Synthesis and Mesomorphic Properties of Cholesteric Elastomers Based on Chiral Mesogenic Crosslinking Agent

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ABSTRACT: Six chiral monomers (M_1–M_6), and their corresponding polymers (P_1, P_4) and elastomers (P_2, P_3, P_5, P_6) derived from chiral mesogenic crosslinking agent were synthesized. The chemical structures of M_1–M_6 were confirmed by FTIR and ^{1}H NMR spectroscopy. The structure-property relationships of M_1–M_6 and P_1–P_6 were discussed. Their mesomorphic properties and phase behavior were investigated by differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), polarizing optical microscopy (POM), and X-ray diffractometer (XRD) measurements. All monomers obtained, except M_2 and M_5, showed typical oily streaks texture and focal conic texture of cholesteric phase on heating and cooling cycles. The selective reflection of cholesteric monomers and elastomers shifted to the short wavelength region with increasing temperature. The elastomers P_2 and P_5 did not reveal the mesomorphic properties, and P_3 and P_6 showed cholesteric phase. TGA showed that P_1–P_6 had a high thermal stability. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1343–1349, 2008

Key words: liquid-crystalline polymers; elastomers; chiral; crosslinking

INTRODUCTION

As a new supramolecular system, research into liquid-crystalline networks (LCNs) with anisotropic properties and macroscopic features has recently expanded rapidly.[1–15] According to density of crosslinking, two new classes of the LCNs emerge: (i) highly crosslinked liquid-crystalline thermosets (LCTs); and (ii) lightly crosslinked liquid-crystalline elastomers (LCEs). In the last decade, the LCTs have been extensively investigated because the macroscopic structure of mesophase is permanently fixed and the anisotropic properties become temperature independent.[16–22] In contrast to the LCTs, the LCEs combine basic features of polymer elastomers with the anisotropy of physical properties of liquid-crystalline (LC). Consequently, the LCEs not only hold the entropic elasticity but also show reversible mesophase transitions on heating and cooling cycles. From a scientific point of view, the LCEs are fascinating because they allow a study of the interplay of electrical and mechanical forces in a rubbery material. This happens because the reorientation of the mesogenic groups in the electric field creates stress in the network of the polymer chains.

Compared with conventional LCEs, cholesteric LCEs show unusual piezoelectricity,[23–29] tunable mirrorless lasing,[30,31] and photonics[32] besides mechanical properties. Cholesteric LCEs have the potential to act as a device that transforms a mechanical signal into an electrical signal when stress is applied parallel to the cholesteric helix, and considered as a candidate for the novel piezoelectric device. However, to the best of our knowledge, cholesteric LCEs derived from chiral mesogenic crosslinking agent are not reported. It has therefore been necessary to synthesize various kinds of side-chain cholesteric LCEs to explore their potential applications.

In previous study, we reported the synthesis and properties of side-chain cholesteric LCEs derived from smectic, nematic, and nonmesogenic crosslinking agent, respectively.[33–35] In this study, new cholesteric LCEs based on chiral mesogenic crosslinking agent were synthesized. The mesomorphic properties of the monomers and elastomers obtained were characterized with DSC, TGA, POM, and XRD.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, $\overline{M}_n$ = 700–800) was purchased from Jilin Chemical Industry Co. (Jilin, China). 4-Hydroxybenzoic acid was purchased from Beijing Fuxing Chemical Industry Co. (Beijing, China). 3,5-Dihydroxybenzoic acid was purchased from Beijing Chemical Reagent Co. (Beijing, China). Undecylenic acid was purchased from Beijing Jinlong chemical Reagent Co. (Beijing, China). Cholesterol was purchased from Henan Xiayi Medical Co. (Xiayi, China). Toluene used in the hydrosilylation reaction was purified by treatment with LiAlH$_4$ and distilled before use. All other solvents and reagents were purified by standard methods.

