Synthesis, Structure, and Properties of Chiral Liquid Crystal Monomers and Polymers Based on Menthol

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Received 26 April 2012; accepted 16 August 2012; published online DOI: 10.1002/pola.26350

ABSTRACT: To study structure-mesomorphism relationships of the monomers and polymers based on menthol, four new chiral monomers (M_1-M_4) and the corresponding homopolymers (P_1-P_4) with menthyl group were synthesized. Their chemical structures, formula, phase behavior, and thermal stability were characterized by FTIR, ¹H NMR, ¹³C NMR, elemental analyses, differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction, and thermogravimetric analysis. The selective reflection of light was investigated with ultraviolet/visible spectrometer. The influence of the mesogenic core rigidity, spacer length, and menthyl steric effect on the mesomorphism of M_1-M_4 and P_1-P_4 was examined. By inserting a flexible spacer between the mesogenic core and the terminal menthyl groups, four target monomers and polymers could form the expected mesophase. Moreover, their melting temperature (T_m) , glass transition temperature (T_g) , clearing temperature (T_i) , and

INTRODUCTION From a scientific and commercial point of view, chiral liquid crystal (LC) materials are fascinating because they possess excellent electro-optical properties, including selective reflection of light, thermochromism, ferroelectricity, and circular dichroism, and many important potential applications in various areas such as nonlinear optical devices, flat-panel displays, thermal imaging, rewritable full-color image recording, and photostable UV screens.¹⁻²⁰ For side-chain LC polymers, their mesomorphism or phase behavior mainly depends on the nature of polymer backbone, the type of mesogen, the flexible spacer and its length, and the nature of terminal groups. The mesogens are usually attached to the polymer backbone through a flexible spacer, which is generally an aliphatic hydrocarbon chain containing, normally, more than two methylene units. In fact, depending on the odd/even number of carbon atoms on the spacer, the mesogens couple to the polymer backbone and induce a local anisotropy of the polymer chains (oblate or prolate conformation). This effect vanishes when the spacer is too long (more than seven carbon atoms), and no coupling is observed.²¹ Depending on the chemical structure, it can

mesophase range (ΔT) increased with increasing the mesogenic core rigidity; whereas the T_m and T_g decreased, T_i and ΔT increased with an increase of the spacer length. M_1 and M_2 showed monotropic and enantiotropic cholesteric phase, respectively, whereas M_3 and M_4 all revealed chiral smectic C (SmC*), cholesteric and cubic blue phases. In addition, with increasing temperature, the selective reflection of light shifted to the long wavelength region at the SmC* phase range and to the short wavelength region at the cholesteric range, respectively. P_1 and P_2 only showed a smectic A (SmA) phase, whereas P_3 and P_4 exhibited the SmC* and SmA phases. All the obtained polymers had very good thermal stability. © 2012 Wiley Periodicals, Inc. J. Polym. Sci. Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: chiral; liquid crystalline polymers (LCPs); liquid crystal polymer; menthol; phase behavior; synthesis

achieve a macroscopic alignment of the chiral mesophase domains. In recent years, many chiral side-chain LC polymers, mostly adopting commercially available chiral compounds such as cholesterol and (*S*)-(+)-2-methyl-1-butanol, have been extensively studied.²²⁻³⁴

Menthol has three chiral center and strong optical activity, so the LC materials based on menthol are expected to obtain excellent mesomorphism and wide applications. At present, menthol has been used to synthesize chiral monomers and side-chain polymers.³⁵⁻⁴² In these articles, the cholesteric phase was induced by the copolymerization of the nematic LC monomer and nonmesogenic chiral monomer containing menthyl group. However, to the best of our knowledge, no research on the LC monomers and homopolymers based on menthol has been reported until now. Liu and Yang³⁹ reported the synthesis and characterization of novel monomers and homopolymers containing menthyl groups. Although these chiral monomers contained two or three phenyl rings, their mesogenic cores were directly linked to terminal menthyl groups, and the existence of the bulky steric menthyl groups prevented the orientation of the mesogenic

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molecular, so they showed no mesophase. However, our recent research showed that the monomers with three phenyl rings and their polymers derived from menthol could form and exhibit LC phase when a flexible linkage chain was inserted between the mesogenic core and the bulky terminal menthyl fragments by reducing the steric effect.⁴² Therefore, it is necessary to design and synthesize a series of novel chiral LC monomers and polymers derived from menthol to study their structure-property relationships and explore their potential applications.

In this study, we reported on the synthesis, structure, and properties of four new chiral LC monomers and homopolymers based on menthol. Their phase behavior and thermal stability were characterized with differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The structure-mesomorphism relationships of these obtained monomers and polymers were discussed in detail. The effect of the mesogenic rigidity and flexible spacer length on the phase behavior of the monomers and homopolymers was investigated.

EXPERIMENTAL

Materials

All chemicals were obtained from the indicated sources and used as received. L-Menthol was purchased from Shanghai Kabo Chemical (Shanghai, China), chloroacetic acid from Tianjin Bodi Chemical (Tianjin, China), 4-hydroxybenzoic acid from Shanghai Wulian Chemical Plant (Shanghai, China), ethylene chlorohydrin from Tianjin Dagu Chemical Plant (Tianjin, China), hexamethylene chlorohydrin from Zhouping Mingxing Chemical Engineering (Zhouping, China), and undec-10-enoic acid from Beijing Jinlong Chemical Reagent (Beijing, China). 4,4'-Dihydroxybiphenyl (from Aldrich) was used as received. Polymethylhydrosiloxane (PMHS) was purchased from Jilin Chemical Industry (Jilin, China). All other solvents and reagents used were purified by standard methods.

