

Effect of Mesogenic Crosslinking Units on the Mesomorphic Phases of Cholesteric Liquid Crystalline Polymers

Fan-Bao Meng, Bao-Yan Zhang, Ai-Juan Zhou, Xi-Zhi Li

Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, People's Republic of China

Received 21 March 2006; accepted 1 November 2006

DOI 10.1002/app.25741

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of cyclosiloxane-based cholesteric liquid crystalline polymers were synthesized from cholest-5-en-3-ol (3 β)-4-(2-propenyloxy)benzoate and a nematic crosslinking monomer biphenyl-4,4'-diol bis[4-(2-propenyloxy)-benzoate], containing mesogenic crosslinking contents among 0–7.8 wt %. Swelling experiments of the elastomers were employed to determine the effective crosslink density (M_c). With increase of mesogenic crosslinking component in the polymers, the isotropic temperature decreases, but both the temperature of glass transition and melting point change irregularly. All the polymers have high thermal stability and percentage weight loss occurred at 460°C decreases with increase of crosslinking units. The inten-

sity of X-ray diffraction peak at $2\theta \approx 17^\circ$ decreases with increase of mesogenic crosslinking units, suggesting that the order between two neighbor liquid crystalline molecules disturbed by the mesogenic crosslinking agents. The maximum reflection bands shift slightly to long wavelength and become broad, indicating that the helical structure is partially disrupted because of both the constraint of chemical crosslinking agents and the different mesogenic units. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1161–1168, 2007

Key words: LCP; elastomers; polysiloxanes

INTRODUCTION

Recently, since cholesteric mesophases exhibit interesting optical properties such as the selective reflection of circular polarized light and an angular dependence of the reflected wavelength, cholesteric liquid-crystalline polymer networks (LCN) have been intensively investigated both in the theoretical and experimental aspects because of their unique optical properties and potential applications in numerous areas.^{1–4} There are two classes of cholesteric LCNs: highly crosslinked cholesteric liquid crystalline thermosets (LCTs) and lightly crosslinked cholesteric liquid crystalline elastomers (LCEs), according to the crosslink density. The formation of highly crosslinked polymer networks with a cholesteric structure has

attracted interest because the helical structure of the cholesteric phase is permanently frozen-in and so the optical properties become temperature independent.^{5,6} Contrary to highly crosslinked networks, cholesteric LCEs combine basic features of polymer elastomers with anisotropy of physical properties of cholesteric liquid crystals. Cholesteric LCEs not only hold entropic elasticity, but also show reversible phase transition on heating and cooling cycles. Compared with conventional LCEs, cholesteric LCEs show unusual properties such as piezoelectric properties besides electro-optical and mechanical properties because of the deformation of helical structure of cholesteric phase.^{7–10}

The helical structure and the pitch of cholesteric liquid crystalline polymers depend on the temperature and the concentration of the chiral constituents. The pitch can be locked either by polymerization or with a polymer network to stabilize the cholesteric structure.¹¹ However, it is important to study how the crosslink units change the helical structure of cholesteric phase, the pitch and liquid crystalline behaviors for cholesteric LCEs.

In previous work, we have studied effect of ionic and nonmesogenic crosslinking units on the mesomorphic phases of cholesteric liquid crystalline polymers.^{12,13} Now, we are interested in cholesteric LCEs using mesogenic component as crosslinking units. We would like to know the fundamental link between

Correspondence to: B.-Y. Zhang (baoyanzhang@hotmail.com).

Contract grant sponsors: National Natural Science Fundamental Committee of China, HI-Tech Research and development program (863) of China, National Basic Research Priorities Program (973) of China, Science and Technology Research Major Project of Ministry of Education of China, Specialized Research Fund for the Doctoral Program of Higher Education, the Science and Technology Department of Liaoning Province.

Journal of Applied Polymer Science, Vol. 104, 1161–1168 (2007)
© 2007 Wiley Periodicals, Inc.

mesogenic crosslinking component in the networks and the behavior of cholesteric mesophases. Furthermore, it is interesting to investigate how the mesogenic crosslinking agents modify liquid-crystalline structures of cholesteric networks.

In synthetic categories, networks with cholesteric structures have been made by the photocrosslinking of cholesteric main-chain or side-chain liquid-crystal polymers.¹⁴ They can also be made through the thermally or chemically induced crosslinking of cholesteric mixtures consisting of nematic and chiral monomers.¹⁵ We prepared cholesteric LCEs in a one-step reaction, in which both the liquid crystalline monomer and mesogenic crosslinking agent are linked to the polymer backbone.

EXPERIMENTAL

Material and measurements

Hexachloroplatinic acid hydrate, 4-hydroxy-benzoic acid, potassium hydroxide, potassium iodide, toluene, and thionyl chloride were obtained from Shenyang Chemical Co. Bromopropene, cholesterol, biphenyl-4,4'-diol, tetrahydrofuran (THF), and pyridine were obtained from Beijing Chemical Co. Cyclo(methylhydrogeno)siloxane (CMHS) ($M_n = 200\text{--}300$) was from Jilin Chemical Industry Company. Pyridine was purified by distillation over KOH and NaH before using. All other solvents and reagents were purified by standard methods.

