Structures and Properties of Side-Chain Cholesteric Liquid Crystalline Polyacrylates

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ABSTRACT: The synthesis and mesomorphic properties of four monomers and three side-chain cholesteric liquid crystalline polymers containing 4-cholesteryl-4′-(acryloyloxy-*n*-alkyloxy)benzoate mesogenic side groups are described. The structure-property relationships of monomers M-1–M-4 and polymers P-1–P-3 are discussed. Phase behavior and optical properties were investigated by differential scanning calorimetry, thermogravimetric analyses, and polarizing optical microscopy. Monomers M-1–M-4 and polymers P-1–P-3 revealed cholesteric phase. Cholesteric texture and reflection color of the polymers were frozen by quenching. The experimental results demonstrated that selective reflection of M-1–M-4 and P-1–P-3 shifted to the long wavelength region with rigidity of the mesogen or decrease of flexible spacer length. Polymers with flexible spacer showed lower phase transition temperatures, wider mesomorphic temperature ranges and higher thermal stability compared with the polymer with no flexible spacer.
KEY WORDS Cholesteric Phase / Oily Streak Texture / Grandjean Texture / Liquid Crystalline Polymers /

Thermotropic cholesteric liquid crystalline polymers (ChLCPs) are of fundamental interest, mainly because of unique optical properties, including selective reflection of light, thermochromism and circular dichroism, and potential applications in numerous areas, especially in flat-panel displays, full-color thermal imaging and organic pigment.[1–11] The outstanding optical properties of ChLCPs are related to the helical supermolecular structure of the cholesteric phase, the pitch of which controls the wavelength of selective reflection of light. Reflection color can be observed if pitch coincides with the wavelength of visible light. For side-chain ChLCPs, mesomorphic properties depend on the nature of polymer backbone, rigidity of mesogen, and flexible spacer length.[12–15] Mesogens are usually attached to the polymer backbone *via* a flexible spacer, which is generally an aliphatic hydrocarbon chain containing, normally, more than two methylene units. The polymer backbone and mesogenic units have antagonistic tendencies. The polymer backbone is driven towards a random coil type configuration, while the mesogenic units stabilize with long range orientation order. The flexible spacer decouples the mesogenic side groups from the polymer backbone. However, when a rigid mesogenic unit is directly attached to the polymer backbone, liquid crystalline polymers can be obtained. Poly(4-cyclohexylphenyl acrylate),[16] poly(4-biphenyl acrylate),[17] poly(4-biphenyloxycarbonylphenyl methacrylate),[18] and so on, are side-chain liquid crystalline polymers, which exhibit mesomorphic properties without flexible spacer.
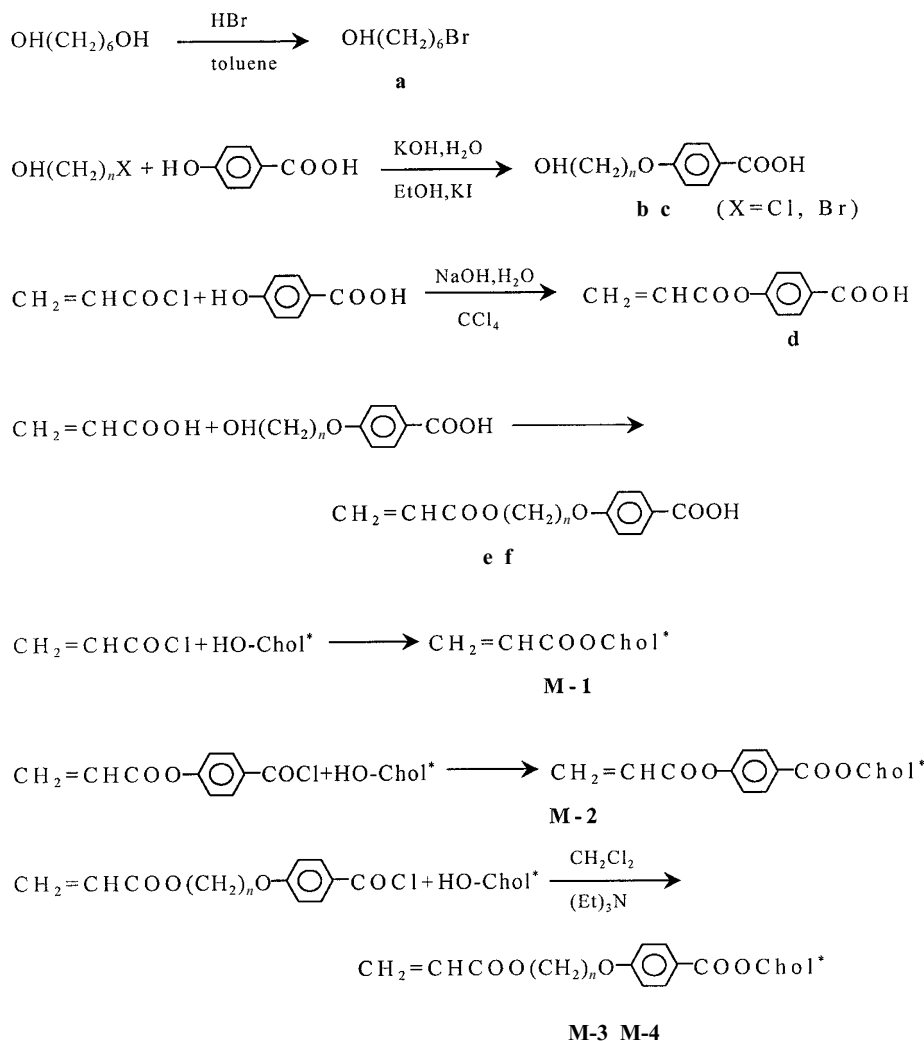
The aims of the present research are: (i) to study structure-property relationships of side-chain ChLCPs; (ii) explore applications in optical switch, color filter, organic pigments and lacquers; and (iii) supply necessary data to synthesize cholesteric liquid crystalline networks. Previous studies reported the synthesis and phase behavior of side-chain ChLCPs.[19, 20] In this study, the synthesis of side-chain cholesteric liquid crystalline polyacrylates containing both 4-cholesteryl-4′-(acryloyloxy-*n*-alkyloxy)benzoate mesogenic side groups is presented. Phase behavior and optical properties were characterized by differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), and polarizing optical microscopy (POM). The influence of the rigidity of mesogen and flexible spacer length on phase behavior and optical properties was discussed.

