

# Effect of Nonmesogenic Crosslinking Units on the Mesogenic Properties of Side-Chain Cholesteric Liquid Crystalline Elastomers

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**ABSTRACT:** A series of cyclosiloxane-based cholesteric liquid crystalline elastomers were synthesized by using cholest-5-en-3-ol(3 $\beta$ )-4-(2-propenyloxy)benzoate and a soft nonmesogenic crosslinking agent, acryloyl-hexyl acrylate. The polymers were prepared in a one-step reaction with the crosslinking contents ranging between 0 and 5.6 weight %. The effective crosslink density ( $M_c$ ) was determined by swelling experiments employing Flory–Rehner models. All the polymers exhibited thermotropic LC properties and revealed a cholesteric phase. With increase of the crosslinking component in the polymers, the melting behavior disappeared and the enthalpy of transition decreased. But the

temperature of glass transition and clear point changed little and did not show uptrend or downtrend. Reflection spectra of the cholesteric mesophase of the polymers showed that the reflected wavelength became broad and shifted to long wavelength with increase of the soft crosslinking component in the polymer systems. All these results originate from the effect of the soft nonmesogenic chemical crosslinking. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 625–631, 2005

**Key words:** liquid crystalline elastomers; cholesteric phase; polysiloxanes

## INTRODUCTION

Slightly crosslinked liquid crystalline (LC) polymers that combine the properties of liquid crystalline phases and the elastic properties and form stability of polymeric networks are known as liquid crystalline elastomers (LCEs). They possess unique features originating from rubber elasticity, and the orientation of the mesogens can be controlled by mechanical forces as well as by electric and magnetic fields.

The potential for LCEs to exhibit unusual properties was first suggested by de Gennes.<sup>1</sup> Subsequently, some LCEs have been prepared and their resultant properties investigated.<sup>2–5</sup> In general, the elastomers most frequently studied have been those based on side-chain liquid crystalline polymers rather than the main-chain systems because of rather more thermally accessible liquid crystalline phases for side-chain liquid crystalline polymers.

Research into cholesteric liquid-crystalline networks has expanded rapidly in recent years because they have outstanding optical properties.<sup>6</sup> 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 formation of highly crosslinked polymer networks with a cholesteric structure has attracted considerable interest because the helical structure of the cholesteric phase is permanently frozen-in and so the optical properties become temperature independent.<sup>7,8</sup> Contrary to highly crosslinked networks, cholesteric liquid crystalline elastomers (ChLCEs) combine basic features of polymer elastomers with anisotropy of physical properties of cholesteric LCs. ChLCEs not only hold entropic elasticity, but also show reversible phase transition on heating and cooling cycles. Compared with conventional LCEs, ChLCEs show unusual properties, such as piezoelectric properties, besides electro-optical and mechanical properties due to the deformation of helical structure of the cholesteric phase. Therefore, ChLCEs have a potential to act as a device that transforms a mechanical signal into an optical signal.<sup>9–12</sup>

We are interested in cholesteric liquid crystalline elastomers using nonmesogenic components as crosslinking units. We would like to know the fundamental link between the crosslinking component in the networks and the behavior of cholesteric mesophases. Furthermore, it is of interest to investigate how the chemical crosslinking components modify liquid-crystalline structures of such kinds of cholesteric networks.

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In the present study, we prepared a series of cyclosiloxane-based cholesteric LCEs with cholesteryl groups using the nonmesogenic crosslinking agent acryloyl-hexyl acrylate. Elastomers of this type were readily prepared in a one-step reaction, in which both the liquid crystalline monomer and nonmesogenic crosslinking agent are linked to the polymer backbone.