Characterization

FTIR spectra were measured on a PerkinElmer spectrum One (B) spectrometer (PerkinElmer, Foster City, CA). ¹H NMR spectra were obtained with a Bruker ARX400 spectrometer (Bruker, Swiss). ¹³C NMR (75.4 MHz) spectra were obtained with a Varian Gemini 300 spectrometer (Varian Associates, Palo Alto, CA). The elemental analyses were carried out with an Elementar Vario EL III (Elementar, Hanau, Germany). The special optical rotations were obtained on a PerkinElmer 341 polarimeter. The average molecular weight of the polymer was obtained with Waters GPC 1515. The selective reflection wavelength was measured using a PerkinElmer 950 ultraviolet/visible (UV/VIS) spectrometer with hot stage. The phase behavior was determined with a Netzsch DSC 204 (Netzsch, Hanau, Germany) equipped with a cooling system. The thermal stability of the polymers under nitrogen atmosphere was measured with a Netzsch TGA 209C thermogravimetric analyzer. The mesomorphism was observed with a Leica DMRX POM (Leica, Germany) equipped with a Linkam



SCHEME 1 Synthetic route of the intermediate compounds **1–10**.

THMSE-600 (Linkam, UK) cool and hot stage. XRD measurements were performed with a nickel-filtered Cu-K α (λ = 1.542 Å) radiation with a DMAX-3A Rigaku (Rigaku, Japan) powder diffractometer.

Synthesis of the Intermediate Compounds

The synthetic route of the intermediate compounds is shown in Scheme 1. Menthyloxyacetic acid (1), 4-menthyloxyacetoxybenzoic acid (3), 4-(2-hydroxy-ethoxy)benzoic acid (5), 4-(6-hydroxyhexyloxy)benzoic acid (6), and 4-(2-undec-10enoyloxyethoxy)benzoic acid (7) were prepared according to the method reported by Hu et al.⁴³⁻⁴⁵

4-(6-Undec-10-enoyloxyhexyloxy)benzoic Acid (8)

The synthesis of **8** is similar to that for **7** as described above. White crystal **8** was obtained by recrystallization from ethanol. Yield: 80%, mp: 89 °C.

IR (KBr, cm⁻¹): 2928, 2853 (-CH₂-); 1728, 1688 (C=0); 1641 (C=C); 1607, 1514 (Ar-), 1255 (C-O-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 1.35–1.82 [m, 20H, CH₂=CHCH₂(CH₂)₆CH₂— and —COOCH₂(CH₂)₄CH₂O—]; 2.10 [m, 2H, CH₂=CHCH₂(CH₂)₇—]; 2.65 [t, 2H, J = 7.2, CH₂= CH(CH₂)₇CH₂—]; 4.05 [t, 2H, J = 6.5, —COO(CH₂)₅CH₂O—]; 4.13 [t, 2H, J = 6.6, —COOCH₂(CH₂)₅O—]; 4.95–5.03 (m, 2H, CH₂=CH—); 5.77–6.90 (m, 1H, CH₂=CH—); 7.11 (d, 2H, J = 8.5); 8.12 (d, 2H, J = 8.5); 10.91 (s, 1H, —COOH).

Elem. Anal. calcd for $C_{24}H_{36}O_5{:}$ C, 71.26%; H, 8.97%. Found: C, 71.41%; H, 9.06%.

4-Hydroxybiphenyl-4'-(2-undec-10-enoyloxyethoxy) benzoate (9)

4-(2-Undec-10-enoyloxyethoxy)benzoyl chloride was prepared through the reaction of **7** with excess thionyl chloride.



SCHEME 2 Synthetic route of the monomers M1-M4.

The acid chloride obtained (3.66 g, 10 mmol) was added dropwise to a solution of 4,4'-dihydroxybiphenyl (5.58 g, 30 mmol) in 50 mL of THF and 0.8 mL of pyridine under quick stirring. The mixture was reacted for 6 h at room temperature and for 8 h at 65 °C. After the mixture was concentrated, the crude product was precipitated by adding ice-water to the residue, washed with 1.5% NaOH solution, and then neutralized with diluted HCl. The solid **9** was obtained by recrystallization from ethanol/acetone (3:1). Yield: 43%, mp: 153 °C.

IR (KBr, cm⁻¹): 3415 (-OH); 2924, 2852 (-CH₂-); 1734 (C=O); 1641 (C=C); 1609, 1500 (Ar-), 1262 (C-O-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 1.34–1.80 [m, 12H, CH₂=CHCH₂(CH₂)₆CH₂—]; 2.05 [m, 2H, CH₂=CHCH₂ (CH₂)₇—]; 2.61 [t, 2H, J = 7.2, CH₂=CH(CH₂)₇CH₂—]; 4.25– 4.54 [m, 4H, -COO(CH₂)₂O—]; 4.95–5.03 (m, 2H, CH₂=CH—); 5.75–6.90 (m, 1H, CH₂=CH—); 6.9 (d, 2H, J =8.4); 7.1 (d, 2H, J = 8.6); 7.2 (d, 2H, J = 8.6); 7.7 (d, 2H, J =8.5); 7.92 (d, 2H, J = 8.5); 8.11 (d, 2H, J = 8.6); 6.92–8.03 (m, 12H, Ar—H); 9.23 (s, 1H, -OH).