EXPERIMENTAL

Materials

Acrylic acid and chloro-ethanol was purchased from Shenyang Xinxi Chemical Reagent Co. (China). 4-Hydroxybenzoic acid was purchased from Beijing Fuxing Chemical Industry Co. (China). 1,6-Hexanediol was purchased from Beijing Hongyu Chemical Industry Co. (China). Cholesterol was from Henan Xiayi Medical Co. (China). All other solvents and reagents were purified by standard methods.

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$$OH(CH_2)_6OH \xrightarrow[\text{toluene}]{HBr} OH(CH_2)_6Br$$
<div align="center">a</div>

$$OH(CH_2)_nX + HO-\!\langle\bigcirc\rangle\!-COOH \xrightarrow[\text{EtOH,KI}]{KOH,H_2O} OH(CH_2)_nO-\!\langle\bigcirc\rangle\!-COOH$$
<div align="center">b c   (X = Cl, Br)</div>

$$CH_2=CHCOCl + HO-\!\langle\bigcirc\rangle\!-COOH \xrightarrow[\text{CCl}_4]{NaOH,H_2O} CH_2=CHCOO-\!\langle\bigcirc\rangle\!-COOH$$
<div align="center">d</div>

$$CH_2=CHCOOH + OH(CH_2)_nO-\!\langle\bigcirc\rangle\!-COOH \longrightarrow$$

$$CH_2=CHCOO(CH_2)_nO-\!\langle\bigcirc\rangle\!-COOH$$
<div align="center">e f</div>