Characterization

FTIR spectra were measured on a Perkin–Elmer spectrum One (B) spectrometer (Perkin–Elmer, Foster City, CA). ^{1}H NMR spectra (400 MHz) were obtained with a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). The phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 (Netzsch, Wittelsbacherstr, Germany) equipped with a liquid nitrogen cooling system. The heating and cooling rates were 10°C/min. The thermal stability of the polymers under nitrogen gas was measured with a Netzsch TG 209C thermogravimetric analyzer. A Leica DMRX (Leica, Wetzlar, Germany) POM equipped with a Linkam THMSE-600 (Linkam, Surrey, England) hot stage was used under inert atmosphere to observe phase transition temperatures and analyze mesomorphic properties for the monomers and polymers through observation of optical textures. XRD measurements were performed with nickel-filtered Cu-K$_\alpha$ radiation with a DMAX-3A Rigaku (Rigaku, Tokyo, Japan) powder diffractometer.

Synthesis of the intermediate compounds

The synthetic route to the intermediate compounds is carried out in Scheme 1. The yield, melting temperatures and IR characterization, of compounds 1–6 are showed in Table I. 4-Allyloxybenzoic acid (1) and 4-(10-undecylen-1-yloxy)benzoic acid (4) were prepared according to the method reported previously by Hu et al.[33,36]

3,5-Diallyloxybenzoic acid (2)

3,5-Dihydroxybenzoic acid (15.4 g, 0.1 mol) and potassium carbonate (29.7 g, 0.3 mol) were dissolved in 150 mL of dimethyl sulfoxide (DMSO). 3-Bromopropene (36.3 g, 0.3 mol) was added dropwise to the above mixture. After reacting for 36 h at 75°C, the mixture

was extracted by ethyl ether. After concentrating the extracted solution, the sodium hydroxide (4 g, 0.1 mol) and 100 mL of methanol were added into the residue. The mixture was refluxed 1 h, and then poured into cold water and acidified with 20% chlorhydric acid. The crude product was recrystallized from ethanol.

3,5-Di(4-allyloxybenzoyloxy)benzoic acid (3);
3,5-Di(10-undecylen-1-yloxy)benzoic acid (5);
3,5-Di[4-(10-undecylen-1-yloxy)benzoyloxy]benzoic acid (6)

The compounds 3, 5, and 6 were prepared by the same method. The synthesis of 6 is described below as an example.

4-(10-Undecylen-1-yloxy)benzoyl chloride was prepared through the reaction of compound 4 with excess thionyl chloride according to the reported literature.[36] The acid chloride obtained (32.3 g, 0.1 mol) was dissolved in 30 mL of dry tetrahydrofuran (THF), and then added dropwise to a cold solution of 3,5-dihydroxybenzoic acid (7.7 g, 0.05 mol) in 70 mL of THF and 8 mL of pyridine. The mixture was heated to reflux for 15 h. After concentrating the reaction solution, the residue was poured into a beaker filled with 300 mL of water. The crude product was obtained by filtration, and recrystallized from ethanol.

Synthesis of the monomers

The synthesis of chiral monomers is shown in Scheme 2. Cholesteryl 4-allyloxybenzoate (M$_1$) and cholesteryl 4-(10-undecylen-1-yloxy) benzoate (M$_4$) were synthesized according to the reported literature.[33,36]

Cholesteryl 3,5-diallyloxybenzoate (M$_2$), Cholesteryl 3,5-di(4-allyloxybenzoyloxy)benzoate (M$_3$), Cholesteryl 3,5-di(10-undecylen-1-yloxy)benzoate (M$_5$), Cholesteryl 3,5-di[4-(10-undecylen-1-yloxy) benzoyloxy]benzoate (M$_6$)

Four monomers M$_2$, M$_3$, M$_5$, and M$_6$ were prepared by the same method. The synthesis of M$_2$ is described below as an example.

