

# Mesomorphic Properties of Cholesteric Side-Chain Liquid Crystalline Polysiloxanes and Elastomers

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**ABSTRACT:** A series of crosslinked liquid crystalline polymers and corresponding uncrosslinked liquid crystalline polymers were prepared by graft copolymerization. Their liquid crystalline properties were characterized by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction measurements. The results showed that the crosslinking obtained in the isotropic state and the introduction of nonmesogenic crosslinking units into a polymeric structure could cause additional reduction of the clearing point ( $T_i$ ) of the crosslinked polymers, com-

pared with the corresponding uncrosslinked polymers. The crosslinked polymers (P-2–P-4) with a low crosslinking density exhibited cholesteric phases as did the uncrosslinked polymers. In contrast, a high crosslinking density made the crosslinked polymer P-5 lose its thermotropic liquid crystalline property. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 773–778, 2004

**Key words:** polysiloxanes; liquid-crystalline polymers (LCP); elastomers

## INTRODUCTION

Thermotropic cholesteric liquid crystalline polymers (ChLCPs) always attract considerable attention and interest, mainly because cholesteric mesophases exhibit interesting optical properties such as the selective reflection of light, thermochromism, and circular dichroism. So, ChLCPs have many potential applications in numerous areas, especially in the field of nonlinear optical materials, electrooptical materials, and fast switching materials.<sup>1–9</sup>

In the past decade, the formation of lightly crosslinked ChLCPs with chiral groups, that is, cholesteric liquid crystalline elastomers (ChLCEs), has attracted more and more interest, because ChLCEs not only hold entropic elasticity, but also show a reversible phase transition during heating and cooling cycles. Compared with conventional LCEs, ChLCEs show unusual piezoelectric properties besides electrooptical and mechanical properties due to the formation of the helical structure of the cholesteric phase. Recent theoretical and experimental studies have suggested that piezoelectric properties can be obtained from ChLCEs.<sup>10,11</sup> ChLCEs have the potential to act as a device that transforms a mechanical signal into an

optical signal.<sup>12</sup> Consequently, ChLCEs have been considered to be a candidate for a piezoelectric device. However, to the best of our knowledge, research on ChLCEs has been seldom reported.<sup>10–14</sup> Therefore, it is both necessary and useful to synthesize various kinds of ChLCEs to explore their potential application.

In this article, we present the synthesis of side-chain ChLCEs using cholesteric liquid crystal as mesogenic units and a flexible nonmesogenic trivinyl compound as crosslinking units. For comparison, corresponding ChLCPs without crosslinking units were also prepared, and the influence of the crosslinking on the mesogenic properties of ChLCEs is discussed.

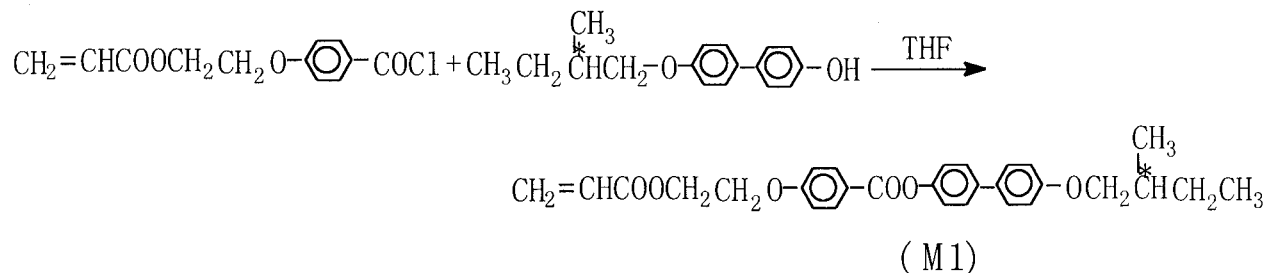
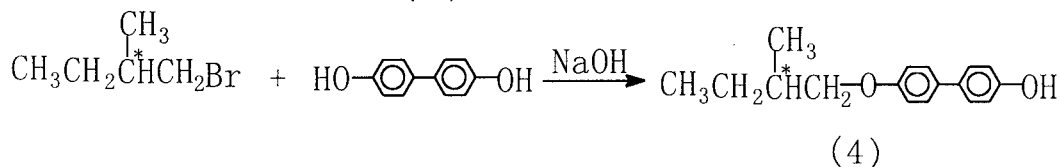
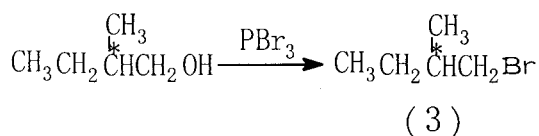
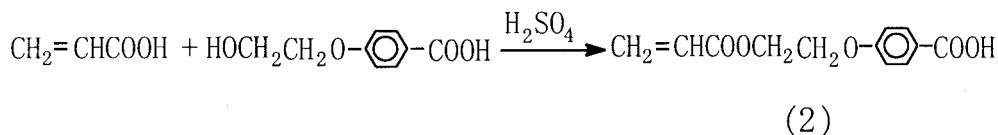
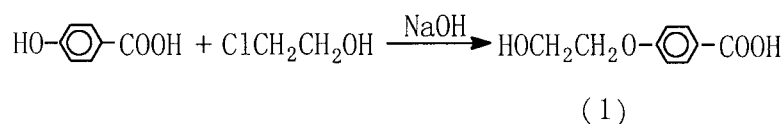
## EXPERIMENTAL