¹H NMR spectra (300 MHz) were recorded on a Varian WH-90 spectrometer (Varian Associates, Palo Alto, CA). Fourier transform infrared spectroscopy (FTIR) of the synthesized polymers and monomers in solid state were obtained by the KBr method performed on a Nicolet 510P FTIR Spectrometer (Nicolet Instruments, Madison, WI). The element analyses (EA) were carried out by using Elementar Vario EL III (Elementar, Germany). X-ray measurements of the samples were performed using Cu K α ($\lambda = 1.542 \text{ \AA}$) radiation monochromatized with a Rigaku DMAX-3A X-ray diffractometer (Rigaku, Japan). Thermal transition properties were characterized by a NETZSCH Instruments DSC 204 (Netzsch, Wittelsbacherstr, Germany) at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The thermal stability of the polymers under atmosphere was measured with a NETZSCH TGA 209C thermogravimetric analyzer. Visual observation of liquid-crystalline transitions and optical textures under cross polarized light was made by a Leica DMRX (Leica, Wetzlar, Germany) polarizing optical microscope (POM) equipped with a Linkam THMSE-600 (Linkam, Surrey, England) hot stage. Ultraviolet-visible spectrophotometry was measured by PerkinElmer instruments Lambda 950 (PerkinElmer, Foster City, CA). Reflection spectra of cholesteric mesophase

were measured by reflective light with beam's incident angle of 8° .

Synthesis of cholest-5-en-3-ol(3 β)-4-(2-propenyloxy)-benzoate (M1)

The liquid crystalline monomer cholest-5-en-3-ol(3 β)-4-(2-propenyloxy)-benzoate (monomer M1) was prepared according to previously reported synthetic method.¹⁶ It showed cholesteric mesophase between 116°C and 243°C .

Yield: 73%. mp: 116°C . IR (KBr, cm^{-1}): 3051 ($=\text{C}-\text{H}$), 2971–2854 ($-\text{CH}_3$, $-\text{CH}_2-$), 1706 ($\text{C}=\text{O}$), 1608, 1511 (Ar—), 1277, 1172 ($\text{C}-\text{O}-\text{C}$). ¹H NMR (CDCl_3 , δ , ppm): 7.98–6.92 (m, 4H, Ar—H), 6.02 (m, 2H, $\text{CH}_2=\text{CH}-$), 5.36 (m, 1H, $=\text{CH}-$ in cholesteryl), 5.18–4.69 (m, 1H, $\text{CH}_2=\text{CH}=\text{}$), 4.47 (t, 2H, $-\text{OCH}_2-$), 2.03–0.67 (m, 43H, cholesteryl-H).

Synthesis of biphenyl-4,4'-diol bis[4-(2-propenyloxy)-benzoate] (M2)

Potassium hydroxide (80.0 g, 1.43 mol) and potassium iodide (0.60 g, 0.029 mol) were dissolved in 100 mL water to form a solution. The aqueous solution, 4-hydroxy-benzoic acid (84.0 g, 0.60 mol) and 300 mL ethanol were added into a round flask equipped with a condenser at room temperature. Bromopropene (90.0 g, 0.74 mol) was added dropwise to the round flask. The mixture was stirred at room temperature for 2 h, then heated to 85°C and kept for 16 h in a water bath to ensure that the reaction finished. The mixture was cooled, and poured in 500 mL of cold water, and acidified with 6N H_2SO_4 . The precipitated product was filtered and recrystallized from ethanol and dried overnight at 85°C under vacuum to obtain a white powder of 4-(2-propenyloxy)-benzoic acid in the yield of 72%, m.p. 164°C .

4-(2-Propenyloxy)-benzoic acid (20.0 g, 0.11 mol) and thionyl chloride (25.0 g, 0.21 mol) were added into a round flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 2 h, then heated to 60°C and kept for 3 h. The excess thionyl chloride was removed under reduced pressure to give 4-(2-propenyloxy)-benzoyl chloride in the yield of 60%.

Biphenyl-4,4'-diol (6.2 g, 0.033 mol) was dissolved in 120 mL THF and 30 mL pyridine to form a solution. 4-(2-Propenyloxy)-benzoyl chloride (13.0 g, 0.066 mol) was added to the solution and reacted at 60°C for 12 h, cooled, poured in 500 mL of cold water and acidified with 6N H_2SO_4 . The precipitated crude product was filtered and recrystallized from ethanol/chloroform (1/1) and dried overnight at 80°C under vacuum to obtain a white powder of biphenyl-4,4'-diol bis(4-(2-propenyloxy)-benzoate) (M2).

TABLE I
Polymerization and Some Swelling Properties of the Series of Polymers

Sample	Feed			M2% ^a (wt %)	Yield (%)	Density (g/cm ³)	V ₂	M _c (g/mol)
	CMHS (mmol)	M1 (mmol)	M2 (mmol)					
P0	1.0	4.0	0	0	91	1.040	–	–
P1	1.0	3.9	0.05	1.0	91	1.041	0.43	3100
P2	1.0	3.8	0.10	2.1	89	1.044	0.44	2920
P3	1.0	3.7	0.15	3.2	90	1.048	0.46	2686
P4	1.0	3.6	0.20	4.3	87	1.052	0.49	2260
P5	1.0	3.5	0.25	5.4	89	1.058	0.51	1956
P6	1.0	3.4	0.30	6.6	90	1.064	0.54	1718
P7	1.0	3.3	0.35	7.8	87	1.069	0.58	1421

^a Mass fraction of mesogenic crosslinking monomer M2 based on M1 + M2 + CMHS.