3,5-Diallyloxybenzoyl chloride was synthesized through the reaction of compound 2 with excess thionyl chloride according to the similar literature reported previously by Hu et al.[33] The acid chloride obtained (12.6 g, 0.05 mol) was dissolved in 20 mL of chloroform, and then added dropwise to a cold solution of cholesterol (19.4 g, 0.05 mol) in 60 mL of chloroform and 4 mL of pyridine. The reaction mixture was stirred at room temperature for 2 h, and refluxed for 18 h. The precipitate was removed by filtration and the crude product was precipitated by adding ethanol to the filtrate, and recrystallized from ethanol.
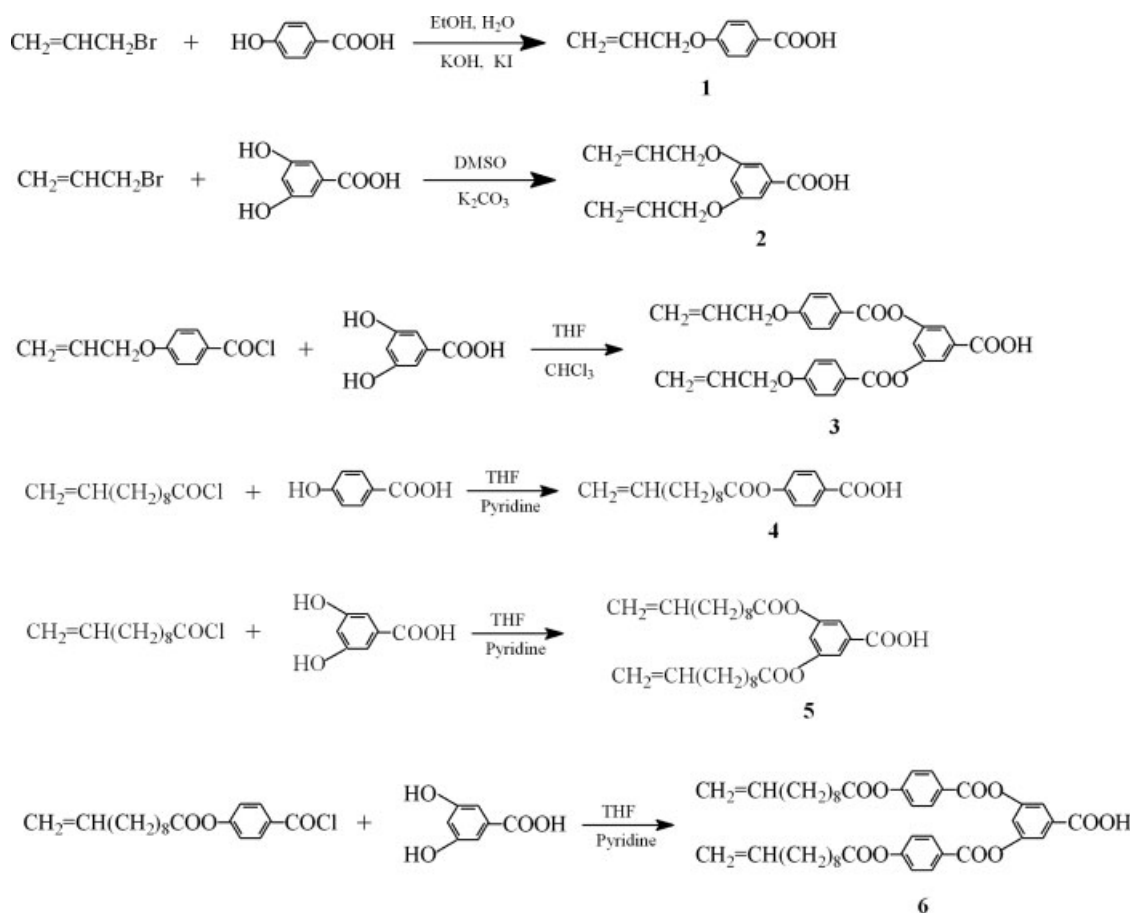
Scheme 1 Synthesis of intermediate compounds.

