Synthesis and Characterization of Network Liquid Crystal Elastomers and Thermosets

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ABSTRACT: A new series of network liquid crystal polymers were synthesized by graft copolymerization of the difunctional mesogenic monomer 4-allyloxy-benzoyloxy-4′-allyloxybiphenyl (M) upon polymethylhydrosiloxane (PMHS). Monomer M acted not only as a mesogenic unit but also as a crosslinker for the network polymers. The chemical structures of the polymers were confirmed by IR spectroscopy. DSC, TGA, and X-ray scattering were used to measure their thermal properties and mesogenic properties. The glass transition temperature (T_g) of these network liquid crystal polymers was increased when the monomer was increased, and T_d (temperature of 5% weight loss) at first went up and reached a maximum at P_1, then went down. The slightly crosslinked polymers (P_0, P_1) show rubber-like elasticity, so it was called liquid-crystal elastomer. Network polymers will lose elasticity property with a highly crosslinked degree, and turn into thermosetting polymers (P_4, P_5). All polymers exhibited a smectic texture by X-ray scattering. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1104–1109, 2002

Key words: liquid crystal; elastomers; networks; thermosets;

INTRODUCTION

Linear liquid crystal polymer can be converted to networks by a crosslinking reaction. These networks completely differ in their physical properties, the most famous being "rubber elasticity." Therefore, such polymers are called liquid crystal elastomers (LCE), and LCE indicates dual characterizations of liquid crystal and elastomer. Since the first synthesis in 1981,[1] LCE have received a lot of interest during recent years, mainly owing to their special optical, mechanical, and piezoelectric properties. The synthesis of these elastomers was always done in two steps. First linear soluble liquid crystal polymers were prepared, which were then crosslinked in the second step[1–5] (polysiloxanes[1–3] and polyacrylates.[4,5]). So far, most of crosslinkers of LCE were nonmesogenic, which may disturb liquid crystal orientation. In this article, we synthesize a difunctional liquid crystal monomer, which is not only a mesogenic unit but also a crosslinker. This is to allow network formation with no perturbation of nonmesogenic, and the polysiloxane main chain was chosen, which is distinguished by its high flexibility; polymers exhibiting the liquid crystal state at room temperature can be expected.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, M_n = 700–800) was offered by Jilin Chemical Industry Company. 1-Bromopropene; *p*-hydroxybenzoic acid, and biphenol were supplied by Beijing Chemical Industry Co. Ltd. Toluene used was first refluxed over sodium and then distilled; all other solvents and reagents were purified before used.

