Synthesis and Phase Behavior of Nematic Liquid-Crystalline Elastomers Derived from Smectic Crosslinking Agent

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ABSTRACT: A mesogenic crosslinking agent M-1 was synthesized to minimize the perturbations of nonmesogenic crosslinking agent for liquid-crystalline elastomers. The synthesis of side-chain liquid-crystalline elastomers containing a rigid mesogenic crosslinking agent M-1 and a nematic monomer M-2 was described by a one-step hydrosilylation reaction. The chemical structures of the obtained monomers and network polymers were confirmed by Fourier transform infrared and ^{1}H-NMR 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 was discussed. The liquid-crystalline elastomers containing less than 15 mol % of the crosslinking units showed elasticity, reversible phase transition, and threaded texture. The experimental results demonstrated that isotropic temperature and liquid-crystalline range of polymers P-1–P-7 decreased a little as the concentration of crosslinking agent M-1 increased, and the use of mesomorphic crosslinking agent M-1 promotes the arrangement of liquid-crystalline units from P-1 to P-5. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1712–1719, 2005

Key words: liquid-crystalline; networks; elastomers; polysiloxane

INTRODUCTION

Crosslinked liquid-crystalline polymers may be divided into two categories, liquid-crystalline elastomers (LCEs) and liquid-crystalline thermosets. Slightly liquid-crystalline polymers exhibit both rubber-like elasticity and liquid-crystalline behavior between the glass transition temperature and liquid-crystalline to isotropic phase transition. Since the first synthesis in 1981,[1] LCEs have received a lot of interest, mainly owing to their special optical, mechanical, ferroelectric, and piezoelectric properties.[2–12] Mesogenic monomers containing two reactive groups, or prepolymers incorporating reactive groups, can be photo or thermally polymerized or crosslinked by one or two steps with the addition of a nonmesogenic crosslinking agent. At present, the backbone of side-chain LCEs is based on polysiloxane,[1,5–9,13–17] polyacrylate, and polymethacrylate.[18–26] In addition, LCEs were also extended to slightly crosslinked main-chain polymers and combined polymers.[19,27–30] The chemical composition of the LCEs, besides the crosslinking unit, is similar. Thus far, most crosslinking agents of LCEs are nonmesogenic flexible chain, 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 liquid-crystalline polymers. However, only a few articles reported that LCEs were synthesized with rigid rod-like crosslinking agents (mesogenic or nonmesogenic).[5,6,17,26]

In this paper, a divinyl smectic liquid-crystalline crosslinking agent (M-1) with a long alkyl chain on one end and a nematic monomer (M-2) were prepared. Liquid-crystalline elastomers were obtained by a one-step process, in which a liquid crystal monomer and a mesomorphic crosslinking agent M-1 were simultaneously attached to the polysiloxane through hydrosilylation reaction. We adopted a rigid divinyl mesomorphic monomer with a long alkyl chain in one end as the crosslinking agent of liquid-crystalline elas-
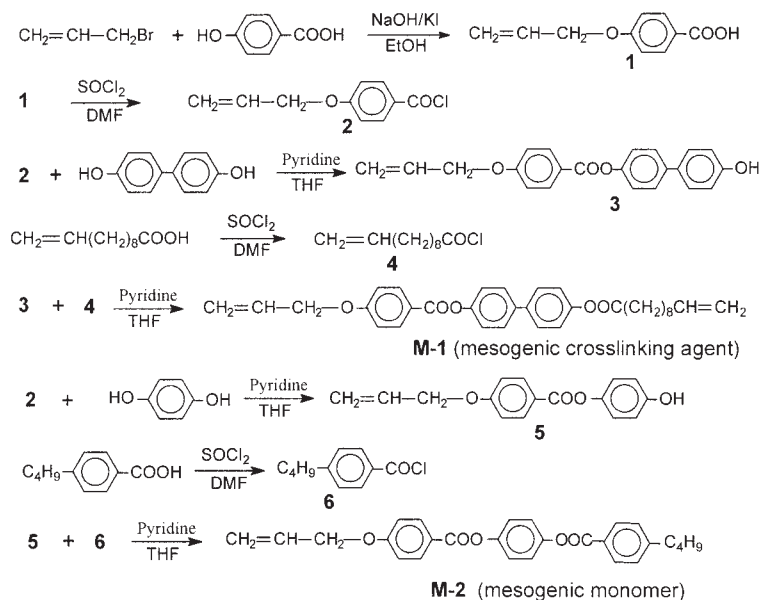
Scheme 1 Synthetic routes of monomers.

