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Synthesis and properties of polysiloxane side chain cholesteric elastomers

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The synthesis of new side chain cholesteric liquid crystalline elastomers containing the flexible non-mesomorphic crosslinking agent M-1 and the cholesteric monomer M-2 by a one-step hydrosilylation reaction is described. The chemical structures of the obtained monomers and network polymers were confirmed by ^{1}H NMR and FTIR spectroscopy. The mesomorphic properties and phase behavior were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The glass transition temperatures and isotropic temperatures of the mesomorphic elastomers decreased as the concentration of crosslinking units increased; in the mesomorphic region the liquid crystalline elastomers showed elasticity, reversible phase transitions and Grandjean texture. The flexible crosslinking agent did not disturb the cholesteric structure; moreover, it was beneficial for adjusting the helix of the cholesteric liquid crystalline polymers, and cholesteric elastomers P-6, P-7, show reversible selective reflection of visible light.

1. Introduction

Liquid crystalline polymers may be lightly crosslinked to form elastomers, known as liquid crystalline elastomers (LCEs). LCEs exhibit both rubber-like elasticity and anisotropic liquid crystalline behaviour between the glass temperature and liquid crystalline to isotropic phase transition. Since their first synthesis in 1981 [1], LCEs have received much interest during recent years. The side chain LCE backbone has been based on polysiloxane [1–11], polyacrylate and polymethacrylate [12–20]; in addition, LCEs have been extended to slightly crosslinked main chain polymers and combined polymers [20–24]. Nematic, cholesteric, smectic A, C and C* phases have been identified in the crosslinked polymers.

As for cholesteric network polymers, in the last decade cholesteric liquid crystalline thermosets (ChLCTs, highly crosslinked) have been extensively investigated because the helical structure of the cholesteric phase is permanently fixed and optical properties become temperature independent [25–30]. ChLCTs are capable of forming a stable Grandjean texture with selective reflection of visible light. They are prepared by photocrosslinking of cholesteric liquid crystalline polymers [25–29], and can also be obtained by the thermal or chemical crosslinking of cholesteric mixtures containing bifunctional nematic and chiral monomers (polyacrylates [25], polymethacrylates [26], polyexpoxides [30, 31], and polyvinylethers [32]).

In contrast to ChLCTs, cholesteric liquid crystalline elastomers (ChLCEs) combine the basic features of elastomers with the properties of cholesteric liquid crystals. Therefore, ChLCEs not only reveal entropic elasticity, but also show reversible phase transitions during heating and cooling cycles. Moreover, compared with nematic elastomers, networks containing chiral side groups have been shown to exhibit piezoelectric and non-linear optical activity in the cholesteric and smectic C* phases, because of their helicoidal superstructure [33]; a completely new type of piezoelectric or optical element may thus be available. Therefore, it is both necessary and useful to synthesize various kinds of side chain ChLCEs to explore their potential application.

In this paper, we describe the one-step synthesis of side chain ChLCEs containing flexible ethanediol diundecylenate (M-1) as crosslinking units and cholesteryl 4-allyloxybenzoate (M-2) as mesomorphic units. The cholesteric monomer and crosslinking agent were simultaneously attached to the polysiloxane through a hydrosilylation reaction. Three aspects of the use of a flexible crosslinking agent were considered: (1) the development of networks; (2) while the T_g of cholesteric polymers is high, a flexible crosslinking agent and siloxane can reduce T_g; (3) it is beneficial to adjust the

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helix of cholesteric liquid crystalline polymers, and cholesteric elastomers may show reversible selective reflection of visible light. The mesomorphic properties and phase behaviour of the mesomorphic monomer and elastomers were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The effect of the concentration of crosslinking units on phase behaviour, cholesteric order and the helix is discussed.

2. Experimental

2.1. *Materials*

Polymethylhydrosiloxane (PMHS, $n=7$) was purchased from the Jilin Chemical Industry Company (China); 1-bromopropene and undecylenic acid were purchased from Beijing Jinlong Chemical Reagent Co., Ltd (China). Cholesterol was purchased from Henan Xiayi Medical Co. (China), 4-hydroxybenzoic acid and ethanediol were purchased from Beijing Fuxing Chemical Industry Co. (China). Toluene used in the hydrosilylation reaction was first heated at reflux over sodium and then distilled. All other solvents and reagents were purified by standard methods.