Yield: 63%. mp: 182°C. ELEM. ANAL. Calcd. For C₃₂H₂₆O₆: C, 75.88%; H, 5.17%. Found: C, 76.01%; H, 5.21%. IR (KBr, cm⁻¹): 3071 (=C–H), 2954, 2856 (–CH₂–), 1730 (–C=O), 16.4, 1511 (Ar–), 1261 (C–O–C). ¹H NMR (CDCl₃, TMS, δ, ppm): 4.54 (t, 2H, –CH₂O–), 6.05 (m, 1H, CH₂=CH–), 5.56 (d, 2H, CH₂=CH–), 6.86 (d, 2H, Ar–H), 7.21 (d, 2H, Ar–H), 7.62 (d, 2H, Ar–H), 7.85 (d, 2H, Ar–H).

Synthesis of the polymers

For synthesis of polymers P0–P7, the same method was adopted. The detailed polymerization experiments and yields were summarized in Table I. The synthetic route of the polymers and the schematic representation of elastomers are shown in Figure 1. The synthesis of polymer P6 was given as an example. Biphenyl-4,4'-diol-bis(4-(2-propenyloxy)benzoate) (0.15 g, 0.30 mmol, mesogenic crosslinking monomer M2) was dissolved in 50 mL of dry, fresh distilled toluene. To the stirred solution, Cholest-5-en-3-ol(3β)-4-

(2-propenyloxy)benzoate (1.91 g, 3.40 mmol, cholesteric LC monomer M1), CMHS (0.24 g, 1.0 mmol), and 2 mL of H₂PtCl₆/THF (0.50 g hexachloroplatinic acid hydrate dissolved in 50 mL THF) were added and heated under nitrogen and anhydrous conditions at 65°C for 48 h. The solution was cooled and poured into 200 mL methanol. After filtration, the product was dried overnight under vacuum to obtain 2.07 g of polymer in the yield of 90%.

IR (KBr, cm⁻¹): 2980–2850 (CH₃– and –CH₂–), 1730 (C=O), 1605, 1510 (phenyl), 1272 (Si–C), 1252 (C–O), 1167–1011 (Si–O–Si).

RESULTS AND DISCUSSION

FTIR spectra

The polymers were prepared by a one-step hydrosilylation reaction between Si–H groups of CMHS and olefinic C=C of M1 and M2 in toluene, using hexachloroplatinic acid hydrate as catalyst at 65°C. Figure 2 shows the FTIR spectra of noncrosslinked LC polymer P0, LC

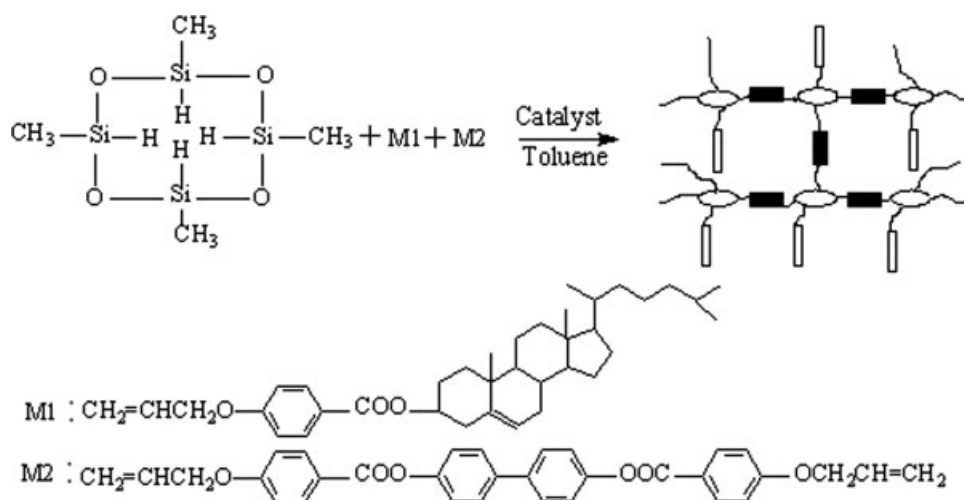


Figure 1 Schematic representation of the series of liquid crystalline elastomers.

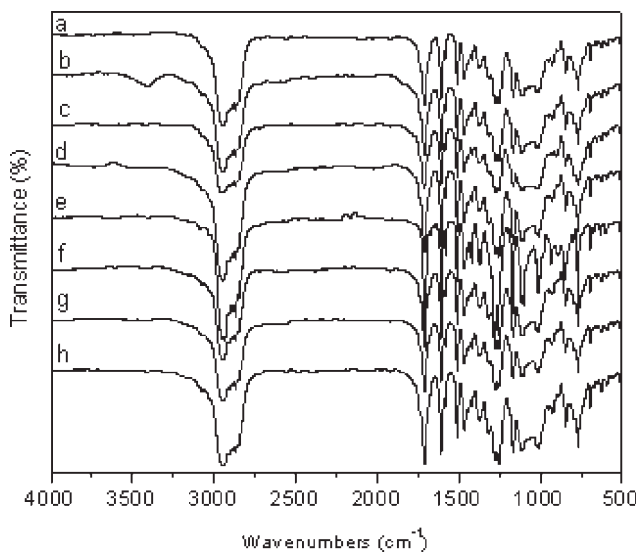


Figure 2 FTIR spectra for (a) P0, (b) P1, (c) P2, (d) P3, (e) P4, (f) P5, (g) P6, and (h) P7.