$$CH_2=CHCOCl + HO\text{-}Chol^* \longrightarrow CH_2=CHCOOChol^*$$
<div align="center">**M-1**</div>

$$CH_2=CHCOO-\!\langle\bigcirc\rangle\!-COCl + HO\text{-}Chol^* \longrightarrow CH_2=CHCOO-\!\langle\bigcirc\rangle\!-COOChol^*$$
<div align="center">**M-2**</div>

$$CH_2=CHCOO(CH_2)_nO-\!\langle\bigcirc\rangle\!-COCl + HO\text{-}Chol^* \xrightarrow[\text{(Et)}_3N]{CH_2Cl_2}$$

$$CH_2=CHCOO(CH_2)_nO-\!\langle\bigcirc\rangle\!-COOChol^*$$

<div align="center">**M-3 M-4**</div>

Scheme 1. Synthetic routes of monomers.

Characterization

Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 510 FT-IR spectrometer (Nicolet Instruments, Madison, WI, U.S.A.). Polymer sample films were obtained *via* casting on a KBr table. Phase transition temperatures and thermodynamic parameters were determined using a PerkinElmer DSC-7 (PerkinElmer, Foster City, CA) equipped with a liquid nitrogen cooling system. Heating and cooling rates were 20 °C min^{-1}. Phase transition temperatures were taken during the second heating and first cooling scans. The thermal stability of the polymers under atmosphere was measured with a PerkinElmer TGA-7 thermograrimetric analyzer at 20 °C min^{-1} heating rate. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and FP 80 central processor were used to observe phase transition temperatures and analyze mesomorphic properties for liquid crystalline monomers and polymers through observation of optical texture.

Table I. Yields and phase transition temperatures of intermediate compounds b–f

Compounds	n	Transition temperature / °C	Yield / %
b	2	K 180 I	64
c	6	K 132 I	58
d	–	K 175 I	73
e	2	K 141 I	90
f	6	K 90 N 98 I	87

K: solid; N: nematic; I: isotropic.

Synthesis of the Monomers

The synthesis of acrylate monomers is performed as shown in Scheme 1. 4-(Hydroxy-n-alkyloxy)benzoic acid was prepared according to the literature.[21,22] Yields and phase transition temperatures of intermediate compounds are summarized in Table I.

4-Acryloyloxybenzoic Acid(d), 4-(2-Acryloyloxyethyloxy)benzoic Acid(e), and 4-(6-Acryloyloxyhexyloxy) benzoic Acid(f). Compound d was synthesized according to literature procedures.[20] Compounds e–f were prepared by the same method. The synthesis of

compound f is described below.

4-(6-Hydroxyhexyloxy)benzoic acid (47.6 g, 0.2 mol) was dissolved in a mixture of acrylic acid (280 mL), 98% H_2SO_4 (2 g) and small amount of 4-methoxyphenol. The solution was reacted at 55 °C for 24 h. The reaction mixture was poured into much water, precipitated, filtered and washed with water. The obtained solid was purified by recrystallization from ethanol.

IR (KBr, cm^{-1}): 2943, 2857 (CH$_2$), 2650, 2562 (COOH), 1721, 1686 (COO), 1635 (C=C), 1607, 1512 (Ar).

Cholesterylacrylate (M-1), 4-Cholesteryl-4'-(acryloyloxy)benzoate (M-2), 4-Cholesteryl-4'-(2-acryloyloxyethyloxy)benzoate (M-3), and 4-Cholesteryl-4'-(6-acryloyloxyhexyloxy)benzoate (M-4). All four acrylate monomers M-1–M-4 were prepared by the same method. The synthesis of monomer M-3 is described below.

4-(2-Acryloyloxyethyloxy) benzoic acid (23.6 g, 0.1 mol) was reacted at room temperature with thionyl chloride (40 mL) containing a few drops of *N,N*-dimethylformamide and trace of *p*-hydroxyanisole for 4 h. Excess thionyl chloride was removed under reduced pressure to give the acid chloride. The acid chloride was dissolved in dry methylene chloride (10 mL), and added dropwise to a cold solution of cholesterol (38.7 g, 0.1 mol) and pyridine (8 mL) in methylene chloride (100 mL). After stirring for 6 h, the precipitate was removed by filtration, the crude product was precipitated by adding ethanol to the filtrate and recrystallized from ethanol.