2.2. *Characterization*

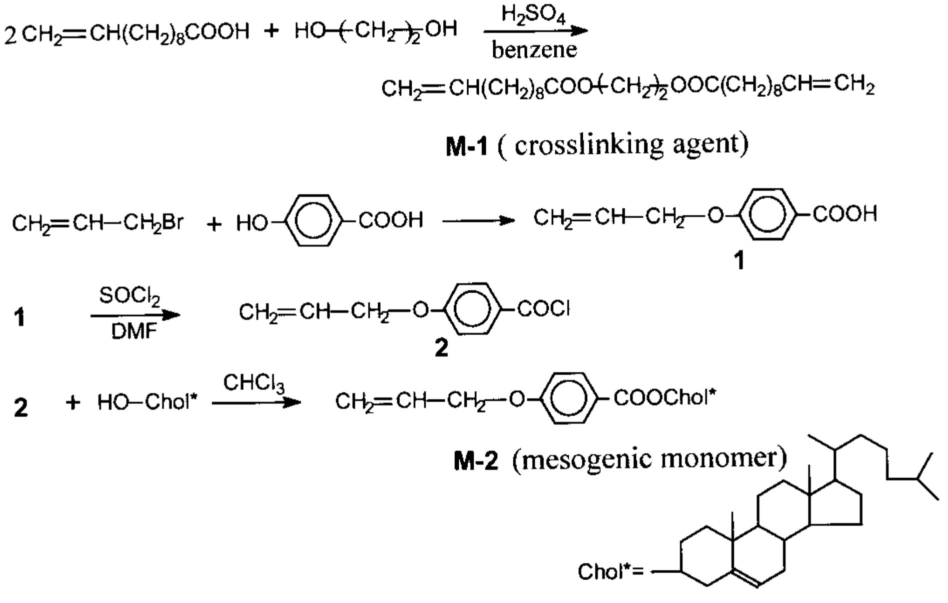
Fourier transform infrared (FTIR) spectra of the synthesized polymers and monomers in the solid state were obtained on a Nicolet 510 FTIR spectrometer via KBr discs. ^{1}H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer. Phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 at a heating rate of 20°C min^{-1} under nitrogen. A Leitz Microphot-FX polarizing optical microscope equipped with a Mettler FP 82 hot stage was used to observe mesophase textures and phase transition temperatures. XRD was performed using a nickel-filtered Cu-K$_\alpha$ ($\lambda = 1.542$ Å) radiation with a Rigaku powder diffractometer.

2.3. *Synthesis*

2.3.1. *Synthesis of the monomers*

The synthesis of flexible crosslinking agent M-1 and mesomorphic monomer M-2 was carried out as shown in scheme 1.

The flexible crosslinking agent ethanediol diundecylenate (M-1) was synthesized by an esterification reaction. Undecylenic acid and ethanediol were dissolved in benzene and then heated under reflux for 8 h with a catalyst of concentrated sulfuric acid. The mixture was neutralized with $NaHCO_3$ solution and washed several times with distilled water. After removing the solvent, the product M-1 was distilled at 172°C under 4 mm Hg pressure. A transparent liquid was obtained, yield 82%. IR (KBr, ν/cm^{-1}): 3076 (=C–H); 2928, 2854 (–CH$_2$–); 1742 (–COOC–); 1640 (C=C); 1237, 1163 (C–O). ^{1}H NMR (CD-Cl$_3$, δ ppm): 1.27–1.62 (m, 24H, $2CH_2{=}CHCH_2\ (C\underline{H_2})_6CH_2COO$–); 2.01–2.03 (m, 4H, $2CH_2{=}CHC\underline{H_2}(CH_2)_6CH_2COO$–); 2.25–2.30 (m, 4H, $2CH_2{=}CHCH_2(CH_2)_6C\underline{H_2}COO$–); 4.02–4.07 (t, 4H, $-OCH_2C\underline{H_2}O$–); 4.93–5.00 (m, 4H, $2C\underline{H_2}{=}CHCH_2(CH_2)_6CH_2COO$–); 5.76–5.87 (m, 2H, $CH_2{=}C\underline{H}(CH_2)_7CH_2COO$–).



