Side-Chain Cholesteric Liquid Crystalline Elastomers Derived from a Mesogenic Cross-Linking Agent

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ABSTRACT: The synthesis of the two monomers  $M_1$  and  $M_2$  and a series of new side-chain cholesteric liquid crystalline elastomers  $P_2-P_8$  is presented. The chemical structures of the monomers and elastomers obtained were confirmed by FTIR or <sup>1</sup>H NMR spectroscopy. The cross-link density of the elastomers was determined by swelling experiments. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements. Monomer  $M_1$  showed a cholesteric phase, and  $M_2$  revealed smectic and nematic phases. The effect of the cross-link density on the phase behavior of  $P_2-P_8$  is discussed. Elastomers  $P_2-P_6$  containing less than 12 mol % of the cross-linking units displayed elasticity, reversible liquid crystalline phase transition, wide mesophase temperature ranges, and high thermal stability. Elastomer  $P_7$  displayed stress-induced birefringence, and  $P_8$  showed only elasticity with no other texture. Experimental results demonstrated that the glass transition temperatures increased, and the isotropization temperatures and the mesophase temperature ranges of  $P_2-P_6$  decreased with increasing cross-link density.

### Introduction

Today, liquid crystalline science is directed toward the development of multifunctional and oriented structures. One example of such supermolecular systems is liquid crystalline networks (LCNs). Recently, research into LCNs with anisotropic properties have expanded rapidly,<sup>1–8</sup> and in particular, LCNs with cholesteric structures have attracted considerable interest, because of their unique properties and potential applications in numerous areas, especially in the fields of nonlinear optical materials and electrooptical materials etc.<sup>9–13</sup> According to the cross-link density, two new classes of cholesteric LCNs emerge: highly cross-linked cholesteric liquid crystalline thermosets (ChLCTs); and lightly cross-linked cholesteric liquid crystalline elastomers (ChLCEs).

In the past decade, ChLCTs have been extensively investigated because the helical structure of cholesteric phase is permanently fixed and optical properties become temperature independent.<sup>14–20</sup> In contrast to ChLCTs, ChLCEs combine the basic features of polymer elastomers with the anisotropy of physical properties of cholesteric liquid crystalline. Consequently, ChLCEs not only hold the entropic elasticity but also show reversible phase transitions between liquid crystalline and isotropic phases on heating and cooling cycles. Compared with conventional LCEs, ChLCEs show unusual piezoelectric properties, besides electrooptical and mechanical properties due to deformation of the helical structure of the cholesteric phase.

Recent theoretical and experimental studies have suggested that piezoelectricity can be obtained from ChLCEs.<sup>21–23</sup> They have the potential to act as a device that transforms a mechanical signal into an optical signal when stress is applied parallel to the cholesteric helix. Therefore, ChLCEs are considered as a candidate for piezoelectric devices. However, to the best of our knowledge, research on ChLCEs is little reported.<sup>21–29</sup> It has therefore been necessary to synthesize various kinds of side-chain ChLCEs to explore their potential applications.

In this study, new side-chain ChLCEs derived from cholesteryl 4-allyloxybiphenyl-4'-carboxylate ( $M_1$ ) and 4-allyloxybenzoyl-4'-(6-acryloyloxyhexyloxy)benzoyl-*p*-benzenediolbisate ( $M_2$ ) were prepared. The mesomorphic properties of the monomers and elastomers obtained were characterized by DSC, TGA, POM, and XRD. The influence of the cross-link density on the phase behavior of the elastomers is discussed.

# **Experimental Section**

**Materials.** Polymethylhydrosiloxane (PMHS) was purchased from Jilin Chemical Industry Co. 4-Hydroxybiphenyl-4'-carboxylic acid (from Aldrich) was used as received. 1,6-Hexanediol was purchased from Beijing Hongyu Chemical Industry Co., and cholesterol was obtained from Henan Xiayi Medical Co. Toluene used in the hydrosilication reaction was first refluxed over sodium and then distilled under nitrogen. All other solvents and reagents were purified by standard methods.

