Synthesis and Structure of Polysiloxane Liquid Crystalline Elastomers with a Mesogenic Crosslinking Agent

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ABSTRACT: A new mesogenic crosslinking agent M-1 was synthesized to minimize the perturbations of a nonmesogenic crosslinking agent for liquid crystalline elastomers. The synthesis of new side-chain liquid crystalline elastomers containing a rigid mesogenic crosslinking agent M-1 and a nematic monomer M-2 is described by a one-step hydrosilylation reaction. The chemical structures of the obtained monomers and elastomers 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 measurements. The influence of the crosslinking units on the phase behavior is discussed. The elastomers containing less than 15 mol % of the crosslinking units showed elasticity, reversible phase transition, and nematic-threaded texture. However, when the crosslinking density reached 21.6 mol %, the mesophase of polymer P-8 disappears. The adoption of a mesogenic crosslinking agent diminishes the perturbation of a nonmesogenic crosslinking agent on mesophase of liquid crystalline elastomers, and isotropic temperature and a mesomorphic temperature range slightly decreased with increasing content of the crosslinking agent. In addition, X-ray analysis shows nematic polydomain network polymers can transform into smectic monodomain by stress induction, leading to the orientation formation macroscopically. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1736–1742, 2004

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

INTRODUCTION

Today, material science is directed toward the development of multifunctional and oriented structures. One example of such supermolecular systems is liquid crystalline elastomers (LCEs), which combine the properties of liquid crystalline with rubber elasticity. Since the first synthesis in 1981,[1] LCEs have received a lot of interest during recent years, mainly owing to their special optical, mechanical, ferroelectric, and piezoelectric properties.[2–11] One of the most remarkable characteristics is the ability to undergo a polydomain-to-monodomain transition; that is, stress-induced macroscopic orientation leading to the formation of "liquid single-crystal elastomers."[12–14] The polymer network structure of the LCEs is usually produced by the introduction of crosslinking into a liquid crystalline polymer, and LCEs were prepared based on crosslinked side-chain polymers with a polysiloxane backbone.[1,5–9,13,15–18] In addition, LCEs were extended to crosslinked side-chain liquid crystal polymers with polyacrylate and polymethacrylate backbones[14,19–26] and also to slightly crosslinked main-chain polymers and combined polymers.[19,27–30] These elastomers, prepared by a one- or two-step process in which monofunctional liquid crystal monomers and bifunctional crosslinking agents, such as divinyl derivatives, were simultaneously or successively attached to the polymer backbone. The chemical composition of the LCEs, besides the crosslinking unit, is similar. So far, most of the crosslinking agents of LCEs were nonmesogenic flexible chains, which may influence the mesophase properties in two ways. First, crosslinking units may act as nonmesogenic diluents, and bring perturbations to the liquid crystalline phase. Second, in a similar way, copolymerization with a nonmesogenic crosslinking agent leads to a downward shift in the clearing point as increasing proportions are added to a liquid crystalline polymer. Moreover, only a few articles reported that LCEs were synthesized with rigid rodlike crosslinking agents (mesogenic or nonmesogenic).[5,6,18,26]

In this article, we synthesize a difunctional liquid crystal monomer as the crosslinking agent, which can minimize the perturbations on the liquid crystalline phase of the LCEs. In addition, the crosslinking agent has long alkyl chains in both ends of liquid crystal core, which can make the mesogenic unit of the LCEs

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orient freely. LCEs were prepared by a one-step process in which a monofunctional liquid crystal monomer and a bifunctional mesogenic crosslinking agent were simultaneously attached to the polysiloxane through hydrosilylation reaction. The mesomorphic properties and phase behavior were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction measurement. The effect of the concentration of the crosslinking units on phase behavior was discussed.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, $M_n = 700-800$) was purchased from Jilin Chemical Industry Company (China). 1-Bromopropene and undecylenic acid were purchased from Beijing Jinlong Chemical Reagent Co., Ltd. (China). 4-Hydroxybenzoic acid, p-dihydroxybenzene, 4,4'-dihydroxy biphenyl and 4-butylbenzoic acid were purchased from Beijing Fuxing Chemical Industry Co. (China). Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

Characterization

Fourier transform infrared (FTIR) spectra of the synthesized monomers and polymers in a solid state were measured on a Nicolet 510 FTIR spectrometer via a KBr table. ^{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 under a nitrogen atmosphere. A Leitz Microphot-FX polarizing optical microscope (POM) equipped with a Mettler FP 82 hot stage was used to observe visual textures and phase transition temperatures for analyzing mesomorphic properties of the liquid crystalline monomers and polymers. X-ray diffraction measurements were performed with a nickel-filtered Cu-K$_\alpha$ ($\lambda = 1.542$ Å) radiation with a Rigaku powder diffractometer.