tomers for three aspects to be considered: (1) the divinyl group through hydrosilylation reaction with polysiloxane is for the formation of network;(2) the rigid mesomorphic group of crosslinking agent is employed to minimize the disturbance of LCEs;(3) a long alkyl chain on one end may permit free orientation of the mesomorphic crosslinking agent. In addition, the mesomorphic properties and phase behavior of monomers and polymers were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction measurement. The effect of the concentration of crosslinking units on phase behavior is discussed.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, M_n = 700–800) was purchased from Jilin Chemical Industry (China). 1-Bromopropene and undecylenic acid were purchased from Beijing Jinlong Chemical Reagent (China). 4-Hydroxybenzoic acid, p-dihydroxybenzene, 4,4'-dihydroxydiphenyl, and 4-butylbenzoic acid were purchased from Beijing Fuxing Chemical Industry (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 polymers and monomers in solid state were measured on a Nicolet 510 FTIR spectrometer via KBr

table. Phase transition temperatures and thermodynamic parameters were determined using a Netzsch DSC 204 at a heating rate of 20 °C/min under nitrogen atmosphere. A Leitz Microphot-FX 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 CuK_α (λ = 1.542 Å) radiation with a Rigaku powder diffractometer.

Synthesis of monomers

The synthesis of the liquid-crystalline crosslinking agent M-1 and the mesogenic monomer M-2 was carried out as shown in Scheme 1.

Synthesis of 4-hydroxy-4'-allyloxybenzoyloxydiphenyl undecylenate (M-1)

4-Allyloxybenzoic acid (**1**) and 4-allyloxybenzoyl chloride (**2**) were prepared according to our previous paper.[16] The synthesis of 4-hydroxy-4'-allyloxybenzoyloxy-diphenyl **3** was obtained as follows: diphenol (36 g, 0.2 mol) was dissolved in 75 mL of THF and 15 mL of pyridine, and then 4-allyloxybenzoyl chloride (**2**) (19.6 g, 0.1 mol) was slowly dropped into the above mixture at 0–5 °C. The mixture reacted at room temperature for 4 h; thereafter it was refluxed for 2 h, and it was poured into 1000 mL of water. The filtered precipitate was added to 500 mL of 5% NaOH aqueous solution for removing unreacted diphenol. The crude product was dried and recrystallized from
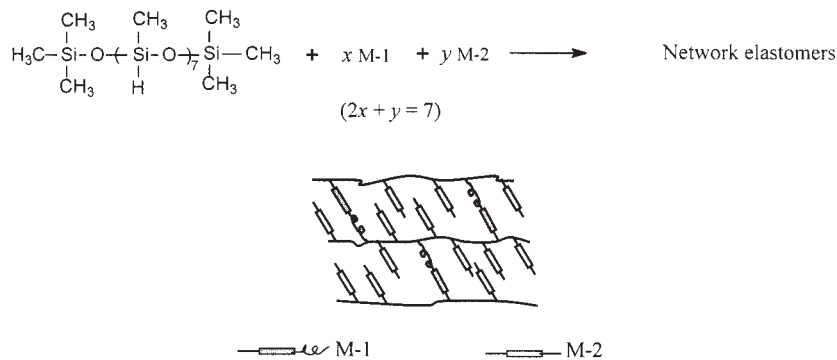
Scheme 2 Synthetic routes of liquid-crystalline elastomers.

mixed solvent of ethanol and acetone. White powder. (mp: 192–194 °C, yield: 51%). IR (KBr, ν/cm^{-1}): 3447 (-OH); 3078 (= C-H); 1706 (-ArCOOAr-); 1643 (C = C); 1605, 1578, 1511, 1497 (Ar); 1262 (C-O).