Scheme 1. Synthetic routes for the monomers.

Cholesteric monomer M-2 was synthesized in a similar maner [34]: 19.3 g (0.05 mol) cholesterol was dissolved in 80 ml of chloroform, and then 9.8 g (0.05 mol) of 4-allyloxybenzoyl chloride was slowly dropped into the mixture. After reacting at room temperature for 2 h, the mixture was heated at reflux for 4 h; it was then precipitated with ethanol and filtered. The crude product was purified by recrystallization from ethanol; white crystals were obtained, yield 90%, m.p. 107°C. IR (KBr, ν/cm^{-1}): 3086 (=C–H); 2931, 2884, 2867 (–CH$_2$–); 1706 (–COO–); 1641 (C=C); 1608, 1579, 1511 (Ar); 1278, 1258 (C–O). ^{1}H NMR (CDCl$_3$, δ ppm): 0.68–2.45, 3.56, 5.45 (m, 45H, H of cholesteryl group); 4.57–4.60 (m, 2H, $CH_2=CHC\underline{H}_2O$–); 5.29–5.39 (m, 2H, $C\underline{H}_2=CHCH_2O$–); 6.04–6.11 (m, 1H, $CH_2=C\underline{H}CH_2O$–); 6.90–8.00 (m, 4H, Ar–H).

2.3.2. *Synthesis of the elastomers*

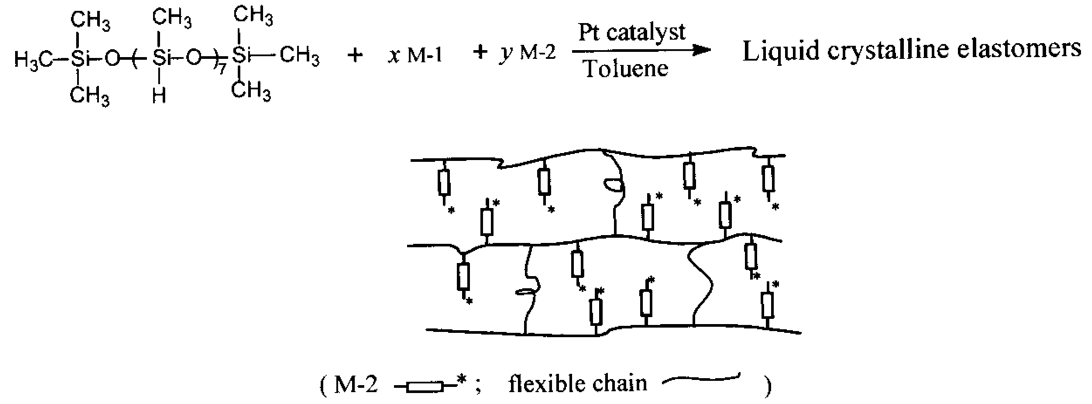
The ChLCEs were prepared by a one-step reaction, in which the di-functional crosslinking agent M-1 and cholesteric monomer M-2 were simultaneously attached to the main chain of the flexible polysiloxane. The synthesis of the elastomers was performed according to scheme 2, with results shown in table 1. The same method was adopted for the synthesis of mesomorphic elastomers P-1–P-8; the synthesis of polymer P-2 is given as an example.

Monomers M-1, M-2, and PMHS were dissolved in dry toluene. The reaction mixture was heated to 65°C under nitrogen, and then 2 ml of 0.5% H_2PtCl_6/THF catalyst solution was injected. The reaction was held at 65°C under nitrogen until the Si–H absorption peak of PMHS at 2160 cm^{-1} disappeared. The elastomers were carefully deswollen with methanol, and then dried under vacuum. IR (KBr, ν/cm^{-1}): 2932, 2867 (–CH$_2$–, –CH$_3$); 1743 (–COOC– of M-1), 1712 (–COOChol of M-2); 1607, 1579, 1510 (Ar); 1273, 1254 (C–O); 1102, 1011 (Si–O–Si).

