

## 지능형 작동기용 실리콘 Cholesteric 액정 고분자

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## Silicone-based Cholesteric Liquid Crystalline Polymers as Smart Actuators

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### 1. Introduction

There is an increasing interest in the development of artificial muscle-type actuators, which are ideal for prototype biomimetic movements as they change their shapes and dimensions according to the applied environments. Polymer actuators play an important role in this field because they provide the advantages such as flexibility, light weight and easy processing. Many polymeric gels[1], conjugated polymers[2], carbon nanotubes, and dielectric elastomers[3] show this type of actuation under various chemical and physical stimuli such as pH, solvent, temperature, electric field, magnetic field, and light. Recently, there is a growing interest on liquid-crystalline elastomers(LCEs) as a result of their unique combination of the anisotropic features coming from liquid crystal(LC) phases and the rubber elasticity coming from polymer networks. Thus poly(methylhydro siloxane)(PMHS)-based partially crosslinked cholesteric liquid crystalline elastomers (ChLCEs) are the most important soft actuation materials because of their unique optical properties characteristics of their cholesteric liquid crystal phase in combination with their good mechanical and thermal properties coming from their network structure[4].

In this paper, a mesomorphic crosslinking agent, M-1 and a cholesteric monomer, M-2 were synthesized to make smart actuator materials. The mesomorphic properties and phase behavior of ChLCEs obtained were characterized by DSC, polarized optical microscopy, and x-ray diffraction measurements, and thermally stimulated actuation behavior was also reported.

### 2. Experimental

#### 2.1. Materials

Polymethyl hydrosiloxane(n=35); 10-undecenoic acid with mp 23-25°C, bp 137°C and density 0.912 g/mL; allyl bromide with mp -119°C, bp 70-71°C, density 1.398 g/mL; hexachloroplatinic acid (8 wt% in water) with density 1.05 g/mL and cholesterol were purchased.

#### 2.2. Synthesis of cross-linking agent (M-1)

Undecylenic acid 22.08 g(0.12 mol) and 5.9 g(0.05 mol) of 1,6-hexanediol were dissolved in 30 ml benzene, and then 1 mL concentrated sulfuric acid was added. After the mixture was mixed

uniformly, it was refluxed for 8 h, and the mixture was poured into 200 ml of water. After removing the water layer, the oil layer was neutralized with 2% NaHCO<sub>3</sub> to pH 7, washed several times with distilled water, and dried with Na<sub>2</sub>SO<sub>4</sub>.

### 2.3. Synthesis of Mesogenic monomer (M-2)

19.3 g(0.05mol) cholesterol was dissolved in 80 ml of chloroform, and then 6.0 g(0.05mol) allyl bromide was slowly dropped into the mixture. After the mixture reacted at room temperature for 2 h and was refluxed at 90°C for 4 h, it was separated with cool ethanol.

### 2.4. Synthesis of LCP

The monomers M-1, M-2, and PMHS were dissolved in dry toluene (Table 1). The reaction mixture was heated to 65°C under nitrogen, and then 2 ml of 0.5 % H<sub>2</sub>PtCl<sub>6</sub>/THF catalyst solution was injected. The reaction was kept at 65°C under nitrogen until the Si-H absorption peak of PMHS at 2160 cm<sup>-1</sup> disappeared.

Table 1. Composition of LCP samples used in this investigation

Sample Code	PMHS (mmol)	M-1 (mmol)	M-2 (mmol)	M-1 (mol%)	Yields (%)
LCP-1	1.00	0.25	5.75	4.16	86
LCP-2	1.00	0.50	5.50	8.33	90
LCP-3	1.00	0.75	5.25	12.50	92
LCP-4	1.00	1.25	4.75	20.83	87
LCP-5	1.00	1.50	4.50	25.00	86

## 3. Results and Discussion

### 3.1. FT-IR analysis

The FT-IR spectra of M-1 shows the characteristic absorbance peaks corresponding to C-H stretching of vinyl at 3035 cm<sup>-1</sup>, C=C of vinyl at 1475 cm<sup>-1</sup>, C-H of methylene at 2925 and 2850 cm<sup>-1</sup> and alkane ester group (-RCOOR-) at 1733 cm<sup>-1</sup> (Figure 1). The cholesteric monomer M-2 shows characteristic absorption peaks corresponding to C-H stretching of vinyl at 3014 cm<sup>-1</sup>, C-H of methylene at 2937 cm<sup>-1</sup>, C=C of vinyl at 1465 and 1376 cm<sup>-1</sup>. FT-IR spectra of network liquid crystalline polymers formed after 12 h reaction show the complete disappearance of the peaks for the Si-H stretching at 2160 cm<sup>-1</sup> and vinyl C=C stretching at about 1475 cm<sup>-1</sup> of the monomers. So we may conclude that the mesogenic monomer (M-2) has been successful reacted with the polysiloxane chain.

### 3.2. Thermo-responsive actuation behavior

The liquid crystal elastomers are found to have good thermo-responsive actuation behavior from their liquid crystalline order as well as from rubber elasticity, which was resulted from the lightly cross-linked structure by using of a mesomorphic crosslinking agent.