ELEM. ANAL. calcd for $C_{32}H_{36}O_6$: C, 74.39%; H, 7.02%. Found: C, 74.24%; H, 7.11%.

4-Hydroxybiphenyl-4'-(6-undec-10-enoyloxyhexyloxy)benzoate (10)

The synthesis of **10** is similar to that for **9** as described above. White solid **10** was obtained by recrystallization from ethanol/acetone (3:1). Yield: 42%, mp: $136 \degree$ C.

IR (KBr, cm⁻¹): 3461 (-OH); 2927, 2854 (-CH₂-); 1732 (C=O); 1641 (C=C); 1608, 1498 (Ar-), 1261 (C-O-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 1.36–1.83 [m, 20H, CH₂=CHCH₂(C**H**₂)₆CH₂— and —COOCH₂(C**H**₂)₄CH₂O—]; 2.09 [m, 2H, CH₂=CHC**H**₂(CH₂)₇—]; 2.64 [t, 2H, J = 7.2, CH₂= CH(CH₂)₇C**H**₂—]; 4.06 [t, 2H, J = 6.4, —COO(CH₂)₅C**H**₂O—]; 4.15 [t, 2H, J = 6.5, —COOC**H**₂(CH₂)₅O—]; 4.97–5.04 (m, 2H, C**H**₂=CH—); 5.76–6.90 (m, 1H, CH₂=C**H**—); 7.02 (d, 2H, J =8.5); 7.12 (d, 2H, J = 8.5); 7.23 (d, 2H, J = 8.5); 7.72 (d, 2H, J = 8.6); 7.91 (d, 2H, J = 8.5); 8.11 (d, 2H, J = 8.5); 9.32 (s, 1H, -OH).

Elem. Anal. calcd for $C_{36}H_{44}O_6{:}$ C, 75.50%; H, 7.74%. Found: C, 75.62%; H, 7.81%.

Synthesis of the Monomers

The synthetic route of the chiral monomers M_1 - M_4 is outlined in Scheme 2. They were prepared by the same method. The synthesis of M_1 is given below as an example.

4-(Menthyloxyacetoxy)biphenyl-4'-(2-(undec-10-enoyloxy) ethoxy)benzoate (M₁)

The compound **2** was prepared according to the reported literature.⁴¹ The acid chloride obtained (2.55 g, 11 mmol) was dissolved in 5 mL of chloroform and then added dropwise to a stirred solution of the compound **9** (5.16 g, 10 mmol) in 40 mL of chloroform and 1 mL of pyridine. The mixture was reacted at room temperature for 2 h and refluxed for 24 h, cooled to room temperature, filtered, and then concentrated. The crude product was precipitated by adding methanol to the filtrate and purified by column chromatography (silica gel, dichloromethane). Yield: 45%. mp: 72 °C.

IR (KBr, cm⁻¹): 2921, 2851 (CH₃—, —CH₂—); 1780, 1729 (C=0); 1640 (C=C); 1610–1497 (Ar—); 1208 (C=O–C).

¹H NMR (δ , ppm from TMS in CDCl₃): 0.81–2.60 [m, 34H, --(CH₂)₈— and in menthyl—H]; 3.28–3.36 (m, 1H, --CH< in menthyl); 4.36–4.45 (m, 2H, --OOCCH₂O—); 4.52–4.63 [m, 4H, --COO(CH₂)₂O—]; 4.92–5.05 (m, 2H, CH₂=); 5.77–5.92 (m, 1H, =CH—); 7.03 (d, 2H, J = 8.5); 7.11 (dd, 4H, J = 8.6); 7.31 (d, 2H, J = 8.6); 7.82 (d, 2H, J = 8.5); 8.23 (d, 2H, J = 8.5).

¹³C NMR (δ, ppm from TMS in CDCl₃): 20.52, 21.43 (3C, CH₃); 23.72, 24.85, 28.74, 29.13, 29.45, 29.64, 29.73, 33.56, 33.66, 34.13, 40.64 (11C, CH₂); 25.82, 31.54, 47.93 (3C, CH); 80.52 (1C, OCH in menthyl); 62.84, 66.15, 67.23 (3C, OCH₂); 113.92, 122.09, 129.56, 130.83 (12C, aromatic tert. C); 114.89, 140.12 (2C, C=C); 121.08, 136.73, 136.84, 147.29,



149.92, 167.54 (6C, aromatic quat. C); 165.54, 166.23, 172.72 (3C, C=0).

ELEM. ANAL. calcd for $C_{44}H_{56}O_8$: C, 74.13%; H, 7.92%. Found: C, 74.21%; H 7.83%.

4-(Menthyloxyacetoxy)biphenyl-4'-(6-(undec-10-enoyloxy)hexyloxy)benzoate (M₂)

Yield: 49%. mp: 63 °C. IR (KBr, cm⁻¹): 2929, 2869 (CH₃-, -CH₂-); 1776, 1728 (C=0); 1641 (C=C); 1604-1492 (Ar-); 1207 (C-O-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 0.79–2.65 [m, 42H, -(CH₂)₈—, -COOCH₂(CH₂)₄CH₂O— and in menthyl—H]; 3.27–3.36 (m, 1H, -CH< in menthyl); 4.06 [t, 2H, J = 6.3, -COO(CH₂)₅CH₂O—]; 4.14 [t, 2H, J = 6.3, -COOCH₂ (CH₂)₅O—]; 4.37–4.48 (t, 2H, J = 6.5, -OOCCH₂O—); 4.93– 5.04 (m, 2H, CH₂=); 5.76–5.90 (m, 1H, =CH—); 7.04 (d, 2H, J = 8.6); 7.12 (dd, 4H, J = 8.5); 7.31 (d, 2H, J = 8.6); 7.82 (d, 2H, J = 8.5); 8.21 (d, 2H, J = 8.5).

