O–CH–), 3.62–3.66 (t, 2H, –CH₂–OH), 5.33–5.35 (d, 1H, –C(CH₂)=CH–). IR (KBr, cm^{–1}): 3451 (O–H stretching), 2840 (aliphatic C–H stretching), 1095 (C–O

stretching). Anal. Calcd for C₃₉H₇₀O₂: C, 82.04; H, 12.36%. Found: C, 82.05; H, 12.45%.

6-Cholesteryloxyhexanol, 2a. Yield 68%, mp 80 °C. ¹H NMR (CDCl₃, δ ppm): 0.67–2.40 (m, 51H, –CH₃, –CH(CH₃)–, –CH–, –CH₂–), 3.12 (m, 1H, –CHO–), 3.42–3.46 (t, 2H, –CH₂–O–CH–), 3.62–3.66 (t, 2H, –CH₂–OH), 5.33–5.35 (d, 1H, –C(CH₂)=CH–). IR (KBr, cm^{–1}): 3451 (O–H stretching), 2840 (aliphatic C–H stretching), 1095 (C–O stretching). Anal. Calcd for C₃₃H₅₈O₂: C, 81.42; H, 12.01%. Found: C, 81.40; H, 12.05%.

8-Cholesteryloxyoctanol, 2b. Yield 66%, mp 73 °C. ¹H NMR (CDCl₃, δ ppm): 0.67–2.40 (m, 55H, –CH₃, –CH(CH₃)–, –CH–, –CH₂–), 3.12 (m, 1H, –CHO–), 3.42–3.46 (t, 2H, –CH₂–O–CH–), 3.62–3.66 (t, 2H, –CH₂–OH), 5.33–5.35 (d,

1H, $-C(CH_2-)=CH-$). IR (KBr, cm^{-1}): 3451 (O–H stretching), 2840 (aliphatic C–H stretching), 1095 (C–O stretching). Anal. Calcd for $C_{35}H_{62}O_2$: C, 81.65; H, 12.14%. Found: C, 81.71; H, 12.20%.

10-Cholesteryloxydecanol, 2c. Yield 65%, mp 74 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 59H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.42–3.46 (t, 2H, $-CH_2-O-CH-$), 3.62–3.66 (t, 2H, $-CH_2-OH$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$). IR (KBr, cm^{-1}): 3451 (O–H stretching), 2840 (aliphatic C–H stretching), 1095 (C–O stretching). Anal. Calcd for $C_{37}H_{66}O_2$: C, 81.85; H, 12.25%. Found: C, 81.83; H, 12.30%.

Dimethyl 2-{12-(Cholesteryloxy)dodecyloxy}terephthalate, 3d. 12-Cholesteryloxydodecanol (**2d**, 4.3 g, 7.5 mmol), dimethyl 2-hydroxyterephthalate (1.4 g, 6.85 mmol), and triphenylphosphine (2.7 g, 10.3 mmol) were dissolved in 100 mL of dry tetrahydrofuran (THF),¹⁸ and the solution was cooled to 0 °C. To this solution added slowly over a period of 30 min was diisopropyl azodicarboxylate^{19,20} (2.1 g, 10.3 mmol). The mixture was stirred for 3 h at 0 °C and then for 12 h at room temperature. After the solvent was removed by distillation from the reaction mixture, the crude product was recrystallized from acetone. The yield was 4.8 g (90%); mp 67 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 63H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 3.90–3.94 (d, 6H, $-O-CH_3$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 2926 (aliphatic C–H stretching), 1732 (C=O stretching), 1613, 1501 (aromatic C=C stretching), 1228, 1110 (C–O stretching). Anal. Calcd for $C_{49}H_{78}O_6$: C, 77.12; H, 10.30%. Found: C, 77.16; H, 10.36%.

Dimethyl 2-{6-(Cholesteryloxy)hexyloxy}terephthalate, 3a. Yield 90%, mp 57 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 51H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 3.90–3.94 (d, 6H, $-O-CH_3$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 2929 (aliphatic C–H stretching), 1733 (C=O stretching), 1613, 1500 (aromatic C=C stretching), 1228, 1110 (C–O stretching). Anal. Calcd for $C_{43}H_{66}O_6$: C, 76.79; H, 10.15%. Found: C, 76.76; H, 10.09%.