Synthesis of monomers

The synthesis of the mesogenic crosslinking agent M-1 was carried out as shown in Scheme 1.

4-undecylenoyloxybenzoic acid (2)

4-Hydroxybenzoic acid (34.5 g, 0.25 mol) was dissolved in 150 mL of tetrahydrofuran (THF) and 16 mL of pyridine. And undecylenoyl chloride (40.5 g, 0.2 mol) was slowly dropped into the above mixture at
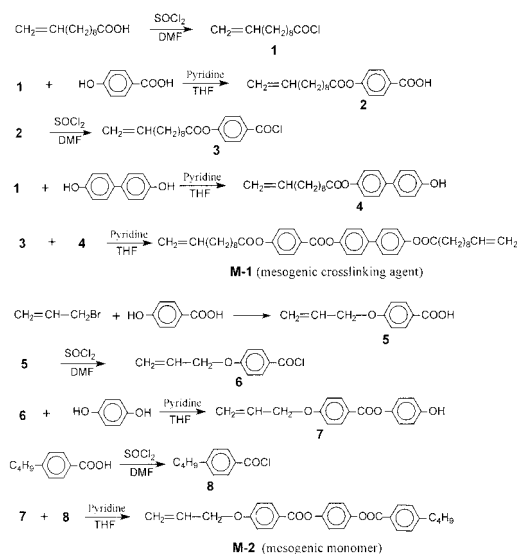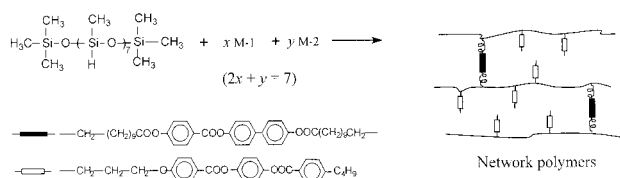

Scheme 1 Synthetic routes of monomers.

5–10°C. After refluxing for 6 h, the reaction mixture was then cooled and poured into water, precipitated, filtered, and washed with water. The crude product was purified by recrystallization from ethanol. White crystals were obtained (m.p.: 123–124°C, yield: 61%). IR (KBr, ν/cm^{-1}): 3080 (=C—H); 2925, 2852 (—CH$_2$—); 2672, 2557 (associated COOH); 1754 (—COO—), 1684 (—COOH); 1641 (C=C); 1602, 1508 (—Ar—).

4-hydroxy-4'-undecylenoyloxy-diphenyl (4)

Biphenol (37.6 g, 0.2 mol) was dissolved in 75 mL of THF and 15 mL of pyridine, then undecylenoyl chloride (20.3 g, 0.1 mol) was slowly dropped into the above mixture at 0–5°C. The mixture reacted at room temperature for 4 h, and thereafter was refluxed for 2 h, and poured into 1000 mL of water. The filtered precipitate was added to 500 mL of 5% NaOH aqueous solution for removing unreacted biphenol, and the dispersion was stirred for 4 h, filtered, and washed with water. The filter cake was dried and dissolved in ethanol, and the mixture was heated to boiling, then cooled and filtered to remove bisate. The filtered solution was slowly evaporated to get the crude product, and purification through recrystallization. White powder. (m.p.: 90°C, yield: 43%). IR (KBr, ν/cm^{-1}): 3381 (—OH); 3073 (=C—H); 2921, 2849 (—CH$_2$—); 1745 (—COO—); 1641 (C=C); 1608, 1593, 1499, 1462 (Ar—).