Measurements. FTIR spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). <sup>1</sup>H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). Phase transition temperatures and thermodynamic parameters were determined by using a Perkin-Elmer DSC-7 (Perkin-Elmer, Foster City, CA) equipped with a liquid nitrogen cooling system. The heating and cooling rates were 10 °C/min. The phase transition temperatures were collected during the second heating and the first cooling scans. The thermal stability of the polymers under atmosphere was measured with a Perkin-Elmer TGA-7 thermograrimetric analyzer. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and FP 80 central processor was used to observe phase transition temperatures and analyze liquid crystalline properties for the monomers and polymers through observation of optical textures. XRD measurements were performed with a nickel-

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Scheme 2. Synthetic Route of Cross-Linking Monomer

Chol\* =



filtered Cu K $\alpha$  radiation with a DMAX-3A Rigaku powder diffractometer (Rigaku, Japan).

**Synthesis of the Monomers.** The synthesis of the olefinic monomers is shown in Schemes 1 and 2. 4-Allyloxybiphenyl-4'-carboxylic acid, 4-hydroxyphenyl-4'-allyloxybenzoate, and 4-(6-acryloyloxyhexyloxy)benzoic acid were prepared according to the literature procedures reported.<sup>30–32</sup>

**Cholesteryl 4-Allyloxybiphenyl-4'-carboxylate (M<sub>1</sub>).** First, 2.54 g (0.01 mol) of 4-allyloxybiphenyl-4'-carboxylic acid was reacted at 60 °C with 15 mL of thionyl chloride containing a few drops of *N*,*N*-dimethylfomamide (DMF) for 3 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. The acid chloride obtained was dissolved in 5 mL of dry chloroform, and added dropwise to a solution of 3.87 g (0.01 mol) of cholesterol in 0.8 mL of pyridine and 15 mL of chloroform. The reaction mixture was refluxed for 10 h. The crude product was precipitated by adding ethanol to the filtrate, and was recrystallized from ethyl acetate/ethanol (1:1). Yield 75%, mp 111 °C. IR (KBr),  $\mu$  (cm<sup>-1</sup>): 3063 (=C-H), 2930, 2852 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1741 (C=O), 1636 (C=C), 1606, 1512 (Ar-), 1152 (C-O-C). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 0.66-2.07 (m, 43H, cholesteryl-*H*); 4.55 (t, 2H, -OCH<sub>2</sub>-); 4.72-5.29 (m, 2H, CH<sub>2</sub>=CH-); 5.51 (m, 1H, =CH- cholesteryl); 6.04 (m, 1H, CH<sub>2</sub>=C*H*-); 7.03–8.06 (m, 8H, Ar-*H*).

**4-Allyloxybenzoyl-4'-(6-acryloyloxyhexyloxy)benzoyl** *p***-benzenediolbisate (M<sub>2</sub>).** First, 2.92 g (0.01 mol) of 4-(6acryloyloxyhexyloxy)benzoic acid was reacted at 40 °C with 15 mL of thionyl chloride containing a few drops of DMF and a trace of *p*-hydroxyanisole for 4 h, and then the excess thionyl chloride was removed under reduced pressure to give the acid chloride.

The acid chloride obtained was dissolved in 5 mL of chloroform and added dropwise to a cold solution of 2.7 g (0.01 mol) of 4-hydroxyphenyl-4'-allyloxybenzoate in 15 mL of chloroform and 1.4 mL of triethylamine. After reacting for 14 h at room temperature, the crude product was precipitated by adding ethanol to the filtrate and recrystallized from ethanol. Yield 47%, mp 75 °C. IR(KBr),  $\mu$  (cm<sup>-1</sup>): 3076 (=C-H); 2938, 2863 (-CH<sub>3</sub>, -CH<sub>2</sub>-); 1736 (C=O); 1643 (C=C); 1610, 1513 (Ar-). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 1.51-1.87 [m, 8H, -(CH<sub>2</sub>)<sub>4</sub>-]; 3.75 (t, 2H, -CH<sub>2</sub>CH<sub>2</sub>O-); 4.18 (t, 2H, -COOCH<sub>2</sub>-); 4.62 (t, 2H, =CHCH<sub>2</sub>O-); 6.01 (m, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>-); 6.20 (m, 1H, CH<sub>2</sub>=CHCOO-); 6.96-8.17 (m, 12H, Ar-H).