## EXPERIMENTAL

### Material and measurements

Acryloyl-hexyl acrylate, cholesterol, and pyridine were purchased from Beijing Chemical Co. Hexachloroplatinic acid hydrate, bromopropene, 4-hydroxybenzoic acid, toluene, and thionyl chloride were obtained from Shenyang Chemical Co. Cyclo(methylhydrogen)siloxane (CMHS) ( $M_n = 200\text{--}300$ ) was obtained from Jilin Chemical Industry Company and used without any further purification. Pyridine was purified by distillation over KOH and NaH before using.

Fourier transform infrared spectroscopy (FTIR) of the synthesized polymers and monomers in solid state was obtained by the KBr method performed on a Nicolet 510P FTIR Spectrometer.  $^1\text{H-NMR}$  spectra (300MHz) were recorded on a Varian WH-90 spectrometer (Varian Associates, Palo Alto, CA). Ultraviolet-visible spectrophotometry was measured by Perkin-Elmer instruments Lambda 900. Reflection spectra of the cholesteric mesophase were measured by reflective light with beam's incident angle of  $8^\circ$ . Thermal transition properties were characterized by a NETZSCH Instruments DSC 204 at a heating rate of  $10^\circ\text{C}/\text{min}^{-1}$  under nitrogen atmosphere. Visual observation of liquid crystalline transitions under cross polarized light was made by a Leitz Laborlux S polarizing optical microscope (POM) equipped with a THMS-600 heating stage. X-ray measurements of the samples were performed using Cu  $K\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) radiation monochromatized with a Rigaku DMAX-3A X-ray diffractometer.

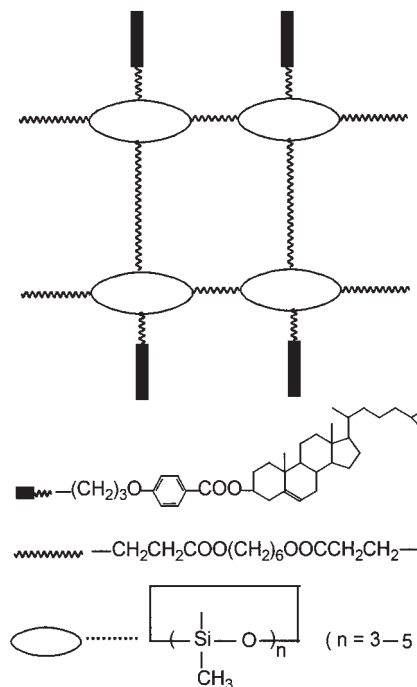
### Synthesis

#### Synthesis of cholest-5-en-3-ol(3 $\beta$ )-4-(2-propenyloxy)benzoate

The liquid crystalline monomer cholest-5-en-3-ol(3 $\beta$ )-4-(2-propenyloxy)benzoate was prepared according to the previously reported synthetic method.<sup>13</sup> The yield was 70%, mp:  $107^\circ\text{C}$ .

IR (KBr,  $\text{cm}^{-1}$ ): 3051 (=C-H), 2971–2854 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1706 (C=O), 1608, 1511 (Ar-), 1277, 1172 (C-O-C).

$^1\text{H-NMR}$  (CDCl<sub>3</sub>,  $\delta$ , ppm): 7.98–6.92 (m, 4H, Ar-H), 6.02 (m, 2H, CH<sub>2</sub>=CH-), 5.36 (m, 1H=CH-in cho-



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

lesteryl), 5.18–4.69(m, 1H, CH<sub>2</sub>=CH-), 4.47 (t, 2H, -OCH<sub>2</sub>-), 2.03–0.67 (m, 43H, cholesteryl-H).