### Materials

Polymethylhydrosiloxane (PMHS),  $M_n = 700–800$ , was purchased from the Jilin Chemical Industry Co. (Jilin, China) and used without any further purification. 1,1,1-Trihydroxymethyl propyl triacrylate (**M2**), used as a crosslinking monomer, was provided by the Liaoning Province Fengcheng Accessory Ingredient Factory (Fengcheng, Liaoning, China) and purified before use. S(-)-2-methyl-1-butanol ( $[\alpha]_D^{20} = -6.3 \pm 0.5^\circ$ ) was purchased from Fluka (Switzerland). 4,4'-Biphenol and 4-hydroxybenzoic acid was purchased from the Beijing Fuxing Chemical Industry Co. (Beijing, China). Acrylic acid and chloroethanol was purchased from the Shenyang Xinxi Chemical Reagent Co. (Shenyang, Liaoning, China). All other solvents and reagents were purified before use.

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Scheme 1 Synthesis routes of monomer M1.

### Characterization

Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). Chiroptical rotation was carried out with a Shanghai WZZ-1S digital polarimeter using THF as a solvent. Phase-transition temperatures were determined by using a TA Q100 DSC under a nitrogen atmosphere. The heating and cooling rates were 20°C/min. The textures of the liquid crystalline phases were observed with a Leitz optical polarizing microscope equipped with a Mettler FP82 hot stage. X-ray diffraction measurements were performed with nickel-filtered CuK $\alpha$  radiation with a Rigaku powder diffractometer.

### Monomer synthesis

The synthesis of the monomer (+)-4-[4-(2-acryloyloxy)ethoxybenzoyloxy]-4'-(2-methyl)butoxy biphenyl (M1) was carried out as shown in Scheme 1. 4-(Hydroxy-*n*-ethoxy)benzoic acid (1) and (+)-1-bromo-2-methylbutane (3,  $[\alpha]_D^{20} = +4.0^\circ$ ) were prepared according to the literature procedures.<sup>15-17</sup>