IR (KBr, cm^{-1}): 2945, 2861 (CH$_3$, CH$_2$), 1734, 1713 (COO), 1645 (C=C), 1608, 1511 (Ar).

Synthesis of the Polymers

The synthetic routes of the polymers are outlined in Scheme 2. For the synthesis of polymers P-1–P-3, the same method was adoped. The synthesis of polymer P-2 is given as an example.

Polymer P-2 was synthesized by radical polymerization of 4-cholesteryl-4'-(2-acryloyloxyethyloxy)benzoate in dry toluene using α,α'-azobisisobutyronitrile (AIBN, 2 mol% to the monomer) as an initiator at 60 °C for 24 h under nitrogen conditions. The polymer was obtained by precipitation with methanol. The crude polymer was dissolved in tetrahydrofuran and reprecipitated with methanol twice. The polymer was dried under vacuum.

IR (KBr, cm^{-1}): 2985, 2863 (CH$_3$, CH$_2$), 1735, 1715 (COO), 1610, 1512(Ar).
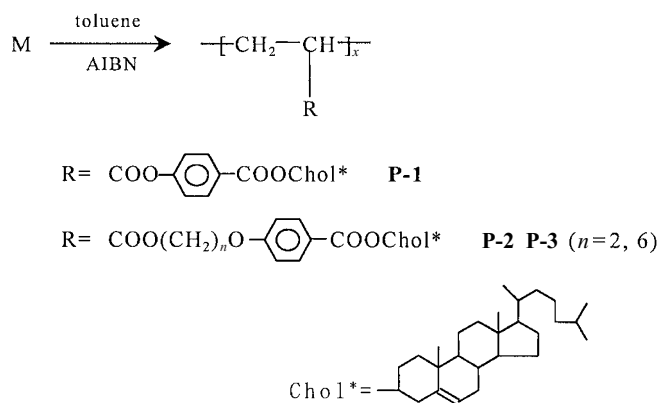
Scheme 2. Synthetic routes of polyacrylates.

RESULTS AND DISCUSSION

Phase Behavior

Phase transition temperatures and corresponding enthalpy changes of M-1–M-4 and P-1–P-3, derived from DSC measurements and POM, are summarized in Tables II, III, and IV, respectively. Representative DSC curves of M-1–M-4 and P-1–P-3, obtained on the second heating scan, are presented in Figures 1 and 2.

DSC heating thermograms of M-1–M-4 show two endothermic peaks of the phase transitions. The first endotherm represents the melting temperature transition, and the second endotherm the transition from the cholesteric phase to isotropic phase. As seen from the data in Tables II and III, the phase behavior of M-1–M-4 was strongly influenced by rigidity of mesogen and the flexible spacer length. Compared with the melting temperature (T_m) and isotropization temperature (T_i) of M-1, T_m and T_i of M-2 increased with rigidity of mesogen. Mesomorphic temperature ranges (ΔT) widened because T_i increased more than T_m. For M-2–M-4, T_m and T_i decreased with spacer length, but T_i decreased less than T_m, so ΔT widened. All phase transitions were reversible during repeated heating and cooling cycles. The phase transition temperatures determined by DSC were consistent with those observed by POM.

During the second heating scans of P-2 and P-3, glass transition and cholesteric phase to isotropic phase transition were observed. According to Tables III and IV, spacer length affected mesomorphic properties of P-2 and P-3. As the spacer length increased, the glass transition temperature (T_g) and isotropization temperature (T_i) decreased, but T_g decreased more than T_i. This suggests that a longer flexible spacer leads to a wider mesomorphic temperature range, and stabilizes mesomorphic properties since a longer flexible spacer always gives higher decoupling between mesogenic side groups and main chains. During the heating scan of P-

