

Synthesis and Characterization of Side-Chain Liquid-Crystalline Elastomers Containing Cholesterol

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ABSTRACT: A series of new smectic and cholesteric liquid-crystalline elastomers were prepared by graft polymerization of mesogenic monomer with the chiral and nonmesogenic crosslinking agent using polymethylhydrosiloxane as backbone. The chemical structures of the monomers and polymers obtained were confirmed by Fourier transform infrared and proton nuclear magnetic resonance spectra. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction measurements. M_1 showed cholesteric phase during the heating and the cooling cycle. Polymer P_1 , elastomers P_2 and P_3 exhibited smectic phase, elastomers

P_4 – P_6 showed chiral smectic C phase, P_7 showed cholesteric phase, and P_8 displayed stress-induced birefringence. The elastomers containing less than 15 mol % M_2 displayed elasticity and reversible phase transition with wide mesophase temperature ranges. Experimental results demonstrated that the glass transition temperatures, the isotropization temperatures, and the mesophase temperature ranges decreased with increasing content of the crosslinking unit. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 383–390, 2005

Key words: chiral; elastomers; crosslinking agent

INTRODUCTION

Since the synthesis of liquid crystalline elastomers (LCEs) was reported in 1981, much attention has been paid to the novel materials that combine the properties of LC phase with rubber elasticity.^{1–7} Recently, cholesteric and chiral smectic C(SmC) elastomers have attracted both industrial and scientific interests because of their additional properties, such as nonlinear optical materials, fast optical switch, piezoelectricity, and others. It is especially worthwhile to note that they are ideal material for the investigation of piezoelectric effects,^{8–16} because elastomers prevent macroscopic flow, which disturbs the emergence of piezoelectricity in the conventional low-molar mass ferroelectric liquid crystals.^{17,18} Our group has conducted many studies in the field of cholesteric and smectic LCEs.^{19–21} In our previous study, cholesteric and smectic LCEs were obtained by introducing a chiral crosslinking agent with nematic and smectic–nematic LC monomers. In the present study, we prepared a new series of side-chain LCEs with pendant cholesteric monomer groups (M_1 , cholesteryl 4-allyloxybenzoate) and chiral and nonmesogenic crosslinking

agents (M_2 , isosorbide 4-undecanoyloxy bisate), which linked directly to the polymethylhydrosiloxane backbone with flexible spacers. We expected to obtain S_C^* or cholesteric LCEs by the method and to observe the effect of chirality on the liquid crystal properties. We chose isosorbide because it possesses a high twisting power and can better introduce chirality into LCEs.²² However, to the best of our knowledge, it is necessary and valuable to study various kinds of side-chain cholesteric or S_C^* LCEs with chiral crosslinking agents, because little research has been done on it. The mesomorphic properties of the monomers and elastomers obtained were characterized by DSC, POM, and X-ray. The chirality influence of crosslinking agents on phase behavior of the elastomers was discussed.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, $M_n = 700$ – 800) was purchased from Jilin Chemical Industry Co. (China). Cholesterol was purchased from Beijing Chemical Industry Co.(China). Undecylenic acid was purchased from Beijing Jinlong Chemical Reagent Co. Ltd (China). Isosorbide was bought from Yangzhou Shenzhou New Material Co. Ltd (China). 3-Bromopropene was obtained from Yancheng Longsheng Fine Chemical Industry Co. (China). Toluene used in the hydrosilylation reaction was first refluxed over so-