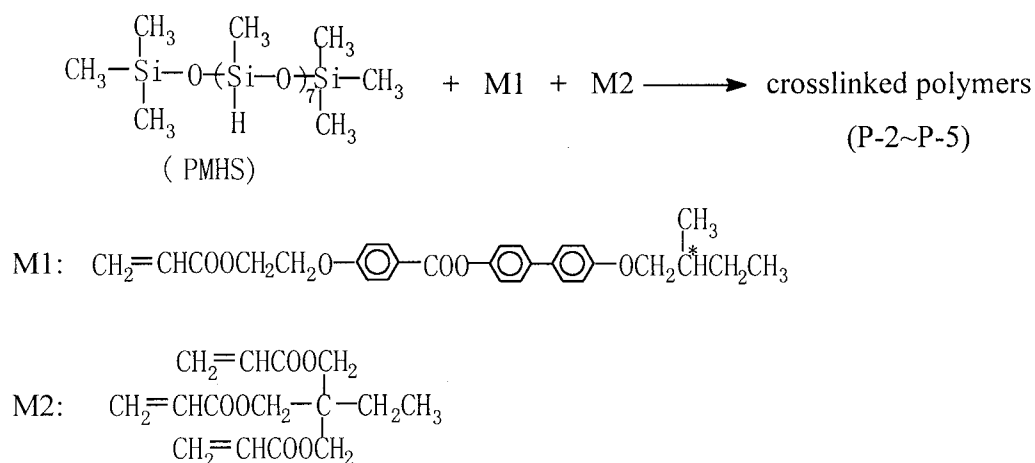
### 4-(2-acryloyloxy)ethoxybenzoic acid (2)

4-(Hydroxy-*n*-ethoxy)benzoic acid (1, 0.2 mol) was dissolved in a mixture of acrylic acid (280 mL), 98% H<sub>2</sub>SO<sub>4</sub> (2 g), and small amount of 4-methoxyphenol. The solution was reacted at 55°C for 24 h. Then, the reaction mixture was poured into water, precipitated, filtered, and washed with water. The obtained solid was purified by recrystallization from ethanol. Yield: 90%; mp: 141–143°C.

IR (cm<sup>-1</sup>): 3040, 3008 (=CH), 2935, 2857 (CH<sub>2</sub>), 2650, 2562 (OH in COOH), 1721, 1686 (C=O), 1635 (C=C), 1607, 1512 (Ar).

### (+)-4'-(2-methyl)butoxy-4-hydroxy biphenyl (4)

4,4'-Biphenol (0.1 mol) was dissolved in a mixture of 50 mL of ethanol and 8 g of sodium hydroxide in 10 mL of water, and a catalytic amount of KI was added. Then, 15 g of (+)-1-bromo-2-methylbutane (3) was added dropwise to the mixture under stirring. After refluxing for 1 h, the reaction mixture was poured into water, precipitated, filtered, and washed with water. The crude product was purified by recrystallization from ethanol and white crystals were obtained. Yield: 52%; mp: 137–139°C;  $[\alpha]_D^{15} = +10.2^\circ$ .



Scheme 2 Synthesis routes of the elastomers.

IR ( $\text{cm}^{-1}$ ): 3441 (OH), 2963, 2878 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 1608, 1510 (Ar), 1248 (COC).

**(+)-4-[4-(2-acryloyloxy)ethoxybenzoyloxy]-4'-(2-methyl)butoxy biphenyl (M1)**

4-(2-Acryloyloxy)ethoxybenzoic acid (**2**, 0.05 mol) was reacted at room temperature, with thionyl chloride (40 mL) containing a few drops of *N,N*-dimethylformamide, for 4 h. Excess thionyl chloride was removed under reduced pressure to give the acid chloride. The acid chloride was added to a cold solution of (+)-4'-(2-methyl)butoxy-4-hydroxy biphenyl (**4**, 0.05 mol) and pyridine (2 mL) in THF (50 mL). The mixture was stirred at 50°C for 8 h and precipitated in water. After being filtered and washed several times with ethanol, the crude product was recrystallized with ethanol and **M1** was obtained. Yield: 65 %; mp: 85°C;  $[\alpha]_D^{15} = +5.8^\circ$ .

IR ( $\text{cm}^{-1}$ ): 3045, 3012 ( $=\text{CH}$ ), 2932, 2868 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 1742, 1720 ( $\text{C}=\text{O}$ ), 1645 ( $\text{C}=\text{C}$ ), 1608, 1511 (Ar).