4-hydroxy-4'-undecylenoyloxy-biphenyl-4-undecylenoyloxybenzoate (M-1)

The synthesis of mesogenic crosslinking agent M-1 was composed of the following two steps. First is the

Scheme 2 Synthetic routes of liquid crystalline elastomers.

synthesis of 4-undecylenoyloxybenzoyl chloride (**3**). 4-Undecylenoyloxybenzoic acid (30.4 g, 0.1 mol) was reacted at 50 °C with 30 mL of thionyl chloride containing a few drops of N,N-dimethylfomamide for 5 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. Yield: 93 %.

Second, 4-hydroxy-4'-undecylenoyloxy-biphenyl (**4**) (17.6 g, 0.05 mol) was dissolved in 60 mL of chloroform. Then, 4-undecylenoyloxybenzoyl chloride (16.5 g, 0.05 mol) in 10 mL of chloroform was added dropwise at 10–15°C. After stirred at room temperature for 2 h, the reaction mixture was refluxed for 4 h. The crude product was precipitated by adding cool ethanol, filtrate, and recrystallized from ethanol. White product was obtained (m.p.: 84°C, yield: 84%). IR (KBr, ν/cm^{-1}): 3073 (=C—H); 2923, 2850 (—CH$_2$—); 1749 (ester group of —RCOOAr—); 1733 (ester group of —ArCOOAr—); 1639 (C=C); 1602, 1494 (Ar). ^{1}H NMR (CDCl$_3$, δ/ppm): 1.33–2.06 [m, 28H, 2CH$_2$=CH(C$\underline{H}_2$)$_7$CH$_2$COO—]; 2.56–2.62 [m, 4H, 2CH$_2$=CH(CH$_2$)$_7$C$\underline{H}_2$COO—]; 4.92–5.02 [m, 4H, 2C$\underline{H}_2$=CH(CH$_2$)$_7$CH$_2$COO—]; 5.77–5.83 [m, 2H, 2CH$_2$=C$\underline{H}$(CH$_2$)$_7$CH$_2$COO—]; 6.91–8.27 [m, 12H, Ar—H].

4-hydroxy-4'-allyloxybenzoyloxy-benzene-4-butylbenzoate (M-2)

The synthetic routes of the liquid crystalline monomer M-2 were outlined in Scheme 1. 4-Allyloxybenzoic acid (**5**), 4-allyloxybenzoyl chloride (**6**), and 4-hydroxy-4'-allyloxy-benzoyloxy-benzene were synthesized according to a reported procedure.[31]

The synthesis of the mesogenic monomers M-2 was composed of the following two steps. First is the synthesis of 4-butylbenzoyl chloride according to product **3** of M-1. Second, 13.5 g (0.05 mol) 4-hydroxy-4'-allyloxy-benzoyloxy-benzene (**7**) was dissolved in 30 mL of tetrahydrofuran (THF) and 10 mL of pyridine, and then 0.05 mol 4-butylbenzoyl chloride (**8**) was slowly dropped into the mixture. After the mixture reacted at room temperature for 2 h and was refluxed for 4 h, it was precipitated with water, and filtered. The crude product was purified by recrystallization from ethanol. White crystalline was obtained (m.p.: 135°C, yield: 91%). IR (KBr, ν/cm^{-1}): 3076 (=C—H); 2963, 2856 (—CH$_2$—); 1736 (—ArCOOAr—); 1641 (C=C);

1607, 1510 (Ar); 1250 (C—O). ^{1}H NMR (CDCl$_3$, δ/ppm): 0.93–0.98 [t, 3H, —CH$_2$(CH$_2$)$_2$C$\underline{H}_3$]; 1.35–1.68 [m, 4H, —CH$_2$(C$\underline{H}_2$)$_2$CH$_3$]; 2.69–2.74 [t, 2H, —C$\underline{H}_2$(CH$_2$)$_2$CH$_3$]; 4.64–4.66 [d, 2H, CH$_2$=CHC$\underline{H}_2$O—]; 5.33–5.49 [m, 2H, C$\underline{H}_2$=CHCH$_2$O—]; 6.04–6.11 [m, 1H, CH$_2$=C$\underline{H}$CH$_2$O—]; 6.91–8.31 [m, 12H, Ar—H].