elastomers **P1-P7** recorded at room temperature in KBr pellets. All the spectra of the elastomers were similar to the noncrosslinked polymer **P0**. The disappearance of the Si—H stretching at 2160 cm^{-1} and the olefinic C=C stretching band at $1643\text{--}1636\text{ cm}^{-1}$ indicates successful incorporation of monomers into the cyclosiloxane chains. In addition, characteristic Si—O—Si stretching bands appeared at $1200\text{--}1000\text{ cm}^{-1}$.

The presence of characteristic bands at 2980 , 2860 , 1730 , and 1605 cm^{-1} was attributed to C—H bond in methylene or methyl group, C=O in ester group and aromatic stretching vibration. However, by reason of introduction of crosslinking agent to the polymers, there were some difference between the spectrum of **P0** and the FTIR spectra of other elastomers. Compared with C—H stretching vibration peaks, the relative absorption intensity of C=O and aromatic

stretching vibration peaks increase slightly with increase of the mesogenic crosslinking component in the polymer systems, suggesting the cholesteryl groups decrease from **P0** to **P7**.

Swelling behavior

To characterize the crosslinking degree, we determine the effective crosslink density, or the average molecular weight between two crosslink points (M_c), by swelling experiments. M_c was calculated according to the Flory and Rehner swelling theory¹⁷

$$M_c = -\rho V_1 (V_2^{1/3} - V_2/2) / [\ln(1 - V_2) + V_2 + \chi V_2^2] \quad (1)$$

where M_c is the number average molecular weight between crosslinks; χ is polymer-swelling agent interaction parameter; V_1 is the molar volume of the swelling solvent; V_2 is the volume fraction of polymer network at swelling equilibrium; and ρ is the density of the polymer before swelling.

The polymer-swelling agent interaction parameter, χ , can be theoretically predicted from the expression:

$$\chi = (\delta_1 - \delta_2)^2 V_1 / R T \quad (2)$$

where δ_1 and δ_2 are solubility parameters of the solvent and polymer; V_1 is the molar volume of the swelling solvent; R is the gas constant; and T is absolute temperature.

The volume fraction of polymer network V_2 was calculated as

$$V_2 = 1/Q \quad (3)$$

The equilibrium/swelling ratio of networks was determined gravimetrically through the following equation:

$$Q = 1 + (W_2/W_1 - 1)\rho_p/\rho_s \quad (4)$$

TABLE II
Thermal and Optical Properties of the Monomers and Polymers

Sample	T_g (°C)	$T_m/\Delta H_m$ (°C)/(J/g)	$T_i/\Delta H_i$ (°C)/(J/g)	ΔT^a (°C)	T_d (°C) ^b	W_d (%) ^c	λ_{ref} (nm) ^d
M1	—	116.3/46.5	243.9/2.35	127.6	—	—	—
M2	—	182.1/46.9	294.3/1.32	112.2	—	—	—
P0	52.4	122.4/21.6	229.3/1.02	106.9	298.2	83.5	320
P1	46.7	122.1/10.3	225.1/2.89	103.0	305.8	61.9	324
P2	52.5	122.0/18.2	224.8/3.23	102.8	306.3	51.0	331
P3	53.1	122.7/19.3	220.2/1.57	97.5	308.6	46.5	335
P4	48.4	118.9/18.7	219.2/1.56	100.3	310.9	40.5	337
P5	53.1	119.2/8.2	216.3/3.21	97.1	313.5	35.4	340
P6	49.2	118.2/11.2	214.6/1.67	96.4	325.0	26.6	349
P7	52.7	120.1/23.8	215.1/1.61	95.0	327.2	19.9	354

^a Mesophase temperature ranges (T_i – T_m).

^b Temperature at which 5% weight loss occurred.

^c Percentage weight loss occurred at 460°C .

^d The maximum reflected wavelength characterized by Perkin-Elmer instruments Lambda 950.

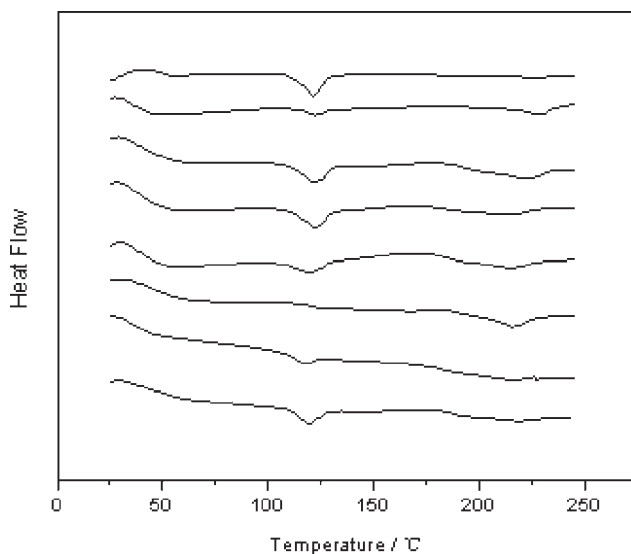


Figure 3 DSC thermograms of the series of polymers on the first heating (10°C/min).