M₂: White solid, yield: 65%, mp 88°C. IR (KBr, cm⁻¹): 3092 (=C—H); 2937, 2887 (—CH₃, —CH₂—); 1716 (C=O); 1596, 1445 (Ar—); 1232 (C—O—C). ¹H NMR (CDCl₃, TMS, δ, ppm): 0.72–2.26 (m, 43H, cholesteryl—H); 3.92 (t, 1H, —COOCH< in cholesteryl); 4.53 (t, 4H, —CH₂O—); 5.20 (m, 4H, CH₂=CH—); 5.33 (m, 1H, =CH— in cholesteryl); 6.02 (m, 2H, CH₂=CH—); 6.50–7.18 (m, 3H, Ar—H).
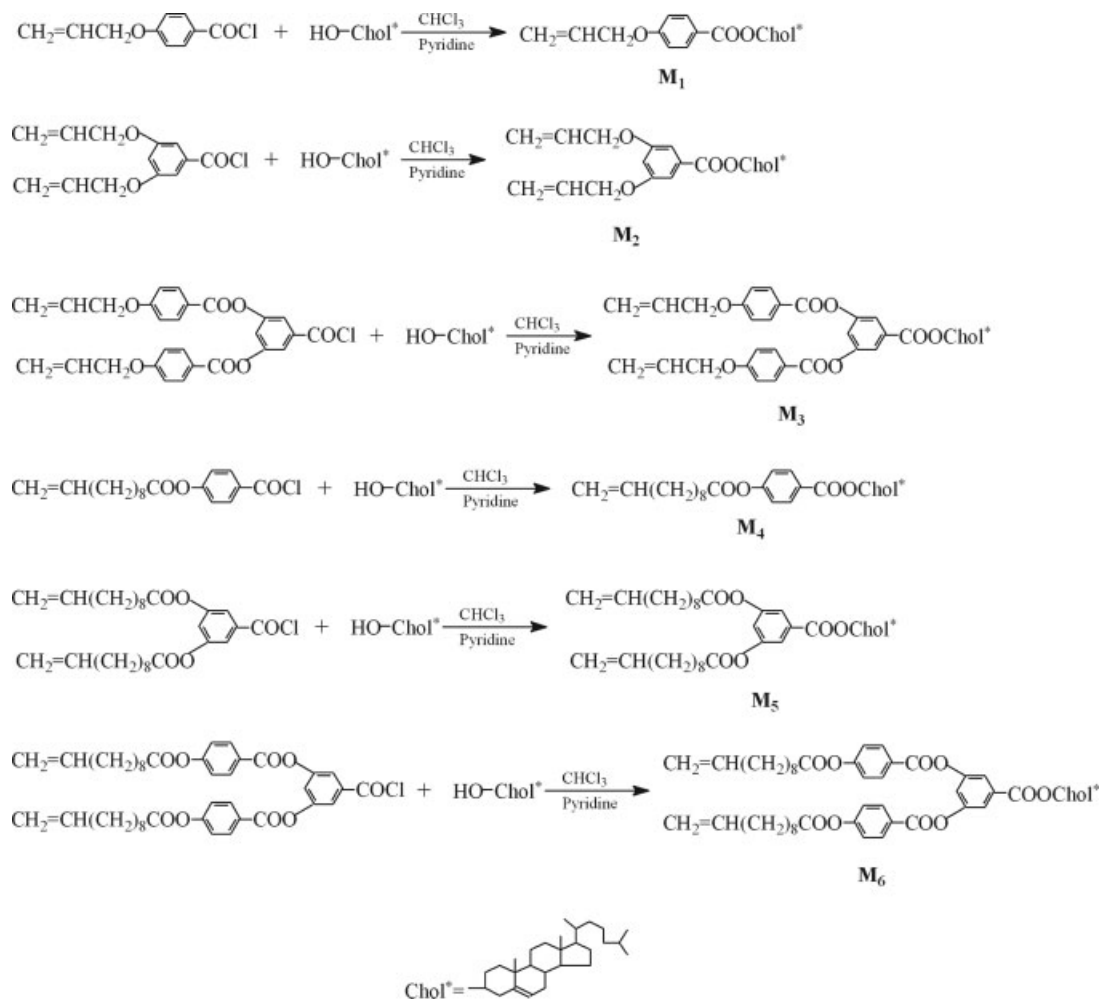
M₃: Recrystallized from ethanol/acetone (1:1), white solid, yield: 68%, mp 105°C. IR (KBr, cm⁻¹):

3097 (=C—H); 2932, 2868 (—CH₃, —CH₂—); 1706 (C=O); 1608, 1511 (Ar—); 1258 (C—O—C). ¹H NMR (CDCl₃, TMS, δ, ppm): 0.71–2.23 (m, 43H, cholesteryl—H); 3.93 (t, 1H, —COOCH< in cholesteryl); 4.51 (t, 4H, —CH₂O—); 5.22 (m, 4H, CH₂=CH—); 5.30 (m, 1H, =CH— in cholesteryl); 6.01 (m, 2H, CH₂=CH—); 7.01–8.11 (m, 11H, Ar—H).