The mesomorphic crosslinking monomer M-1 was prepared by esterification reaction. 4-Hydroxy-4'-allyloxybenzoyloxydiphenyl (**3**) (20.8 g, 0.06 mol) was dissolved in 100 mL of THF and 10 mL of pyridine, and then undecylenoyl chloride (14.2 g, 0.07 mol) (**4**) was slowly dropped into the mixture at 0–5 °C. The mixture reacted at room temperature for 2 h and then was refluxed for 4 h. Afterward the mixture was precipitated with 1000 mL of water. The crude product was dried and recrystallized from ethanol. White powder: (mp: 91–92 °C, yield: 92%). IR (KBr, ν/cm^{-1}): 3071 (= C-H); 2921, 2849 (-CH$_2$-); 1729 (-ArCOOAr-); 1748 (-RCOOAr-); 1644 (C = C); 1607, 1497 (Ar); 1254 (C-O). ^{1}H-NMR (CDCl$_3$, δ/ppm) 1.33–2.06 [m, 14H, CH$_2$ = CH(CH$_2$)$_7$-CH$_2$COO-]; 2.55–2.60 [t, 2H, CH$_2$ = CH(CH$_2$)$_7$CH$_2$COO-]; 4.63–4.65 [d, 2H, CH$_2$ = CHCH$_2$O-]; 4.92–5.02 [m, 2H, CH$_2$ = CH(CH$_2$)$_7$CH$_2$COO-]; 5.32–5.48 [m, 2H, CH$_2$ = CHCH$_2$O-]; 5.76–5.87 [m, 1H, CH$_2$ = CH(CH$_2$)$_7$CH$_2$COO-]; 6.04–6.12 [m, 1H, CH$_2$ = CHCH$_2$O-]; 6.99–8.18 [m, 12H, Ar-H].

Synthesis of 4-hydroxy-4'-allyloxybenzoyloxybenzene 4-butylbenzoate (M-2)

The mesomorphic monomer M-2 was synthesized according to our previously reported paper.[31] White crystalline was obtained (mp: 135 °C, yield: 91%). IR (KBr, ν/cm^{-1}): 3076 (= C-H); 2963, 2856 (-CH$_2$-); 1736 (-ArCOOAr-); 1641 (C = C); 1607, 1577, 1510 (Ar); 1250 (C-O). ^{1}H-NMR (CDCl$_3$, δ/ppm): 0.93–0.98 [t, 3H, CH$_3$(CH$_2$)$_2$CH$_2$-]; 1.35–1.68 [m, 4H, CH$_3$(CH$_2$)$_2$CH$_2$-]; 2.69–2.74 [t, 2H, CH$_3$(CH$_2$)$_2$CH$_2$-]; 4.64–4.66 [d, 2H, CH$_2$ = CHCH$_2$O-]; 5.33–5.49 [m, 2H, CH$_2$ = CHCH$_2$O-]; 6.04–6.11 [m, 1H, CH$_2$ = CHCH$_2$O-]; 6.91–8.31 [m, 12H, Ar-H].

Synthesis of the elastomers

The liquid-crystalline elastomers were prepared according to Scheme 2 and Table I, in which liquid crystal monomer M-2 and a divinyl mesogenic crosslinking agent M-1 simultaneously were grafted to the highly flexible polysiloxane through hydrosilylation reaction. The same method was adopted for the synthesis of polymers P-1–P-8, so the synthesis of elastomer P-3 was given as an example.

TABLE I
Polymerization and Yield

| Polymer | Feed[a] | | | M-1[b] (mol%) | Yields (%) |
	PMHS (mmol)	M-1 (mmol)	M-2 (mmol)		
P-1	1	0.00	7.00	0.00	89
P-2	1	0.125	6.75	1.80	85
P-3	1	0.25	6.50	3.60	87
P-4	1	0.375	6.25	5.40	90
P-5	1	0.50	6.00	7.20	86
P-6	1	0.75	5.50	10.8	91
P-7	1	1.00	5.00	14.4	88
P-8	1	1.50	4.00	21.6	87

[a] PMHS, $n = 7$.
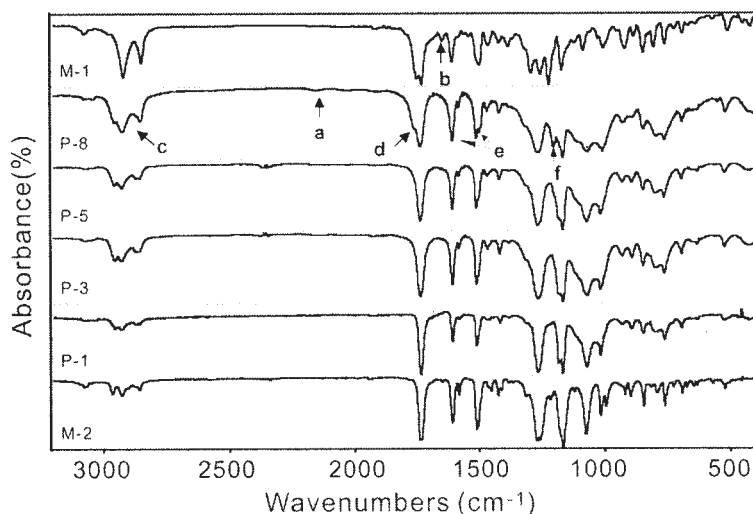[b] Molar fraction of monomer M-1 based on M-1 + M-2.