### Synthesis of the elastomers

For synthesis of polymers P1–P7, the same method was adopted. Their general structure is shown in Figure 1. The polymerization experiments are summarized in Table I. The synthesis of polymer P4 is given as an example. Acryloyl-hexyl acrylate (0.045 g, 0.20 mmol, crosslinking monomer A) was dissolved in 30 mL of dry, fresh distilled toluene. To the stirred solution, Cholest-5-en-3-ol(3 $\beta$ )-4-(2-propenyloxy)benzoate (2.02 g, 3.60 mmol, monomer B), cyclo(methylhydrogen)siloxane (CMHS, 0.24g, 1.0 mmol), and 2 mL of H<sub>2</sub>PtCl<sub>6</sub>/THF (0.50 g hexachloroplatinic acid hydrate dissolved in 50 mL tetrahydrofuran THF) were added and heated under nitrogen and anhydrous conditions at  $65^\circ\text{C}$  for 36 h. The solution was cooled and poured into 100 mL methanol. After filtration, the product was dried at  $80^\circ\text{C}$  for 2 h under vacuum to obtain 2.19 g of polymer in the yield of 95%.

IR(KBr,  $\text{cm}^{-1}$ ): 2960–2850 (CH<sub>3</sub>- and -CH<sub>2</sub>-), 1712 (C=O), 1606, 1510 (phenyl), 1272 (Si-C), 1252 (C-O), 1167(S=O).1102–1011(Si-O-Si).

## RESULTS AND DISCUSSION

### The effective crosslink density

To characterize the crosslinking degree, it is necessary to measure the effective crosslink density (or the av-

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

Sample	Feed			A content <sup>a</sup> (wt %)	Yield (%)	Density (g/cm <sup>3</sup> )	$V_2$	$M_c$ (g/mol)
	CMHS (mmol)	A (mmol)	B (mmol)					
P1	1.0	0	4.00	0	92	1.140	—	—
P2	1.0	0.05	3.90	0.5	93	1.141	0.36	2201
P3	1.0	0.10	3.80	1.0	93	1.141	0.37	2010
P4	1.0	0.20	3.60	2.0	95	1.142	0.39	1688
P5	1.0	0.30	3.40	3.1	95	1.142	0.43	1211
P6	1.0	0.40	3.20	4.3	96	1.143	0.46	958
P7	1.0	0.50	3.00	5.6	97	1.145	0.50	710

<sup>a</sup> Mass content of crosslinking monomer A in the polymer systems.

erage molecular weight between two crosslink points ( $M_c$ ). We determine the effective crosslink density by swelling experiments.

This characteristic was deduced from swelling measurements. It was based on the capability of a good solvent of a polymer to swell the network until it used all the possible volume. The relations of Flory and Rehner<sup>14</sup> led to

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

where  $M_c$  is the number average molecular weight between crosslinks;  $\chi$  is the polymer–swelling agent interaction parameter;  $V_1$  is the molar volume of the swelling solvent;  $V_2$  is the volume fraction of the polymer network at swelling equilibrium; and  $\rho$  is the density of the polymer before swelling.

The polymer–swelling agent interaction parameter,  $\chi$ , can be theoretically predicted from the expression:

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

where  $\delta_1$  and  $\delta_2$  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 the absolute temperature. Solubility parameters can be found in tables or calculated from tabulated values for cohesive energy density (or molar attraction constants). The results thus obtained are qualitative and may vary considerably, depending on the selection of table values both for molar attraction constants and molar volume of the groups. Our solubility parameters were calculated using Hoy's Table values<sup>15</sup> for the molar attraction constants  $F$ . The solubility parameter, which is the ratio of  $F$  and molar volume  $V_i$ , was calculated from the expression

$$\delta = \Sigma F_i / \Sigma V_i \quad (3)$$

The calculated solubility parameter for the cyclosiloxane-based polymer is 20.9. The solubility parameter for dimethyl formamide (DMF) is reported<sup>15</sup> to be 24.9 J<sup>1/2</sup>/cm<sup>3/2</sup>. Therefore, the polymer–swelling agent interaction parameter  $\chi$ , calculated from eq. (2), is 0.5 at 298 K.