**Synthesis of the Elastomers.** For the synthesis of the elastomers  $P_2-P_8$ , the same method was adopted. The synthesis of  $P_3$  is given as an example. Monomers  $M_1$ ,  $M_2$ , and **PMHS** were dissolved in dry, freshly distilled toluene. The mixture was heated to 65 °C under nitrogen and anhydrous conditions, and then a proper amount of THF solution of hexchloroplatinate hydrate catalyst was injected with a syringe. After holding the reaction mixture at 65 °C for 48 h, the networks were obtained with methanol, and then dried under vacuum. IR (KBr),  $\mu$  (cm<sup>-1</sup>): 3000–2800 (-CH<sub>3</sub>, -CH<sub>2</sub>-); 1735, 1711 (C=O); 1606, 1512 (Ar-); 1200–1000 (Si–O–Si).

#### **Results and Discussion**

Syntheses. The synthetic routes for the target monomers are shown in Schemes 1 and 2. The structural characterization of the monomers and elastomers obtained were in agreement well with the prediction. 4-Allyloxybiphenyl-4'-carboxylic acid (1), 4-hydroxyphenyl-4'-allyloxybenzoate (3), and 4-(6-acryloyloxyhexyloxy)benzoic acid (5) were synthesized according to a route described by Hu et al.<sup>26–28</sup> The synthetic methods for  $M_1$  and  $M_2$  are the same. First, activation of compounds 1 and 5 was obtained with thionyl chloride and then reacted, respectively, with cholesterol and **3** in chloroform to prepare cholesteric monomer  $M_1$  and cross-linking monomer  $M_2$ . IR spectra of  $M_1$  and  $M_2$ showed characteristic bands at 1741–1736, 1643–1636, and 1610–1512 cm<sup>-1</sup> attributed to ester C=O, olefinic C=C, and aromatic C=C stretching band. <sup>1</sup>H NMR spectra of  $M_1$  and  $M_2$  showed multiplets at 0.61-4.62, 4.72–6.04, and 6.96–8.17 ppm corresponding to methyl and methylene protons, olefinic protons, and aromatic protons, respectively.

The elastomers were prepared by a one-step hydrosilication reaction between Si–H groups of **PMHS** and olefinic C=C of  $M_1$  and  $M_2$  in toluene, using hexchloroplatinate hydrate as catalyst at 65 °C. Yields and detailed polymerization are summarized in Table 1. Schematic representation of the elastomers obtained is presented in Figure 1. IR spectra of the elastomers showed the complete disappearance of the Si–H stretching band at 2166 cm<sup>-1</sup> and the olefinic C=C stretching band at 1643–1636 cm<sup>-1</sup>. Characteristic Si–O–Si stretching bands appeared at 1200–1000 cm<sup>-1</sup>. In addition, the absorption bands of ester C=O and aromatic still existed.

Table 1. Polymerization and Solubility

	feed (mmol)		$M_2^a$	vield	solubility <sup>b</sup>		
polymer	<b>M</b> <sub>1</sub>	<b>M</b> <sub>2</sub>	(mol %)	(%)	toluene	xylene	DMF
P1	7.000	0.000	0	82	+	+	+
$\mathbf{P}_2$	6.861	0.069	1	84	_	_	_
$\mathbf{P}_3$	6.726	0.137	2	89	_	_	_
$\mathbf{P}_4$	6.462	0.269	4	90	_	_	_
$P_5$	5.963	0.519	8	86	_	_	_
$\mathbf{P}_{6}$	5.500	0.750	12	85	-	_	_
$\mathbf{P}_7$	5.069	0.966	16	84	-	_	_
P <sub>8</sub>	4.667	1.167	20	79	_	_	_

<sup>*a*</sup> Molar fraction of  $\mathbf{M}_1$  based on  $\mathbf{M}_1 + \mathbf{M}_2$ . <sup>*b*</sup> Key: (+) dissolve; (-) insolubility or swelling.



**Figure 1.** Schematic representation of side-chain liquid crystalline elastomers.

**Swelling Properties.** The degree of swelling and the cross-link density of the elastomers could be determined by swelling experiments or by stress—strain measurements. From swelling experiments, the cross-link density or the average molar mass of the network chains between two cross-links,  $\bar{M}_c$ , was calculated according to the Flory swelling theory

$$\bar{M}_{\rm c} = \rho_{\rm e} \cdot V_1 \, (0.5 - \chi_1)^{-1} \cdot q^{5/3} \tag{1}$$

where  $\rho_e$  is the density of the elastomer,  $V_1$  is the molar volume of the swelling solvent, q is the equilibrium ratio of the volumes of the swollen and unswollen elastomers, and  $\chi_1$  is the Flory–Huggins parameter or the interaction parameter between the solvent and the elastomer.