Figure 1 FTIR spectrum of monomers and elastomers.

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_2PtCl_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} disappeared. The elastomer was carefully deswollen with methanol and then dried under vacuum. IR (KBr, ν/cm^{-1}): 2924, 2853 (-CH_2-, -CH_3); 1759 (-RCOOAr-), 1735 (-ArCOOAr-); 1605, 1576, 1509, 1496 (Ar); 1200–1000 (Si-O-Si).

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of mesogenic crosslinking agent M-1, mesogenic monomer M-2 and some liquid-crystalline elastomers are presented in Figure 1. The FTIR spectrum of M-1 shows the characteristic absorbance peaks, respectively, corresponding to C-H stretching of vinyl at 3071 cm^{-1}, C = C of vinyl at 1643 cm^{-1}, C-H of methyl, methylene at 2921 and 2849 cm^{-1}, alkane ester group (-RCOOAr-) at 1748 cm^{-1} and aromatic ester (-ArCOOAr-) at 1729 cm^{-1}, aromatic C = C of diphenyl at 1607 and 1497 cm^{-1}, and C-H in-plane bending vibration of diphenyl rings at 1219 and 1169 cm^{-1}. In addition, M-2 monomer shows similar characteristic absorption bands, which corresponding to the ester group (-ArCOOCAr-) at 1736 cm^{-1} and C = C vibration of aromatic ring at 1607 and 1510 cm^{-1}.

As seen in Figure 1, the FTIR spectra of network liquid-crystalline polymers show the complete disappearance of the peaks for the Si-H stretching at 2160 cm^{-1} [Fig. 1(a)] and vinyl C = C stretching at about 1640 cm^{-1} [Fig. 1(b)] of the monomers. In addition,

with the increasing content of crosslinking agent M-1 from P-1 to P-8, C-H vibration of methyl, methylene [Fig. 1(c)] enhances and the obvious new peaks of the ester group (-RCOOAr-) of M-1 at 1759 cm^{-1} [Fig. 1(d)], C = C vibration at 1496 cm^{-1} [Fig. 1(e)], and C-H in-plane bending vibration 1201 cm^{-1} [Fig. 1(f)] of diphenyl rings of M-1 appear and increase, so we can conclude that successful incorporation of the monomers into polysiloxane was made as we expected.

Liquid-crystalline behavior analysis

Liquid-crystalline properties of the monomers M-1, M-2, and liquid-crystalline polymers P-1–P-8 were determined by DSC and POM. Thermal behavior determined by DSC was consistent with POM observation results.
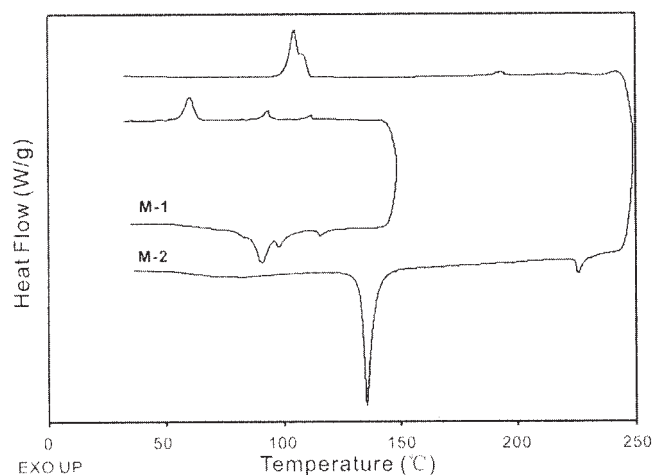

Figure 2 DSC thermograms of monomers.