Dimethyl 2-{8-(Cholesteryloxy)octyloxy}terephthalate, 3b. Yield 88%, mp 61 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 55H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 3.90–3.94 (d, 6H, $-O-CH_3$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 2926 (aliphatic C–H stretching), 1732 (C=O stretching), 1613, 1501 (aromatic C=C stretching), 1228, 1109 (C–O stretching). Anal. Calcd for $C_{45}H_{70}O_6$: C, 76.44; H, 9.98%. Found: C, 76.45; H, 10.02%.

Dimethyl 2-{10-(Cholesteryloxy)decyloxy}terephthalate, 3c. Yield 91%, mp 64 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 59H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 3.90–3.94 (d, 6H, $-O-CH_3$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 2926 (aliphatic C–H stretching), 1732 (C=O stretching), 1614, 1502 (aromatic C=C stretching), 1230, 1107 (C–O stretching). Anal. Calcd for $C_{47}H_{74}O_6$: C, 76.79; H, 10.15%. Found: C, 76.75; H, 10.18%.

2-{12-(Cholesteryloxy)dodecyloxy}terephthalic Acid, 4d. Diester **3d** (3.2 g, 4.11 mmol), potassium hydroxide (3.2 g, 57.5 mmol), and 5 mL of distilled water were dissolved in 100 mL of ethanol. The mixture was refluxed for 24 h and was poured into 500 mL of distilled water. The solution was acidified to pH 1 by adding concentrated hydrochloric acid. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The yield was 3.0 g (98%); mp 197 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 63H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 3300–2500 (O–H stretching), 2929 (aliphatic

C–H stretching), 1699 (C=O stretching), 1610, 1496 (aromatic C=C stretching), 1245, 1107 (C–O stretching). Anal. Calcd for $C_{47}H_{74}O_6$: C, 76.79; H, 10.15%. Found: C, 76.75; H, 10.16%.

2-{6-(Cholesteryloxy)hexyloxy}terephthalic Acid, 4a. Yield 98%, mp 217 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 51H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 3300–2500 (O–H stretching), 2929 (aliphatic C–H stretching), 1699 (C=O stretching), 1610, 1496 (aromatic C=C stretching), 1245, 1107 (C–O stretching). Anal. Calcd for $C_{41}H_{62}O_6$: C, 75.65; H, 9.60%. Found: C, 76.70; H, 9.63%.

2-{8-(Cholesteryloxy)octyloxy}terephthalic Acid, 4b. Yield 97%, mp 208 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 55H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 3300–2500 (O–H stretching), 2929 (aliphatic C–H stretching), 1699 (C=O stretching), 1610, 1496 (aromatic C=C stretching), 1245, 1107 (C–O stretching). Anal. Calcd for $C_{43}H_{66}O_6$: C, 76.06; H, 9.80%. Found: C, 76.05; H, 9.78%.

2-{10-(Cholesteryloxy)decyloxy}terephthalic Acid, 4c. Yield 98%, mp 202 °C. 1H NMR ($CDCl_3$, δ ppm): 0.67–2.40 (m, 59H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.44–3.49 (t, 2H, $-CH_2-O-CH-$), 4.31–4.35 (t, 2H, $-CH_2-O-Ar$), 5.33–5.35 (d, 1H, $-C(CH_2-)=CH-$), 7.76–8.28 (m, 3H, $ArCH$). IR (KBr, cm^{-1}): 3300–2500 (O–H stretching), 2929 (aliphatic C–H stretching), 1699 (C=O stretching), 1610, 1496 (aromatic C=C stretching), 1245, 1107 (C–O stretching). Anal. Calcd for $C_{45}H_{70}O_6$: C, 76.44; H, 9.98%. Found: C, 76.50; H, 10.01%.