Where Q is the swelling ratio of networks by volume; W_1 is weight of the network before swelling; W_2 is the weight of the network at equilibrium swelling; ρ_p and ρ_s are densities of polymer and solvent, respectively.

Swelling measurements were made in 10 mL of THF with samples of 0.3 g in initial weight. Swelling experiment was accomplished in several days at room temperature to achieve equilibrium. Swollen elastomers removed from solvents at regular intervals were dried superficially with filter paper, weighed, and placed in the same condition. The measurements were continued until a constant weight was reached for each sample.

Some of the information about the swelling experiments of the elastomers was shown in Table I. The value V_2 increases with increase of the mesogenic crosslinking agents, corresponding to a higher crosslink density and a lower degree of swelling. As a result, the molecular weight between the crosslink points (M_c) decreases with increase of the mesogenic crosslinking component.

Thermal behavior

The phase-transition temperatures and corresponding enthalpy changes of monomers (**M1**, **M2**) and polymers (**P0-P7**) are summarized in Table II. All the DSC thermograms were obtained on the second heating and the first cooling scan, and all phase transitions were reversible and did not change on repeated heating and cooling cycles. The phase-transition temperatures determined by DSC were consistent with POM observation results.

DSC heating thermogram of **M2** contained two endotherms of the phase, which represented a melting

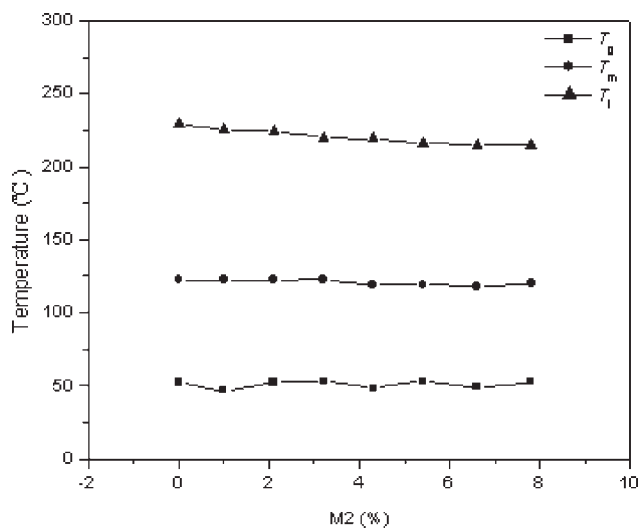


Figure 4 Effect of mesogenic crosslinking component (**M2**) on the phase-transition temperatures of the polymers.

transition at 182.1°C and a nematic-isotropic phase transition at 294.3°C. On cooling scans of **M2**, an isotropic-nematic phase transition appeared at 274.8°C and crystallization appeared at 168.9°C.

For the polymers, Figure 3 displays the DSC thermograms on the second heating. All of the polymers display three kinds of phase-transition behavior corresponding to glass transition, melting point, and clear point. Figure 4 shows the influence of the mesogenic crosslinking component on the phase behavior of the cholesteric liquid crystalline polymers. With increase of mesogenic crosslinking groups in the polymers **P1-P7**, the isotropic temperature (T_i) decrease, but the temperature of melting point (T_m) and the glass-transition temperature (T_g) changes a little and does not show uptrend or downtrend. In Table II, **P0-P7** displayed wide mesophase temperature ranges (ΔT). ΔT

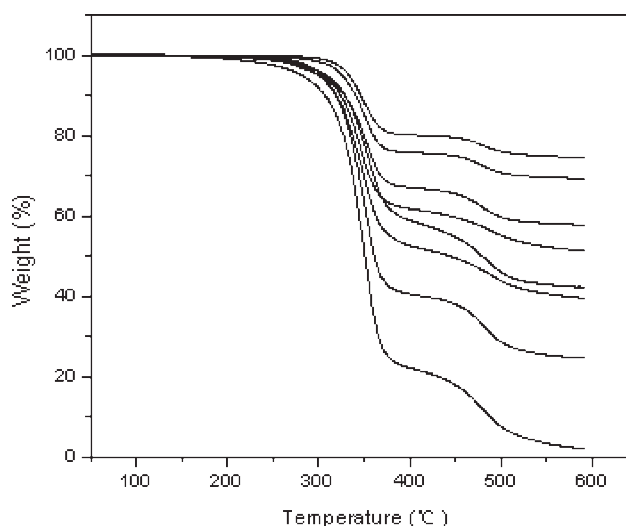


Figure 5 TGA thermograms of the polymers.