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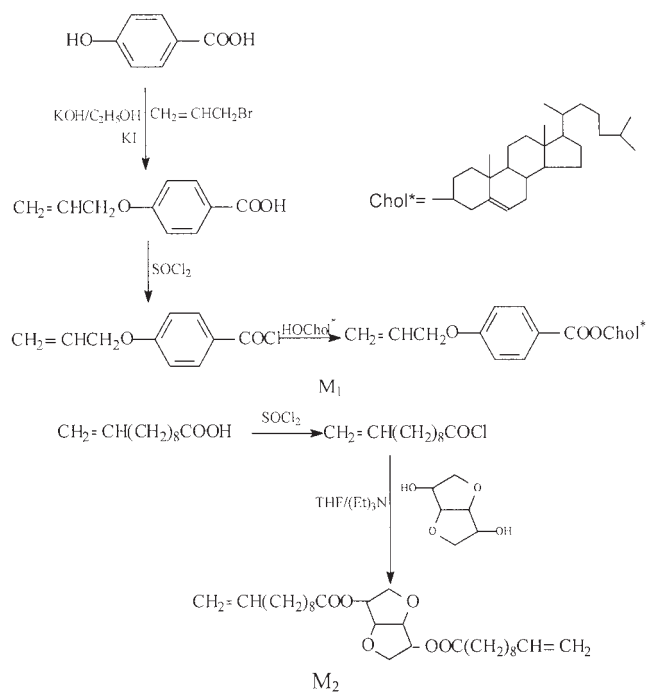
dium and then distilled under nitrogen. All other solvents and reagents were purified by standard methods.

Characterization

IR spectra were measured on a Perkin–Elmer spectrum one FTIR spectrometer (Perkin–Elmer Instruments, Wellesley, MA). $^1\text{H-NMR}$ spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Palo Alto, CA). Specific rotation was performed with a Perkin–Elmer 341 polarimeter (Perkin–Elmer Instruments, UK). Phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 (Netzsch, Germany) with a liquid nitrogen cooling system. The heating and cooling rates were $10^\circ\text{C}/\text{min}$. A Leica DMRX (Leica, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe phase transition temperatures and to analyze LC properties for the monomers and polymers through observation of optical textures. XRD measurements were performed with nickel-filtered $\text{Cu-K}\alpha$ ($\lambda = 0.1542 \text{ nm}$) radiation with a DMAX-3A Rigaku (Rigaku, Japan) powder diffractometer. Specific rotation of M_1 and M_2 of solutions of 8 g/mL in the toluene were measured in 2 mL cuvettes of 100 mm length using the light of a Na lamp at $\lambda = 589 \text{ nm}$ and at 18.0°C .

Synthesis of the monomers

The synthesis of the olefinic monomers is shown in Scheme 1.



Scheme 1 Synthetic route of monomers.

Synthesis of cholesteryl 4-allyloxybenzoate (M_1)

A few drops of DMF was added to a suspension of 4-allyloxy-benzoic acid (0.1 mol) in freshly distilled thionyl chloride (40 mL) and the reaction mixture was refluxed for 10 h and the excess thionyl chloride then was removed under reduced pressure to give the corresponding acid chloride. Cholesterol (0.026 mol) was dissolved in a mixture of dry triethylamine (10 mL) and dry chloroform (100 mL); the 4-allyloxy-benzoic

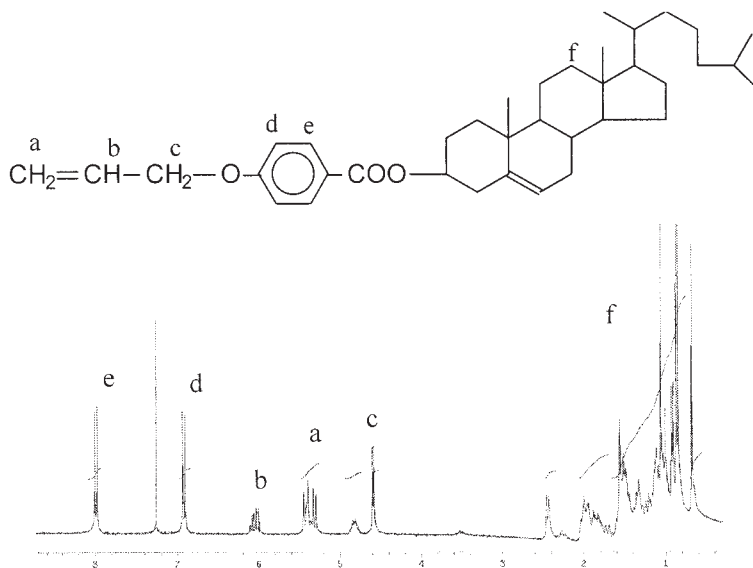


Figure 1 $^1\text{H-NMR}$ spectra of M_1 .

acid chloride was then added slowly at once in an ice bath, and the reaction mixture was stirred for 10 h at room temperature, and then reacted for 2 h at 60°C. The cold reaction mixture was precipitated into water; the precipitated product was isolated by filtration and was recrystallized from glacial acetic acid: yield 86%, mp 113.2°C, $[\alpha]_{589}^{18.0} = -5.45^\circ$.