3. Results and discussion

3.1. *FTIR analysis*

The structures of crosslinking agent M-1 and cholesteric monomer M-2 were characterized by ^{1}H NMR and FTIR. As the proportion of crosslinking agent M-1 increased from P-1 to P-8, changes in absorption peaks of the mesomorphic elastomers were seen in the FTIR spectrum. FTIR thus provides an effective method for following the synthesis of the elastomers. The FTIR spectra of crosslinking agent M-1, mesomorphic monomer M-2 and some elastomers



Scheme 2. Synthetic routes for the liquid crystalline elastomers.

Table 1. Polymer compositions and yields.

	Feed				
Polymer	PMHS/mmol	M-1/mmol	M-2/mmol	M-1[a]/mol%	Yield/%
P-1	1	0.00	7.00	0.00	90
P-2	1	0.125	6.75	1.80	85
P-3	1	0.25	6.50	3.60	82
P-4	1	0.375	6.25	5.40	80
P-5	1	0.50	6.00	7.20	87
P-6	1	0.75	5.50	10.8	87
P-7	1	1.00	5.00	14.4	91
P-8	1	1.50	4.00	21.6	88

[a] Molar fraction of monomer M-1 based on M-1 + M-2.

are presented in figure 1. The mesomorphic elastomers show characteristic absorptions corresponding to (1) the ester group absorption of M-2 at 1712 cm^{-1}, (2) the ester group of M-1 at 1743 cm^{-1}, (3) benzene ring stretching at 1607, 1579 and 1511 cm^{-1}, and (4) the Si–O–Si group at 1102 and 1011 cm^{-1}. Moreover, from the disappearance of vinyl group C–H stretching peaks at 3076 cm^{-1} (a), vinyl C=C stretching at about 1640 cm^{-1} (b) of the monomers, and Si–H stretching at 2160 cm^{-1} (c), as well as the appearance and enhancement of the ester group at 1743 cm^{-1} (d), and methylene scissors bending vibration at 1459 cm^{-1} (e), we can conclude that successful incorporation of monomers into the polysiloxane was achieved.

3.2. *Mesophase behaviour*

The mesophase properties of M-2 and elastomers P-1–P-8 were determined by DSC and POM. M-2 showed two endothermic peaks during heating, corresponding to the crystal-to-melting transition at 107.1°C and the mesophase-to-isotropic phase transition at 225.3°C. DSC thermograms of liquid crystalline elastomers P-1–P-8 are shown in figure 2. Thermal behaviour determined by DSC was consistent with POM observations; the results for the synthesized polymers are summarized in table 2. The homopolymer P-1 and mesomorphic elastomers P-2–P-8 exhibit DSC curves of similar shape, chemical crosslinking with the flexible crosslinking agent leads only to a downshift of the phase transition temperature. Figure 3 shows the effect of the concentration of crosslinking units on the phase behaviour of elastomers.

For side chain LCEs, the glass transition temperature (T_g) is influenced by the nature of the polymer backbone, mesomorphic group, flexible spacer length and crosslinking density. For the homopolymer P-1 with a rigid mesomorphic unit in the side chain, the flexible

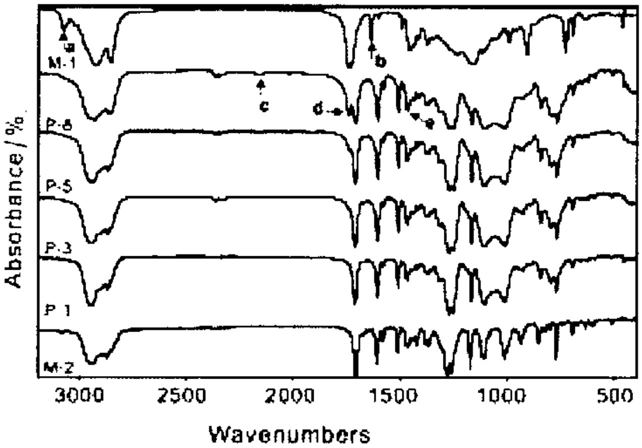


Figure 1. FTIR spectra of monomers and elastomers.