TABLE II
Thermal Properties of Monomers

| Monomer	Phase transition temperatures[a] (°C) (Corresponding enthalpy changes in J/g) Heating / Cooling	Yield (%)	ΔT^b (°C)
M-1	K90.6(15.68)S_C97.8(2.92)S_A115.6 (1.16) I I111.7(1.70)S_A93.4(4.6)S_C60.0(20.8)K	92	25.0
M-2	K135.4(57.5)N 225.6 (3.9)I I193.4(2.1)N104.8(50.4) K	91	90.2

Note. 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.

Typical DSC curves of M-1 and M-2 are shown in Figure 2, and phase transition temperatures and corresponding enthalpy changes are listed in Table II.

DSC thermograms of M-1 present three endothermic peaks. Combined with POM micrograph [Fig. 3(a,b)] we can confirm that crystal to smectic C transition at
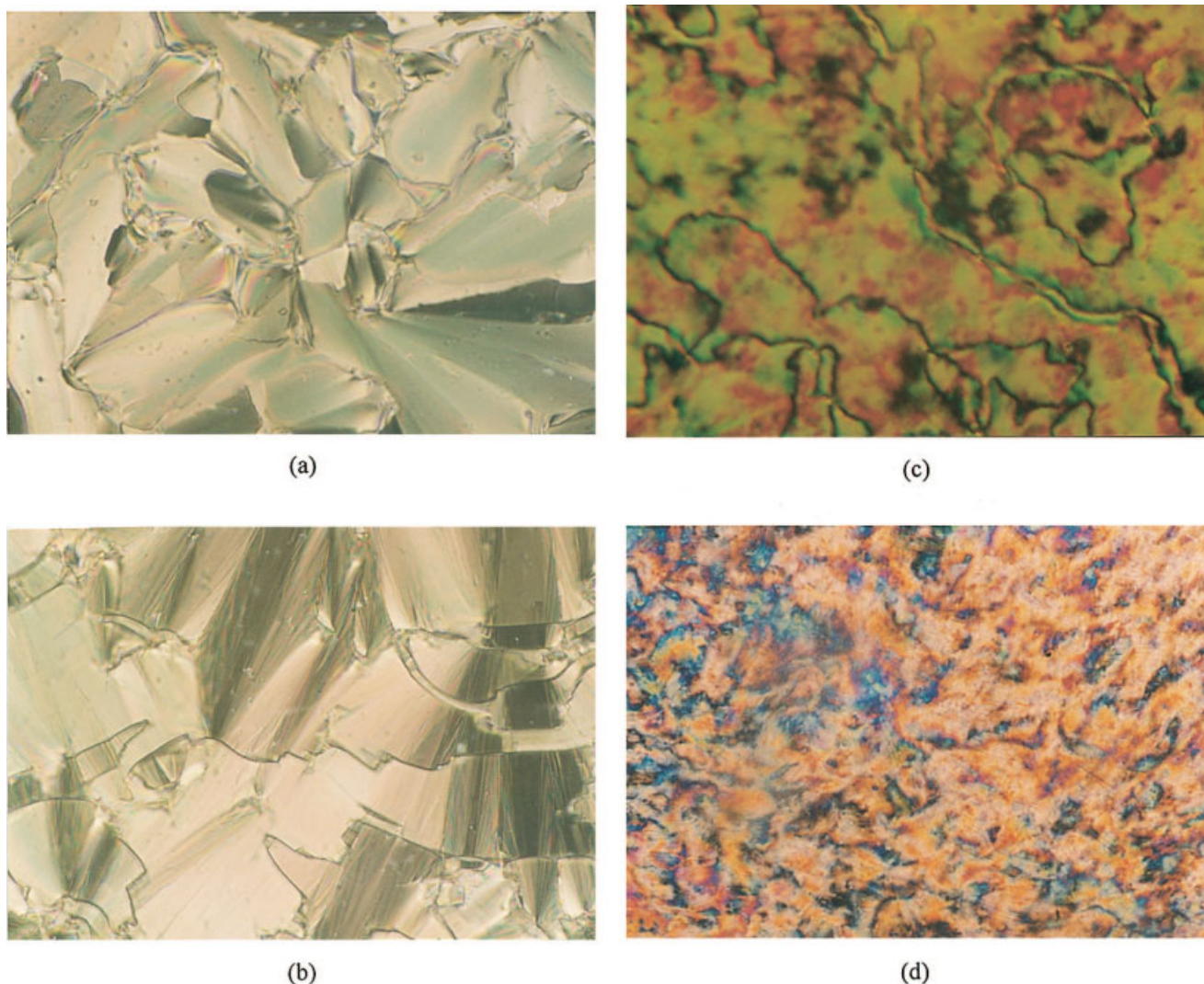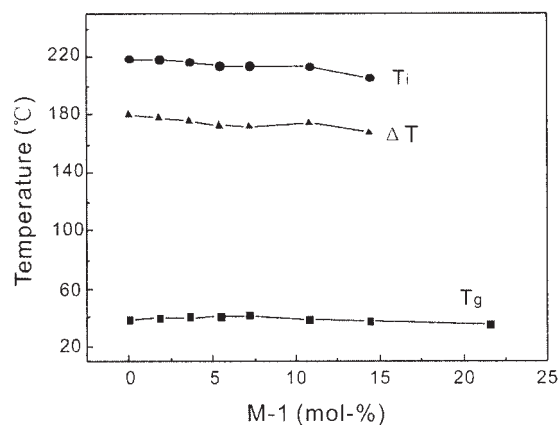