M₅: Recrystallized from ethanol, sticky matter, yield: 55%. IR (KBr, cm⁻¹): 3077 (=C—H); 2929, 2854 (—CH₃, —CH₂—); 1769, 1723 (C=O); 1641

TABLE I
Yield, Melting Temperatures, and IR Characterization of Intermediate Compounds

Compounds	Yield (%)	Recrystallized solvent	T_m (°C)	IR (KBr) (cm⁻¹)
1	67	Ethanol	164	3300–2500 (—COOH); 1682 (C=O); 1604, 1450 (—Ar); 1251 (C—O—C)
2	48	Ethanol	52	3300–2500 (—COOH); 1692 (C=O); 1600, 1447 (—Ar); 1255 (C—O—C)
3	53	Ethanol/acetone (1 : 1)	157	3300–2500 (—COOH); 1714, 1698 (C=O); 1600, 1440 (—Ar); 1250 (C—O—C)
4	58	Ethanol	128	3300–2500 (—COOH); 2975, 2852 (—CH₂—); 1754, 1682 (C=O); 1640 (C=C); 1602, 1508 (—Ar)
5	52	Ethanol	58	3300–2500 (—COOH); 2924, 2853 (—CH₂—); 1770, 1698 (C=O); 1642 (C=C); 1594, 1470 (—Ar)
6	55	Ethanol/acetone (2 : 1)	94	3300–2500 (—COOH); 2922, 2850 (—CH₂—); 1752, 1684 (C=O); 1641 (C=C); 1601, 1502 (—Ar)

Scheme 2 Synthesis of chiral monomers.

(C=C); 1594, 1444 (Ar—). ^{1}H NMR (CDCl$_3$, TMS, δ, ppm): 0.63–2.39 [m, 75H, —CH$_2$— and choles-teryl—H]; 4.11 (t, 1H, —COOCH< in cholesteryl); 5.08 (m, 4H, CH$_2$=CH—); 5.33 (m, 1H, =CH— in cholesteryl); 5.97 (m, 2H, CH$_2$=CH—); 7.01–7.75 (m, 3H, Ar—H).

M$_6$: Recrystallized from ethanol/acetone (2:1), sticky matter, yield: 57%. IR (KBr, cm^{-1}): 3079 (=C—H); 2932, 2867 (—CH$_3$, —CH$_2$—); 1766, 1722 (C=O); 1642 (C=C); 1605, 1466 (Ar—). ^{1}H NMR (CDCl$_3$, TMS, δ, ppm): 0.65–2.43 [m, 75H, —CH$_2$— and cholesteryl—H]; 4.07 (t, 1H, —COOCH< in cho-lesteryl); 5.02 (m, 4H, CH$_2$=CH—); 5.38 (m, 1H, =CH— in cholesteryl); 6.01 (m, 2H, CH$_2$=CH—); 7.18–8.20 (m, 11H, Ar—H).

Synthesis of the polymers and elastomers

The polymers **P$_1$** and **P$_4$** were synthesized according to the reported literature.[33,36] The elastomers **P$_2$, P$_3$, P$_5$,** and **P$_6$** were prepared by a one-step hydrosilyla-tion reaction. The synthesis of **P$_6$** is described below

as an example. PMHS and **M$_6$** [feed ratio (mol) = 1:3.5] were dissolved in dried toluene. The reaction mixture was heated to 65°C under nitrogen, and then 2 mL of THF solution of the Pt catalyst (5 mg/mL) was injected with a syringe. The mixture was reacted for 48 h. **P$_6$** was obtained by the reprecipita-tion from toluene solutions into methanol, purified by the filtration from hot ethanol, and then dried *in vacuo*. IR spectra of **P$_6$** showed the disappearance of the Si—H stretching band at 2166 cm^{-1} and the ole-finic C=C stretching band at 1641 cm^{-1}. Characteris-tic Si—O—Si and Si—C stretching bands appeared at 1300−1000 cm^{-1}. In addition, the absorption bands of the ester C=O and aromatic still existed. **P$_1$** and **P$_4$** were dissolved in toluene, however, the elas-tomers obtained were insoluble in hot toluene.

RESULTS AND DISCUSSION

Thermal analysis

The thermal properties and phase behavior of **M$_1$**−**M$_6$** and **P$_1$**−**P$_6$** were investigated with DSC.