Preparation of Polymers. General Procedure. All of the CHOL-*n* (*n* = 6, 8, 10, and 12) polyesters were prepared by melt polycondensation reaction of 1,4-diacetoxybenzene and terephthalic acid derivatives bearing pendants consisting of an oxyalkyleneoxy spacer and the cholesteryl moiety, i.e., compounds **4**. Since all of them were synthesized in the same manner, only a representative procedure is described for the preparation of CHOL-12. 2-{12-(Cholesteryloxy)dodecyloxy}terephthalic acid, **4d** (1.50 g, 2.04×10^{-3} mol), and 1,4-diacetoxybenzene (0.396 g, 2.04×10^{-3} mol) were placed in a polymerization tube which was equipped with a mechanical stirrer, an argon inlet, and a vacuum connection. The tube was immersed in a salt bath at 200 °C. The reaction mixture was stirred at 200 °C for 120 min, at 220 °C for 120 min, at 240 °C for 120 min, at 260 °C for 120 min, at 280 °C for 120 min, and then at 300 °C for 60 min under an argon atmosphere. Finally, the pressure was reduced to and kept at 0.3 Torr at 300 °C for 60 min. The product obtained was dissolved in chloroform and then precipitated in methanol. The product was white powder. It was subjected to Soxhlet extraction with ethanol for 3 days and dried in a vacuum oven for 2 days. The recovered yield was 1.30 g (76%). 1H NMR ($CDCl_3$, δ ppm): 0.66–2.37 (m, 63H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.11 (m, 1H, $-CHO-$), 3.43 (t, 2H, $-CH_2-O-CH-$), 4.18–4.33 (t, 2H, $-CH_2-O-Ar$), 5.30 (d, 1H, $-C(CH_2-)=CH-$), 6.88–8.06 (m, 7H, $ArCH$). IR (KBr, cm^{-1}): 2933 (aliphatic C–H stretching), 1743 (C=O stretching), 1615, 1503 (aromatic C=C stretching), 1225, 1100 (C–O stretching). Anal. Calcd for $(C_{53}H_{76}O_6)_n$: C, 78.67; H, 9.47%. Found: C, 78.98; H, 9.65%.

CHOL-6. The recovered yield was 1.60 g (85%). 1H NMR ($CDCl_3$, δ ppm): 0.66–2.37 (m, 51H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.11 (m, 1H, $-CHO-$), 3.43 (t, 2H, $-CH_2-O-CH-$), 4.18–4.33 (t, 2H, $-CH_2-O-Ar$), 5.30 (d, 1H, $-C(CH_2-)=CH-$), 6.88–8.06 (m, 7H, $ArCH$). IR (KBr, cm^{-1}): 2933 (aliphatic C–H stretching), 1743 (C=O stretching), 1615, 1503 (aromatic C=C stretching), 1225, 1100 (C–O stretching). Anal. Calcd for $(C_{47}H_{64}O_6)_n$: C, 77.86; H, 8.90%. Found: C, 77.50; H, 8.71%.

CHOL-8. The recovered yield was 0.95 g (72%). 1H NMR ($CDCl_3$, δ ppm): 0.66–2.37 (m, 55H, $-CH_3$, $-CH(CH_3)-$,

Table 1. General Properties of Polymers CHOL-*n*'s^a

polymer	η_{inh} (dL/g)	$\overline{M}_w \times 10^3$	$\overline{M}_w/\overline{M}_n$	$(DP)_n$	T_β (°C)	T_g (°C)	T_i (°C)
CHOL-6	0.53	140	7.5	25.8	56	156	260 (254–268)
CHOL-8	0.45	50.4	5.2	12.9	44	134	227 (220–235)
CHOL-10	0.42	27.2	4.1	8.5	37	104	184 (170–196)
CHOL-12	0.32	23.1	4.0	6.9	34	94	169 (160–178)

^a T_β , T_g , and T_i stand for the β - and glass transitions and isotropization temperature, respectively.

–CH–, –CH₂–), 3.11 (m, 1H, –CHO–), 3.43 (t, 2H, –CH₂–O–CH–), 4.18–4.33 (t, 2H, –CH₂–O–Ar), 5.30 (d, 1H, –C(CH₂)=CH–), 6.88–8.06 (m, 7H, ArCH). IR (KBr, cm^{–1}): 2933 (aliphatic C–H stretching), 1743 (C=O stretching), 1615, 1503 (aromatic C=C stretching), 1225, 1100 (C–O stretching). Anal. Calcd for (C₄₉H₆₈O₆)_n: C, 78.15; H, 9.10%. Found: C, 77.50; H, 9.02%.