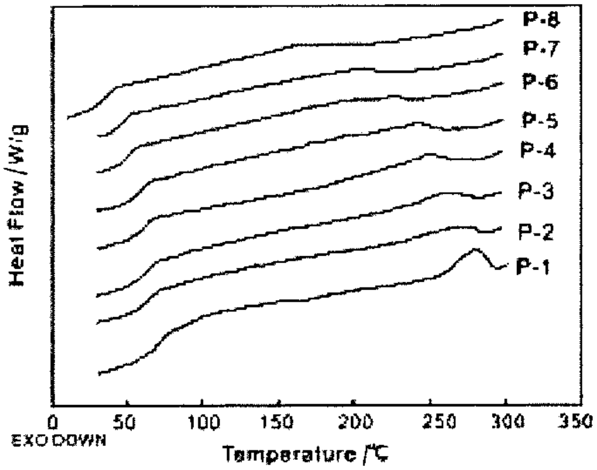


Figure 2. DSC thermograms of the liquid crystalline elastomers.

Table 2. DSC and POM results for the mesomorphic elastomers.

Elastomer	DSC T_g/°C	DSC T_i/°C	DSC ΔH_i^a/J g^{-1}	ΔT^b/°C	Selective reflection
P-1	71.4	275.3	4.86	203.9	no
P-2	64.3	272.7	3.14	208.4	no
P-3	61.8	264.8	2.95	203.0	no
P-4	60.2	250.0	2.27	189.8	no
P-5	57.4	243.2	1.56	185.8	no
P-6	49.4	227.5	1.06	178.1	yes
P-7	45.6	205.8	0.98	160.2	yes
P-8	34.4	163.7	0.34	129.3	no

[a] Enthalpy changes of isotropic transition.
[b] Mesogenic temperature range ($T_i - T_g$).

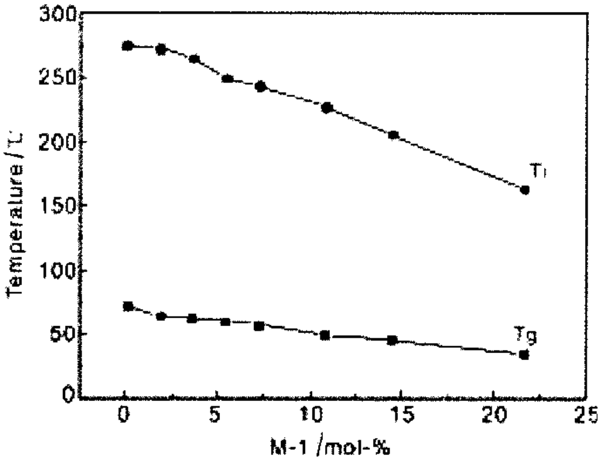


Figure 3. Effect of M-1 concentration on phase transition temperatures of liquid crystalline elastomers.

crosslinking chain is similar to the plasticizer, and this will lead to a decrease in T_g. So, the T_g of the mesomorphic elastomers decreases from 71.4°C for P-1 to 34.4°C for P-8, as the crosslinking agent increases. Chemical crosslinking with a non-mesomorphic crosslinking agent may act as diluent, downward shifting T_i with increasing proportions of the non-mesomorphic crosslinking agent added to a liquid crystalline polymer. As the proportion of crosslinking M-1 units increases from 0 to 21 mol%, T_i of the mesomorphic elastomers decreases from 275.3°C to 163.7°C, and the enthalpy changes of isotropic transition (ΔH_i) decrease from 4.86 to 0.34 J g^{-1}.

The liquid crystalline behaviour of the mesomorphic polymers occurs over a restricted temperature range, between the isotropic transition temperature (T_i) and the glass transition temperature (T_g); the mesomorphic range (ΔT) was determined as $T_i - T_g$. Because the T_g of P-2 decreased more than its T_i, ΔT of P-2 widened, as compared with homopolymer P-1. However, ΔT of liquid crystalline elastomers P-2–P-8 decrease markedly (see figure 3) indicating the diluent effect of the non-mesomorphic crosslinking agent. In the liquid crystal range P-2–P-8 exhibit both elasticity (due to the crosslinked polymer backbones) and reversible liquid crystalline behaviour.

3.3. *Optical properties*

The liquid crystalline texture of monomer M-2 and the liquid crystalline elastomers was observed by POM with a hot stage, under nitrogen. The cholesteric monomer M-2 revealed an oily-streak texture during heating. On cooling the focal-conic texture was formed, which easily transformed to an oily-streak texture by shearing the mesomorphic phase. By POM observation, the flexible crosslinking agent M-1 did not change mesomorphic type, and LCPs P-1–P-8 displayed similar Grandjean textures on heating or cooling.