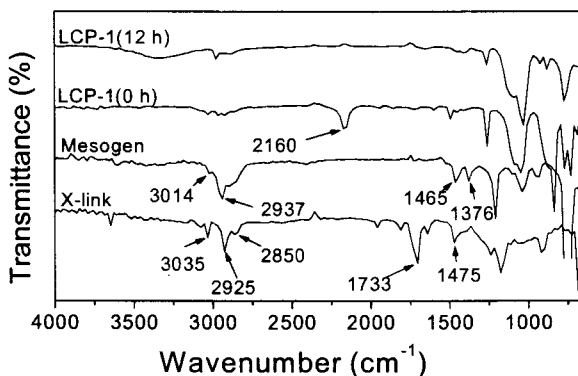


Figure 1. FT-IR spectra of M-1, M-2 and LCP-1.

### 3.3. DSC thermal analysis

LCP-1 - LCP-3 reveal a glass transition at low temperature and isotropic transition at high temperature (Figure 2). However, LCP-4 and LCP-5 show only glass transition.  $T_g$  of lightly crosslinked liquid crystal polymers is shifted to a lower value. For side-chain ChLCEs, the glass transition temperature ( $T_g$ ) is influenced by the polymer backbone, mesogenic group, flexible spacer length and crosslinking density. In general, chemical crosslinking imposes additional constraints on the motion of chain segments, and makes  $T_g$  increase. On the other hand, the flexible chain of the crosslinking agent similar to the plasticization will cause  $T_g$  decrease. So, with the increasing concentration of crosslinking agent from 4.16 to 25.00 mol%,  $T_g$  decreases from 39.7°C for LCP-1 to 34.5°C for LCP-5. As the density of crosslinking M-1 units increased from 4.16 to 12.50 mol%,  $T_i$  reduced from 212.1°C for LCP-1 to 207.6°C for LCP-3, and  $T_i$  of LCP-4 and LCP-5 disappeared for high crosslinking density. Thus in the liquid crystal range, LCP-1 - LCP-3 revealed elasticity and reversible phase transitions on heating and cooling cycles.

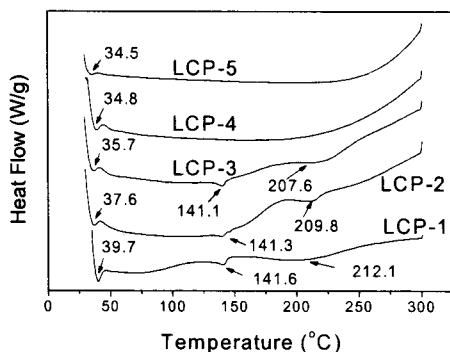


Figure 2. DSC thermograms of LCPs.

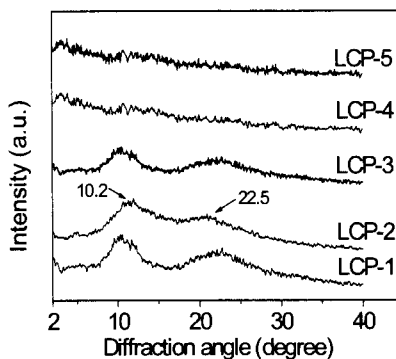


Figure 3. WAXS curves of LCPs.

### 3.4. X-ray diffraction and POM observation

The nematic and cholesteric liquid crystalline phases show broad peak in the wide angle region. Thus the two broad peaks associated with the lateral packing at wide angle appeared at about  $2\theta=10.2$  and  $22.5^\circ$  in wide angle X-ray diffraction region (Figure 3). Therefore, the cholesteric phase structure of LCP-1-LCP-3 was confirmed by X-ray diffraction. Figure 4(a) and 4(b) show POM photographs of ChLCE at  $30^\circ\text{C}$ . At  $209^\circ\text{C}$  it starts melting (Figure 4(c)) and at  $210^\circ\text{C}$  the melting is complete (Figure 4(d)).

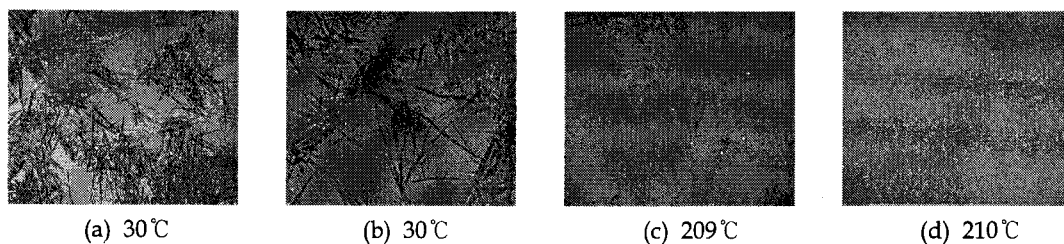


Figure 4. POM images of LCP-1 at different temperatures.

## 4. Conclusion

A series of side chain liquid crystalline network elastomers containing both mesomorphic crosslinking agent and a cholesteric monomer have been synthesized. Isotropic transition temperature decreases with increase in mesomorphic crosslinking agent. However, the flexible chains at both ends of M-1 still lead to decrease the  $T_g$  values. In the mesogenic range, the liquid crystalline elastomers LCP-1 - LCP-3, containing less than 12.50 mol% crosslinking agent, reveals elasticity and reversible phase transition on heating and cooling cycles. X-ray analysis shows that crosslinking agent affects the liquid crystalline order at high proportion of x-linking agent. The cholesteric phase structure of the synthesized polymers was confirmed by X-ray scattering, DSC and POM results.

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## References

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