**Polymer synthesis**

The crosslinked polymers' synthesis is illustrated in Scheme 2, and the polymerization experiments are summarized in Table I. The crosslinked liquid crystalline polymers P-2–P-5, containing the mesogenic monomer (+)-4-[4-(2-acryloyloxy)ethoxybenzoyloxy]-4'-(2-methyl)butoxy biphenyl (**M1**) and the crosslinking monomer 1,1,1-trihydroxymethyl propyl triacrylate (**M2**) with different mol ratios in the side chain of the polymethylhydrosiloxane (PMHS) backbone were synthesized by graft copolymerization. The trivinyl monomer **M2**, which acted as a crosslinker, reacted with Si–H of PMHS to form a network structure, while the mesogenic monomer **M1** gave the crosslinked polymers liquid crystalline properties in the presence of the catalyst hydrogenhexchloroplatinate hydrate, using dry toluene as a solvent. The reaction mixture was stirred at 60–70°C until the IR spectra showed that the Si–H absorption peak of PMHS at 2160  $\text{cm}^{-1}$  disappeared. Uncrosslinked polymers P-1, P-6, and P-7, which are the corresponding

**TABLE I**  
Polymerization and the Thermal Analysis Results of the Polymers

Polymer	Feed		DSC		
	PMHS/M1/M2 (mmol)	M2 <sup>a</sup> (mol %)	$T_g$ (°C)	$T_i$ (°C)	$\Delta T^b$ (°C)
P-1	1.00/7.00/0.00	0.00	62.7	140.5	77.8
P-2	1.00/6.40/0.20	3.03	63.4	138.6	75.2
P-3	1.00/5.80/0.40	6.45	63.7	128.3	65.2
P-4	1.00/5.20/0.60	10.34	62.3	124.9	62.6
P-5	1.00/4.60/0.80	14.81	63.8	— <sup>c</sup>	—
P-6	1.00/5.80/0.00	0.00	65.4	132.6	67.2
P-7	1.00/4.60/0.00	0.00	64.5	129.6	65.1

<sup>a</sup> Mol percent of **M2** based on **M1** + **M2**.

<sup>b</sup> Mesomorphic temperature range ( $T_i - T_g$ ).

<sup>c</sup> No transition peak existing in DSC curve.



**Figure 1** Polarized optical micrograph of **M1** at 82°C.

polymers to P-3 and P-5, were synthesized in a similar way with the same feed of **M1** and no **M2**, and the reaction took the same time as that of the crosslinked polymers.

IR ( $\text{cm}^{-1}$ ), P-1–P-5: 2932, 2868 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 1740, 1722 ( $\text{C}=\text{O}$ ), 1608, 1511 (Ar), 1150–1020 ( $\text{Si}-\text{O}-\text{Si}$ ). P-6 and P-7: 2932, 2868 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 2160 ( $\text{SiH}$ ), 1740, 1722 ( $\text{C}=\text{O}$ ), 1608, 1511 (Ar), 1150–1020 ( $\text{Si}-\text{O}-\text{Si}$ ). P-1:  $[\alpha]_D^{15} = +3.7^\circ$ , P-6:  $[\alpha]_D^{15} = +3.2^\circ$ , P-7:  $[\alpha]_D^{15} = +2.8^\circ$ , while for the crosslinked polymers P-2–P-5, the dry samples were swollen in solvent, so no specific rotatory power was gained.

## RESULTS AND DISCUSSION

### Liquid crystalline behavior of monomer **M1**

The liquid crystalline property of monomer **M1** was characterized with differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The mesomorphic temperature ranges of **M1** were from 85.3°C ( $T_m$ ) to 135.6°C ( $T_i$ ) during the heating cycle and from 130.3 ( $T_c$ ) to 81.8°C ( $T_k$ ) during the cooling cycle. **M1** exhibited an oily streak texture when heated over  $T_m$ , and the texture did not change until  $T_i$ . When **M1** was cooled from the isotropic phase, a focal conic texture was observed at first and it turned to a fingerprint texture (shown in Fig. 1) at temperatures slightly above the  $T_k$ ; then, **M1** began to crystallize, indicating that the monomer **M1** was an enantiotropic cholesteric liquid crystal.