Synthesis of the elastomers

LCEs were prepared using the liquid crystal monomer M-2 and the bifunctional mesogenic crosslinking agent M-1 simultaneously attached to the highly flexible polysiloxane through hydrosilylation reaction.

The synthesis of the polymers was performed according to Scheme 2 and Table I. The same method was adopted for the synthesis of polymers P-1–P-8, and the synthesis of the elastomer P-3 was given as an example. The 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$_2$PtCl$_6$/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^{-1} disappears. The elastomers were carefully deswollen with methanol, and then dried under vacuum. IR (KBr, ν/cm^{-1}): 2924, 2853 (—CH$_2$—, —CH$_3$); 1752 (ester group of —RCOOAr—); 1735 (ester group of —ArCOOAr—); 1602, 1501(Ar); 1200–1000 (Si—O—Si).

RESULTS AND DISCUSSION

FTIR analysis

FTIR spectrum of the mesogenic crosslinking agent M-1, mesogenic monomer M-2, and some elastomers are shown in Figure 1. FTIR studies can reflect all these changes with stepping from P-1 to P-8, and provide an effective method for verification in synthesis of all polymers. From the disappearance of the peaks for the Si—H stretching at 2160 cm^{-1} (a) and vinyl C=C stretching at 1638 cm^{-1} (b) of monomers in Figure 1,

TABLE I
Polymerization and Yield

Polymer	Feed			M-1[a] (mol %)	Yield (%)
	PMHS (mmol)	M-1 (mmol)	M-2 (mmol)		
P-1	1	0.00	7.00	0.00	92
P-2	1	0.125	6.75	1.80	90
P-3	1	0.25	6.50	3.60	87
P-4	1	0.375	6.25	5.40	93
P-5	1	0.50	6.00	7.20	90
P-6	1	0.75	5.50	10.8	93
P-7	1	1.00	5.00	14.4	84
P-8	1	1.50	4.00	21.6	91

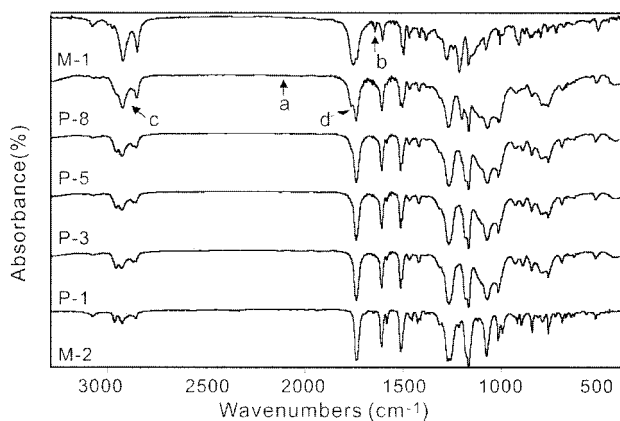[a] Molar fraction of monomer M-1 based on M-1 + M-2.

Figure 1 FTIR spectrum of monomers and polymers.

as well as with the increasing content of the crosslinking agent M-1 from P-1 to P-8, the alkyl stretching bands about 2845 and 2920 cm^{-1} (c) strengthened and an obvious new peak (—RCOOAr—) at 1752 cm^{-1} (d) of M-1 appeared, so we can conclude that successful incorporation of monomers into polysiloxane was made as we expected. Other characteristic absorption bands respectively belong to ester group peak of —ArCOOAr— at 1735 cm^{-1}, aromatic peaks at 1605 and 1502 cm^{-1}, and an Si—O—Si peak at 1200–1000 cm^{-1}.

Liquid crystalline behavior

Liquid crystalline properties of the monomers M-1, M-2, and polymers P-1–P-8 were determined by DSC and POM. Thermal behavior determined by DSC was consistent with POM observation results. Typical DSC curves of M-1 and M-2 are shown in Figure 2. Phase transition temperatures and corresponding enthalpy changes are listed in Table II.