Figure 3 Optical polarizing micrographs of samples (200×): (a) smectic A texture of M-1 at 105 °C, (b) smectic C texture of M-1 at 70 °C, (c) threaded texture of M-2 at 175 °C, (d) thread texture of P-2 at 216 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
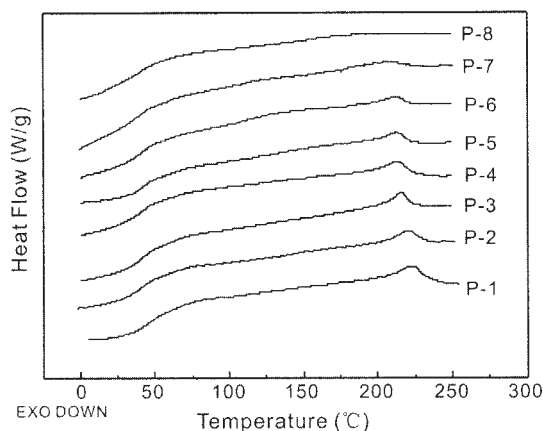
Figure 4 DSC thermograms of liquid-crystalline elastomers.

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

90.6 °C, smectic C to smectic A phase transition at 97.8 °C, and smectic A to isotropic transition at 115.6 °C. Figure 3(a,b) are polarized optical micrographs of M-1 on cooling course, which corresponds to focal conic texture smectic A at 105 °C and smectic C at 70 °C, respectively. In addition, DSC thermograms of M-2 showed two endothermic peaks, a melting transition at 135.4 °C and a nematic to isotropic phase transition at 225.6 °C on the heating course. The monomers display reversible phase transition on the heating or cooling course. A polarized micrograph of M-2 at 175 °C is shown in Figure 3(c), which is a typical nematic threaded texture.

As can be seen in Figure 4, network liquid-crystalline elastomers P-1–P-7 reveal a glass transition at low temperature and mesomorphic phase to isotropic transition at high temperature; however, polymer P-8 only shows glass transition and no liquid-crystalline to isotropic temperature is seen. The corresponding phase transition temperatures and enthalpy changes of the all polymers are listed in Table III. Light chemical crosslinking for P-2–P-7 did not remarkably influ-

ence the phase behavior, and only the phase transition temperature shifted a little; reversible phase transitions were observed because of the adequate motion and ready mesogenic orientation. However, high crosslinking has a strong effect on the phase behavior of polymer P-8. This could cause the mesomorphic phase to disappear due to depression of the high crosslinking on the liquid-crystalline order. Figure 5 shows the effect of the concentration of crosslinking units on phase behavior of liquid-crystalline elastomers.

For side-chain LCEs, 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 crosslinking agent similar to plasticization also affects T_g, which leads to decrease of T_g. At first, the crosslinking limit on the motion of chain segments is the main influence factor of T_g, which leads to T_g of polymers P-1–P-5 increases from 38.2 to 41.4 °C, and then T_g decreases from 39.0 °C for P-6 to 35.6 °C for P-8 due to plasticization of the flexible chain of M-1. Both effects together make the T_g of polymers P-1–P-8 change a little.

