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## Liquid Crystals

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# Mesomorphic properties of liquid crystalline polysiloxanes and elastomers based on a tri-vinyl crosslinker

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A series of crosslinked liquid crystalline polymers and the corresponding uncrosslinked liquid crystalline polymers were prepared by graft copolymerization; their liquid crystalline properties were characterized by DSC, POM and X-ray measurements. The results show that the crosslinking obtained in the isotropic state leads to a reduction of the clearing point ( $T_c$ ) of the crosslinked polymers, as compared with the corresponding uncrosslinked polymers. The crosslinked polymers with low crosslinking density ( $P_1$ – $P_7$ ) exhibit nematic mesogenic phases, as do the uncrosslinked polymers. In contrast, a high crosslinking density leads to the crosslinked polymers  $P_8$  and  $P_9$  losing their thermotropic liquid crystalline phases; they instead exhibit stress-induced orientation.

## 1. Introduction

In recent years, much attention has been paid to liquid crystalline network polymers (LCNPs), which are also called liquid crystalline elastomers (LCEs), because of their ‘rubber-like elasticity’; this is mainly due to their special optical, mechanical, piezoelectric and thermal stability properties. Since the first synthesis in 1981 [1], LCNPs based on polysiloxane, polyacrylate and epoxy, and also combined main chain/side chain polymers, have been realized [2–8]; most crosslinking monomers were bifunctional compounds.

In our previous study [9], a rigid bifunctional liquid crystalline monomer was used to prepare LCNPs; it acted not only as a mesogenic unit but also as crosslinker. In the present work, a flexible non-mesogenic trivinyl compound was used as crosslinking monomer to prepare a series of LCNPs. To study the influence of the crosslinking, the corresponding uncrosslinked liquid crystalline polymers were synthesized for comparison with the crosslinked products. The results show that, as long as the crosslinking density is not too high, the LC phase structure will not be disrupted, although the crosslinking narrows the mesophase ranges of the LCNPs.

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## 2. Experimental

### 2.1. Materials

Polymethylhydrosiloxane (PMHS) with  $M_n = 700$ – $800$  was purchased from Jilin Chemical Industry Company and used without further purification. 1,1,1-Trihydroxymethylpropyl triacrylate (M2), used as crosslinking monomer, was obtained from Liaoning Province Fengcheng Accessory Ingredient Factory, and was purified before used. 4-Allyloxybenzoyl-4'-(4-*n*-amylbenzoyl)-*p*-benzenediol bisate (M1), which is a nematic monomer with a broad mesomorphic phase from 107.6 to 223.7°C, was prepared in this laboratory; figure 1 shows a polarized optical micrograph of M1. All other solvents and reagents were purified before used.

### 2.2. Characterization

Thermal transitions were measured with a Perkin-Elmer DSC-7 instrument equipped with a PE 7300 data station at heating and cooling rates of 20°C min<sup>-1</sup> under a nitrogen atmosphere. The textures of the liquid crystalline phases were observed with a Leitz polarizing optical microscope (POM) equipped with a Mettler FP82 hot stage. X-ray diffraction analysis of the quenched samples was carried out with a Rigaku DMAX-3A X-ray diffractometer at room temperature, using  $CuK_{\alpha}$  radiation.

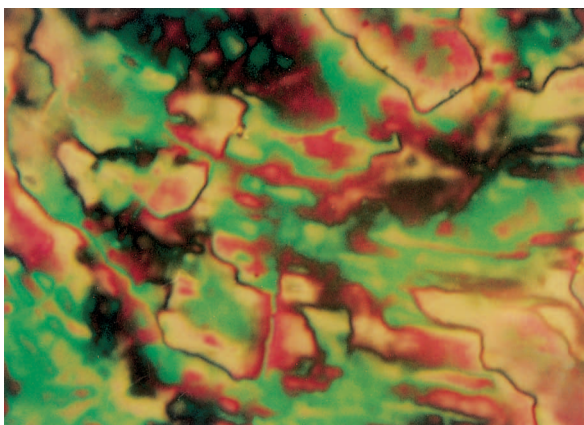
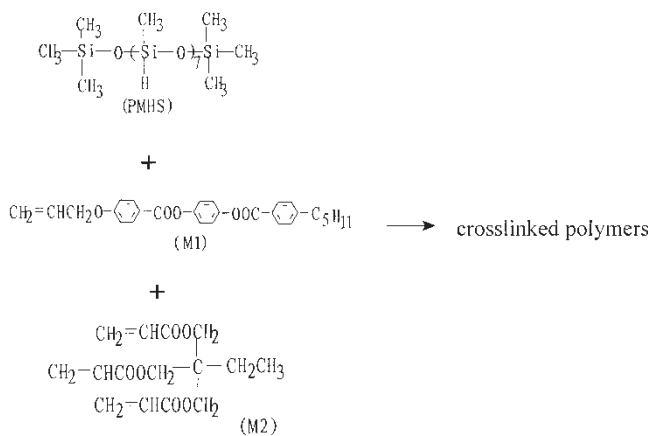