DSC heating thermograms of M-1 showed four endothermic peaks, which corresponding to different mesogenic phase transition. By the observation with POM, we can confirm that the four peaks in DSC thermogram respectively represented a melting transition at 84.0°C, a smectic C-to-smectic A transition at 118.3°C, a smectic A-to-nematic transition at 169.6°C, and a nematic-to-isotropic phase transition at 180.0°C. On the cooling scans, an isotropic-to-nematic phase transition appeared at 176.6°C, a nematic-to-smectic A transition at 166.5°C, a smectic A-to-smectic C transision at 113.5°C, as well as a crystallization transition at 74.0°C. POM observation showed that crosslinking monomer M-1 exhibited enantiotropic nematic schlieren texture, smectic A, and smectic C during heating and cooling cycles. For long alkyl chains in both ends, curly chain leads to formation of smectic mesophase of M-1. Polarizing micrographs of M-1 at 161 and 104°C are shown in Figure 3(a) and (b) on the cooling course, which respectively corresponding to a

focal–conic texture of smectic A phase and a fan-shape texture of the smectic C phase.

In addition, monomer M-2 showed two endothermic peaks on the heating course, corresponding to a melting transition at 135.4°C and a nematic to isotropic phase transition at 225.6°C. On the cooling course, an isotropic to nematic phase transition appeared at 193.4°C, and a crystallization temperature occured at 104.8°C. A polarizing micrograph of M-2 at 175.0°C in Figure 3(c) indicates a nematic schlieren texture.

The liquid crystalline behavior of mesogenic polymers only occured over a restricted temperature range with an upper limit set by the mesogenic–isotropic transition temperature and a lower limit set by the glass transition. DSC thermograms of polymers P-1–P-8 are shown in Figure 4. The thermal results of the synthesized polymers are summarized in Table III. It was clearly seen that a low concentration of the crosslinking agent M-1 did not remarkably influence phase behavior, and the phase transition temperatures were not shifted significantly. However, a high crosslinking density has a strong effect on the phase behavior of the LCEs; this could cause the mesophase to disappear. Thus, for polymer P-8 only the glass transition is observed in the DSC curve. Figure 5 shows the effect of the concentration of the crosslinking agent M-1 on the phase behavior of the liquid crystalline elastomers.

For side-chain LCEs, T_g is affected by the polymer backbone, mesogenic group, flexible spacer length, and crosslinking density. In general, crosslinking imposes additional constraints on the motion of chain segments, which makes T_g increase. On the other hand, the flexible chains of the crosslinking agent are similar to plasticization, and this will cause T_g of the elastomers to decrease. Because of the long flexible chains in both sides of M-1, the plasticization effect is more significant than crosslinking. So, the T_g of the elastomers from P-2 to P-8 is shifted to a low temperature compared with the homopolymer P-1. When the concentration of the crosslinking agent M-1 increased from 0 to 21.6 mol %, the T_g of elastomers decreased from 40.5°C for P-1 to 30.2°C for P-8.
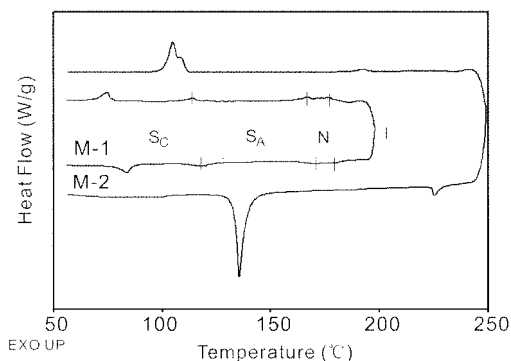

Figure 2 DSC thermograms of monomers.

TABLE II
Thermal Properties of Monomers

Monomer	Phase transition temperatures[a] in °C (Corresponding enthalpy changes in J/g) Heating / Cooling	Yield (%)	ΔT^{b} (°C)
M-1	K84.0(11.16)S$_C$118.3 (4.7)S$_A$ 169.6 (2.4)N180.0(0.92)I I176.6 (1.1)N166.5(2.1)S$_A$113.5(3.4)S$_C$74.0(11.1)K	84	96.0
M-2	K135.4(57.5)N 225.6 (3.9)I I193.4(2.1)N104.8(50.4)K	91	90.2

K = solid, S$_C$ = smectic C, S$_A$ = smectic A, N = nematic, I = isotropic.
[a] Peak temperatures were taken as the phase transition temperature.
[b] Mesomorphic temperature ranges.