### Liquid crystalline behavior of polymers

#### Thermal analysis

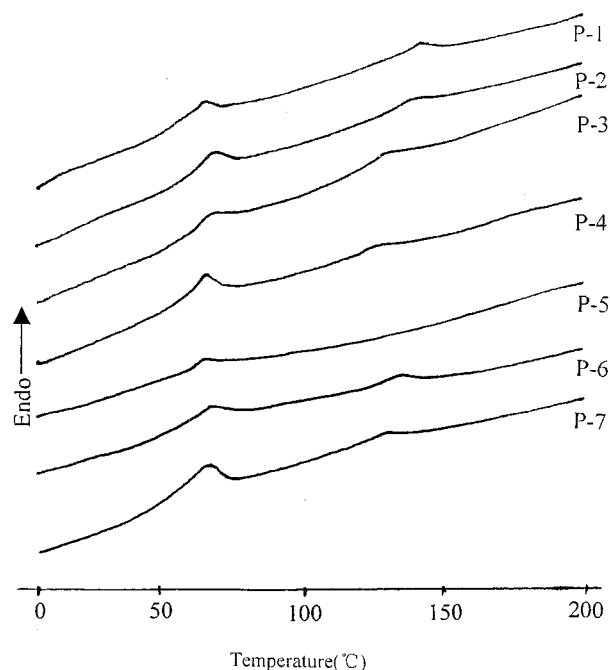
The thermal behavior of all polymers synthesized is summarized in Table I. The DSC thermograms are given in Figure 2.

Generally, crosslinking imposes additional constraints on the segmental motion of polymer chains, and the increase of the glass transition temperatures ( $T_g$ ) may be expected. However, the effect is small for lightly crosslinked polymers. Also, opposing this effect is the influence of the flexible crosslinking units as a plasticizer<sup>18</sup>; therefore, the  $T_g$  of the crosslinked polymers P-3 and P-5 were lower, compared with the corresponding uncrosslinked polymers P-6 and P-7, while for crosslinked polymers P-2–P-5, the crosslinking units **M2** acted as two controversial roles simultaneously: Crosslinking made the  $T_g$  increase and plasticization of **M2** caused the  $T_g$  to decrease, so their  $T_g$ 's remained almost the same.

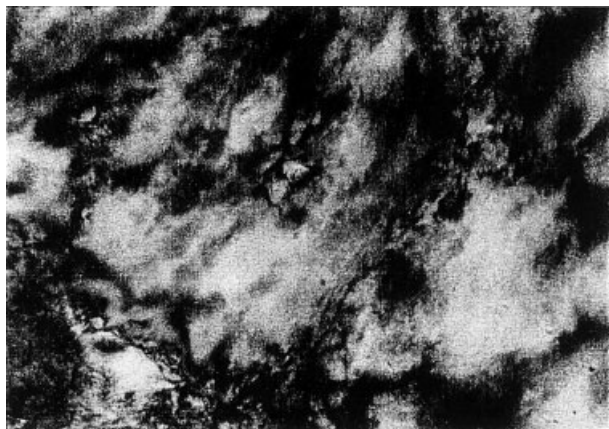
Table I shows that clearing point ( $T_i$ ) of the uncrosslinked LCs P-1, P-6, and P-7 was reduced along with a decrease of the mesogenic monomer **M1**, which resulted in the narrowing of the mesophase ranges. This is easy to understand because the contents of mesogenic units in those polymers were reduced.

In addition, with the increase of **M2**, namely, the decrease of the mesogenic monomer **M1**, the  $T_i$  of the crosslinked LCs also tended to decrease. Meanwhile, their  $T_i$  were lower compared with those of the corresponding uncrosslinked polymers, so their mesophase ranges ( $\Delta T = T_i - T_g$ ) were narrower than those of the uncrosslinked polymers. The reason is that crosslinking units may act as a nonmesogenic diluent and destabilize the liquid crystalline phase, just as impurities lead to freezing point depression in liquids.