IR (KBr): 3082(=CH), 2951, 2850 (–CH₃, –CH₂), 1711 (C=O), 1645 (C=C), 1605–1450 (Ar–), 1258 cm^{–1} (C–O–C).

¹H NMR (CHCl₃) δ~ (ppm): 0.68–2.45, 3.56, 5.45 (m, 45H, cholesterol), 4.57–4.60 (d, 2H, CH₂ = CHCH₂), 5.29–5.39 (m, 2H, CH₂=CH), 6.04–6.11 (m, 1H, CH₂ = CH), 6.90–8.00 (m, 4H, Ar–H). In Figure 1, the ¹H-NMR spectra of M₁ is shown.

Isosorbide 4- undecanoyloxy bisate (M₂)

M₂ was prepared by similar procedures according to a previously reported study.²³

Isosorbide(0.03 mol) was dissolved in a mixture of dry triethylamine (10 mL) and dry THF (100 mL); the undecylenic acid chloride was then added at once to the ice bath and then the reaction mixture was refluxed for 72 h at room temperature. The crude product was obtained by layering and extracting with toluene. The organic layer was washed by water, dilute alkali, and water and then dried by magnesium sulfate. The product was obtained by evaporating toluene thoroughly under reduce pressure: yield 65%, mp 22°C, $[\alpha]_{589}^{18.0} = +63.2^\circ$.

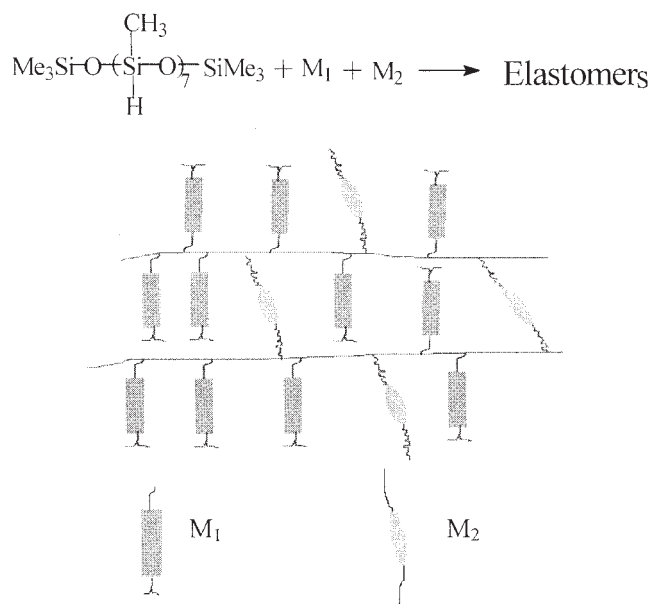
IR(kbr): 3057(=ch), 2975, 2855(–ch₃, –ch₂), 1742(c=o), 1640(c=c), 1605–1450 (ar–), 1235 cm^{–1} (c–o–c).

¹H NMR (CHCl₃) δ~ (ppm): 1.29–1.66(m, 12H, (–CH₂–)₆), 2.00–2.07(d, 2H, CH₂=CHCH₂), 2.28–2.39(m, 2H, –CH₂CH₂COO), 3.77–4.48 (m, 8H, sosorbide), 4.81–5.19 (m, 2H, CH₂ = CH), 5.74–5.85(m, 1H, CH₂ = CH).

Synthesis of the polymers

The synthetic ways of uncrosslinked and crosslinked polymers (elastomers) are on the similar plan. The synthetic routes and schematic representation of elastomers are outlined in Scheme 2. The mesogenic monomers and the different contents of chiral crosslinking agents reacted with Si–H of PMHS to form elastomers in the presence of the Pt catalyst. The detailed processes are similar to our previous work.²¹ The obtained elastomers were insoluble in toluene, xylene, DMF, chloroform, etc. but could swell in these solvents. All polymerization and solubility values for the polymers are listed in Table I.