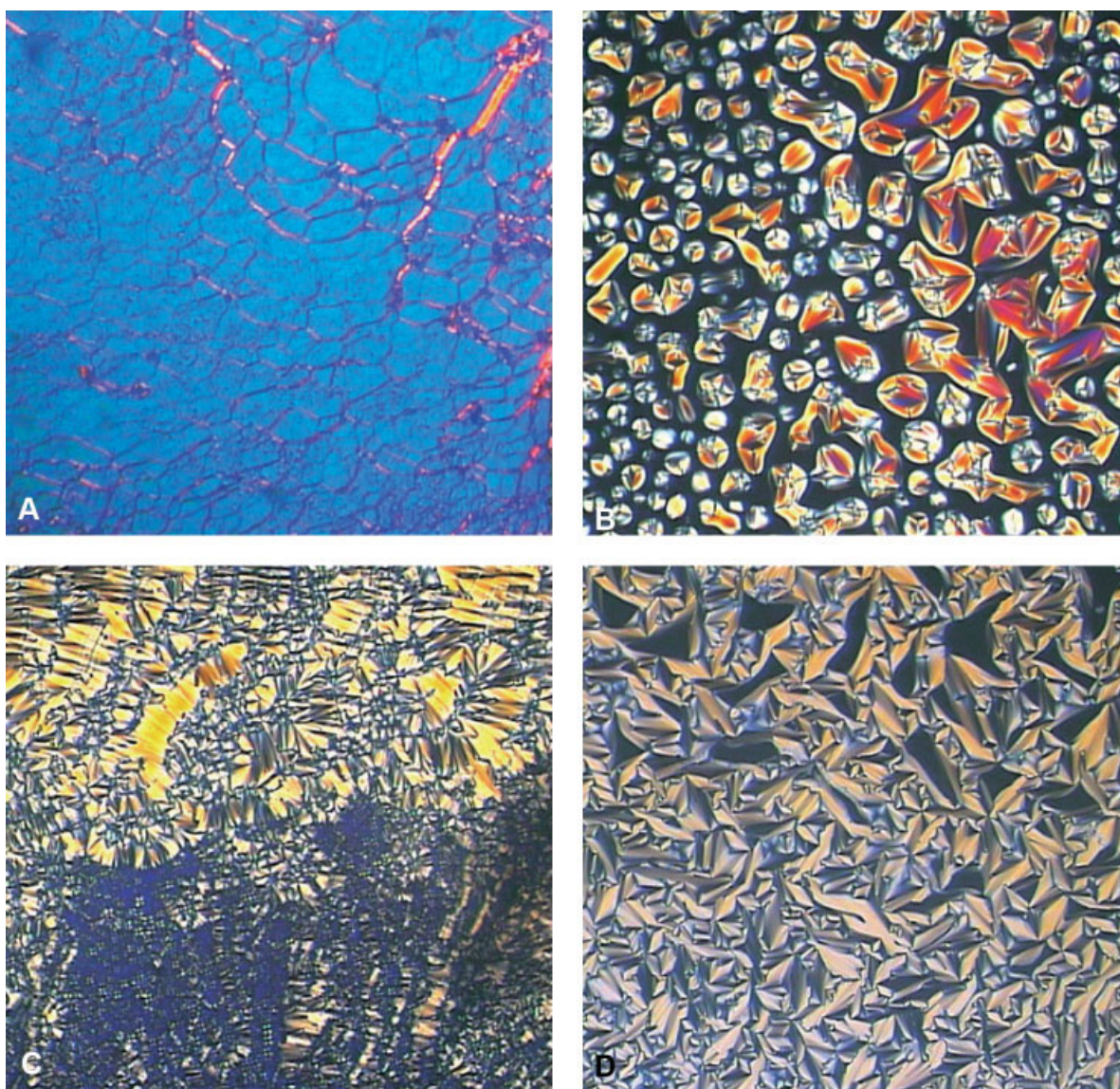


Figure 6 Optical textures of the polymers ($\times 200$): (a) oily-streak texture on heating to 223.9°C for **P1**, (b) droplet texture on cooling to 218.6°C for **P3**, (c) fan-shaped focal conic texture on heating to 215.7°C for **P5**, and (d) fan-like texture on cooling to 209.3°C for **P7**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of elastomers decreased with increasing mesogenic crosslink density.

For side-chain LCs, T_g is influenced by the nature of the polymer backbone, the length of the flexible spacer, and the rigidity of the mesogenic groups. In general, chemical crosslinking imposes additional constraints on the segmental motion of polymer chains, and might be expected to raise the glass-transition temperatures.¹⁶ However, T_g is also affected by the length of the flexible spacer of side groups, which could lead to the plasticization effect. Because the soft aliphatic chain of the cholesteric LC monomer **M1** is as long as that of nematic crosslinking monomer **M2**, T_g of the series of polymers would change irregularly with increase of the mesogenic crosslinking component.

Similar to T_g , T_i is also influenced by the nature of the crosslinked polymer systems. The flexible chains

on the mesogenic crosslinking component acted as plasticizer and led to a decrease in the T_i value; on the other hand, chemical crosslinking units could prevent the formation of mesogenic orientation order in the networks with increasing crosslink density. Besides, a kind of different liquid crystalline core was induced into the cholesteric LCP systems with increase of mesogenic crosslinking unit **M2**, so the mesogenic orientation order would decrease. According to Table II, the T_i value of **P0-P7** decreased from 229.3 to 215.1°C when the concentration of mesogenic crosslinking units increased from 0 to 7.8 wt %.

Figure 5 presents TGA thermograms of the polymers and some TGA value is listed in Table II. The TGA results showed that the temperatures at which 5% weight loss occurred (T_d) were greater than 300°C for **P1-P7**, suggesting that the synthesized elastomers

have high thermal stability. Besides, T_d increases with increase of mesogenic crosslinking component in the polymer systems. In Figure 5, speed-up weight loss occurred at 460°C for all the polymers. In addition, percentage weight loss occurred at 460°C decrease with increase of mesogenic crosslinking component.