TABLE III
DSC and POM Results of Elastomers

Polymer	DSC				POM	
	T_g (°C)	T_i (°C)	ΔH_i (J/g)	ΔT^a (°C)	T_{cl}^b (°C)	T_{lc}^c (°C)
P-1	38.2	218.4	4.43	180.2	218	215
P-2	39.9	217.9	3.08	178.0	221	217
P-3	40.4	216.3	2.86	175.9	216	215
P-4	41.0	213.7	2.69	172.7	215	214
P-5	41.4	213.2	1.99	171.8	213	211
P-6	39.0	213.0	1.52	174.0	213	210
P-7	37.8	205.5	0.95	167.7	206	209
P-8	35.6	—	—	—	—	—

[a] Mesogenic temperature range (T_i–T_g).
[b] Temperature at which the birefringence disappeared completely.
[c] Temperature at which the mesogenic phase occurred.

For the network liquid-crystalline polymers chemical crosslinking agent also has an effect on the isotropic temperature (T_i). Commonly, the flexible alkane crosslinking agent acted as a diluent and led to decrease of T_i remarkably with increasing concentration of crosslinking agent. To reduce this effect on T_i, a mesomorphic crosslinking agent M-1 containing rigid core was adopted for the synthesis of liquid-crystalline elastomers. Compared with the absolute flexible crosslinking agent, the flexible chains on both ends of the mesogenic crosslinking agent have a very small effect on the T_i of liquid-crystalline elastomers. Just as we can see from Figure 4 and Table III, the T_i of polymers P-1–P-7 decrease a little. The same effect also makes the enthalpy changes (ΔH_i) decrease. As the mesogenic crosslinking agent M-1 increase from 0 to 14.4 mol %, T_i of the elastomers decreases from 218.4 to 205.5 °C and ΔH_i is reduced from 4.43 J g^{-1} for P-1 to 0.95 J g^{-1} for P-7. When the crosslinking density reaches 21.6 mol %, the T_i of P-8 disappears due to the depression of high crosslinking on the liquid-crystalline order.

During the heating and cooling cycles, homopolymer P-1 and liquid-crystalline elastomers P-2–P-7 show a nematic-threaded texture. A photomicrograph of P-2 at 216 °C is given in Figure 3(d) as an example. But P-8 only showed elasticity and no texture was observed; this is consistent with the result of DSC. Thus, through the observation of DSC and POM, when the concentration of the crosslinking agent is less than 15 mol % for P-1–P-7, the liquid-crystalline phase type did not change.

X-ray diffraction analysis

X-ray scattering has been used extensively to determine structural features of liquid-crystalline materials. The peaks ($1° < 2\theta < 3°$) in the small-angle X-ray scattering region reveal long-range order or laminated structure of liquid-crystalline polymer, but a broad peak ($16° < 2\theta < 21°$) at the wide-angle region shows short-range or lateral packing order of liquid-crystalline molecules. In general, the smectic liquid-crystalline phase shows sharp and strong peaks in the small-angle region, together with a broad peak in the wide-angle region. However, nematic and cholesteric liquid-crystalline phases only produce a broad peak in wide-angle region.

A sharp peak associated with the smectic layer in the small-angle region was not observed for the precursor P-1 and the synthesized elastomers. In the wide-angle scattering region, the elastomers show a amorphous diffractive peak at 20°, which could be attributed to the lateral spacing between the liquid-crystalline molecules. Figure 6 shows X-ray scattering curves of the synthesized polymers in the wide-angle region. The peak intensity increases from P-1 to P-5,
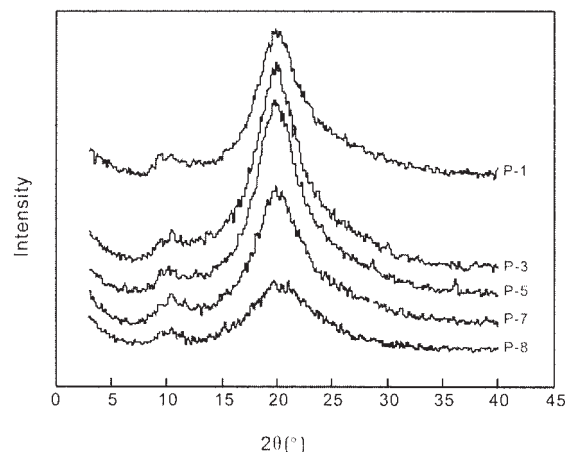
Figure 6　Wide-angle X-ray diffraction patterns of network polymers.

which reveals that crosslinking agent M-1 promotes the arrangement of mesomorphic unit and short-range order parameter increase. But, with further increasing content of crosslinking agent M-1, degree of orientation decreases due to the depression of the crosslinking on lateral packing order. The elastomer P-8 indicates a low-intensity broad peak at 20° for the disappearance of mesophase. So, the nematic phase structure of P-1–P-7 was confirmed by X-ray scattering, DSC, and POM results.