¹³C NMR (δ, ppm from TMS in CDCl₃): 20.53, 21.43 (3C, CH₃); 23.71, 24.86, 25.52, 25.82, 28.74, 28.88, 29.16, 29.43, 29.57, 29.66, 29.75, 33.55, 33.63, 34.15, 40.66 (15C, CH₂); 25.82, 31.55, 47.92 (3C, CH); 80.51 (1C, OCH in menthyl); 62.85, 66.13, 67.24 (3C, OCH₂); 113.93, 122.11, 129.55, 130.85 (12C, aromatic tert. C); 114.89, 140.13 (2C, C=C); 121.09, 136.72, 136.83, 147.29, 149.93, 167.55 (6C, aromatic quat. C); 165.53, 166.22, 172.73 (3C, C=O).

ELEM. ANAL. calcd for $C_{48}H_{64}O_8$: C, 74.97%; H, 8.39%. Found: C, 74.86%; H, 8.48%.

4-(Menthyloxyacetoxybenzoyloxy)biphenyl-4'-(2-(undec-10enoyloxy)ethoxy)benzoate (M₃)

Yield: 54%. mp: 108 °C. IR (KBr, cm⁻¹): 2925, 2853 (CH₃-, -CH₂-); 1781, 1733 (C=0); 1641 (C=C); 1606-1495 (Ar-); 1212 (C-0-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 0.83–2.64 [m, 34H, –(C H_2)₈— and in menthyl—H]; 3.27–3.35 (m, 1H, —CH< in menthyl); 4.35–4.48 (m, 2H, —OOCC H_2 O—); 4.54–4.65 [m, 4H, —COO(C H_2)₂O—]; 4.93–5.05 (m, 2H, C H_2 =); 5.78–5.90 (m, 1H, =CH—); 7.13 (d, 2H, J = 8.5); 7.33 (dd, 2H, J = 8.6); 7.54 (d, 2H, J = 8.5); 7.93 (dd, 4H, J = 8.6); 8.14 (d, 4H, J = 8.5); 8.31 (d, 2H, J = 8.5).

¹³C NMR (δ, ppm from TMS in CDCl₃): 20.51, 21.45 (3C, CH₃); 23.71, 24.84, 28.75, 29.11, 29.42, 29.65, 29.72, 33.56, 33.65, 34.12, 40.66 (11C, CH₂); 25.83, 31.55, 47.92 (3C, CH); 80.51 (1C, OCH in menthyl); 62.85, 66.13, 67.24 (3C, OCH₂); 113.91, 121.48, 122.11, 129.55, 130.56, 130.83 (16C, aromatic tert. C); 114.91, 140.12 (2C, C=C); 121.13, 126.88, 136.74, 136.81, 147.29, 147.31, 156.38, 167.57 (8C, aromatic quat. C); 165.52, 165.54, 166.23, 172.73 (4C, C=O).

Elem. Anal. calcd for $C_{51}H_{60}O_{10}{:}$ C, 73.53%; H, 7.26%. Found: C, 74.02%; H 7.37%.

4-(Menthyloxyacetoxybenzoyloxy)biphenyl-4'-(2-(undec-10enoyloxyhexyloxy)-benzoate (M_4)

Yield: 56%. mp: 82 °C. IR (KBr, cm⁻¹): 2927, 2855 (CH₃-, -CH₂-); 1787, 1731 (C=0); 1641 (C=C); 1604-1492 (Ar-); 1205 (C-O-C).

¹H NMR (δ , ppm from TMS in CDCl₃): 0.81–2.64 [m, 42H, –(CH₂)₈–, –COOCH₂(CH₂)₄CH₂O– and in menthyl–H]; 3.28–3.36 (m, 1H, –CH< in menthyl); 4.02 [t, 2H, J = 6.4, –COO(CH₂)₅CH₂O–]; 4.13 [t, 2H, J = 6.3, –COOCH₂ (CH₂)₅O–]; 4.35–4.47 (m, 2H, J = 6.5, –OOCCH₂O–); 4.92– 5.04 (m, 2H, CH₂=); 5.76–5.91 (m, 1H, =CH–); 7.03 (d, 2H, J = 8.5); 7.24 (dd, 2H, J = 8.6); 7.53 (d, 2H, J = 8.5); 7.94 (dd, 4H, J = 8.6); 8.15 (d, 4H, J = 8.5); 8.32 (d, 2H, J = 8.5).

¹³C NMR (δ, ppm from TMS in CDCl₃): 20.51, 21.43 (3C, CH₃); 23.73, 24.85, 25.53, 25.84, 28.75, 28.86, 29.15, 29.44, 29.56, 29.66, 29.77, 33.53, 33.64, 34.16, 40.66 (15C, CH₂); 25.82, 31.56, 47.93 (3C, CH); 80.53 (1C, OCH in menthyl); 62.83, 66.15, 67.25 (3C, OCH₂); 113.92, 121.51, 122.13, 129.54, 130.55, 130.85 (16C, aromatic tert. C); 114.92, 140.11 (2C, C=C); 121.14, 126.88, 136.75, 136.83, 147.31, 147.34, 156.39, 167.59 (8C, aromatic quat. C); 165.52, 165.55, 166.24, 172.72 (4C, C=O).