TABLE II
Phase Transition Temperatures of Monomers

Monomers	T_m (°C)	ΔH_m (J g^{-1})	T_i (°C)	ΔH_i/(J g^{-1})	LC phase	Reflection color
M_1	108.2	42.5	223.7	1.6	Ch	Red, green, blue
M_2	88.2	29.9	–	–	–	–
M_3	104.7	22.2	218.3	1.5	Ch	Green, blue
M_4	110.0	20.6	195.5	1.8	Ch	Green
M_5	–	–	–	–	–	–
M_6	–	–	61.2	0.9	Ch	Green

Their phase transition temperatures and corresponding enthalpy changes, obtained on the second heating scan, are summarized in Tables II and III. Representative DSC heating and cooling thermograms of M_3 are presented in Figure 1.

As seen from the data listed in Table II, the molecular structure had a considerable effect on the phase behavior of M_1–M_6. Compared with the melting temperature (T_m) and the clearing temperature (T_i) of M_1, T_m of M_2 decreased by 20.0°C, and T_i disappeared when the allyloxy side groups were introduced into 3- and 5-position of the phenyl ring. The reason is that (1) the molecular coplanarity is broken, and (2) the molecular width increases, which makes the intermolecular distance increase and intermolecular force decrease. The above two effects can make T_i fall, and even disappear. So DSC thermograms of M_2 only showed a melting transition. This indicated that M_2 did not display the mesomorphic properties, which is consistent with POM results. With increasing the rigidity of the side groups, the intermolecular force increased, and it made T_m increase and the mesomorphic properties appear again. Compared with those of M_2, T_m of M_3 increased by 16.5°, and T_i appeared when the rigid 4-allyloxybenzoyloxy groups were introduced into 3- and 5-position of the phenyl ring. Similarly, compared with M_4, M_5 did not show the mesomorphic properties and M_6 displayed a cholesteric to isotropic phase transition. Moreover, DSC thermograms of M_5 and M_6 did not reveal the melting transition at above 0°C.

The thermal properties of P_1 and P_4 have been reported by Hu et al.[33,36] DSC heating thermograms of the elastomers P_2, P_3, P_5, and P_6 only showed a glass transition, but POM results showed that P_3 and P_6 exhibited the mesomorphic properties. For the elastomers containing the same flexible spacer, the glass transition temperature (T_g) increased with increasing the rigidity of the side groups. T_g of P_3 increased by 29.2°C than that of P_2, and T_g of P_6 increased by 38.5°C than that of P_5. Moreover, T_g of the elastomers containing the decoyloxy spacer was less than that of the elastomers containing the propoxy spacer. According to Table III, T_g of P_5 decreased by 47.9°C than that of P_2, and T_g of P_6 decreased by 38.6°C than that of P_3.

The thermal stability of P_1–P_6 was detected with TGA. The corresponding data are shown in Table III. Typical TGA curve of P_1–P_3 is shown in Figure 2. TGA results showed that the temperatures at which 5% weight loss occurred (T_d) were greater than 310°C for P_1–P_6, this displayed that all these polymers had a high thermal stability. Moreover, the thermal stability of the elastomers was higher than that of the uncrosslinking polymers.
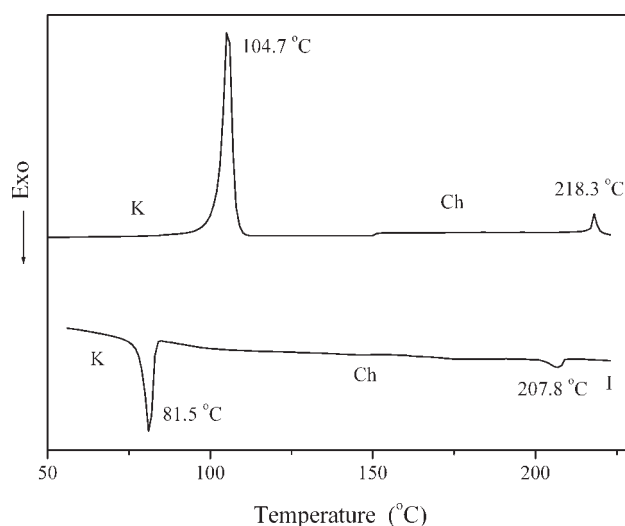
TABLE III
Thermal Properties of Polymers and Elastomers