The parameter  $\chi_1$  was calculated from the second virial coefficient  $A_2$  according to eq 2

$$\chi_1 = 0.5 - A_2 \rho_{\rm u}^{2} V_1 \tag{2}$$

where  $\rho_u$  is the density of the un-cross-linked polymer. From eqs 1 and 2,  $\overline{M}_c$  was obtained.

The equilibrium ratio of the elastomers was determined through the following equation

$$q = 1 + (W_2/W_1 - 1)\rho_p/\rho_s \tag{3}$$

where  $W_1$  and  $W_2$  are the weights of the elastomers before swelling and at equilibrium swelling, and  $\rho_p$  and  $\rho_s$  are the densities of the polymer and solvent, respectively.

Swelling experiments were measured in 10 mL of toluene with 0.5 g of samples. The samples were placed into glass vial closed hermetically. They were subsequently homogenized at room temperature by strong shaking. Each vial was weighed before and after homogenization. After the vial was sealed, they were left

**Table 2. Physical Properties of Polymers** 

	-		_	-
polymer	density (g/cm³)	q	$ar{M}_{ m c}$ (g/mol)	degree of swelling <sup>a</sup> (wt %)
<b>P</b> <sub>1</sub>	1.056			
$\mathbf{P}_2$	1.064	4.07	11 039	350
$P_3$	1.063	3.82	9923	330
$\mathbf{P}_4$	1.068	3.46	8453	300
$\mathbf{P}_{5}$	1.076	3.23	7594	280
$\mathbf{P}_{6}$	1.075	2.74	5768	240
$\mathbf{P}_7$	1.082	2.37	4558	210
P <sub>8</sub>	1.098	2.01	3515	180

 $^a$  Toluene uptake in weight % at room temperature, referring to the weight of the extracted polymer.

in a constant temperature insulated. 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. Table 2 shows swelling properties of the elastomers. As seen from the data listed in Table 2, with increasing the concentration of cross-linking units in the networks,  $\bar{M}_c$  and the degree of swelling reduced, that is to say, the cross-link density increased.

Thermal Properties. In general, the phase behavior of side-chain LCEs mainly depends on the nature of the polymer backbone, the rigidity of the mesogenic unit, the length of the flexible spacer, and the cross-link density. The polymer backbones are primarily polyacrylates, polymethacrylates and polysiloxanes. However, polyacrylates and polymethacrylates show higher glass transition temperatures because of their backbones. To obtain mesomorphic properties and elasticity at moderate temperature, polysiloxanes backbone and flexible spacer are usually adopted. The polymer backbone and the mesogenic units have antagonistic tendency: the polymer backbone is driven toward a random coil-type configuration, whereas the mesogenic units stabilize with long-range orientation order. The mesogenic units are usually attached to the polymer backbone by a flexible spacer. The flexible spacer decouples the mesogenic side groups from the polymer backbone and renders the mesogenic units to order.

The thermal properties of the monomers  $M_1$  and  $M_2$ and polymers  $P_1-P_8$  were determined by DSC and POM measurement. The phase transition temperatures and corresponding enthalpy changes are summarized in Tables 3 and 4, respectively. According to the data listed in Table 3, a melting transition and a cholesteric to isotropic phase transition for  $M_1$  appeared at 111.6 and 251.7 °C; a melting transition, a smectic to nematic phase, and a nematic to isotropic phase transition for  $M_2$  occurred at 76.5, 86.5, and 199.0 °C, respectively.

For the elastomers  $P_2-P_6$ , a glass transition at low temperature and a cholesteric to isotropic transition at high temperature appeared on DSC curves. As seen from the data in Table 3, low cross-link density did not significantly affect the phase behavior of the elastomers, and reversible phase transitions were observed because of enough molecular motion. In contrast, higher crosslink density had strong influence on the phase behavior, it could cause liquid crystalline phase to disappear due to the disturbance of mesogenic order. Therefore, DSC curves of  $P_7$  and  $P_8$  only showed a glass transition. Above all, the phase transitions are reversible and do not change on repeated heating and cooling cycles.