ELEM. ANAL. calcd for $C_{55}H_{68}O_{10}$: C, 74.30%; H, 7.71%. Found: C, 74.36%; H, 7.83%.

Synthesis of the Polymers

The synthetic route of the polymers P_1-P_4 is outlined in Scheme 3. The yields and average molecular weights of P_1-P_4 are listed in Table 1. These polymers were prepared by the same method, and the synthesis of P_1 is given as an example. M_1 (2 mol % excess vs. the Si—H groups in PMHS) and PMHS were dissolved in dry toluene. The reaction mixture was heated to 70 °C under nitrogen and anhydrous conditions, and then 2 mL of THF solution with the H₂PtCl₆ catalyst (5 mg/mL) was injected into mixture with a syringe. When the reaction was finished, P_1 was obtained by precipitation from toluene solution into methanol, purified by several filtrations from hot ethanol, and then dried *in vacuo*.

IR (KBr, cm⁻¹): 2923, 2853 (-CH₃, -CH₂-); 1780, 1737 (C=0); 1607, 1496 (Ar-); 1275, 779 (Si-C); 1210 (C-0-C); 1200-1006 (Si-0-S).

¹H NMR (δ , ppm from TMS in CDCl₃): 0.17–2.53 [m, 59H, CH₃Si—, $-(CH_2)_{10}$ — and in menthyl—H]; 3.30 (m, 1H, -CH < in menthyl); 4.41 (m, 2H, $-OOCCH_2O$ —); 4.55–4.62 [m, 4H, $-COO(CH_2)_2O$ —]; 7.09–8.31 (m, 12H, Ar—H).

RESULTS AND DISCUSSION

Synthesis and Characterization

Until now, research on the design and synthesis of new chiral LC materials has all long attracted considerable interest. It is well known that menthol has three chiral centers and strong optical activity, so the LC materials based on menthol are expected to obtain a chiral smectic C and cholesteric phases and show excellent mesomorphism. To investigate the effect of spacer length and rigid mesogenic core on physical properties and phase behavior of target monomers and polymers, we designed and prepared four new chiral LC monomers (with same terminal group, different mesogenic rigidity, and spacer length) and their corresponding homopolymers containing menthyl group.

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SCHEME 3 Synthetic route of the polymers P1-P4.

For the purification of 9, the byproduct for biphenyl-4,4'-diyl bis(4-(2-undec-10-enoyloxy)ethoxy)benzoate) was removed by washing with 1.5% NaOH solution, and the compound 9 was obtained by recrystallization from ethanol/acetone (3:1) to remove the unreacted material 4,4'-dihydroxybiphenyl. The purification process of **10** is same as **9**. The synthesis of the monomers M_1-M_4 is performed by the same method. They were prepared by reacting 2 or 4 with 9 and 10, respectively, in chloroform in the presence of pyridine. The chemical structures of the monomers M_1 - M_4 were characterized by FTIR and ¹H NMR. IR spectra of M_1-M_4 showed characteristic stretching bands at 1787-1776 cm⁻¹ attributed to ester C=0 in menthyloxyacetate, 1733-1728 cm^{-1} attributed to ester C=0 in undecylenate and substituted benzoate, 1641 cm^{-1} attributed to olefinic C=C, and 1606-1495 cm⁻¹ attributed to aromatic C=C. ¹H NMR spectra of M_1-M_4 multiplet at the chemical shift values nearby 0.83-4.65, 4.93-5.90, and 7.00-8.28 ppm correspond to methyl and methylene protons, olefinic protons, and aromatic protons, respectively. ¹H NMR spectra of M_2 as an example are shown in Figure 1. The spectra suggested that the purity of these monomers was high, and this was confirmed by the elemental analyses.

tion reaction using an excess amount of olefinic monomers. The unreacted monomers were removed by several reprecipitation from toluene solutions into methanol and filtrations from hot ethanol. The progress of the hydrosilylation reaction, monitored by the Si—H stretch intensity, went to completion, as indicated by IR when the complete disappearance of Si—H stretching band at 2165 cm⁻¹ and olefinic C=C stretching band at 1640 cm⁻¹. Characteristic Si—C bands at about 1269 and 782 cm⁻¹, and Si—O—Si bands at about 1203, 1166, 1117, 1071, and 1005 cm⁻¹ appeared.

The polymers P_1 - P_4 were prepared through the hydrosilyla-

Specific Optical Rotations

The specific optical rotations of M_1-M_4 and P_1-P_4 were evaluated at 25 °C in chloroform and toluene, respectively, and the obtained results are summarized in Table 1. As can be seen from the data listed in Table 1the specific optical rotations of M_1-M_4 and P_1-P_4 were all left handed; moreover, the specific optical rotation absolute values decreased with increasing the aryl number in the mesogenic units; for example, compared with M_1 ($[\alpha]_D^{25} = -38.4^\circ)$, M_3 with more aryl

TABLE 1 Specific Optical Rotation, Yields, and Average

 Molecular Weight of Sample

Monomer	$[\alpha]_{D}^{25a}$	Polymer	$[\alpha]_{D}^{25b}$	Yield (%)	$M_{ m n} imes$ 10 ⁻³
M ₁	-38.4	P ₁	-32.4	86	8.2
M ₂	-37.9	P ₂	-32.0	88	9.3
M ₃	-22.5	P ₃	-18.1	83	10.1
M ₄	-20.4	P ₄	-13.7	82	10.9

^a Specific optical rotation, about 0.21 g in 100 mL of CHCl₃.