Samples	T_g (°C)	T_i (°C)	T_{onset}[a] (°C)	T_d[b] (°C)	Weight loss (%)		
					300°C	350°C	400°C
P_1	71.6	278.3	308.2	332.4	0.5	16.9	63.2
P_2	57.3	–	309.5	334.2	0.5	15.8	53.0
P_3	86.5	–	313.8	337.7	0.2	12.5	42.2
P_4	38.6	233.6	276.4	316.3	2.6	21.4	61.2
P_5	9.4	–	285.3	321.3	1.8	19.2	60.8
P_6	47.9	–	291.8	324.7	1.4	17.5	58.4

[a] Temperature of initial thermal decomposition.
[b] Temperature at which 5% weight loss occurred.

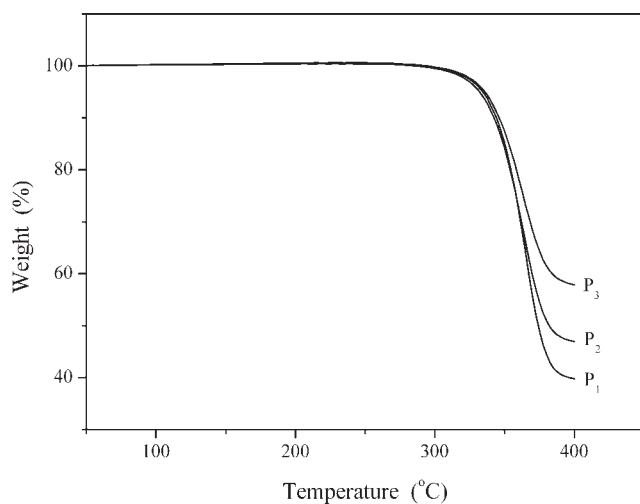**Figure 1** DSC thermograms of M_3.

**Figure 2** TGA curves of P_1-P_3.

Textures analysis

The cholesteric optical textures of M_1-M_6 and P_1-P_6 were studied by POM with hot stage. The optical textures of M_1, M_4, P_1, and P_4 have been reported by Hu et al.[33,36] POM results showed that M_3 and M_6 exhibited enantiotropic cholesteric phase on heating and cooling cycles, and M_2 and M_5 did not show any texture and birefringence, this is consistent with the results obtained by DSC. When M_3 was heated to 104°C, the sample began to melt, typical oily streaks texture of the cholesteric phase and selective reflection gradually appeared. The reflection color changed from green to blue with increasing temperature. Texture disappeared at 225°C. When the isotropic state was cooled to 221°C, the focal conic appeared, if a mechanical field was superimposed on the sample at that time, for example, slight shearing the melt would cause macroscopic orientation of the cholesteric domains, and the focal conic texture transformed to oily streaks texture and the selective reflection appeared again, which is typical characteristic of cholesteric LC. The reflection color changed from blue to green, yellow, and red with decreasing temperature. Optical textures of M_3 are shown in Figure 3(a,b). M_6 showed the cholesteric texture and selective reflection at room temperature, and the reflection color was green. The mesomorphic properties and texture disappeared at 67°C.

P_2 and P_5 did not reveal any texture and stress-induced birefringence, but showed the elasticity. P_3 showed the stress-induced birefringence, which is similar to those described by Mitchell et al.[37] The reflection color of P_3 changed from red to green with increasing temperature under stress, but the good texture pictures could not been obtained because of the elasticity. P_6 also showed the stress-induced bire-

fringence and selective reflection. The elasticity of the polymer networks obtained became better with increasing temperatures.