Table 3. Phase Transition Temperatures (°C) of Monomers<sup>a</sup>

	transition temp <sup><math>b</math></sup>		
	(corresponding enthalpy changes/J·g <sup>-1</sup> )		
monomer	heating/cooling	$\Delta T_1^c$	$\Delta T_2^{d}$
<b>M</b> <sub>1</sub>	K111.6(35.6)Ch251.7(1.3)I/I234.2(0.8)Ch81.5(29.7)K	140.1	152.7
$M_2$	$K76.5(22.2)S_{A}86.5(3.7)N199.0(2.7)I/I194.7(1.5)S_{A}77.1(2.2)N36.3(17.2)$	122.5	158.4

<sup>*a*</sup> Key: K, solid; Ch, cholesteric; S<sub>A</sub>, smectic A; N, nematic; I, isotropic. <sup>*b*</sup> Peak temperatures were taken as the phase transition temperature. <sup>*c*</sup> Mesophase temperature ranges during heating cycle. <sup>*d*</sup> Mesophase temperature ranges during cooling cycle.

polymer	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm i}/^{\circ}{\rm C}$	$\Delta H J \cdot g^{-1}$	$\Delta T^a$	$T_{\rm cl}{}^b/{}^{\circ}{\rm C}$	$T_{\rm d}c/^{\circ}{\rm C}$	$\lambda_m d/nm$
<b>P</b> <sub>1</sub>	65.4	312.5	2.8	247.1	315	348.9	
$\mathbf{P}_2$	63.8	311.2	2.0	247.4	316	332.5	1215
$\mathbf{P}_3$	64.2	308.5	1.7	244.3	314	345.4	1224
$\mathbf{P}_4$	65.9	294.6	1.8	228.7	301	342.2	1381
$\mathbf{P}_{5}$	69.8	295.7	1.4	225.9	302	335.2	1426
$\mathbf{P}_{6}$	77.1	288.2	0.9	211.1	298	319.5	1459
$\mathbf{P}_7$	79.4				264	331.4	
P <sub>8</sub>	85.6					328.4	

<sup>*a*</sup> Mesophase temperature ranges  $(T_i - T_g)$ . <sup>*b*</sup> Temperature at which the birefringence disappeared completely. <sup>*c*</sup> Temperature at which 5% weight loss occurred. <sup>*d*</sup> Reflection wavelength measured by UV/vis spectra at cholesteric phase.

The glass transition temperature  $(T_g)$  is an important parameter in connection with structures and properties. In general, chemical cross-linking imposes additional constraints on the motion of chain segments, and causes an increase in the  $T_g$  value. However, the effect may be small for lightly cross-linked polymers, and the  $T_g$  value is also affected by the flexible cross-linking chains similar to the plasticization effect. Compared with the un-cross-linked polymer,  $T_g$  values of lightly cross-linked polymers may fall. Taking the cross-linking effect and plasticization effect into account,  $T_g$  is given by

$$T_{\rm g} = T_{\rm go} - \mathbf{K}_{\rm x} \rho_{\rm x} \tag{4}$$

$$T_{\rm g} = T_{\rm go} + K_{\rm x} \rho_{\rm x} \tag{5}$$

where  $T_g$  and  $T_{go}$  are the glass transition temperatures of cross-linked and un-cross-linked polymers,  $K_x$  is constant, and  $\rho_x$  is the cross-link density. When the cross-link density is less than a certain critical value, the plasticization effect of flexible cross-linking chains is predominant, and eq 4 is adopted. Conversely, the cross-linking effect is predominant, and eq 5 is adopted. Figure 2 shows the effect of the concentration of crosslinking units on the phase transition temperatures of  $P_1-P_8$ . It can be seen that  $T_g$  value of  $P_2$  and  $P_3$ decreased by 1.6 and 1.2 °C compared with  $P_1$ . However, general tendency is toward an increased  $T_g$  value with increasing cross-link density. For  $P_2-P_8$ , when the concentration of cross-linking units increased from 1 to 20 mol %, the  $T_g$  value increased from 63.8 to 85.6 °C.

20 mol %, the  $T_g$  value increased from 63.8 to 85.6 °C. Similar to  $T_g$ , chemical cross-linking affected isotropization temperature ( $T_i$ ) in two ways. On one hand, the flexible cross-linking chains acted as diluents and led to a decrease in the  $T_i$  value; on the other hand, chemical cross-linking could prevent the motion and orientation of mesogenic molecule at and in the vicinity of the cross-linking sites and did not favor the formation of mesogenic orientation order in the networks with increasing cross-link density. Consequently,  $T_i$  disappeared when the cross-link density was greater than a certain critical value. According to Table 4, the  $T_i$  value of  $\mathbf{P_1}-\mathbf{P_6}$  decreased from 311.2 to 288.2 °C when the concentration of cross-linking units increased from 1 to 12 mol %. In addition,  $\mathbf{P_1}-\mathbf{P_6}$  displayed wide mesophase



**Figure 2.** Effect of  $M_2$  content on phase transition temperatures of the elastomers. Key: (**I**)  $T_{g}$ ; (**O**)  $T_{i}$ ; (**A**)  $\Delta T$ .