^b Specific optical rotation, about 0.15 g in 100 mL of toluene.





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	Mesophase, Phase Transition Temperature (°C), and Enthalpy Changes (J/g)					
Monomer	Heating Cycle	Cooling Cycle				
M ₁	K 72.3 (70.7) I	l 66.2 (4.7) Ch 43.9 (19.9) K				
M ₂	K 63.0 (38.8) Ch 81.1 (3.5) I	l 79.6 (3.5) Ch 35.1 (12.9) K				
M ₃	K 108.1 (7.7) SmC* 147.0 (1.0) Ch 175.4 (0.4) I	l 173.0 (1.1) Ch 141.1 (0.6) SmC* 96.1 (5.8) K				
M ₄	K81.5 (20.3) SmC* 148.9 (2.2) Ch 180.8 (0.5) I	l 180.0 (0.4) Ch 148.0 (2.4) SmC* 74.1 (12.0) K				

TABLE 2 The Phase Transition Temperatures and Mesophase of Monomers

K, solid; SmC*, chiral smectic C phase; Ch, cholesteric phase; I, isotropic.

segments showed lower specific optical rotation absolute values. The results suggested that the existence of more phenyl segments affected the molecular polarity leading to the decrease of the specific rotation absolute values, which is in agreement with the results reported by Liu and Yang.³⁹

The specific optical rotation of P_1-P_4 showed the same tendency as the above monomers. In addition, the specific optical rotation absolute values of P_1-P_4 were less than those of the corresponding monomers. This indicated that the concentration of optically active sites decreased because these polymers consisted of optically inactive polysiloxane. This of course affected the amount of optically active sites and this in turn decreased the optical rotation absolute values.

Thermal Properties

The thermal properties of M_1-M_4 and P_1-P_4 were studied with DSC. Their phase transition temperatures and corresponding enthalpy changes, obtained on the second heating and cooling scans from DSC, are summarized in Tables 2 and 3. Representative DSC curves of M_4 are shown in Figure 2. The DSC heating and cooling rates were 10 °C/min.

According to DSC curves, M_1 showed an endothermic peak on heating and two exothermic peaks on cooling process, and exhibited monotropic cholesteric phase. M_2 showed two endothermic peaks and two exothermic peaks, and exhibited enantiotropic cholesteric phase. M_3 and M_4 showed three endothermic peaks, which represent a melting transition, a chiral smectic C (SmC*) to cholesteric phase transition, and a cholesteric to isotropic phase transition, respectively. On cooling, three exothermic peaks were seen, which represent an isotropic to cholesteric phase transition, a cholesteric to

TABLE 3 The Phase Transition Temperatures of Polymers

Polymer	Phase Transition Temperature (°C)
P ₁	g 28.3 SmA 116.2 (2.8) I
P ₂	g 16.5 SmA 124.1 (3.0) l
P ₃	g 41.1 SmC* 101.5 (0.8) SmA 226.3 (1.4) I
P ₄	g 27.2 SmC* 105.2 (1.1) SmA 228.2 (1.6) I

g, glass state; SmA, smectic A phase; SmC*, chiral smectic C phase; I, isotropic.



FIGURE 2 DSC curves of M₄.

SmC* phase transition, and a SmC* to crystallization transition, respectively.

The mesogenic rigidity and flexible spacer length had a considerable influence on the phase behavior of the monomers. The different phase ranges of M_1-M_4 are presented in Figure 3. M_1 only showed the melting temperature (T_m) on heating process, and the isotropic temperature (T_i) was not seen. Although the same mesogenic core as M1, M2 with longer flexible spacer showed good mesomorphism, similar results could be seen for M_3 and M_4 . With increasing the number of the flexible methylene, the corresponding $T_{\rm m}$ decreased from 108.1 °C for M_3 to 81.5 °C for $M_4,$ whereas the T_i increased from 175.4 °C for M_3 to 180.0 °C for M_4 , so the mesophase range (ΔT) widen. In addition, it was clearly seen in Figure 3 that the SmC* phase temperature range increased more than the cholesteric phase temperature range. With increasing the number of aryl rings or mesogenic rigidity, the two mesophase and higher phase transition temperatures were seen. Different from M_1 and M_2 , M_3 and M_4 showed the SmC^{*} besides cholesteric phase.



FIGURE 3 Different mesophase ranges of M_1-M_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Polymer

FIGURE 4 Different mesophase ranges of P1-P4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Moreover, compared with $T_{\rm m}$ and $T_{\rm i}$ of M_2 , those of M_4 increased by 18.5 and 99.7 °C, respectively, and ΔT widened from 18.1 °C for M_2 to 99.3 °C for M_4 because the T_i increased greater than $T_{\rm m}$ with increasing the mesogenic core rigidity.

The polymers P_1 and P_2 showed a glass transition at low temperature and a LC to isotropic phase transition at high temperature, whereas P_3 and P_4 all showed a glass transition, SmC* to SmA phase transition, and SmA to isotropic phase transition, respectively. For the side-chain LC polymers, it is well known that their phase behavior mainly depended on the polymer backbone, mesogenic core, flexible spacer, and terminal groups. For P_1 - P_4 , because of the same polysiloxanes backbone and terminal groups, their phase behavior mainly depended on the mesogenic rigidity and spacer length. According to Table 3the influence of the mesogenic rigidity and spacer length on the phase behavior of P_1-P_4 showed the same tendency as those described above for the monomers. Namely, with increasing the mesogenic rigidity, the glass transition temperature (T_g) and T_i all increased; as the spacer length increased, the $T_{\rm g}$ decreased while $T_{\rm i}$ increased. This result suggested that a longer spacer tended to stabilize the mesophase more than a shorter one because longer spacer could give higher degree of decoupling between the mesogenic side groups and main chains. In addition, the mesophase ranges of P_1-P_4 , presented in Figure 4 were greater than those of the corresponding monomers. This indicated that the polymerization could further stabilize and widen the mesophase range. In a word, a flexible polysiloxane backbone and a long flexible spacer had a tendency toward a low glass transition temperature and wide mesophase range.