Figure 1. Polarizing optical micrograph of M1 at 217°C (200×).

### 2.3. Polymer synthesis

The crosslinked LC polymers were synthesized according to the description in the scheme; the polymerization experiments are summarized in the table.



Scheme. Synthesis of the polymers.

The crosslinked polymers P<sub>1</sub>–P<sub>9</sub> were prepared by graft copolymerization of the mesogenic monomer 4-allyloxybenzoyl-4-(4-*n*-amylbenzoyl)-*p*-benzenediol bisate (M1) and the trivinyl crosslinking monomer 1,1,1-trihydroxymethylpropyl triacrylate (M2) upon polymethylhydrosiloxane (PMHS) in different proportions, using dry toluene as solvent and hexachloroplatinic acid as catalyst. The reaction was carried out at 60–70°C until the IR spectrum showed disappearance of the Si–H absorption peak of PMHS at 2160 cm<sup>-1</sup>. The corresponding uncrosslinked polymers P<sub>0</sub> and P<sub>C2</sub>–P<sub>C9</sub> were synthesized in a similar way, with the same feed of M1 and no M2; the reaction took the same time as for the crosslinked polymers.

Table. Polymerization and thermal analysis results for the polymers.

Polymer	Feed		DSC		
	PMHS/M1/M2 mmol	M2 <sup>a</sup> mol%	T <sub>g</sub> <sup>c</sup> °C	T <sub>c</sub> <sup>b</sup> °C	T <sub>i-1</sub> <sup>c</sup> °C
P <sub>0</sub>	1.00/7.00/0.00	0.0	53.1	225.3	210.2
P <sub>1</sub>	1.00/6.70/0.10	1.5	50.1	207.7	199.7
P <sub>2</sub>	1.00/6.10/0.30	4.7	50.4	199.2	192.5
P <sub>3</sub>	1.00/5.50/0.50	8.3	50.4	194.6	188.9
P <sub>4</sub>	1.00/4.90/0.70	12.5	53.1	191.3	186.3
P <sub>5</sub>	1.00/4.30/0.90	17.3	53.4	179.7	172.4
P <sub>6</sub>	1.00/3.70/1.10	22.9	49.8	164.4	<sup>d</sup>
P <sub>7</sub>	1.00/3.10/1.30	29.6	48.3	143.7	<sup>d</sup>
P <sub>8</sub>	1.00/2.50/1.50	37.5	44.2	<sup>d</sup>	<sup>d</sup>
P <sub>9</sub>	1.00/1.90/1.70	47.2	47.1	<sup>d</sup>	<sup>d</sup>
P <sub>C2</sub>	1.00/6.10/0.00	0.0	52.8	203.5	194.7
P <sub>C4</sub>	1.00/4.90/0.00	0.0	52.2	193.7	191.9
P <sub>C6</sub>	1.00/3.70/0.00	0.0	52.2	176.8	166 <sup>e</sup>
P <sub>C7</sub>	1.00/3.10/0.00	0.0	51.6	153.2	158 <sup>e</sup>
P <sub>C9</sub>	1.00/1.90/0.00	0.0	47.9	124.8	130 <sup>e</sup>

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

<sup>b</sup>Clearing point temperature.

<sup>c</sup>The isotropic to liquid crystalline transition temperature during cooling.

<sup>d</sup>No transition peaks existing in DSC curves.

<sup>e</sup>Obtained by POM.