IR(kbr): 2950–2868(–ch₃, –ch₂), 1714(c=o), 1605–1450(ar–), 1200–1000 cm^{–1} (si–o–si).



Scheme 2 Synthesis and schematic representation of elastomers.

RESULTS AND DISCUSSION

Synthesis

The monomers, a cholesteric liquid crystalline (M₁) and a chiral crosslinking agent (M₂), were synthesized. The reaction pathways to the M₁ and M₂ are shown in Scheme 1. M₁ was prepared by esterification of cholesterol with 4-allyloxy benzoic acid chloride. M₂ was prepared by esterification of 4-undecenoic acid chloride with isosorbide. The chemical structures of the two monomers were characterized by FTIR and ¹H-NMR spectroscopy. The FTIR of M₁ and M₂, respectively, showed characteristic bands at 1714–1711 (cm^{–1}) originating from ester.

C=O stretching (1645–1640 cm^{–1}) was due to olefinic C=C stretching. The ¹H-NMR spectra of M₁ showed a multiplet at 6.90–8.00 ppm: 6.04 ~ 6.11, 5.29 ~ 5.39, 4.57 ~ 4.60, and 0.68–2.45, 3.56, and 5.45 ppm corresponding to aromatic, vinyl, methyleneoxy, and cholesterol protons. The ¹H-NMR spectra of M₂ showed a multiplet at 5.74–5.85 ppm: 4.81–5.19, 3.77–4.88, 2.28–2.39, and 1.29–2.07 ppm corresponding to vinyl, isosorbide, methylene linked to ester, and methylene protons. The new series of elastomers P₂–P₈ were prepared by a one-step hydrosilylation reaction between Si–H groups of PMHS and olefinic C=C of the cholesteric monomer and difunctional chiral crosslinking agent in toluene, using hexachloroplatinate as catalyst at 60°C. The yields and properties of P₁–P₈ are summarized in Table I. The obtained elastomers P₂–P₈ were insoluble in toluene, xylene, DMF, chloroform, etc. but could swell in these solvents. The FTIR spectra of P₁–P₈ showed the complete disappear-

TABLE I
Polymerization of P₁-P₈

Polymers	Feed/mmol			M ₂ ^a (mol %)	Yields (%)	Solubility ^b	
	PMHS	M ₁	M ₂			Toluene	DMF
P ₁	0.500	3.500	0.000	0	86.5	+	+
P ₂	0.500	3.360	0.070	2	83.9	—	—
P ₃	0.500	3.220	0.140	4	85.2	—	—
P ₄	0.500	3.080	0.210	6	79.5	—	—
P ₅	0.500	2.940	0.280	8	81.6	—	—
P ₆	0.500	2.800	0.350	10	82.5	—	—
P ₇	0.500	2.450	0.525	15	75.3	—	—
P ₈	0.500	2.100	0.700	20	69.8	—	—

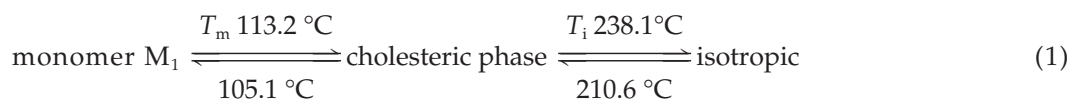
^a Molar fraction of M₂ based on M₁ + M₂.

^b +, dissolve; —, insolubility or swelling.

ance of Si-H stretching band at 2166 cm⁻¹. Characteristic absorption bands appeared at 1714, 1605–1450, and 1200–1000 cm⁻¹ attaching to the stretching of ester C=O, aromatic, and Si-O-Si, respectively. That is, the chemical structures of obtained monomers and polymers are consistent with the molecular design.