The volume fraction of polymer network  $V_2$  was calculated as

$$V_2 = 1/Q \quad (4)$$

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

$$Q = 1 + (W_2/W_1 - 1)\rho_p/\rho_s \quad (5)$$

where  $Q$  is the swelling ratio of networks by volume;  $W_1$  is the weight of the network before swelling;  $W_2$  is the weight of the network at equilibrium swelling;  $\rho_p$  and  $\rho_s$  are densities of the polymer and the solvent, respectively.

Using eqs. (4) and (5), we can obtain the following equation:

$$V_2 = 1/[1 + (W_2/W_1 - 1)\rho_p/\rho_s] \quad (6)$$

Swelling measurements were made in 10 mL of DMF with samples of about 0.2g in initial weight. Swelling was accomplished in two days at various temperature. 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 collected in Table I. The molar volume  $V_1$  of the swelling solvent DMF is 77.8 cm<sup>3</sup>/mol. By using both the experimentally measured polymer volume fractions  $V_2$  of the elastomers in their equilibrium-swollen state at room temperature and

**TABLE II**  
**Thermal Properties and the Maximum Reflected Wavelengths of the Polymers**

Sample	DSC			$\lambda_{\text{ref}}^a$ (nm)
	$T_g$ (°C)	$T_m$ (°C)	$T_c$ (°C)	
P1	61.1	110.1	229.3	319
P2	58.9	119.9	219.7	332
P3	57.6	121.0	223.7	338
P4	52.5	122.5	229.2	339
P5	58.5	108.2	227.7	342
P6	60.2	-	228.1	346
P7	60.6	-	232.3	355–647

<sup>a</sup> The maximum reflected wavelength characterized by Perkin–Elmer instruments Lambda 900.

the above-mentioned data, we can calculate the values of  $M_c$  according to eq. (1), which are listed in Table I.

From the results listed in Table I one can see that the value  $V_2$  becomes higher for an increasing functionality of the 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 soft crosslinking component.

### Liquid-crystalline behavior

All the polymers were studied by DSC and X-ray and observed by polarizing microscopy. The thermal behaviors are included in Table II, and Figure 2 displays the DSC thermograms of all the polymers synthesized.

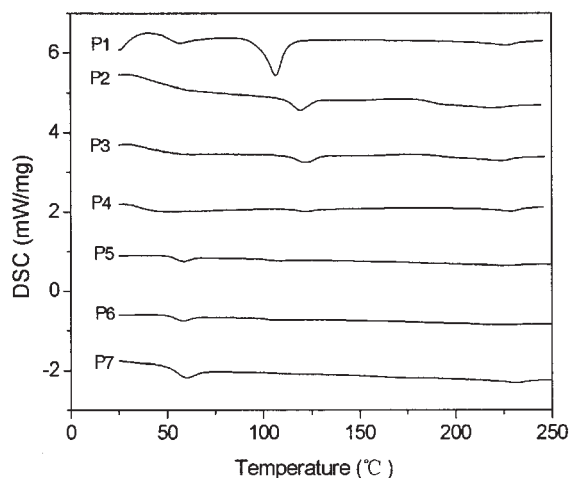
In the DSC thermogram, some of the polymers display three kinds of phase transition behavior corresponding to glass transition, melting point, and clear point, but the others (P6 and P7) show glass transition and clear point. In Figure 2, with increase of the crosslinking groups in the polymers P1–P7, the temperature of the melting point increases slightly while the enthalpy of the phase transition decreases. The temperature of the clear point and the glass transition temperature changes little and doesn't show uptrend or downtrend.