Similar to T_{g}, a chemical crosslinking also affected the liquid crystalline phase-to-isotropic phase transition behavior. In general, nonmesogenic crosslinking units acted as a diluent, and did not make for the formation of mesogenic orientation in the networks. Consequently, the effect could lead to a markedly T_i decrease with increasing concentration of the nonmesogenic crosslinking units. So, a mesogenic crosslinking agent (M-1) was adopted to reduce this effect on T_i. In addition, the rigid mesogenic core of M-1 may promote the formation of the mesophase. So, the cooperation of these effects leads to the T_i of the elas-
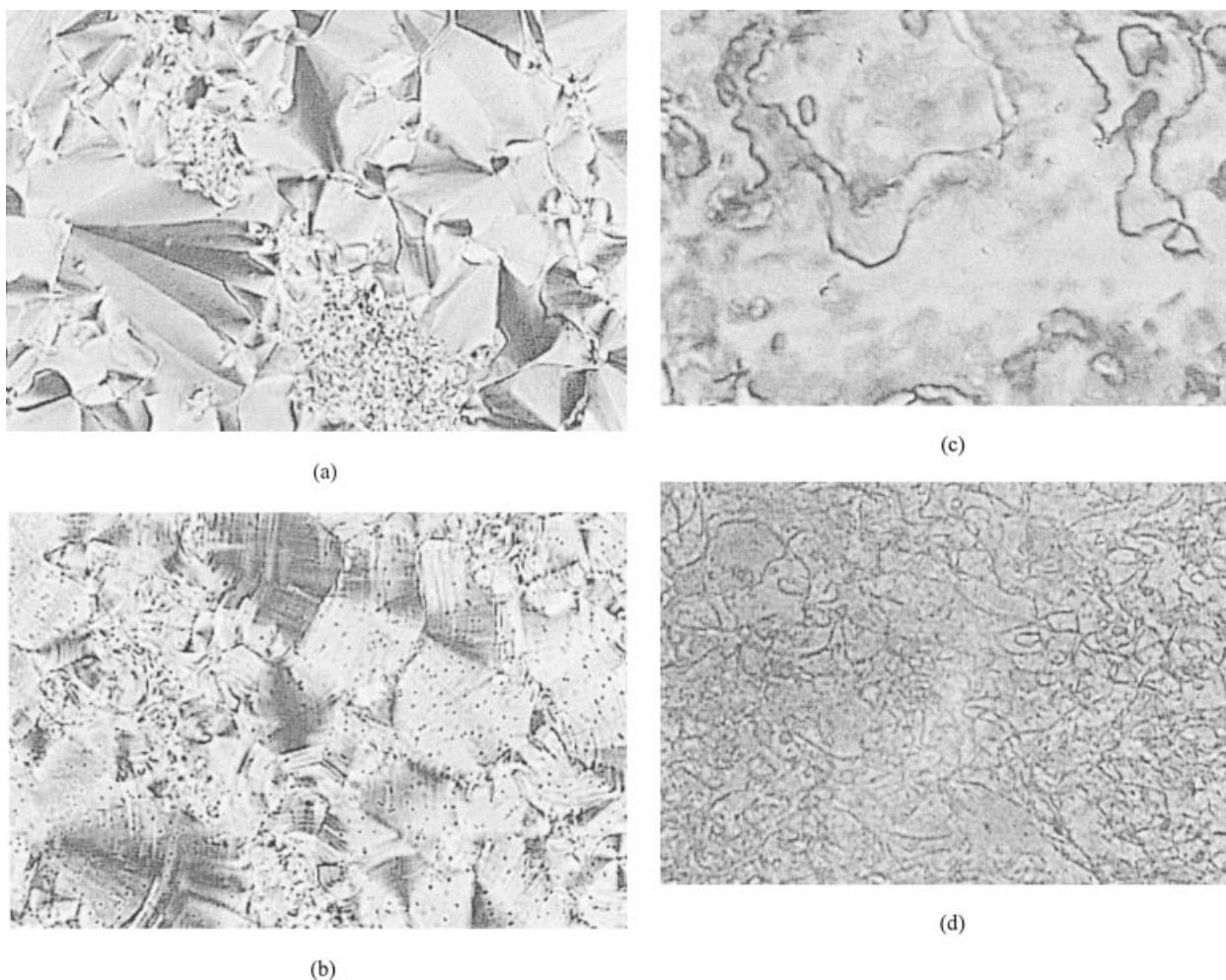