CHOL-10. The recovered yield was 1.10 g (78%). ¹H NMR (CDCl₃, δ ppm): 0.66–2.37 (m, 59H, –CH₃, –CH(CH₃)–, –CH–, –CH₂–), 3.11 (m, 1H, –CHO–), 3.43 (t, 2H, –CH₂–O–CH–), 4.18–4.33 (t, 2H, –CH₂–O–Ar), 5.30 (d, 1H, –C(CH₂)=CH–), 6.88–8.06 (m, 7H, ArCH). IR (KBr, cm^{–1}): 2933 (aliphatic C–H stretching), 1743 (C=O stretching), 1615, 1503 (aromatic C=C stretching), 1225, 1100 (C–O stretching). Anal. Calcd for (C₅₁H₇₂O₆)_n: C, 78.42; H, 9.29%. Found: C, 78.50; H, 9.37%.

Instrumentation. Elemental analysis was performed by the Center for Organic Reactions, Sogang University, Seoul, Korea, using an Eager 200 elemental analyzer. The inherent viscosity values of the polymers were measured at 30 °C for solutions of 0.2 g/dL in cyclohexanone. The IR and ¹H NMR spectra were recorded respectively on a Bomem MB FT-IR instrument and a Varian AM 300 spectrometer. DSC thermograms were obtained under a nitrogen atmosphere at the heating rate of 10 °C/min. The instrument used for thermal analysis was Mettler 821^e. The temperatures where initial slope changes were observed were taken as relaxation temperatures, whereas peak minimum temperatures were taken as clearing temperatures. The X-ray analysis was conducted at the Pohang Laboratory of Synchrotron using a radiation of 1.542 Å. The powder sample holder was equipped with a heating and cooling thermostat. Optical textures were observed on a polarizing microscope (Olympus BH-2) equipped with a Mettler FP82HT hot stage. Molecular weights of the polymers were determined against polystyrene standard by gel permeation chromatography (GPC; Waters model 440 attached with 410 diffraction refractometer) using tetrahydrofuran as an eluent.

Results and Discussion

Synthesis and General Properties of Polymers.

All the present polyesters, CHOL-*n*'s, were prepared by polymerizing dicarboxylic acid monomers **4**'s with 1,4-diacetoxybenzene in melt. Monomers **4**'s are terephthalic acid derivatives bearing pendants consisting of an oxyalkyleneoxy spacer and the cholesteryl moiety. The monomers were synthesized following the multi-step synthetic route shown in Scheme 1. The structures of intermediates, monomers, and polymers were confirmed by IR and ¹H NMR spectroscopy and elemental analysis.

Polymers are soluble at room temperature in such organic solvents as methylene chloride, chloroform, tetrahydrofuran, and cyclohexanone. Their inherent solution viscosity values were measured at 30 °C for 0.2 g/dL solutions in a mixed solvent of 1,1,2,2-tetrachloroethane/phenol = 1:1 by volume. They range from 0.32 to 0.53 g/dL (Table 1), and their molecular weights determined by GPC range from 20 000 to 140 000. According to the GPC analyses, their polydispersity indices are relatively high (ca. 4–7.5). Probably, not enough efficient stirring of the reaction mixtures caused

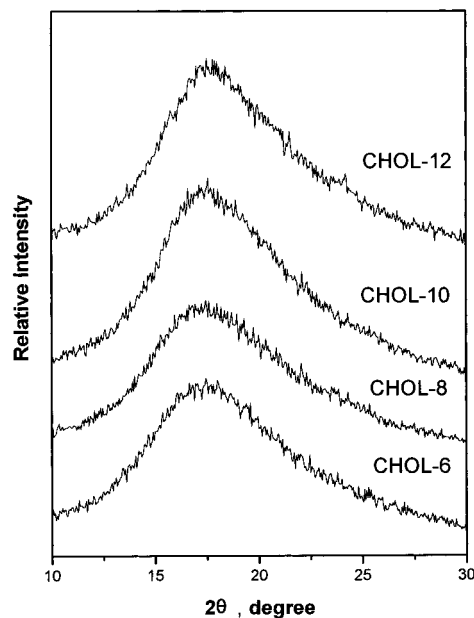
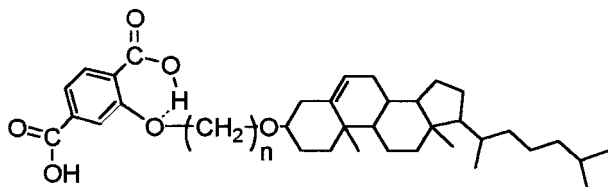


Figure 1. Wide-angle X-ray diffractograms of polymers CHOL-*n*'s at room temperature.

the rather broad molecular weight distributions. All of the present polymers are found to be amorphous as shown by their X-ray diffractograms as given in Figure 1. This is ascribed to the two structural factors: non-regioregular placement and bulkiness of the pendants. Since the pendant in the dicarboxylic acid monomers **4**'s is located at the 2-position of the benzene ring of terephthalic acid and, thus, the dicarboxylic acid monomers are not symmetrically substituted, the pendant groups are to be oriented in a nonregioregular manner when the monomers **4**'s are polymerized with 1,4-diacetoxybenzene.