All the polymers exhibit thermotropic LC properties and reveal cholesteric phase. Mesophase identification has been accomplished by X-ray measurement and polarized optical microscopic observation. The optical textures of the polymers were investigated via POM with cold and hot stages under a nitrogen atmosphere. All the polymers showed similar cholesteric phase textures on heating and cooling cycles. The representative textures are shown in Figure 3. For polymer P4, when it was heated from the room temperature to 123°C, the viewing field became bright and a grandjean texture (see Fig. 3a) appeared. When it was heated to 220°C, the typical oily-streak texture gradu-

ally appeared (see Fig. 3b), and the selective reflection color changed from red to blue with increasing temperature; the texture disappeared at 230°C. When the isotropic state was cooled to 208°C, the broken focal-conic texture appeared (see Fig. 3c). When a mechanical force was superimposed on the sample, such as slight shearing, the melt caused macroscopic orientation of the cholesteric domains, and the broken focal-conic texture immediately transformed into the oily-streak texture (see Fig. 3d), which is typical of cholesteric liquid crystals.

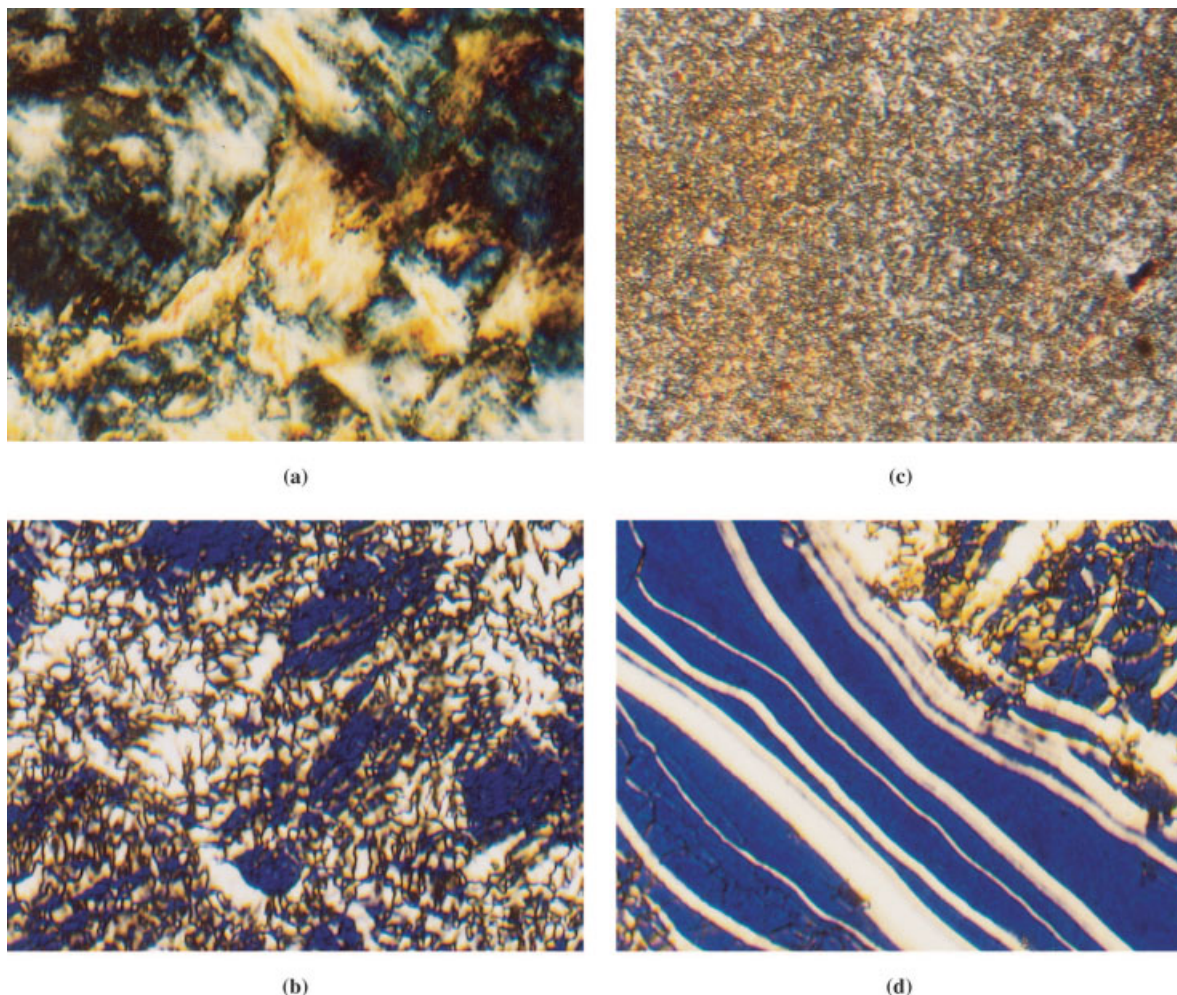
The cholesteric mesophase has also been confirmed by X-ray diffraction. Figure 4 shows the X-ray diffraction diagrams of samples P1, P3, P5, and P7. A broad diffraction peak around  $2\theta = 17^\circ$  is observed for all the polymers, which suggests the average distance of 5 Å between two neighbor LC molecules within the layers of the mesophase. The diffraction peak around  $2\theta = 10^\circ$  corresponding to spacing 9.4 Å suggests the ordered structure. The intensity of the diffraction peak around  $2\theta = 17^\circ$  decreases with increase of the crosslinking component in the polymer systems from P1 to P7, suggesting the order between two neighbor LC molecules disturbed by the soft crosslinking agents.