Table II. Phase transition temperatures of monomers

Monomers	n	Transition temperature in °C (Corresponding enthalpy changes in J g^{-1}) Heating / Cooling	Yield (%)	ΔT
M-1	–	K79.6(48.82)Ch124.3(1.25)I / I119.1(0.93)Ch25.5(10.29)K	62	44.7
M-2	–	K122.7(18.42)Ch220.8(1.14)I / I213.8(0.49)Ch98.8(11.72)K	48	98.1
M-3	2	K92.6(15.27)Ch188.2(1.58)I / I180.1(0.78)Ch	43	95.6
M-4	6	K72.9(18.53)Ch176.4(1.08)I / I171.1(0.63)Ch	45	103.5

K: solid; Ch: cholesteric; I: isotropic.

Table III. POM for monomers and polymers

Samples	T_m /°C	T_r^a /°C	T_i^b /°C	T_{ai}^c /°C	Textures	Main Reflected Color
M-1	78	78	127	125	oily streak focal-conic	violet
M-2	120	126	225	223	oily streak focal-conic	red
M-3	89	103	191	190	oily streak focal-conic	green
M-4	71	140	182	181	oily streak focal-conic	blue
P-1	158	160	273	271	oily streak focal-conic	red
P-2	–	88	227	218	grandjean oily streak	yellow
P-3	–	94	216	209	grandjean oily streak	green

[a]Temperature at which the reflection color occurred. [b]Temperature at which the birefringence disappeared completely. [c]Temperature at which the mesomorphic phase occurred.

Table IV. DSC and TGA for polymers

Polymers	n	Yields /%	T_g /°C	T_m /°C	T_i /°C	ΔT^b	T_d^c /°C
P-1	–	94	–	156.6	273[a]	116.4	264.7
P-2	2	96	56.8	–	217.8	161.0	305.4
P-3	6	92	48.3	–	213.3	165.0	314.9

[a]Observed by POM at 10 °C min^{-1}. [b]Mesomorphic temperature ranges. [c]Temperature at which 5% weight loss occurred.

1, only a melting transition was seen. Due to thermal degradation, isotropization of the cholesteric melt is not shown. T_i of P-1 was thus determined by POM.

For side-chain ChLCPs, T_g is strongly influenced by polymer backbone, mesogenic unit, and flexible spacer length. T_g involves mobility of chain segments, and T_g increases with decrease in mobility of chain segments. When spacer length of P-2 and P-3 increases, the interchain distance increases, and intermolecular force decreases, which makes the mobility of chain segments increase, so T_g decreases. From Table IV and DSC curves, shortening of the spacer length from $n = 6$ to $n = 2$ increased T_g by 8.5 °C.

The phase transition temperatures of the polymers containing a flexible spacer were lower than those of the polymer with no flexible spacer. Mesomorphic temperature ranges of P-1–P-3 were wider compared with monomers M-2–M-4, which indicates that polymerization results in stabilization of the mesomorphic phase. TGA indicated temperatures at 5% weight loss (T_d) were greater than 260 °C for P-1–P-3, showing that synthesized side-chain cholesteric liquid crystalline polyacrylates had higher thermal stability.

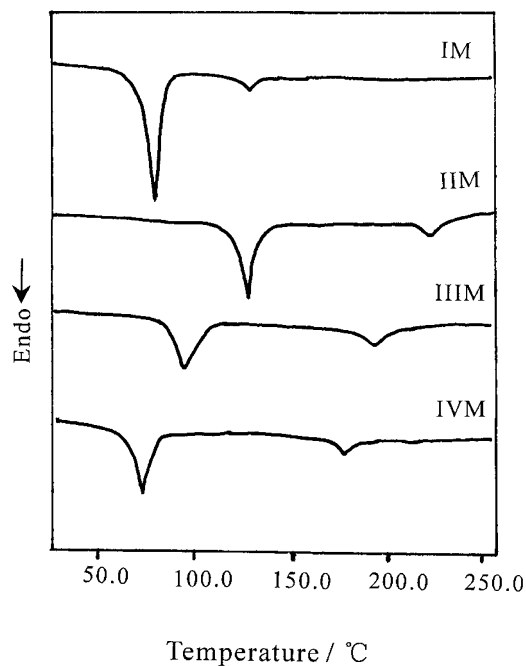By comparison of the phase transitions of P-1–P-3, a