Thermal Properties of Intermediates and Polymers. Among the intermediates **2**–**4**, compounds **2**, (ω -hydroxyalkylcholesteryl ether)s, were found to be thermotropic. They formed a smectic and the cholesteric phases in melt. Compounds **3**, (dimethyl 2-(ω -cholesteryloxypolymethyleneoxy)terephthalates), all were only monotropically liquid crystalline. But we did not try to identify their nature. This must be due to the presence of the terephthalate terminals that broaden the breadth of the molecules to such an extent that they lose their ability to form stable mesophases. Compounds **4**, however, did not form any mesophase in melt. It was expected that compounds **4** may be thermotropic as the two carboxylic acid groups may form hydrogen-bonded chains resulted from the formation of intermolecular cyclic dimers. Such structures are very similar to the so-called side chain LCPs bearing mesogenic pendants. Probably, intramolecular hydrogen bond formation between one of the acid groups and the oxygen atom in the side group hinders the formation of hydrogen-bonded linear long chains.



Thermal transition data for compounds **2** are tabulated in Table 2. Their isotropization temperature diminishes with increasing length of the tail. Longer tails are known to diminish the thermal stability of mesophases due to a higher degree of conformational freedom when compared with compounds with shorter tails.^{21,22}

Thermal transition behavior of the present polymers was studied by DSC, and their thermograms are shown in Figure 2. Since all of the polymers are amorphous, they do not exhibit any melting transition. We can still recognize three endothermic transitions on the heating DSC curves. The first ones occur at 34–56 °C, the second at 94–156 °C, and the last at 169–260 °C with all the transition temperatures being decreasing as the length of tails lengthens. Combined with observations made on optical textures of polymer melts on the polarizing microscope, we can judge that highest temperature transitions correspond to isotropization or clearing. Since isotropization occurs over a very broad temperature range, the DSC values given in Table 1 are the temperatures where peak maxima are located. At the same time, the temperature range over which isotropization occurs on the hot stage also was included in Table 1. Nonetheless, it is clear that isotropization temperature, T_i , drops down with increasing length of the spacers. The T_i value of CHOL-6 is 260 °C, whereas the value of CHOL-12 is much lower, 169 °C. A longer spacer must undergo conformational changes in melt much more readily than the shorter ones, which is believed to be the main reason for such a dependence of T_i on the spacer length, n . Similar phenomena were reported earlier by us for the previous series of combined type LCPs.^{3–5}

As alluded above, two more thermal transitions (T_β and T_g in Table 1) are observed for the present polymers before isotropization. We⁴ believe that the low-temperature transitions arise mainly from the motion of the pendants and spacers, i.e., β -relaxations, and the second, higher temperature transitions correspond to the segmental motion (α -relaxation) of the backbone or glass transition (T_g) in the conventional sense. The first, low transition temperature (T_β) of CHOL-6 is 56 °C, whereas the corresponding temperature of CHOL-12 is 34 °C. In other words, this transition also clearly depends on the length of spacer and drops down with increasing length of the spacers. Also, the second transition temperatures (T_g 's) appear to be dependent on the spacer length. For example, the T_g of CHOL-6 and CHOL-12 is 156 and 94 °C, respectively. Longer spacers should have a higher degree of conformational freedom than shorter spacers, which, in turn, would decrease the first transition temperature (T_β) because of easier vibrational and rotational motions of side branches. Since longer spacers, at the same time, will result in a greater free volume, the T_g values are expected to diminish as the spacer length increases. This is what we observe for the present series. When the pendant mesogens are involved in a stronger interaction with the backbone, the T_g values are much less dependent on the spacer length as we observed

Table 2. Phase Behavior of Compounds **2**

compound	phase transition ^a (°C)
2a	K 82.5 S 104.9 N* 107.9 I
2b	K 74.2 S 95.4 N* 103.2 I
2c	K 73.7 S 93.6 N* 99.9 I
2d	K 79.8 S 86.7 N* 93.5 I

^a Estimated from the DSC thermograms of the first heating cycle under a nitrogen atmosphere at the heating rate of 5 °C/min.