CONCLUSIONS

In this paper, we synthesized a series of side-chain liquid-crystalline network polymers containing liquid-crystalline crosslinking agent M-1 and mesogenic monomer M-2. Light chemical crosslinking of polymers with a mesogenic crosslinking agent did not markedly affect phase behavior. However, high crosslinking density depressed molecular motion and liquid-crystalline order, which leads to the disappearance of the mesomorphic phase of P-8. The liquid-crystalline elastomers P-2–P-7 containing less than 15 mol % of crosslinking agent revealed elasticity and reversible phase transition. Isotropic temperature and liquid-crystalline range decrease a little with increasing concentration of crosslinking agent. X-ray analysis shows that the use of mesomorphic crosslinking agent promotes the arrangement of liquid-crystalline units from P-1 to P-5.

References

1. Finkelmann, H.; Kock, H. J.; Macromo. Chem Rapid Commun 1981, 2, 317.
2. Meier, W.; Finkelmann, H., Makromol Chem Rapid Commun 1990, 11, 599.
3. Davis, F. G.; Mitchell, G. R. Polym Commun 1987, 28, 8.

4. Kaufhold, W.; Finkelmann, H.; Brand, H. R. Makromol Chem 1991, 192, 2555.
5. Zentel, R.; Gebhard, E. Macromol Chem Phys 2000, 201, 902.
6. Zentel, R.; Gebhard, E. Macromol Chem Phys 2000, 201, 911.
7. Vallerien, S. U.; Kremer, F. Makromol Chem Rapid Commun 1990, 11, 593.
8. Hirshchmann, H.; Finkelmann, H. J Phys II 1991, 1, 559.
9. Mauzac, M.; Nguyen, H. T. Chem Phys Lett 1995, 240, 461.
10. Brehmer, M.; Zentel, R. Liq Cryst 1996, 21, 589.
11. Symons, A. J.; Davis, F. J.; Mitchell, G. R. Polymer 1999, 40, 5365.
12. Kupfer, J.; Finkelmann, H. Macromol Rapid Commun 1991, 12, 717.
13. Twomey, C. J.; Blanton, T. N. Liq Cryst 1995, 19, 339.
14. Schatale, J.; Finkelmann, H. Mol Cryst Liq Cryst 1987, 142, 85.
15. Gleim, W.; Finkelmann, H. Makromol Chem 1987, 188, 1489.
16. Jia, Y. G.; Zhang, B. Y. J Appl Polym Sci 2002, 85, 1104.
17. Skupin, H.; Zentel, R. J. Macromo. Sci Phys 1999, B38, 709.
18. Mitchell, G. R.; Ahn, K. H. Polym Prep 1996, 48.
19. Zentel, R.; Reckert, G. Macromol Chem 1986, 187 1915.
20. Zentel, R. Liq Cryst 1986, 1, 589.
21. Davis, F. J.; Gibert, A. J Chem Soc Chem Commun 1986, 1333.
22. Mitchell, G. R.; Davis, F. J. Polymer 1987, 28, 639.
23. Andersson, H. Chem Phys Lett 1996, A33, 1427.
24. Trollsas, H. Macromolecules 1996, 29, 2590.
25. Trollsas, H. J Am Chem Soc 1996, 118, 8524.
26. Pfaffernoschke, M.; Rubner, J. Macromol Chem Phys 1998, 199, 2247.
27. Zentel, R.; Schmidt, G. F.; Meyer, J. Liq Cryst 1987, 2, 651.
28. Bualek, S.; Zentel, R. Macromol Chem 1988, 189, 791.
29. Bergmann, H. F.; Finkelmann, H. Macromol Rapid Commun 1997, 18, 353.
30. Donnio, B.; Finkelmann, H. Macromolecules 2000, 33, 7724.
31. Jia, Y. G.; Zhang, B. Y.; Tian, M.; Pan, W. J Appl Polym Sci 2004, 93, 1736.