Figure 3 Optical polarizing micrographs of samples (200×). (a) Smectic A texture of M-1 at 161°C, (b) Smectic C texture of M-1 at 104°C, (c) Schlieren texture of M-2 at 175°C, (d) threaded texture of P-3 at 182°C.
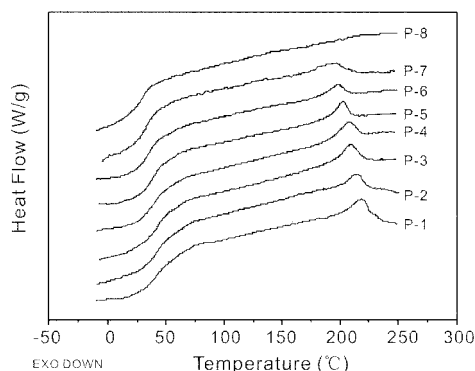
Figure 4 DSC thermograms of liquid crystal elastomers.

Figure 5 Effect of M-1 concentration on phase transition temperatures of elastomers.

tomers to decrease slightly. When the concentration of crosslinking units increased from 0 to 14.6 mol %, according to Table III, T_i decreased from 218.4°C for P-1 to 197.4°C for P-7. In addition, ΔH_i of the mesogenic–isotropic transition decreased from 4.43 Jg^{-1} for P-1 to 0.96 Jg^{-1} for P-7. Compared to the nonmesogenic flexible crosslinking agent, the effect of the mesogenic crosslinking agent on T_i of the elastomers is minor. T_i of the polymer P-8 disappeared due to the depression of crosslinking on liquid crystalline order.

Between the glass transition temperature and liquid crystalline-to-isotropic phase transition, liquid crystalline elastomers exhibited both rubberlike elasticity (due to the crosslinked polymer backbones) and anisotropic liquid crystalline behavior. Through the POM analysis, homopolymer P-1 and elastomers P-2–P-7 showed nematic threaded texture, but with the crosslinking degree increasing, this threaded texture became unclear. A polarizing photomicrograph of elastomers P-3 at 182°C is shown in Figure 3(d) as an example. Polymer P-8 did not reveal a mesophase; this was consistent with the DSC result. For adapting the mesogenic crosslinking agent ΔT of the network polymers P-1–P-7 decreased a little compared with the elastomers containing a nonmesogenic crosslinking agent. With the increasing density of the crosslinking agent, the influence of the mesogenic crosslinking agent on ΔT of the elastomers is shown in Table III and Figure 5.

X-ray diffraction analysis

X-ray scattering from liquid crystalline materials has been used extensively to determine structural features, including the order parameter. One of the most remarkable characterizations of LCEs is the ability to undergo a polydomain-to-monodomain transition. This phenomenon is a well-known universal characteristic of both main-chain and side-chain nematic and smectic LCEs, regardless of chemical structure.[10–14,30,32]

The orientation of the network polymers for X-ray measurement were annealed for 30 min under stress induction at 150°C, and then frozen by cooling the system down to about 0°C (far below T_g). Wide-angle and small-angle X-ray scattering of the polymers P-1, P-3, P-5, and P-7 are, respectively, shown in Figures 6 and 7. In the wide-angle scattering region, the polymers revealed a strong amorphous diffractive peak at 20° ($d_1 \approx 4.4$ Å), which could be attributed to the short-range positional order of the side groups. At the

TABLE III
DSC Results of Liquid Crystalline Elastomers

| Elastomer | DSC | | | |
	T_g (°C)	T_i (°C)	ΔH_i^a (J/g)	ΔT^b (°C)
P-1	40.5	218.4	4.43	177.9
P-2	40.0	213.6	2.83	173.6
P-3	39.3	211.6	2.76	172.3
P-4	37.5	204.8	1.92	167.3
P-5	36.2	204.5	1.70	168.3
P-6	35.1	199.4	1.17	164.3
P-7	32.0	197.4	0.96	165.4
P-8	30.2	—	—	—