Thermal analysis

The DSC curves of M₁ are shown in Figure 2, and the phase transition temperature of M₁ during heating and cooling runs as follows:



When there is a small molecular weight liquid crystalline occurred phase transition, there will be strict enthalpy changes that are the direct result of the degree of acting force between the liquid crystalline molecule and the ordered arrangement. The heating cycle thermogram clearly showed two endotherms at 113.2 and 238.1°C; on the subsequent cooling cycle, there were two corresponding endotherms at 210.6 and 105.1°C. The DSC measurements revealed a melting to

the cholesteric phase at 113.2°C and a clearing at 238.1°C. On cooling from the isotropic phase into the cholesteric phase at 210.6°C, and cholesteric phase to crystalline at 105.1°C. As seen from Figure 2, the enthalpy values changing from crystalline to melting are large and those from cholesteric to isotropic phase are small. Monomer M₁ is an enantiotropy cholesteric liquid crystalline. The results of thermal and optical analyses are consistent.

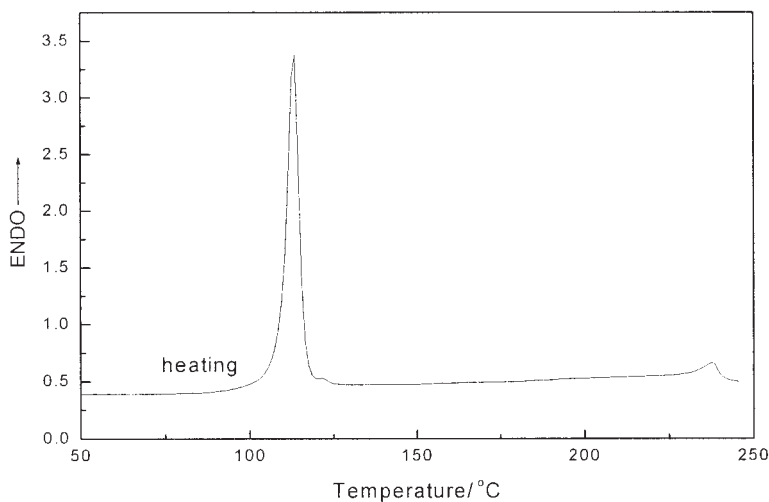


Figure 2 DSC thermographs of liquid crystalline monomer.

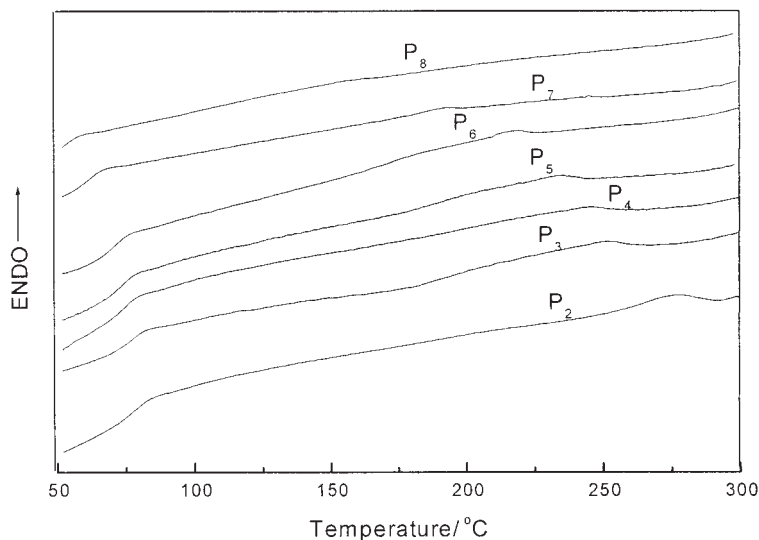


Figure 3 DSC thermographs of liquid crystalline elastomers.

Representative DSC curves of elastomers, obtained on the second heating scan, are presented in Figure 3; phase transition temperatures and the results of thermal analysis are shown in Table II; and the effect of the content of crosslinking units on the phase transition are shown in Figure 4. DSC curves show a glass transition temperature and the temperature of mesophase to isotropic phase transition. All transitions are reversible and do not change on repeated heating and cooling cycles; the phase transition temperatures showed in the DSC thermograms are consistent with the mesomorphic transition temperatures observed by POM.