Texture analysis

All the polymers exhibit thermotropic LC properties and reveal enantiotropic mesomorphic phase. Mesophase identification has been accomplished by X-ray measurement and POM observation.

The optical textures of the monomers and polymers were investigated via POM with cold and hot stages under a nitrogen atmosphere. **M1** exhibited enantiotropic cholesteric phase; **M2** revealed nematic phases and all the polymers showed cholesteric phase textures on heating and cooling cycles.

Figure 6 shows representative textures of the polymers. For polymer **P1**, when it was heated up to 122.8°C, the sample melted and a grandjean texture appeared. When it was heated to 223.9°C, the typical oily streak texture gradually appeared [see Fig. 6(a)], showing cholesteric mesomorphic phase. Via visual observation, the selective reflection color changed from red to blue with increasing temperature. For polymer **P3**, when the isotropic melt was cooled to 218.6°C, cholesteric droplets of the mesophase separated from the melt, suggesting different colors corresponding to different twist states [see Fig. 6(b)]. When **P5** was heated to 215.7°C, a fan-shaped focal conic texture appeared [see Fig. 6(c)], indicating a short pitch cholesteric phase. Figure 6(d) showed a fan-like texture on cooling to 209.3°C for **P7**, revealing its cholesteric phase with a short pitch. Within individual fans, the helix axis is oriented uniformly.

X-ray diffraction analysis

The cholesteric mesophase has also been confirmed by X-ray diffraction analysis. XRD studies can provide more detailed information on the liquid crystalline structure and type. In general, for smectic mesophase structure, a sharp and strong peak at low angle ($1^\circ < 2\theta < 4^\circ$) in the small angle X-ray scattering (SAXS) curve can be observed; but no peak appears in the SAXS curve for nematic and cholesteric polymer structure. In the wide angle X-ray diffraction (WAXD) curve, a broad peak at $2\theta \approx 20^\circ$ can usually be observed for nematic polymers, but a broad peak appears generally at $2\theta \approx 17^\circ$ for cholesteric polymers.

For **P0-P7**, a sharp peak associated with the smectic layers at low angles did not appear in the SAXS curves. Figure 7 shows the X-ray diffraction diagrams of all the polymers **P0-P7**. A broad diffraction peak at $2\theta \approx 17^\circ$ is observed for all the polymers, which sug-

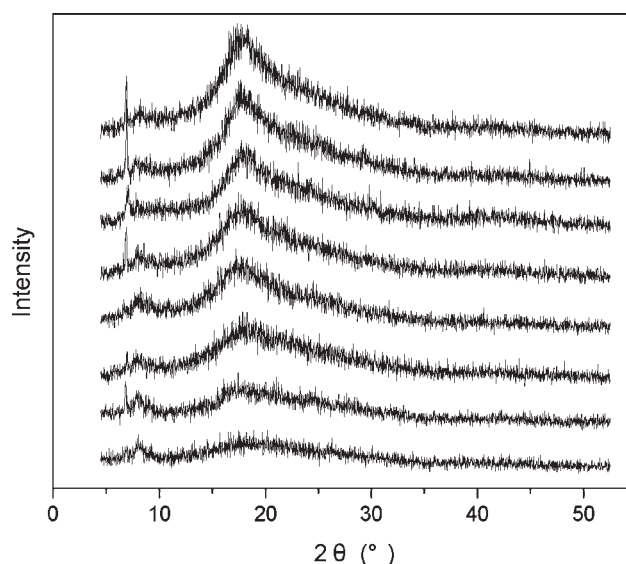


Figure 7 X-ray diffraction diagrams of the polymers from **P0** to **P7** (from the top down).

gests the average distance of 5 Å between two neighbor LC molecules within the layers of the mesophase. Besides, a weak diffraction peak around $2\theta = 8-10^\circ$ was observed for the polymers. The intensity of the diffraction peak at $2\theta \approx 17^\circ$ decrease with increase of mesogenic crosslinking component in the polymer systems from **P0** to **P7**, suggesting the order between two neighbor LC molecules disturbed by the mesogenic crosslinking agents.

Reflection spectra of cholesteric mesophase

Cholesteric mesophases exhibit interesting optical properties such as the selective reflection of circular polarized light and an angular dependence of the reflected wavelength. If the reflected wavelength is in the visible range of the spectrum, the cholesteric phase appears colored. The unique optical properties of cholesteric liquid crystalline are related to the helical supermolecular structure of the cholesteric phase. The wavelength, λ_{\max} , of reflected light from a cholesteric sample is given by

$$\lambda = nP \sin\phi \quad (5)$$

where n is the average refractive index of the liquid crystalline phase, P is the pitch height of the helicoidal arrangement, and ϕ is the incident angle of beam. The helical pitch P depends on many factors such as the concentration of the chiral substance, the temperature and an external field of mechanical, electric, or magnetic origin, etc.¹⁸

The reflected wavelengths of the samples **P1-P7** were characterized by PerkinElmer instruments Lambda 950 when the samples were heated at 210.0°C