Experimental Techniques

^{1}H-NMR spectra were recorded on a Varian avance-300 in CDCl$_3$. IR spectra were obtained on a Perkin-Elmer 1320 spectrometer. Thermal transitions and thermodynamic parameters were determined by using Perkin-Elmer DSC at a heating and cooling rate of 20°C/min under nitrogen atmosphere, and TGA were used to determined thermal stability of polymers. A Leitz optical polarizing microscope equipped with a Mettler FP82 hot stage were used to observe the
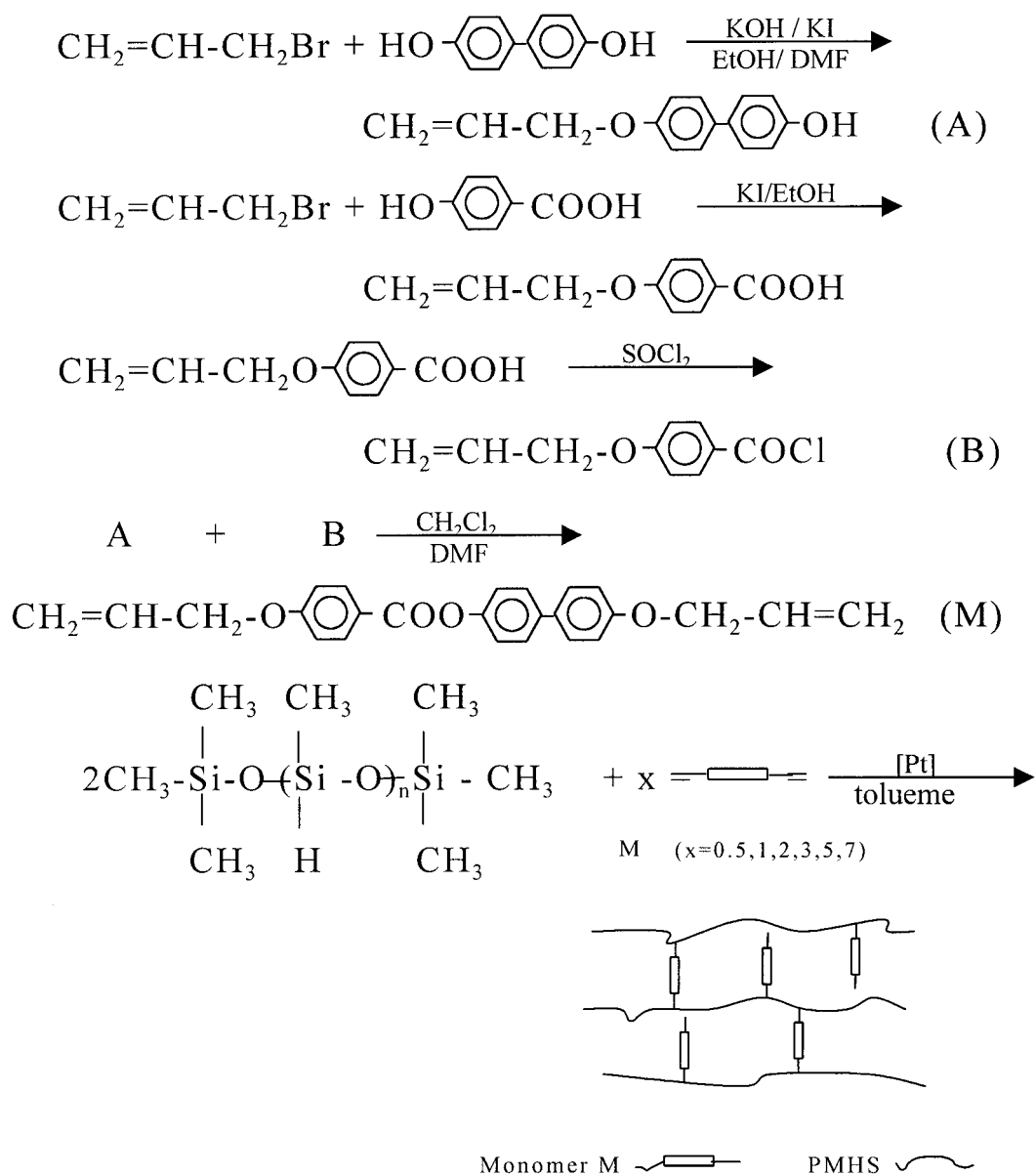
Scheme 1 Synthetic routes of monomer and network polymers.

Table I   Polymerization and Thermal Analysis Results of Polymers

Sample	PMHS (mmol)	M (mmol)	M[a] (mol %)	T_g (°C)	ΔH[b] (J/g)	T_d[c] (°C)
P_0	2	0.5	20.0	−10.12	80.88	305.26
P_1	2	1	33.3	−5.06	28.24	392.59
P_2	2	2	50.0	−4.86	9.04	375.44
P_3	2	3	60.0	−4.01	6.04	341.04
P_4	2	5	71.4	−2.07	—	362.56
P_5	2	7	77.8	−2.77	—	351.64

[a] Based on PMHS (2 mmol) + M.
[b] Exothermic enthalpy transition.
[c] Temperature at which 5% loss occurred.

liquid crystal textures. The X-ray diffraction analysis was performed with a Rigaku DMAX X-ray instrument, and all samples were quenched at 120°C.

Monomer Synthesis

The synthetic routines of mesogenic monomer are shown in Scheme 1. Monomer M was synthesized by the following procedure. 4-Allyloxy benzoic acid and 4-allyloxybenzoyl chloride were prepared according to ref. 6, and 4-allyloxy-4′-hydroxy biphenyl was prepared according to ref. 7. The 4-allyloxybenzoyl chloride (0.03 mol) was slowly added to a 30-mL dichloromethane solution containing 4-allyloxy-4′-hydroxy biphenyl (0.026 mol), and then was reacted for 2 h at room temperature and refluxed for 4 h. The mixture was concentrated, and thereafter precipitated with ethanol. The crude product was recrystallized with ethanol (m.p.: 142°C; yields: 90%). IR(KBr), ν/cm^{-1}:3030(H_2C=CH—), 1728(—C=O), 1601,1508 (⬡), 1257(—C—O—C—); ^{1}H-NMR(δ,CDCl$_3$): 5.10–6.10(6H, m, with maxima at 5.17, 5.34 and 6.04, 2H_2C=CH—), 4.53 and 4.48 (2H, 2H, m, 2—H_2CO—), 6.88 and 7.99 (4H, m, —O—⬡—COO—), 7.08, 7.42, 7.34 and 6.88 (8H, m, —COO—⬡—⬡—O—).