As seen from the data in Table II and Figure 4, T_g values decreased with the increase in the content of chiral crosslinking agent. It is well known the influential factors of T_g are summarized as the property of polymer backbone, the rigidity of mesogenic unit, the flexible spacer length, and the content of the crosslinking agent. The polysiloxanes backbone is inclined to reduce the T_g value; the rigid mesogenic unit with a short carbochain is inclined to increase T_g value. The crosslinking agent has two opposite actions: crosslink-

ing and plasticization. Crosslinking imposes additional constraints on the segment motion of polymer chains and might be expected to raise the glass transition temperature. Plasticization inclines to reduce the glass transition temperature. The molecular lengths of M_1 and M_2 are 22.5 and 30.5 Å, respectively; it is shown that the monomer has relatively enough space to move in the elastomers. As we know, the cholesteryl has a rigid steroid structure and the space-hindered effect is large, so, when the long, flexible chiral crosslinker is introduced into the elastomers, the plasticizer becomes dominant and this effect remains as the main factor until the properties of LCE disappear. It can be seen from Table II that the T_g values of P_1 – P_8 were reduced from 77.8 to 52.8°C, which is the influence of plasticization.

Similar to T_g , crosslinking may influence the clearing point (T_i) in two ways. On the one hand, crosslinking units may act as a nonmesogenic diluent and lead to a downward shift in the clearing point as increasing content is added to a LC polymer; on the other hand, for a crosslinked sample, heating to the isotropic state requires additional energy to distort the polymer backbone from the anisotropic state at crosslinking and leads to a forward shift in the clearing point with increasing content of the chiral crosslinking agent. In this study, a non-LC chiral crosslinking agent is introduced into the polymer backbone, so the first factor is predominant. It can be seen that the T_i value was reduced with the increasing content of crosslinking agent. When the concentration of crosslinking units increased from 0 to 15%, the T_i value of P_1 – P_8 decreased from 275.3 to 191.8°C, and, at the same time, P_1 – P_8 displayed wide mesophase temperature ranges (ΔT) from 198.4 to 130.0°C and ΔT values of elastomers decreased with increasing contents of the

TABLE II
Thermal Properties of Polymers P_1 – P_8

Polymer	T_g (°C)	T_i (°C)	ΔH ($J \cdot g^{-1}$)	ΔT^a
P_1	76.6	275.3	4.72	198.7
P_2	77.8	276.2	4.20	198.4
P_3	75.9	249.0	4.41	173.1
P_4	74.2	243.0	2.47	168.8
P_5	71.0	233.7	2.85	162.7
P_6	70.3	215.0	2.01	144.7
P_7	61.8	191.8	0.40	130.0
P_8	52.8	—	—	—

^a Mesophase temperature ranges (T_i – T_g).

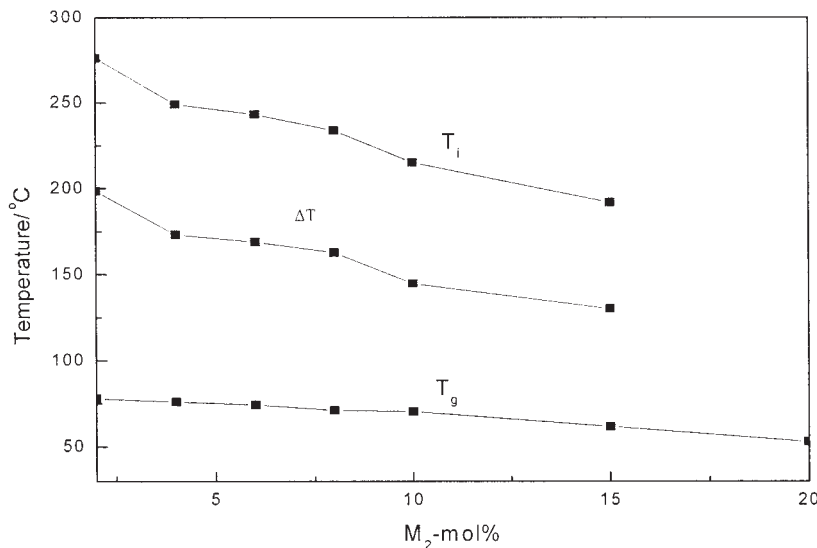


Figure 4 Effect of M_2 content on phase transition temperature of the elastomers.

crosslinking agent. The DSC curve of P_8 only showed a glass transition and no mesophase to isotropic transition due to high levels of crosslinking, which disturbed the LC order.