Figure 1. DSC thermograms of monomers M-1–M-4.
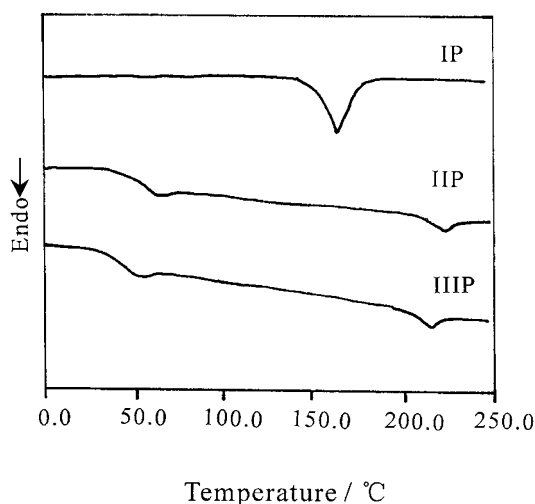

Figure 2. DSC thermograms of polymers P-1–P-3.

flexible polymer backbone and longer flexible spacer exhibited lower phase transition temperatures, wider mesomorphic temperature ranges and higher thermal stability.

Optical Properties

The cholesteric phase is formed by rod-like, chiral molecules responsible for macroscopical alignment of cholesteric domains. The periodic helical structure of cholesteric phase selectively reflects visible light like an ordinary diffraction grating. The wavelength of selective reflection of light obeys the Bragg condition:[23, 24]

$$\lambda_m = np \cos \phi \qquad (1)$$

where n is average refractive index of cholesteric phase,

p pitch of cholesteric helix, and ϕ angle of incidence. When selective reflection of light takes place at visible wavelength, brilliant color is observed. Because of the angular dependence of reflection, different observation angles lead to different color. The transmitted light shows complementary color. In reality, the orientation of the helices is not exactly perpendicular to the cell surface. Taking this into account, eq 1 becomes

$$\lambda_m = np \cos \left\{ \frac{1}{2} \left[\sin^{-1}\left(\frac{\sin \alpha}{n}\right) + \sin^{-1}\left(\frac{\sin \beta}{n}\right) \right] \right\} \qquad (2)$$

Where α and β are angles of incidence and observation, respectively.[25]

From a technological point of view, two important questions about cholesteric materials are (1) how to adjust pitch and (2) how to keep pitch constant once it has been adjusted. For side-chain ChLCPs, pitch and reflection color of cholesteric phase depend on chemical structure, content of chiral constituents in the copolymer, temperature, and outer field. Cholesteric texture and reflection color can in principle be fixed: (a) quenching the cholesteric phase below the glass transition temperature; (b) photocrosslinking, when suitable photocure reactive groups are present; (c) thermal crosslinking. In the present research, the influence of chemical structure on the selective reflection of light and technology of fixing the cholesteric colored films are discussed.

Texture and main reflection color of M-1–M-4 and P-1–P-3 observed by POM under nitrogen atmosphere are given in Table III. According to Table III, rigidity of the mesogenic unit and flexible spacer length influenced the reflection color of cholesteric phase. Selective reflection of light shifted to the long wavelength region (red shift) with rigidity of the mesogenic unit or decrease of the flexible spacer length.