Because of the helical superstructure of the cholesteric phase, cholesteric mesophases may show interesting optical properties, such as selective reflection and an angular dependence of the reflected wavelength. If selective reflection takes place at a visible wavelength, the cholesteric phase appears coloured. The wavelength of selective reflection of light obeys the Bragg condition. When M-2 is heated into the liquid crystalline phase, it appears red in color in the vertical direction and green in the oblique direction; on further heating to about 190°C, red in the vertical direction changes into green and blue in the oblique direction; the selective reflection disappears at the isotropic temperature.

As can be seen in table 2, the rigidity of the mesomorphic unit and the flexible crosslinking agent strongly influences the pitch and selective reflection. Only polymers P-6 and P-7 show the property of selective reflection. The selective reflection of P-6 and P-7 was similar to that of monomer M-2: red–green selective reflection at different angles is seen at about 160°C, green–blue appears at about 180°C, disappearing at the isotropic temperature. Thus an appreciable proportion of the flexible part is beneficial for the adjustment of the cholesteric phase pitch, leading to selective reflection in the visible light region.

3.4. *X-ray diffraction*

X-ray diffraction studies are carried out to obtain more detailed information on the mesophase structure of liquid crystalline materials. In general, a smectic mesophase will display peaks in small angle ($1° < 2\theta < 3°$) and wide angle ($15° < 2\theta < 21°$) regions, which reveals the long-range and short-range order, respectively, of smectic materials. Nematic and cholesteric mesophases show only an amorphous broad peak in the wide angle region, at about 20° for the nematic phase, and 17° for the cholesteric phase.

For mesomorphic polymers P-1–P-8, no sharp peaks associated with a smectic structure appeared in the small angle region; and only a broad amorphous peak at 17.5° occurred in the wide angle region, revealing short-range order or lateral packing for the cholesteric structure of homopolymer P-1 and elastomers P-2–P-8. Figure 4 shows representative X-ray diffraction curves of the mesomorphic polymers in the wide angle region. The peak intensity for the polymers is almost the same, increasing with the concentration of crosslinking agent M-1 in the networks, which suggests that the flexible

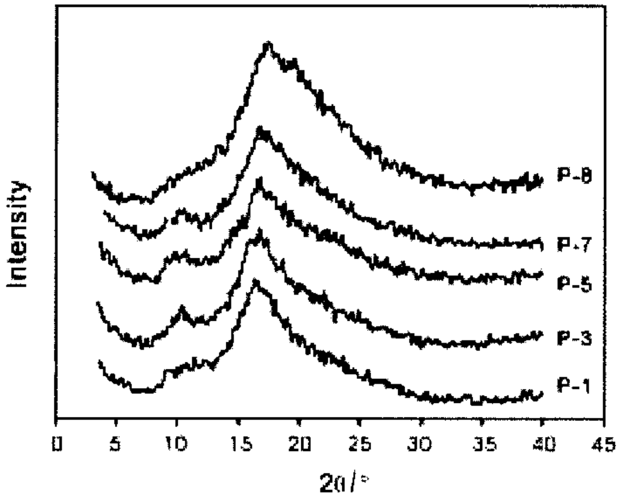


Figure 4. Wide-angle X-ray diffraction patterns of mesomorphic elastomers.

crosslinking agent does not disturb the liquid crystalline order for polymers P-2–P-8.

4. Conclusion

In this study, we synthesized a series of side chain liquid crystalline elastomers containing ethanediol diundecylenate (M-1) and cholesteryl 4-allyloxybenzoate (M-2). With the crosslinking density increasing from P-1 to P-8, T_g and T_i decrease because of the incorporation of flexible crosslinking agent. In the mesomorphic range, the network polymers revealed elasticity and reversible phase transitions during heating and cooling, and exhibited a cholesteric Grandjean texture. X-ray analysis showed that the use of a flexible crosslinking agent did not disturb the structure of the cholesteric mesophase. Moreover, the flexible crosslinking agent aids the adjustment of pitch of the cholesteric liquid crystal, and P-6, P-7 exhibit reversible selective reflection.

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