Optical Texture

To observe and record the optical textures of M_1-M_4 and P_1-P_4 , a POM with hot stage was used. POM results showed that M_1 only exhibited focal conic texture of a cholesteric phase during cooling process, whereas M₂ exhibited enantiotropic oily streak texture and focal conic texture of the



The blue phase is frustrated defect phase, generally observed in a temperature interval smaller than 1 °C, between the isotropic phase and the cholesteric phase of highly chiral mesogens, and reveals different color corresponding to different

cholesteric phase. For M_3 and $M_4, \, \mbox{they all exhibited broken}$ fan-shaped texture of a SmC* phase, oily streak and focal

conic textures of cholesteric phase, and platelet texture of a

cubic blue phase. The optical textures of M_4 , as an example,

are shown in Figure 5(a-d).

lattice planes, which shows Bragg scattering at different wavelengths, because the condition for constructive interference depends on the distance between lattice planes and their orientation with respect to the direction of incident light. Because of much smaller enthalpies for subsequent transition between the blue phase and into the cholesteric phase,⁴⁶ the transition trace of the blue phase using traditional DSC cannot be seen, but the visual appearance of the cubic blue phase with POM is quite characteristic. On very slow cooling of 0.2 °C/min, single crystals of the blue phase can be obtained, further cooling the blue phase results in a transition to the cholesteric phase. The platelet texture of the blue phase was clearly seen on slow cooling to 173.9 °C for M₃ and 179.7 °C for M₄, and gradually transformed to the focal conic texture of the cholesteric phase at 172.8 °C for M₃ and 177.9 °C for M₄.

The polymers P_1 and P_2 exhibited an enantiotropic fanshaped texture of a smectic A (SmA) phase; in this case, the smectic layers are basically perpendicular to the substrate plane. This indicated that the more ordered SmA phase was formed by the polymerization compared with the corresponding monomers shown cholesteric phase. In addition, P_3 and P₄ showed broken fan-shaped texture of the SmC* phase besides SmA phase. This behavior was attributed to an increased density of the mesogenic units in side chain and hence an ordered organization into the LC phases. The optical texture of P_4 on cooling is shown in Figure 6.

The Selective Reflection of Light

The unique optical properties of SmC* and cholesteric LC are related to their helical supermolecular structure. The periodic helical structure selectively reflects visible light like an ordinary diffraction grating, the pitch of which controls the wavelength of the selective reflection of light. If the reflected wavelength lies in the visible range of the spectrum, both SmC* and cholesteric phases exhibit brilliant colors. Because of the angular dependence of the reflection conditions, the wavelength of the selective reflection of light λ obeys the Bragg condition:

$$\lambda = \overline{n}P\cos\theta,\tag{1}$$

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where \overline{n} is the average index, $n = (n_e + n_o)/2$, n_e and n_o are the extraordinary and ordinary indices of refraction, respectively. P is the pitch of SmC* or cholesteric phase, defined as the spatial distance over which the director rotates 360°, and θ is the incidence angle. The width of the selective reflection band $\Delta \lambda$ is equal to $p\Delta n$, where $\Delta n = n_e - n_o$ is the birefringent of a LC layer perpendicular to the helix axis.



FIGURE 5 Optical textures of M_4 (×200). (a) Oily streak texture of cholesteric phase on heating to 171 °C; (b) platelet texture of a cubic blue phase on cooling to 179 °C; (c) focal conic texture of cholesteric phase on cooling to 175 °C; and (d) broken fan-shaped texture of SmC* phase on cooling to 138 °C.

In fact, the helical axis of SmC^* or cholesteric phase is not completely normal to substrate plane, so eq 1 was revised to eq 2:

$$\lambda = \overline{n}P\cos\frac{1}{2}\left[\arcsin\left(\frac{\sin\theta_1}{\overline{n}}\right) + \arcsin\left(\frac{\sin\theta_2}{\overline{n}}\right)\right], \quad (2)$$

where θ_1 and θ_2 are the incidence angle and reflection angle of light, respectively. When the normal incidence occurred, $\theta = 0^{\circ}$, a maximum wavelength λ_m is described as follows:

$$\lambda_{\rm m} = \overline{n}P.$$
 (3)



FIGURE 6 Optical textures of P4 (×200). (a) Broken fan-shaped texture at 100 °C and (b) fan-shaped texture at 180 °C.



FIGURE 7 UV/Vis spectra of M_4 at SmC* (a) and cholesteric (b) phase temperature ranges.

The selective reflection wavelength depends on the pitch, and the pitch depends on the molecular structure and external field. For M_2-M_4 , the structure affected not only the



FIGURE 8 XRD curve of P₄ at different mesophase ranges.