## 3. Results and discussion

### 3.1. Thermal analysis

The phase behaviour of the LC polymers P<sub>0</sub>–P<sub>9</sub> and P<sub>C2</sub>–P<sub>C9</sub> evaluated by DSC are summarized in the table. The representative DSC thermograms are shown in figures 2 and 3, respectively. Although the content

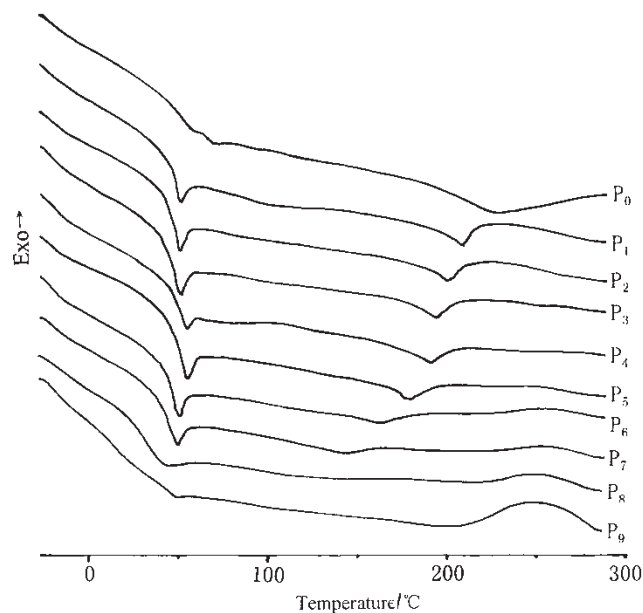


Figure 2. DSC thermograms (second heating) of polymers P<sub>0</sub>–P<sub>9</sub>.

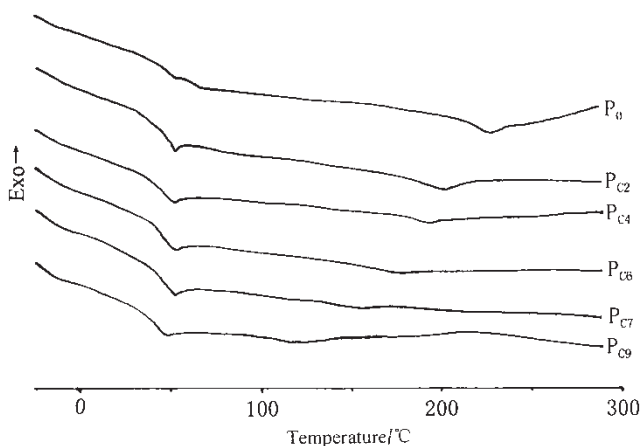


Figure 3. DSC thermograms (second heating) of polymers  $P_0$ ,  $P_{C2}$ – $P_{C9}$ .

of mesogenic unit M1 in the uncrosslinked polymers decreases from  $P_0$ ,  $P_{C2}$  to  $P_{C9}$ , their glass transition temperatures ( $T_g$ ) remain almost the same.

Generally, crosslinking imposes additional constraints on the segmental motion of polymer chains; therefore, an increase in the glass transition temperature  $T_g$  might be expected. However experimental results show that this effect is relatively small in the case of lightly crosslinked polymers. This implies that another role has been played by the flexible crosslinking units simultaneously: that of a plasticizer [10]. The existence of a plasticizer causes the decrease in  $T_g$  of lightly crosslinked polymers, as compared with the corresponding uncrosslinked ones. These two opposing functions of the crosslinker balance each other, so that  $T_g$  does not change greatly.

The table shows that the clearing point ( $T_c$ ) of the uncrosslinked LC polymers  $P_0$  and  $P_{C2}$ – $P_{C9}$  falls with the decreasing content of mesogenic monomer M1, resulting in the narrowing of mesophase ranges (see figure 4). This is easy to understand, since the content of mesogenic units in these polymers is reduced.

In addition, with increasing content of M2, the  $T_c$  of the crosslinked LC polymers also tend to decrease. Meanwhile, their  $T_c$  values are lower than those of the corresponding uncrosslinked polymers, resulting in narrower mesophase ranges than for the uncrosslinked polymers, which can be seen clearly from figure 4. This is due to the crosslinking, because crosslinking units may act as a non-mesogenic diluent and destabilize the LC phase, just as an impurity leads to freezing point depression in a liquid. The rule that clearing points decrease with the increase of non-mesogenic units has been demonstrated in previous work [11]. Moreover,  $T_{i-1}$ , the isotropic to LC transition temperature during cooling, also tends to decrease with the decrease of