Polymer Synthesis

The synthetic routes of network polymers are outlined in Scheme 1. The divinyl mesogenic monomer M, which also acts as a crosslinker, reacted with Si—H of PMHS to form network polymers in the presence of a Pt catalyst. All polymers synthesized are listed in Table I.

The monomer M and PMHS were dissolved in dried toluene. A hydrochloroplatinic (IV) acid hydrate/THF solution was added to the above solution with the mol ratio of Pt/alkene was 1 : 10^3. The reaction was carried out at 60–70°C for 3 days under a nitrogen atmosphere, and then precipitated with methanol. The products were dried in a vacuum at room temperature. With M increasing from P_0 to P_5, samples morphology changed from soft, rubber-like elastomers to powder, thermosetting polymers. IR(KBr), ν/cm^{-1}: 2800–3000 (—CH$_3$, —CH$_2$—), 2159(—Si—H), 1734(C=O), 1606, 1508(—Ar), 1250 (—C—O—C), and 1000–1150 (Si—O—Si).
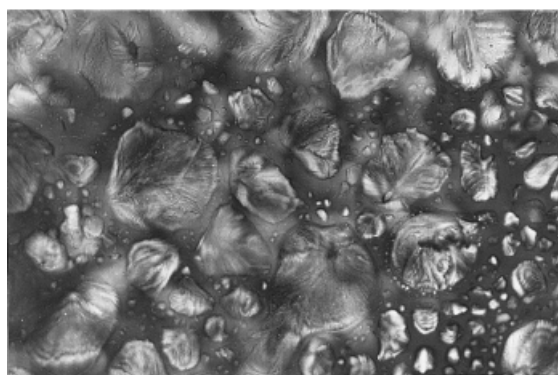
RESULT AND DISCUSSION

Monomer

The DSC thermogram of monomer M was shown in Figure 1. Upon heating, there are two endothermic peaks at 142 and 241°C, respectively, corresponding to a melting point and a clearing point. The liquid crystal range of M is 99°C. From the cooling curve, two exothermic peaks revealed
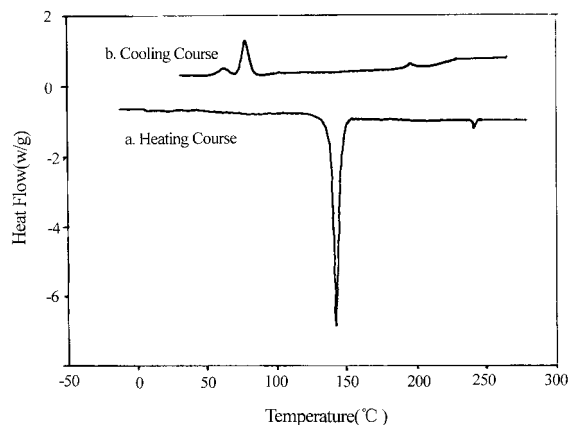
Figure 1   DSC thermogram of mesogenic monomer M.
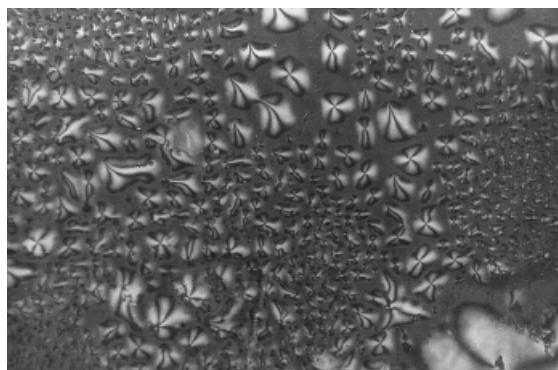
Figure 2 Optical polarizing micrographs of monomer M (×192). (a) Monomer M at 122°C; (b) monomer M at 85°C.

the transition temperature of isotropic to liquid crystal at 198°C and liquid crystal to crystal at 75°C.

Figure 2 shows optical polarizing micrographs of monomer M at different temperatures. Upon cooling, the monomer respectively shows a smectic droplet at 122°C [Fig.2(a)] and fan-shaped at 85°C [Fig.2(b)], which are typical smectic textures.