XRD analysis

In general, a sharp and strong peak at low angle (1° $< 2\theta < 5°$) in small-angle X-ray scattering (SAXS) curves and a broad peak associated with lateral packing at $2\theta \approx 20°$ in wide-angle X-ray diffraction (WAXD) curves were observed for smectic structure. For nematic structure, no peak appeared in SAXS curve, but a broad peak at $2\theta \approx 20°$ in WAXD curve was observed. For cholesteric structure, no peak appeared in SAXS curve, however, we discovered that a broad peak occurred at $2\theta = 16–18°$ in WAXD curve.[33–35] Representative XRD curves of P_3 and P_6
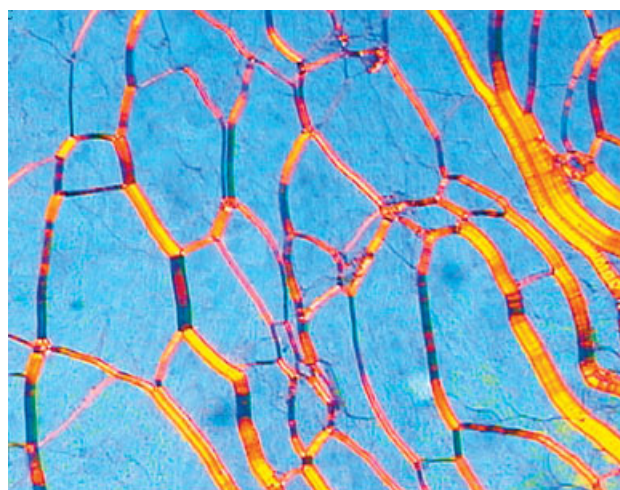
(a)
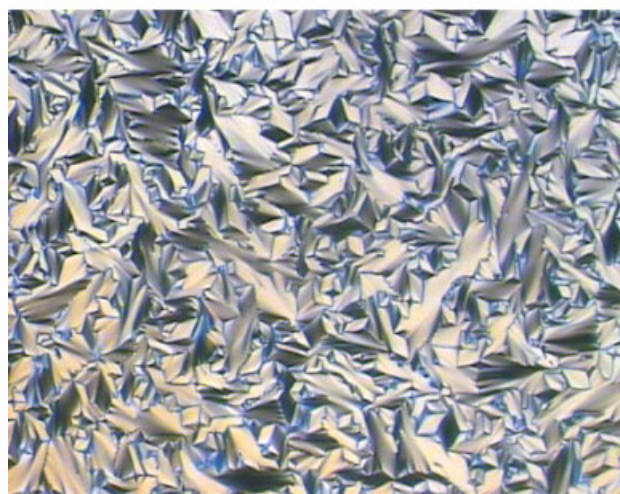
(b)

Figure 3 Optical textures of M_3 (×200): (a) oily streaks texture at 179°C; (b) focal conic texture at 211°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
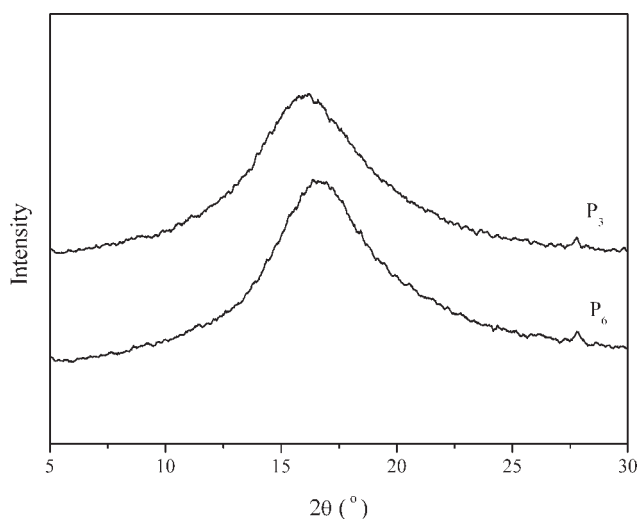
Figure 4 XRD patterns of P_3 and P_6.

are shown in Figure 4. A sharp peak did not appear in SAXS curves, and a broad peak was observed at $2\theta = 16–17°$ in WAXD curves. Therefore, the cholesteric structure of P_3 and P_6 was confirmed with POM and XRD.

CONCLUSIONS

The six chiral monomers, two polymers and four elastomers were prepared and characterized. All monomers, except M_2 and M_5, showed cholesteric phase. The elastomers P_2 and P_5 only revealed the elasticity, and P_3 and P_6 showed cholesteric phase. All of the obtained elastomers displayed a high thermal stability. The increase of the molecular width did not favor the formation of the mesogenic orientational order. T_g of the elastomers increased with increasing the rigidity of the side groups or decreasing the length of the flexible spacer.

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