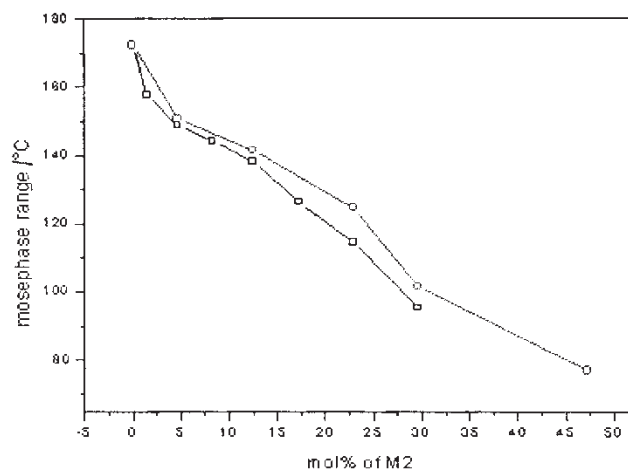


Figure 4. Mesophase range of crosslinked polymers ( $\square$ ) as a function of M2 content, and mesophase range of the corresponding uncrosslinked polymers ( $\circ$ ).

mole ratio of mesogenic monomer M1; and the  $T_{i-1}$  of the crosslinked polymers is lower than that of corresponding uncrosslinked polymers. The trends of  $T_{i-1}$  and  $T_c$  are identical with decreasing content of mesogenic monomer M1.

The DSC curve of  $P_8$  (see figure 2) with 63 mol% of M1, suggests that no liquid crystalline to isotropic transition exists; that is to say, crosslinked polymers with more than 37 mol% of M2 have no thermotropic liquid crystalline properties. In contrast, the uncrosslinked polymer  $P_{C9}$ , whose M1 content is as much as that of crosslinked polymer  $P_9$  and less than in  $P_8$ , still has thermotropic liquid crystalline properties, with a broad mesomorphic region over  $75^\circ\text{C}$ , as shown by DSC and POM. This is attributed to the formation of a network structure in the non-mesogenic state, as well as to the dilution of the non-mesogenic crosslinking units. Since crosslinking obtained in the non-mesogenic state tends to maintain the polymer backbones in the isotropic state, it will reduce the energy of disorientation of polymer molecules in the LC phase with the increase of crosslinking densities. So low levels of crosslinking do not obviously affect the phase behaviour of network polymers; in contrast, high levels of crosslinking may have more drastic influences, with the loss of LC phases [10]. We consider, that there is a critical crosslinking density for crosslinked liquid crystalline polymers; network polymers formed in the isotropic state will lose mesophase as soon as their crosslinking densities exceed the critical density. When the critical crosslinking density is exceeded, a sample crosslinked in the anisotropic state will retain mesophase at any temperature and no  $T_c$  can be observed.

Figure 2 also shows that polymers  $P_7$ – $P_9$  have



exothermic peaks at about 220–280°C during heating; the enthalpy corresponding to these peaks increases from 1.8 to 9.7 J g<sup>-1</sup> with the increase of crosslinking units M2, the reason for which we do not yet understand.

### 3.2. Texture analysis

The textures of polymers P<sub>0</sub>–P<sub>9</sub> and P<sub>C2</sub>–P<sub>C9</sub> observed by POM are shown in figure 5; P<sub>0</sub>–P<sub>7</sub> and P<sub>C2</sub>–P<sub>C9</sub> exhibit thermotropic LC properties during heating and cooling. P<sub>0</sub> and P<sub>C2</sub>–P<sub>C9</sub> show typical nematic threadlike textures [12], see figure 5(a, b), however the lightly crosslinked polymers P<sub>1</sub>–P<sub>7</sub> exhibit the texture shown in figure 5(c). Although the DSC curves of P<sub>6</sub> and P<sub>7</sub> show no isotropic to LC transition peaks, during cooling they display birefringence, too faint to be photographed. As suggested by the DSC curves, P<sub>8</sub> and P<sub>9</sub> show no texture under crossed polarizers when heated over  $T_g$ , so these two crosslinked polymers are not thermotropic LC polymers. However, under stress, P<sub>8</sub> and P<sub>9</sub> form semi-transparent thin films at room temperature, and birefringence can be observed under POM. When the thin film is heated, its birefringence slowly disappears. At temperatures higher than  $T_g$ , the thin films suddenly exhibit coloured textures, see figure 5(d), under mechanical stress; on removing the stress the textures vanish. Although P<sub>8</sub> and P<sub>9</sub> show no thermotropic liquid crystalline properties, they exhibit stress-induced orientation. P<sub>4</sub>–P<sub>7</sub> also display a rubber-like behaviour when

heated over  $T_g$ , however, their textures do not change on stressing or pressing P<sub>4</sub>–P<sub>7</sub> to form thin films below  $T_g$ ; they show no birefringence with polarized light.