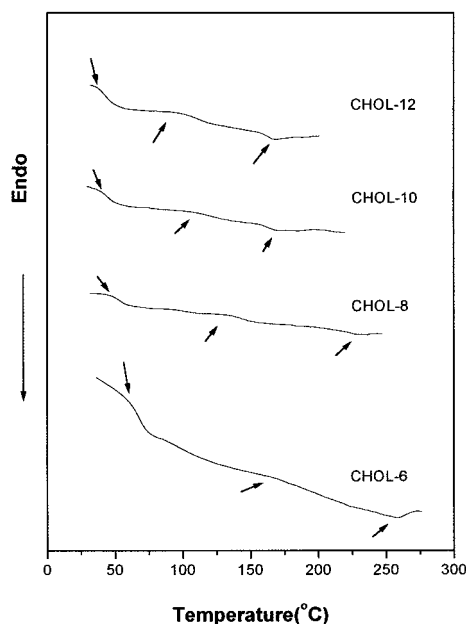


Figure 2. DSC thermograms of polymers CHOL- n 's (heating rate: 10 °C/min).

earlier for another series of combined type LCPs bearing very polar azobenzene mesogenic pendants because motions of pendants are expected to be more coupled with the segmental motion of the backbone.^{3–5} Occurrence of such two distinct relaxations was reported earlier by us for a similar series of combined type LCPs having the same backbone but with azobenzene type pendant mesogens.^{3–5} Differential mechanical thermal analysis (DMTA) was found to provide us with more definitive information on the two relaxations.⁴ Even the magnitudes of the two transitions of the present polymers are not much different from the values reported by us for the earlier series.

Nature of Mesophases Formed by Polymers. The nature of mesophases formed by present polymers was studied by observing optical textures of the melts on a polarizing microscope and their X-ray analysis (Figure 3). All of the polymers revealed optical textures without any specific feature by which the morphology of the mesophases could not be clearly identified. They appeared similar either to so-called grainy textures or to cholesteric planar textures. They, however, failed in showing any threaded Schlieren textures. Anyway, observed optical textures did not provide us with clear clues regarding the nature of their mesophases.

In contrast, X-ray analysis of the melts gave us better information about the structure of mesophases formed by the polymers. As one can see from Figure 3, all the polymers exhibit two or three diffractions for the liquid crystalline melts, one or two at the small-angle region, and the other at the wide-angle region. The peak at the small-angle region becomes sharper with increasing

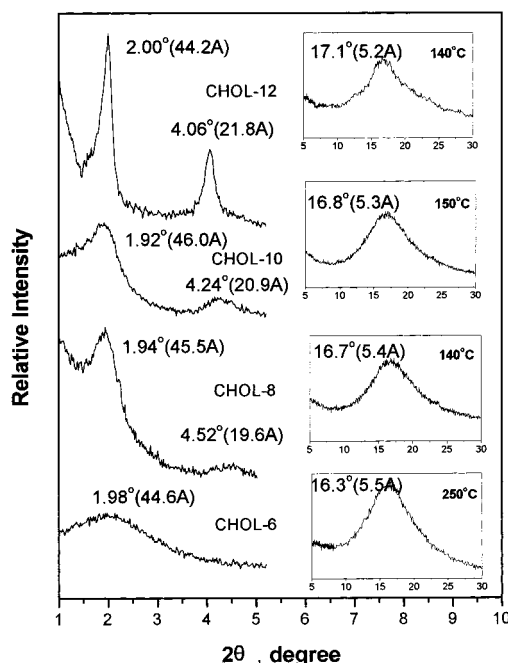


Figure 3. X-ray diffractograms of polymers CHOL-*n*'s.