Optical analysis

The optical properties of monomer M_1 and polymers were characterized by POM with hot stage under nitrogen atmosphere. The visual observation under POM revealed that M_1 exhibited an enantiotropic cholesteric phase. When the sample of M_1 was heated to 113.2°C, it began to melt and flow and appeared first as a broken focal conic and then a platelet texture, which is the typical texture of the cholesteric phase. During the heating process, the background color changed from red, yellow, green, to blue. Continuing heated to 238.1°C and then turned into the isotropic phase. On the cooling process, the texture of M_1 underwent focal-conic texture at 215.8°C, and the color of the texture changed from gray to red. Photomicrographs of M_1 are shown in Figure 5(a–c), respectively. At the same time, selective reflection can be seen during the heating and cooling processes. The results suggested that M_1 showed the cholesteric phase on the heating cycle and the subsequent cooling cycle. The uncrosslinked polymer P_1 showed bright color, but the textures cannot be clearly made out; crosslinked polymer P_2 and P_3 showed smectic step particle texture, which is the typical texture of smectic A and B; elastomers P_4 – P_6 exhibited lined textures, which is the typical texture of chiral smectic C or cholesteric phase, while P_7 showed lined texture during the heating process and underwent Grandjean-orange-yellow-blue texture during the cooling process and P_8 displayed stress-induced birefringence. Photomicro-

graphs of elastomers are shown in Figure 6(a–d), respectively. The special rotation of M_1 and M_2 is in a contrary direction, but special rotation of M_2 is greater than that of M_1 , and the chirality effect of M_2 is predominant on properties of the LCEs. It may be concluded that chirality has a promoter action on the optical properties of LCEs. The type of LC phase of polymers was further characterized by X-ray diffraction.

X-ray diffraction

XRD analysis allowed for a complementary assessment of the nature of the phases observed by DSC and

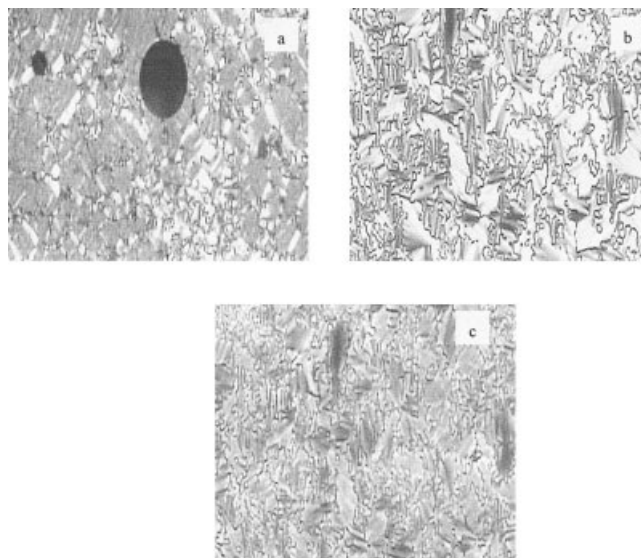


Figure 5 Optical texture of monomer M_1 ($\times 200$). (a) Platelet texture of M_1 at heating to 124.7°C. (b) Focal-conic of M_1 at cooling to 212.5°C. (c) Focal-conic texture of M_1 at cooling to 129.0°C.

POM, giving additional information about their structural parameters. XRD patterns of elastomers are shown in Figure 7. X-ray diffraction pattern of the quenched polymer P_1 – P_6 films showed a sharp reflection peak at 2θ of 3.23° ($d = 27.32 \text{ \AA}$). The d value was longer than the molecular lengths of the fully stretched mesomorphic units, which were calculated to 20.45 \AA . The results are due to the interpenetration between molecules, and they are inclined to arrange sloppily, which can weaken the acting force between molecules.²⁴ The films of P_1 – P_6 showed broad peaks at 2θ of $22.78 \sim 23.08^\circ$ ($d = 3.89 \sim 3.85 \text{ \AA}$), which are due to the distance between the mesogenic side groups in the smectic layer.^{24,25} The peak of reflection for P_7 is different. It has only a wide peak at 22.78° ($d = 3.89 \text{ \AA}$). Combining polarizing microscopy with X-ray diffraction measurements may reveal²⁵ that polymers P_1 – P_3 were smectic phase and elastomers P_4 – P_6 were chiral smectic C phase, while P_7 were cholesteric elastomers and P_8 displayed stress-induced birefringence. And at the same time, the chirality of the chiral crosslinking agent has a strong effect on the phase of polymers during the increasing of the crosslinker contents.