Figure 3. TGA thermograms of the elastomers.

temperature ranges ( $\Delta T$ ).  $\Delta T$  of elastomers decreased with increasing cross-link density because the  $T_g$  value increased, whereas the  $T_i$  value decreased.

Figure 3 presents TGA thermograms of the elastomers. TGA results showed that the temperatures at which 5% weight loss occurred ( $T_d$ ) were greater than 300 °C for  $P_2-P_8$ ; this reveals that the synthesized elastomers have a high thermal stability.

**Optical Properties.** The unique optical properties of cholesteric liquid crystalline are related to the helical supermolecular structure of the cholesteric phase. The periodic helical structure of the cholesteric phase selectively reflects visible light like an ordinary diffraction grating, the pitch of which controls the wavelength of selective reflection of light. If the reflected wavelength lies in the visible range of the spectrum, the cholesteric phase exhibits brilliant colors. The transmitted light shows complementary color. The wavelength of selective reflection of light  $\lambda_m$  obeys the Bragg condition

$$\lambda_{\rm m} = \bar{n}P \tag{6}$$

where  $\bar{n}$  is the average index of refraction and *P* is the pitch of the cholesteric phase, defined as the spatial distance over which the director rotates 360°.

Because of the angular dependence of the reflection conditions, different colors are seen depending on different observation angles. So  $\lambda_m$  is given by

$$\lambda_{\rm m} = \bar{n} P \cos \varphi \tag{7}$$

where  $\varphi$  is the incidence angle. When  $\varphi = 0^{\circ}$  (normal incidence),  $\lambda_{\rm m} = \lambda_0 = \bar{n}P$ . The intensity of reflected light is a maximum at  $\lambda_{\rm m} = \lambda_0$ , and it falls off very rapidly on either side of  $\lambda_0$ .

In reality, the orientation of the cholesteric helices is not exactly perpendicular to the cell surface. Taking this into account, eq 2 becomes

$$\lambda_{\rm m} = \bar{n}P\cos\left(\frac{1}{2}\left[\sin^{-1}\left(\frac{\sin\alpha}{\bar{n}}\right) + \sin^{-1}\left(\frac{\sin\beta}{\bar{n}}\right)\right]\right\} \quad (8)$$

where  $\alpha$  and  $\beta$  are the incidence angle and observation angle, respectively.

The helical pitch is an important parameter in connection with optical properties of the cholesteric phase. Although the microscopic origins of the helical pitch are still a subject of study, it is known that the helical pitch and optical properties of side-chain cholesteric liquid crystalline networks mainly depend on the polymer backbone, the rigidity of mesogenic units, the length of the flexible spacer, the cross-link density, and the outer condition (such as temperature, force field, electric field and magnetic field). For each elastomer, the maximum reflection wavelength  $\lambda_m$  was measured with UV-vis spectra. The  $\lambda_m$  values are summarized in Table 4. As can be seen from Table 4, the reflection color could not be observed because  $\lambda_m$  value was greater than the wavelength of visible light. Moreover,  $\lambda_m$  values increased, that is to say, the helical pitch also increased with an increase in the concentration of cross-linking units.

The optical textures of the monomers and polymers are studied by POM with hot stage under nitrogen atmosphere. POM observation results showed that  $M_1$ exhibited enantiotropic cholesteric phase and  $M_2$  revealed smectic and nematic phases on heating and cooling cycles. When  $M_1$  was heated to 111 °C, the sample began to melt, the typical cholesteric oily streak texture gradually appeared, and the texture disappeared at 257 °C. When the isotropic state was cooled to 253 °C, the focal-conic texture appeared. If a mechanical field was superimposed on the sample right now, for example, slight shearing of the melt would cause macroscopic orientation of the cholesteric domains, and the focal-conic texture transformed to an oily streak texture, which is a typical characteristic of cholesteric liquid crystalline. When M2 was heated to 75 °C, a smectic fan-shaped texture appeared, and then heating continued to 88 °C, nematic schlieren texture gradually occurred, and mesomorphic behavior disappeared at 203 °C. Photomicrographs of M1 and M2 are shown in Figure 4 parts a–c.