The DSC curve of P-5, whose mol percent of **M1** was about 85 mol %, suggested no liquid crystalline-to-



**Figure 2** DSC thermograms (second heating) of polymers P-1–P-7.



**Figure 3** Polarized optical micrograph of P-3 at 94°C (200×).

isotropic transition, that is, crosslinked polymers with more than 15 mol % of **M2** did not show thermotropic liquid crystalline properties. In contrast, the uncrosslinked polymer P-7, whose content of **M1** was as much as that of the crosslinked polymer P-5, still had a thermotropic liquid crystalline property with a broad mesomorphic temperature range about 65°C, which was proved by DSC and POM. It was attributed to the formation of a network structure in the nonmesogenic state, as well as the dilution of the nonmesogenic crosslinking units. Since crosslinking obtained in the nonmesogenic state tends to maintain the polymer backbones at the isotropic state, less energy was required to distort the orientating mesogenic units from the anisotropic state to the isotropic state with an increase of the crosslinking densities. So, low levels of crosslinking did not obviously affect the phase behavior of the crosslinked polymers; in contrast, high levels of crosslinking may have a more drastic influence and liquid crystalline phases may disappear.

#### Texture analysis

The textures of polymers P-1–P-7 were observed with polarizing optical micrographs, while P-1–P-4, P-6, and P-7 exhibited thermotropic liquid crystalline properties during heating and cooling cycles. The temperatures of the transition obtained from POM were confirmed with the thermal data gained from the DSC.

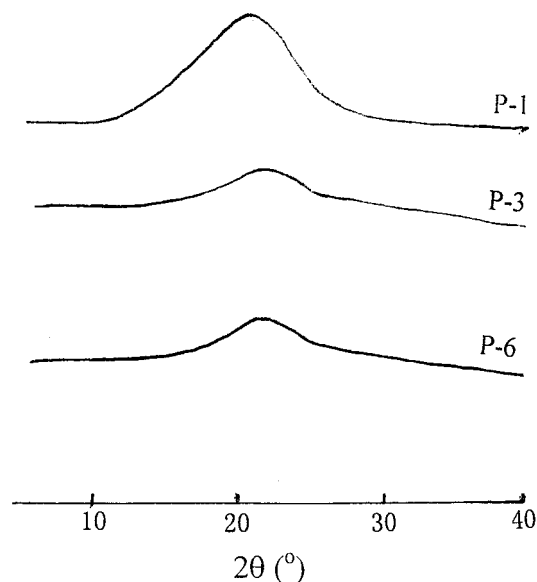
The crosslinked polymers P-2–P-4 displayed a cholesteric Grand-jean texture just like that of the uncrosslinked polymers P-1, P-6, and P-7. A photomicrograph of P-3 is shown in Figure 3 as an example, which indicated that the introduction of a nonmesogenic crosslinking monomer **M2** to the LCPs' structure did not remarkably affect their texture. As suggested by the DSC curve, P-5 showed only elasticity, and no mesomorphic property was observed on repeated heating and cooling cycles.

#### X-ray diffraction analysis

X-ray diffraction studies were carried out to obtain more detailed information on the liquid crystalline phase structure. Figure 4 reveals representative X-ray diffraction curves of P-1, P-3, and P-6. A sharp peak associated with the smectic layers did not appear at the lower Bragg angle region, and a broad amorphous diffuse peak at about 20° occurred in the wide-angle X-ray diffraction curves for all the three quenched samples. Therefore, the cholesteric phase structure of the crosslinked LCPs P-2–P-4 and the uncrosslinked liquid crystalline polymers P-1, P-6, and P-7 was confirmed by X-ray diffraction, which coincides with the DSC and POM results described. It also indicated that the formation of a network structure in the polymers did not change their mesogenic types.

#### CONCLUSIONS

In this work, a series of cholesteric crosslinked LCPs and cholesteric uncrosslinked LCPs were prepared by graft copolymerization. Their liquid crystalline properties showed that the crosslinking obtained in the isotropic state and the introduction of nonmesogenic crosslinking units into the polymeric structure could cause an additional reduction of the clearing point of the crosslinked polymers, compared with the corresponding uncrosslinked polymers. Light crosslinking did not remarkably affect the phase behavior of the LCPs or change their mesogenic types, so crosslinked polymers P-2–P-4 exhibited cholesteric phases just as did the uncrosslinked polymers. In contrast, a high crosslinking density made the crosslinked polymer P-5 lose its thermotropic liquid crystalline phase.



**Figure 4** X-ray diffractograms of quenched samples P-1, P-3, and P-6.

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