Chemical crosslinking imposes additional constraints on the segmental motion of polymer chains, and might be expected to raise the glass-transition temperatures.<sup>16</sup> The majority of polymers based on siloxane chains are atactic, and the glass-transition temperature may be considered as a measure of the backbone flexibility. Liquid crystalline polymers are most commonly composed of flexible and rigid moieties; thus, the nature of the side-group also influences the glass-transition temperature. For the polymers P1–P7, the rigid moieties containing cholesteryl groups made the polymers possess



**Figure 2** DSC thermograms of the series of polymers on the first heating (10°C/min).





**Figure 3** Optical textures of the polymer P4 (200 $\times$ ): (a) grandjean texture on heating to 123 $^{\circ}$ C, (b) oily-streak texture on heating to 220 $^{\circ}$ C, (c) broken focal-conic texture on cooling to 208 $^{\circ}$ C, and (d) oily-streak texture on cooling to 205 $^{\circ}$ C.

relatively high glass-transition temperatures due to their sterically hindered effect. With increase of the soft crosslinking component in the polymers from P1 to P7, the rigid moieties decrease, leading to decrease of the glass-transition temperatures. In consideration of the two cases, it is possible for the glass-transition temperature of the polymers to change only little and not show uptrend or downtrend. The data of temperatures of clear points illustrates that low levels of crosslinking do not markedly affect this kind of phase behavior of the materials, just as previously reported.<sup>17</sup>

Because liquid crystalline polymers are most commonly composed of flexible and rigid moieties, self-assembly and nanophase separation into specific micro-structures frequently occur due to geometric and chemical dissimilarity of the two moieties. For the polymers that contain less crosslinking component, the organization of the longer hard segments is easier, resulting in a higher degree of crystallinity of the hard phase. These results demonstrate the melting behavior

in polymers P1–P5. For the other polymers, P6 and P7 that contain more soft crosslinking component, the crosslinking units may act as a nonmesogenic diluent and destabilize the phase in a manner analogous to the freezing-point depression in liquids. Therefore, the chemical crosslinking units destroy the degree of order, leading to absence of melting behaviors.