POM observation revealed that monomers M-1–M-4 exhibited oily streak texture and focal conic texture of cholesteric phase during heating and cooling cycles. When the monomers were heated to T_m, the mesomorphic phase appeared, and obvious oily streak texture and the reflection color of cholesteric phase appeared at T_r. On cooling the samples from the isotropic melt, the focal-conic texture was formed, which easily transformed to oily steak texture by shearing the mesomorphic phase. Photomicrographs of M-3 are shown in Figures 3a and 3b. Polymers P-1–P-3 displayed oily streak, grandjean texture and focal conic texture. Photomicrographs of P-3 are shown in Figures 4a and 4b. In general, cholesteric phase at 0 field exhibits two optically contrasting stable states:[26, 27] planar (including oily streak and grandjean) texture and focal-conic texture. When the cholesteric phase exhibits planar tex-
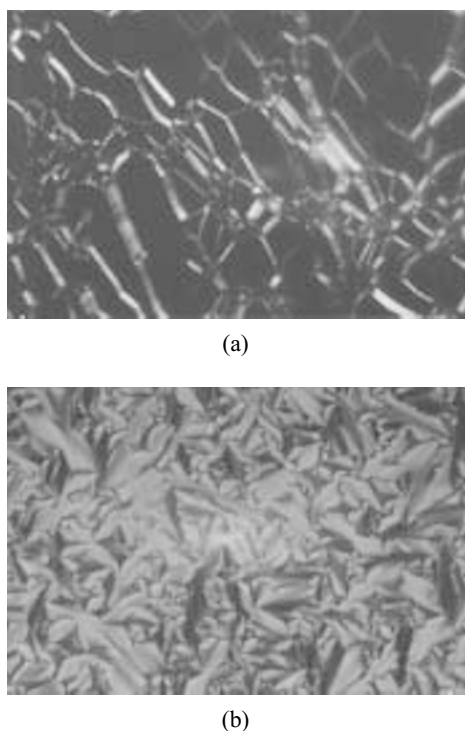
(a)

(b)

Figure 3. POM micrographs of monomer M-3 (320×):
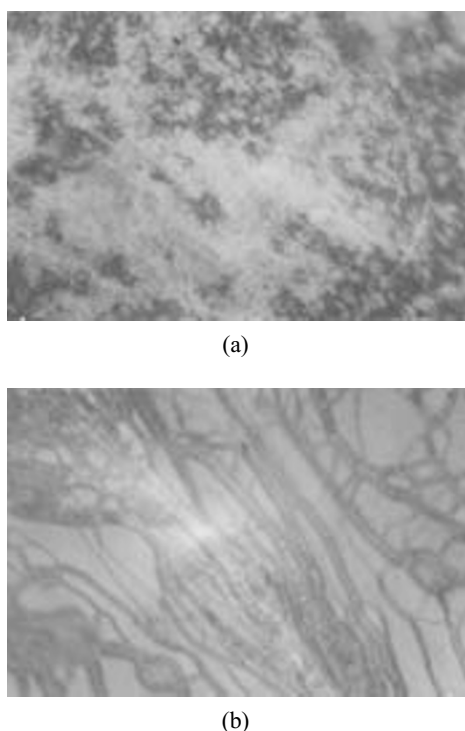(a) oily streak texture at 165 °C ; (b) focal conic texture at 130 °C.

(a)

(b)

Figure 4. POM micrographs of polymer P-3 (320 ×):
(a) grandjean texture at 180 °C, (b) oily streak texture at 200 °C.

ture, the helical axis is perpendicular to the cell surface and the material reflects colored light. When the cholesteric phase has focal-conic texture, the helical axis is more or less parallel to the cell surface and the material scatters and is a black if the black plate of the cell is painted black. If a cholesteric phase has a shorter pitch length than the wavelength of visible light, focal-conic texture is usually observed.

Variously cholesteric colored films were obtained by bringing molten polymers below T_i, followed by quenching to room temperature.

CONCLUSIONS

Side-chain cholesteric liquid crystalline poly-acrylates containing 4-cholesteryl-4′-(acryloyloxy-n-alkyloxy)benzoate mesogenic side groups were prepared. Monomers M-1–M-4 and polymers P-1–P-3 exhibited cholesteric texture. All phase transitions were reversible with repeated heating and cooling. Selective reflection of M-1–M-4 and P-1–P-3 shifted to the long wavelength region with rigidity of the mesogenic unit or shortening flexible spacer length. Cholesteric colored films were obtained by quenching. In polymers P-1–P-3, longer flexible spacer exhibited lower phase transition temperatures, wider mesomorphic temperature range and greater thermal stability.

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