length of the spacers. The spacing also increases as the spacer length lengthens. The long spacings estimated from the diffraction intensity maximum positions are 44.6, 45.5, 46.0, and 44.2 Å for CHOL-6, -8, -10, and -12, respectively. These spacing values are significantly larger than the molecular breadths calculated from molecular models with the assumption that all the methylene groups in the spacers being in the trans anti conformation: 31.7, 34.1, 36.7, and 39.2 Å, respectively. The broad halos at the wide-angle region correspond to the spacing of 5.2–5.5 Å that is believed to be an average interchain distance. The second diffraction peak of the spacing of about 20–22 Å grows very sharp with the increase of the spacer length, *n*. This diffraction is absent for CHOL-6. This spacing matches the length of the cholesterol moiety. This suggests that the layered structure of CHOL-12 in the mesophase is of best defined lateral order by the cholesterol moieties. Such X-ray diffraction characteristics of the mesophase melts of the present polymers, especially CHOL-12, suggest that most probably they form intercalated layered morphology, which is in a great contrast to the previously reported combined type LCPs that bear azobenzene type pendants.^{3–5} In light of its relatively broad diffraction in the small angle region, CHOL-6 forms the least organized mesophase among the four polymers. In fact, its mesophase structure may be very similar to nematic phases with relatively strong lateral interactions among the pendant mesogens. The small-angle diffraction patterns by CHOL-8 and -10 suggest that they reveal the inbetween mesophase ordering. In other words, their layered structures contain much defects and fluctuations in the lateral order. In contrast, CHOL-12 bearing the longest side branch forms a layered mesophase of a smectic order. Formation of intercalated mesophase has been reported for many side-group LCPs²³ and of other combined-type LCPs.²

All of the earlier polymers formed nematic phases, implying that the pendants are oriented more or less parallel to the backbone. This difference can be explained by the very nonpolar nature of the pendants in the present polymers. Since the polymer backbone is of

the polar structure, only repulsive interactions are expected to exist between the backbone and pendants in the case of the present series. At the same time, pendant groups of the present polymers are expected to exhibit attractive interactions among themselves, due to their same nonpolar character. In comparison, attractive interactions are favored between two structural elements in the previous polymers reported earlier by us.^{3–5} In addition, increased sharpness of the small-angle peaks for the polymers with longer spacers suggests that intercalated mesophase structures are better defined with less structural fluctuations than those of shorter spacers.

Since the average degree of polymerization of CHOL-12 is only 6.9 (Table 2), one may concern the effect of the end groups on its liquid crystalline order. We tried to identify the structure of the end groups of CHOL-12 by ¹³C NMR spectroscopy and found that they are acetoxy groups which were identified by the weak resonance by the acetoxy group bearing phenylenic carbon at the chemical shift of 148 ppm. This structure originated from one of monomers, 1,4-diacetoxybenzene. We could not detect the presence of free carboxylic acid terminal groups whose carbonyl carbon is expected to show a resonance peak at 169 ppm. Therefore, in the present case, the terminal groups of CHOL-12 are not anticipated to be involved in such strong inter- and/or intramolecular interactions as hydrogen bonding. In short, it is concluded that the layered smectic order observed for CHOL-12 is derived from its unique structure, not by any specific interactions, caused by terminal groups and has to be further clarified, especially for LC properties of oligomers.

One of the drawbacks of nematic LCPs is their anisotropy in the physical properties arising from their easy molecular orientation during processing. In other words, their mechanical strength is much greater across the orientation or molecular long axis direction than parallel to it. Because of the anisotropy, the compression strength of nematic LCPs is known to be far from satisfaction. Such anisotropy in physical and mechanical properties can be mitigated if one can design the structures of LCPs which can form aligned molecular orientation intercalated perpendicularly through strong interaction among the pendant mesogens. The present polymers, especially CHOL-12, appear to satisfy such requirements, which are expected to reveal a reduced anisotropy in physical properties when processed by conventional processing methods. One may be able to develop high-strength materials from these types of LCPs which reveal a very low degree of anisotropy in mechanical strength.

Conclusion

Relative orientation of pendant mesogenic units in combined-type LCPs with respect to their backbones depends strongly on mutual interactions between the two structural elements. If the two elements are of a great disparity in polarity as in the present series polymers, layered morphology is observed in the mesophase where the pendants are oriented vertically to the backbone. This is especially true when the length of the polymethylene spacer becomes longer.

On the contrary, if both structural constituents are of polar nature as in the previously reported compositions, formation of only nematic mesophases is favored, which is possible only when the orientational directions

of the backbone and pendants are about the same. All the combined-type LCPs reported in this and earlier articles clearly exhibit two relaxational transitions; it is conjectured that one related to the motion of spacer and pendant and the other to the segmental motion of the backbone. All of the present polyesters are amorphous due to the presence of irregularly placed bulky pendant mesogens.

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