### 3.3. X-ray diffraction analysis

The quenched samples of the polymers P<sub>0</sub>, P<sub>2</sub>, P<sub>4</sub> and P<sub>6</sub> were studied by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Their WAXD patterns are shown in figure 6. All four samples show amorphous diffuse peaks at about  $2\theta = 20^\circ$ ; no sharp peak in the lower Bragg angle region is observed. This suggests that the network liquid crystalline polymers P<sub>0</sub>–P<sub>7</sub> exhibit nematic mesophases [12]. It also indicates that the formation of a network structure in the polymers does not change their mesogenic types.

## 4. Conclusion

A series of crosslinked liquid crystalline polymers and uncrosslinked liquid crystalline polymers have been prepared by graft copolymerization. Their liquid crystalline properties show that crosslinking obtained in the isotropic state causes reduction of the clearing point of the crosslinked polymers, as compared with the corresponding uncrosslinked polymers. Light crosslinking hardly affects the phase behaviour of the liquid crystalline polymers, so the crosslinked polymers P<sub>1</sub>–P<sub>7</sub> exhibit nematic mesogenic phases just as the uncrosslinked polymers do. In contrast, a high crosslinking density leads to the crosslinked polymers P<sub>8</sub> and P<sub>9</sub> losing their thermotropic liquid crystalline phases; instead, they exhibit stress-induced orientation.

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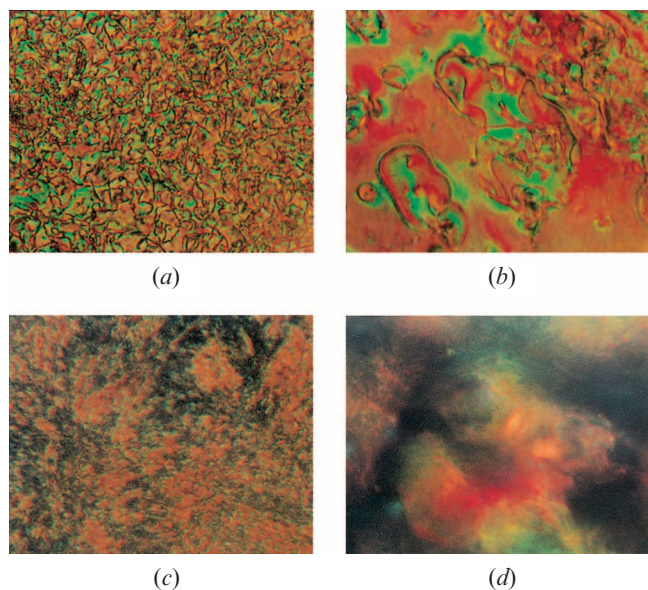


Figure 5. Polarizing optical micrographs of polymers (200×). (a) P<sub>0</sub> at 110°C; (b) P<sub>C6</sub> at 94°C; (c) P<sub>3</sub> at 186°C; (d) stress-induced texture of P<sub>9</sub> at 87°C.

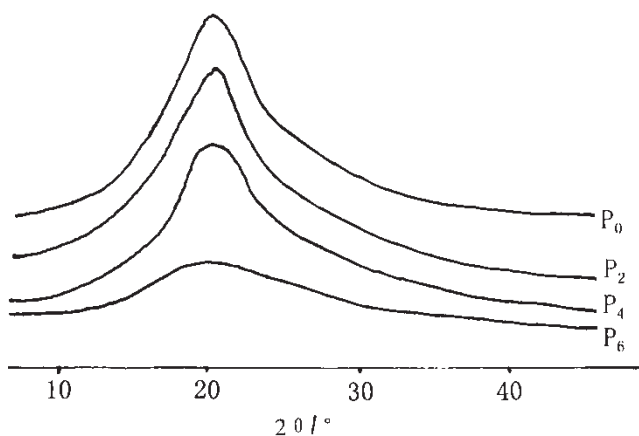


Figure 6. Wide angle X-ray diffraction patterns for polymers P<sub>0</sub>, P<sub>2</sub>, P<sub>4</sub> and P<sub>6</sub>.

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