FIGURE 9 Variation of the *d*-layer spacing as a function of temperature for P_4 .

phase transition temperatures but also the selective reflection wavelength of SmC* and cholesteric phases. With increasing the mesogenic rigidity or reducing the spacer length, the selective reflection of light shifted to the long wavelength region. The reflection color of M2-M4 mainly exhibited red at SmC* phase, and red and green at cholesteric phase. It is well known that dP/dT > 0 for SmC^{*} phase, and dP/dT < 0 for cholesteric phase, so λ_m is temperature dependent. To describe the relationships of $\lambda_{\rm m}$ and temperature, λ_m of M_4 was measured by UV/VIS spectra with hot stage. Figure 7 shows the UV/VIS spectra of M_4 with temperature. λ_m increased from 732 nm at 90 °C to 859 nm at 150 °C at SmC* phase, whereas λ_m decreased from 689 nm at 160 °C to 539 nm at 180 °C at cholesteric phase; this indicated that the selective reflection shifted to the long wavelength region (red shift) at SmC* phase and to the short wavelength region (blue shift) at cholesteric phase with increasing temperature.

Although the polymers P_3 and P_4 also showed the SmC* phase, no selective reflection color was macroscopic seen, and no wavelength of the selective reflection at 200–800 nm was shown in the curves measured by UV/VIS spectra.

TABLE 4 TGA Data of the Polymers

	τa	τ b		Weight Loss (%)			
Polymer	/ d (°C)	/ _{max} (°C)	300 °C	400 °C	500 °C	600 °C	
P ₁	335	374	0.5	62.1	79.9	87.9	
P ₂	338	376	0.5	60.3	79.5	88.1	
P ₃	340	381	0.4	59.1	78.6	87.7	
P ₄	345	380	0.3	58.6	78.2	88.4	

^a Temperature at which 5% weight loss occurred.

^b Temperature of maximum thermal decomposition rate.

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FIGURE 10 TGA curves of P_1 and P_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XRD Studies

To identify mesophase structure, XRD studies were carried out. Figure 8 displays the representative XRD curves of P_4 at 65 and 110 °C. A sharp reflection corresponding to the periodic distance associated with the smectic layers at low angle, and a broad peak associated with the lateral interference of the mesogenic cores or the distance of the local arrangement between the mesogenic side groups in the smectic layer at wide angle were observed. To further confirm the presence of the SmC* and SmA phases, the temperature-dependent *d*-spacing of the smectic layers obtained from powdered samples of P_4 is shown in Figure 9. On cooling from isotropic temperature to 105 °C, the *d*-spacing was practically constant. The *d*spacing of corresponding first-order and second-order reflections was about 40.4 and 20.8 Å, respectively. This result suggested the presence of a SmA phase, which is also confirmed by POM. When the measuring temperature lowered from 100 to 45 $^{\circ}$ C, the *d*-spacing of the first-order reflection gradually decreased from 40.4 to 36.8 Å, which gives strong evidence for the formation of a tilted SmC* phase.

Thermal Stability

The thermal stabilities of the polymers were estimated using TGA, and the corresponding data are listed in Table 4. Representative TGA curves of P_1 and P_4 are shown in Figure 10. The heating rates are 20 °C/min. According to Figure 10two steps of decomposition behavior were observed, the first weight decreased by about 60% from 320 to 400 °C and the second weight decreased by about 22% between 450 and 520 °C. This may be due to the occurrence of the thermal degradation of the mesogenic units in side chain and then the main chain, respectively.

As can be seen in Table 4the temperatures at which 5% weight loss occurred (T_d) were greater than 330 °C; this indicated that **P**₁-**P**₄ had the excellent thermal stability. In addition, the T_d increased with increasing the number of phenyl ring and spacer length; it suggests that the existence

of a biphenyl segment and the longer side chain groups may cause intermolecular $\pi - \pi$ interaction between the mesogenic units in side chain, and interaction between the repeating units and entanglement of the polymer chains, which are expected to increase in the stabilization of the polymer.

CONCLUSIONS

The synthesis and characterization of four new chiral LC monomers and the corresponding polymers based on menthol are described. By inserting a flexible spacer between the mesogenic core and the bulky terminal menthyl fragments, M_1-M_4 all showed mesomorphism and exhibited cholesteric oily streak texture or focal conic texture. In addition, M3 and M_4 also exhibited broken fan-shaped of a SmC* phase and platelet texture of a cubic blue phase. $\lambda_{
m m}$ increased at SmC* phase and decreased at cholesteric phase with increasing temperature. P_1-P_4 exhibited broken fan-shaped texture of the SmC* phase and fan-shaped texture of SmA phase. With increasing the number of aryl rings, the corresponding $T_{\rm m}$ T_{i} and ΔT all increased. With increasing the number of the flexible methylene, the corresponding $T_{\rm m}$ decreased, whereas $T_{\rm i}$ and ΔT increased. In addition, the effect of mesogenic core and spacer length on $T_{\rm g}$ and $T_{\rm i}$ showed the similar tendency as those described for the monomers. Moreover, the mesophase ranges of P_1 - P_4 were greater than those of the corresponding monomers. In addition, the experimental results demonstrated that a flexible siloxane backbone and a long spacer tended to exhibit a low glass transition temperature, more ordered phase, wide mesophase range, and high thermal stability. These experimental results can supply new chiral LC material and theoretical basis to further synthesize and study SmC* or cholesteric elastomers with ferroelectricity or piezoelectricity.

ACKNOWLEDGMENTS

The authors are grateful to Program for Science and Technology Bureau of Shenyang (F12-277-1-44) and Fundamental Research Funds for the Central Universities (N110405006 and N110705001) for financial support of this study.

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