Network Polymers

IR Spectra Analysis

The IR spectra of the polymers are shown in Figure 3. The hydrocarbon absorption bands of olefinic, methyl, and methene at $3100-2800$ cm^{-1} and ester group peaks at 1734 cm^{-1} increased with the increase in the content of monomer M; meanwhile, a two-ended active vinyl bonds of M reacted with the Si—H bond of PMHS in the presence of a catalyst to form network polymers.

The IR absorption peak value of Si—H bond at 2160 cm^{-1} is relative to the reactive degree of the vinyl bond, which determine valid crosslinking degree and thermal properties of polymers.

Thermal Analysis

An M increase leads to a high crosslinking degree, which makes network polymers morphology change from rubber-like to powder. DSC and TGA thermograms of the samples are shown in Figure 4; also, the thermal analysis results are summarized in Table I.

The glass transition temperature (T_g) is an important parameter in connection with structures and properties of polymers. Table I shows that the T_g of the network polymers P_0–P_5 increase with the concentration of mesogenic units (i.e., crosslinker) in the polymers. As we know, T_g involves the mobility of chain segments of the polymers, and it will be increased with the mobility restriction of the chain segment. With an increase in the concentration of the monomer, valid crosslinked density also increases, which made the mobility of the chains segment limited; thus, the T_g increases from -10 to -2°C.

T_d (the temperature at which 5% weight loss occurred) is another important parameter of the polymer's thermal stability (see Table I). In our research, development of network and concentration of M was a pair of contradictory factors for T_d. The former made T_d rise and the later, on the contrary, leads to a decline of T_d. So, at first, the network is a major impact factor for T_d, which made T_d go up and P_1 reached a maximum, then went down with M continuously increasing because M get the run upon. T_d of P_3 was the lowest
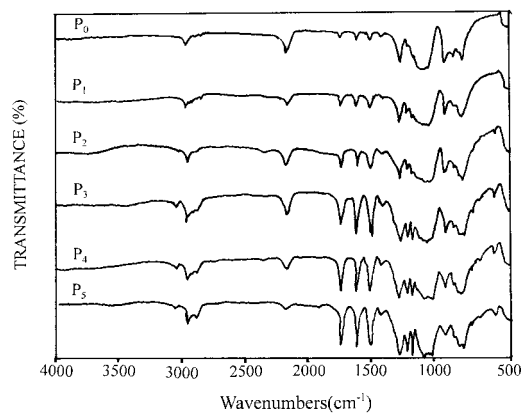
Figure 3 IR spectrums of network liquid crystal polymers.
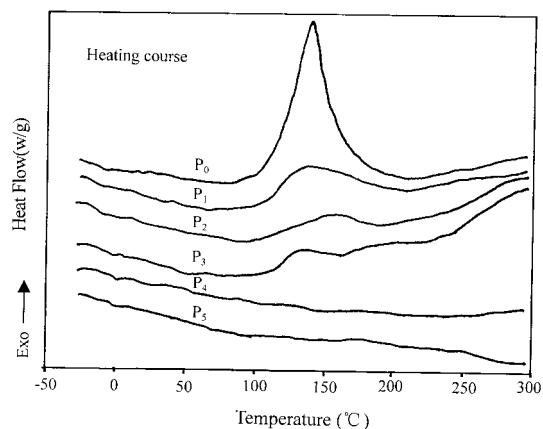
(a)
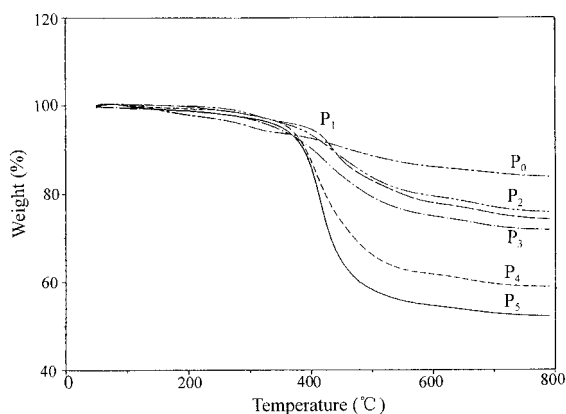
(b)

**Figure 4** Thermographs of network liquid crystal polymers. (a) DSC; (b) TGA.

because in the IR spectrum active Si—H is more unreactive than others, which affect development of the network.