#### Reflection spectra of the 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 wavelength,  $\lambda_{\max}$ , of reflected light from a cholesteric sample is given by

$$\lambda = nP \sin \varphi \quad (7)$$

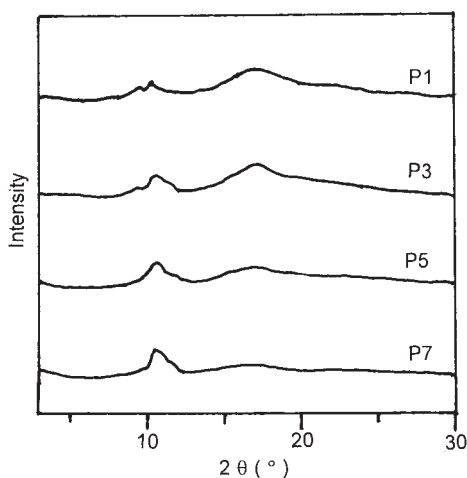
where  $n$  is the average refractive index of the liquid crystalline phase,  $P$  is the pitch height of the helicoidal

arrangement, and  $\varphi$  is the incident angle of beam. The helical pitch  $P$  depends on many factors, such as the concentration of the chiral substance, the temperature, an external field of mechanical, electric, or magnetic origin, etc.<sup>18</sup>

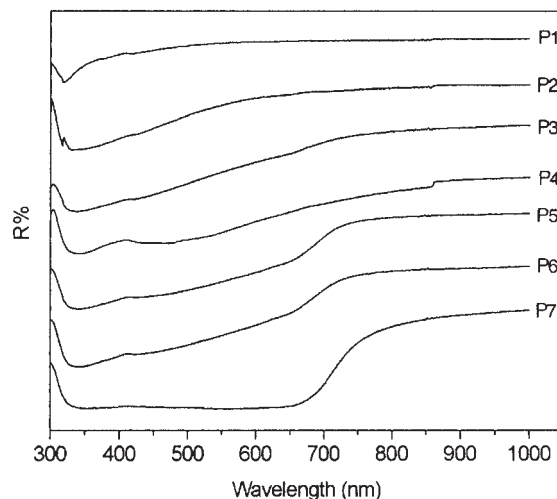
The reflected wavelengths of the samples P1–P7 were characterized by Perkin–Elmer instruments Lambda 900 when the samples were heated at their mesophases (exactly 148.0°C) without any external field, which were listed in Table II. Figure 5 shows the maximum reflected wavelength of the series of polymers. It is shown that the maximum reflection bands become broad from P1 to P7 with increase of the soft crosslinking component in the samples. Furthermore, the data mean that the reflected wavelength shifted to long wavelength from P1 to P7 with increase of the soft crosslinking component in the polymer systems, suggesting the helical pitch  $P$  become longer according to eq. (7). These results are because the helical structure is partially disrupted due to the constraint of chemical crosslinking agents. Consequently, the pitch of the helical structure would become longer with increase of the soft nonmesogenic crosslinking component.

## CONCLUSIONS

We have synthesized a series of cyclosiloxane-based cholesteric LCEs with the nonmesogenic crosslinking contents ranging between 0 and 5.6 weight %. Their chemical structures and liquid-crystalline properties were characterized by FTIR, <sup>1</sup>H-NMR, DSC, POM, and X-ray measurement. We have studied the elastomers with the help of swelling experiments to determine the effective crosslink density ( $M_c$ ), employing Flory–Rehner models. The variety of network structures obtained by varying the soft



**Figure 4** X-ray diffraction diagrams of the polymers P1, P3, P5, and P7.



**Figure 5** The reflected wavelengths of the series of polymers at 148.0°C without any external field.

crosslinking contents leads to different swelling properties in organic solvents.

All the polymers exhibit thermotropic LC properties and reveal a cholesteric phase. With increase of the soft nonmesogenic crosslinking component in the polymers, the melting behavior disappears and the enthalpy of transition decreases. On the other hand, the temperature of glass transition and clear point change little and don't show uptrend or downtrend. These results originate from the effect of the soft nonmesogenic chemical crosslinking.

Reflection spectra of the cholesteric mesophase of the series of polymers showed that the reflected wavelength becomes broad and shifts to long wavelength with increase of the soft crosslinking component in the polymer systems, suggesting that helical pitch  $P$  became long.

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