CONCLUSIONS

In this study, a new series of side-chain chiral smectic C and cholesteric LCEs containing cholesteric monomer groups (M_1 , cholesteryl 4-allyloxybenzoate) and a chiral crosslinking agent (M_2 , isosorbide 4-undecanoyloxy bisate) were synthesized and characterized. All of the obtained polymers showed very wide mesophase temperature ranges and high thermal stability. The

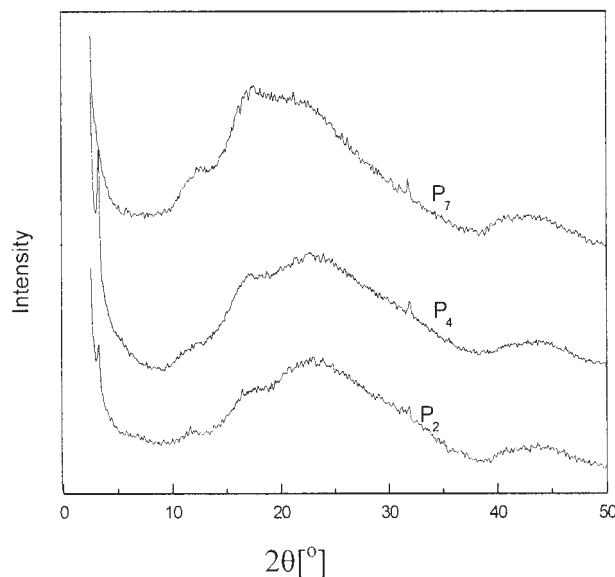


Figure 7 X-ray diffraction patterns of quenched samples.

elastomers containing less than 15% of crosslinking units showed elasticity and reversible phase transition. The liquid crystalline phase of homopolymer and elastomers changed from smectic to chiral smectic C and then to the cholesteric phase with increase in the chiral crosslinker content. For P_1 – P_8 , the glass transition temperatures, isotropization temperatures, and the ranges of the mesophase temperature decreased with increasing the content of the crosslinking agent.

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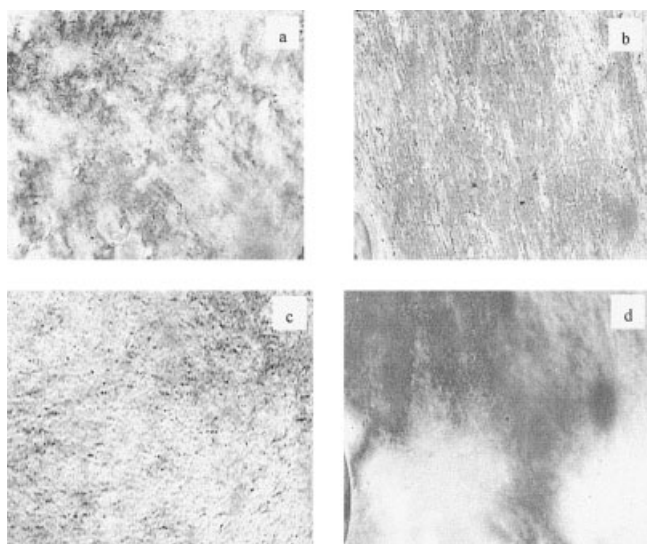


Figure 6 Optical texture of polymers ($\times 200$). (a) Step particle texture of P_2 at heating to 101.4°C . (b) Lined texture of P_6 at heating to 141.1°C . (c) Grandjean blue texture of P_7 at heating to 129.6°C . (d) Grandjean red-orange-yellow-blue texture of P_7 at cooling to 80.6°C .

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