In previous works, the phase transition temperature of lightly crosslinked liquid crystal polymers is shifted at ±5 K, and no difference is observed in the shapes of DSC curves of the linear and the crosslinked polymers.[1–5] There is a difference between ours and others where an additional exothermic peak (ΔH) appears in our DSC thermogram of P_0–P_3. Due to thermal analyzer using a nitrogen atmosphere, the polymer oxidizing was impossible. So, this is a typical elastomer peak because the specific heat capacity (ΔC_p) of the elastomer increases with a rising temperature rising.[8] In previous works no exothermic peak of the elastomer appears in their thermogram because the molecular weight of the linear for the crosslinked polymers is larger, and lightly

crosslinked polymers can be regarded as a similar structure of the linear polymer. On the contrary, the molecular weight is lower, which leads to relatively higher crosslinking density than others, and the network polymers cannot be thought of as a linear structure. It can be seen that the exothermic ΔH reduced and then disappeared with increasing M (i.e., highly crosslinked density). This shows elastic properties decreased from P_0 to P_5. P_0 and P_1 show good elasticity like rubber. In fact, P_4 and P_5 lost elasticity and became thermosets.

Optical Micrograph Analysis

The analysis of the phase behavior of the swollen elastomer failed using polarizing microscopy. Due to stress-induced birefringence of the elastomer caused by varying the temperature, mesophase birefringence is not distinguishable. Therefore,
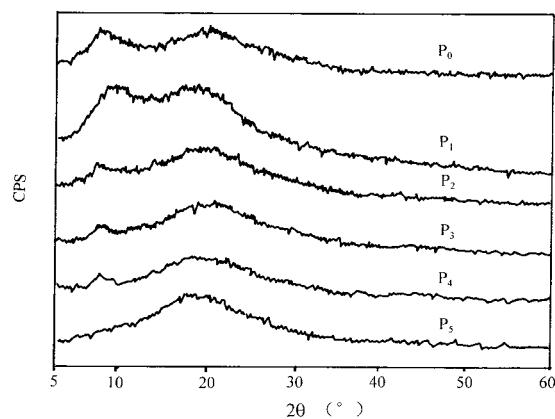
(a)
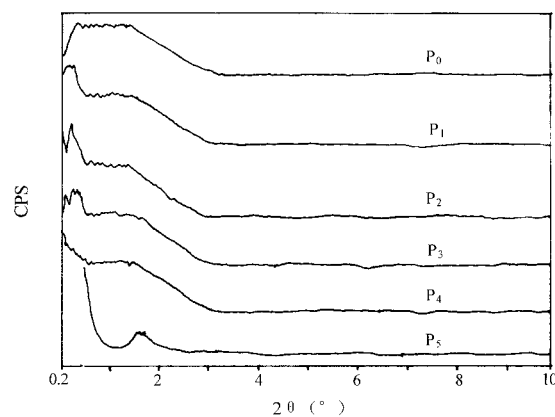
(b)

Figure 5 X-ray diffraction curves of network polymers: (a) wide angle; (b) small angle.

phase transformation temperatures as well as the structure of the elastomer, can only be determined by X-ray diffraction measurement.[9]

X-ray Diffraction Analysis

X-ray diffraction studies were carried out to get more detailed information on both the mesophase structure and crystalline structures of the polymer. Figure 5 reveals the X-ray diffraction diagrams of the samples. A broad reflection in the wide angle is associated with the lateral packing, and reflections in the low angle is associated with the smectic layers. Polymers P_0–P_5 show a broad amorphous diffraction at about 20°C (d = 0.444 nm) in the wide angle [Fig. 5(a)] and a platform diffraction peak from 0.350° (25.218 nm) to 1.20° (7.356 nm) in the small angle [Fig. 5(b)], which reveal a laminated structure of the molecular chain and multiple ways of the order arrangement of layers. A platform peak in the small angle indicates the order of continuous smectic layers, and the layer thickness corresponds to the sharp and shape of the peak. P_5 shows a single diffraction peak in the small angle, which explains that each liquid crystal unit was fixed on the network, and gains a single liquid crystal arrangement. In the wide angle the diffraction peak at 11° (d = 0.804 nm) corresponds to the PMHS decrease with increasing M; this indicates that the order parameter of the main chain arrangement improved greatly.

CONCLUSION

A series of network liquid crystal polymers were synthesized by difunctional Monomer M reacting with PMHS. M is not only a mesogenic unit but also a crosslinker, which removes the perturbation of the nonmesogenic crosslinker. All the obtained polymers have exhibited a smectic phase by X-ray measurement. Lightly crosslinking density polymers show thermal behavior of the elastomer. Thus, P_0, P_1 were liquid crystal elastomers, and P_4, P_5 were liquid crystal thermosetting polymers.

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