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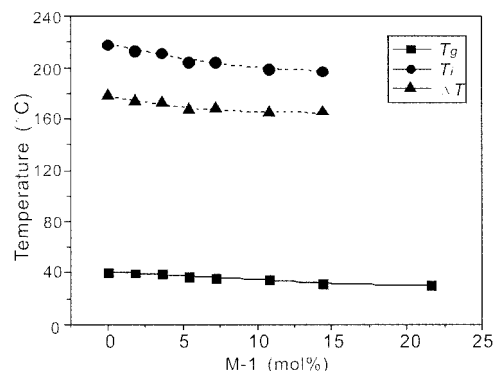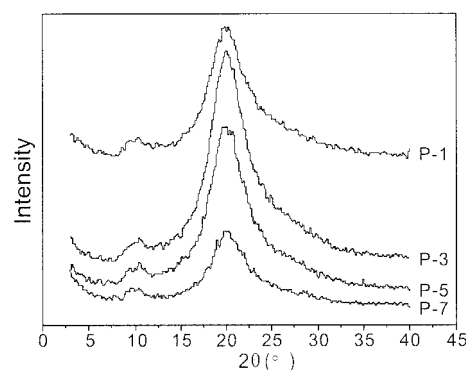^b Mesogenic temperature range ($T_i - T_g$).

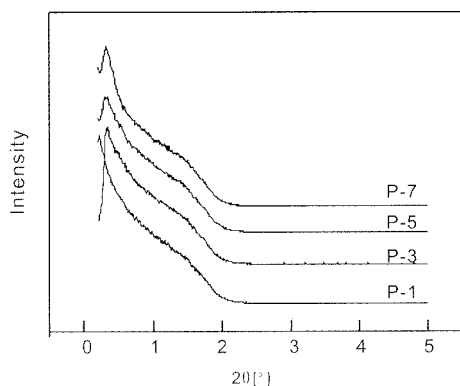**Figure 6** Wide-angle X-ray diffraction patterns of elastomers.

Figure 7 Small-angle X-ray diffraction patterns of elastomers.

same time, the diffractive peak at 20° strengthened at first, which showed short-range positional order between the mesogens enhanced. Then, the intensity of diffractive peak at 20° from elastomer P-3 to P-7 weakened due to the perturbation of crosslinking.

In small-angle X-ray scattering (SAXS), homopolymer P-1 did not displayed peaks, but the elastomers P-3, P-5, and P-7 exhibited a strong peak at about 0.34° ($d_2 \approx 260$ Å), which represented a smectic-laminated structure of the elastomers. Usually, the X-ray scattering patterns of conventional mesogens in the smectic phase did not display such diffuse streaks. Actually, each side chain is chemically linked to a backbone so that when a side chain fluctuates around its mean position in the smectic layer, this fluctuation may be transmitted through the backbone to its other side chains, which leads to a longitudinal correlation length about 260 Å.[33]

Thus, it can be seen that a long period exists in the polymers, and nematic polydomain network polymers can convert to monodomain smectic structures by stress induction.

CONCLUSION

In this study, we synthesized a series of side-chain liquid crystalline network polymers by reacting a liquid crystalline crosslinking agent, 4-hydroxy-4'-undecylenoyloxy-biphenyl-4-undecylenoyloxybenzoate (M-1) and a mesogenic monomer, 4-hydroxy-4'-allyloxybenzoyloxy-benzene-4-butylbenzoate (M-2) with PMHS. Light chemical crosslinking of the linear polymer with the mesogenic crosslinking agent did not markedly affect phase behavior. For P-2–P-8, the glass

transition temperature decreased for the plasticization of long alkyl chains in both ends of M-1. The isotropic temperature and mesomorphic temperature range slightly decreased with increasing the concentration of crosslinking units. The network polymers containing less than 15 mol % of the crosslinking units revealed elasticity and reversible phase transition, and nematic threaded texture. However, when the crosslinking density reached 21.6 mol %, the mesophase of polymer P-8 disappeared. X-ray analysis shows nematic polydomain network polymers can transform into smectic monodomain by stress induction, leading to the orientation formation macroscopically.

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