The un-cross-linked polymer  $P_1$  exhibited a smectic fan-shaped texture, and the expected cholesteric phase





(b)



(c)

**Figure 4.** Optical textures of monomers  $(320 \times)$ : (a) oily streak texture of  $M_1$  at 237 °C; (b) fan-shaped texture of  $M_2$  at 83 °C; (c) Schlieren texture of  $M_2$  at 189 °C.

did not appear, the reason for which is that the polymer chains hinder the formation of the helical supermolecular structure of the mesogens. Because of the introduction of the nematic units, the elastomers  $P_2$  and  $P_3$  exhibited cholesteric oily streak or Grandjean texture, and the types of cholesteric textures of  $P_4$ – $P_6$  were not easily identified because of the viscoeelasticity. Moreover,  $P_7$  displayed stress-induced birefringence although the DSC curve showed no mesophase to isotropic phase transition. This is similar to those described by Mitchell.<sup>33</sup>  $P_8$  showed only elasticity with no other texture; this is consistent with the results obtained by DSC. Photomicrographs of polymers are shown in Figure 5, parts a–c.

**X-ray Diffraction Analysis.** XRD studies were carried out to obtain more detailed information on the liquid crystalline structure and type. In general, a sharp and strong peak at low angle ( $1^{\circ} < 2\theta < 4^{\circ}$ ) in the smallangle X-ray scattering (SAXS) curve and a broad peak associated with lateral packing at  $2\theta \approx 20^{\circ}$  in the wide-



(4)







Figure 5. Optical textures of polymers (320×): (a) fan-shaped texture of  $P_1$  at 213 °C; (b) oily streak texture of  $P_2$  at 256 °C; (c) Grandjean texture of  $P_3$  at 184 °C.

angle X-ray diffraction (WAXD) curve can be observed for smectic structure. For the nematic structure, no peak appears in the SAXS curve, but in the WAXD curve, a broad peak at  $2\theta \approx 20^\circ$  can also be observed. For the cholesteric structure, no peak also appears in the SAXS curve; however, a broad peak occurs at  $2\theta \approx 17^{\circ}$ . The diffraction angles of the cholesteric structure at wide angle are obviously less than those of the smectic and nematic structures, and this is a very important characteristic to judge the cholesteric structure. Moreover, some research also shows that a weak peak at  $2\theta$  = 8–10° is usually observed for cholesteric structure.<sup>34–36</sup> For  $P_2-P_6$ , a sharp peak associated with the smectic layers at low angles did not appear in the SAXS curves, and a weak peak and a broad peak were observed, respectively, at  $2\theta = 8.9-9.6$  and  $16.5-17.4^{\circ}$  in WAXD curves. Moreover, broad peaks were more and more diffuse, and the peak intensity decreased with increas-



Figure 6. X-ray diffraction patterns of quenched samples.

ing cross-link density, which indicates the decrease of liquid crystalline order from  $\mathbf{P}_2$  to  $\mathbf{P}_6$ . Figure 6 shows representative XRD curves of quenched samples of elastomers. According to Bragg equation,  $\lambda = 2d \sin \theta$ , the corresponding *d* spacings were 9.8–9.1 and 5.3–5.0Å, respectively. Therefore, the cholesteric phase structures of  $\mathbf{P}_2-\mathbf{P}_6$  were confirmed by optical texture and XRD results.

#### Conclusions

In this study, a series of new side-chain ChLCEs containing cholesteryl4-allyloxybiphenyl-4'-carboxylate and 4-allyloxybenzoyl-4'-(6-acryloyloxyhexyloxy)benzoyl-*p*-benzenediolbisate side groups were synthesized and characterized. All of the obtained polymers showed very wide mesophase temperature ranges and high thermal stability. Light chemical cross-linking did not markedly affect phase behavior of the elastomers. The elastomers containing less than 12 mol % of cross-linking units showed elasticity, reversible mesophase transition, and cholesteric texture during heating and cooling cycles. For  $P_2-P_6$ , the glass transition temperature increased, and the isotropization temperature and the mesophase temperature range decreased with increasing the cross-link density.

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