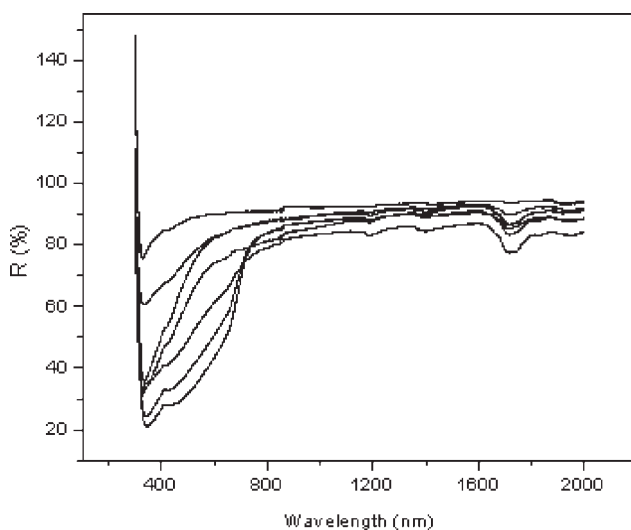


Figure 8 The reflected wavelengths of the series of elastomers P1-P7.

without any external field. Figure 8 shows the maximum reflected wavelength of the series of the elastomers **P1-P7**, and the data were listed in Table II. It is shown that the maximum reflection bands shift slightly to long wavelength and become broad from **P1** to **P7** with increase of mesogenic crosslinking units. According to eq. (5), the data mean that the helical pitch P become longer with increase of the mesogenic crosslinking component. These results suggest that the helical structure is partially disrupted because of both the constraint of chemical crosslinking agents and the different mesogenic units.

CONCLUSIONS

We have synthesized a series of cyclosiloxane-based cholesteric LCEs containing 0–7.8% (weight percentage) of mesogenic crosslinking units. Their chemical structures and liquid-crystalline properties were characterized by FTIR, ^1H NMR, DSC, TGA, POM, and X-ray measurement. Swelling experiments were employed to determine the effective crosslink density (M_c). M_c decreases with increase of the mesogenic crosslinking component.

All the polymers exhibit thermotropic LC properties and reveal cholesteric phase. With increase of meso-

genic crosslinking component in the polymers, the isotropic temperature decreased. On the other hand, the temperature of glass transition and melting point change a little and do not show uptrend or downtrend. TGA analysis suggests that all the polymers have high thermal stability and percentage weight loss occurred at 460°C decreases with increase of mesogenic crosslinking component. The intensity of X-ray diffraction peak at $2\theta \approx 17^\circ$ decrease with increase of mesogenic crosslinking units in the polymer systems, suggesting the order between two neighbor LC molecules disturbed by the mesogenic crosslinking agents. The maximum reflection bands shift slightly to long wavelength and become broad with increase of mesogenic crosslinking component in the polymers, indicating that the helical structure is partially disrupted because of both the constraint of chemical crosslinking agents and the different mesogenic units.

References

1. Van Delden, R. A.; Van Gelder, M. B.; Huck, N. P. M.; Feringa, B. L. *Adv Funct Mater* 2003, 13, 319.
2. Bonet, J.; Callau, L.; Reina, J. A.; Galia, M.; Cadiz, V. *J Polym Sci Part A: Polym Chem* 2002, 40, 3883.
3. Nishikawa, E.; Finkelmann, H. *Macromol Chem Phys* 1999, 200, 312.
4. Zhang, B. Y.; Hu, J. S.; Jia, Y. G.; Du, B. G. *Macromol Chem Phys* 2003, 204, 2123.
5. Pfeuffer, T.; Kurschner, K.; Strohrriegl, P. *Macromol Chem Phys* 1999, 200, 2480.
6. Stohr, A.; Strohrriegl, P. *Macromol Chem Phys* 1998, 199, 751.
7. Gebhard, E.; Zentel, R. *Macromol Chem Phys* 2000, 201, 902.
8. Mauzac, M.; Nguyen, H. T.; Tournilhac, F.G.; Yablonsky, S.V. *Chem Phys Lett* 1995, 240, 461.
9. Gebhard, E.; Zentel, R. *Macromol Chem Phys* 2000, 201, 911.
10. Kricheldorf, H. R.; Krawinkel, T. *Macromol Chem Phys* 1998, 199, 783.
11. Hattori, H.; Uryu, T. *J Polym Sci A: Polym Chem* 2000, 38, 887.
12. Meng, F. B.; Zhang, B. Y.; Xiao, W. Q.; Hu, T. X. *J Appl Polym Sci* 2005, 96, 625.
13. Meng, F. B.; Zhang, B. Y.; Li, Q. Y.; Qi, J. *Polym J* 2005, 37, 277.
14. Sapich, B.; Stumpe, J.; Krawinkel, T.; Kricheldorf, H. R. *Macromolecules* 1998, 31, 1016.
15. Espinosa, M. A.; Cadiz, V.; Galia, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 2847.
16. Meng, F. B.; Zhang, B. Y.; Liu, L. M.; Zang, B. L. *Polymer* 2003, 44, 3935.
17. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 521.
18. Sikorski, P.; Cooper, S. J.; Edward, D.; Atkins, T.; Jaycox, G.; Vog, O. *J Polym Sci A: Polym Chem* 1998, 36, 1855.