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Preparation and properties of siloxane liquid crystalline elastomers with a mesogenic crosslinking agent

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A mesogenic crosslinking agent M-1 was synthesized to minimize the perturbations of non-mesogenic crosslinking agents in liquid crystalline elastomers. The synthesis of new side chain liquid crystalline elastomers containing the rigid mesogenic crosslinking agent M-1 and nematic monomer M-2 by a one-step hydrosilylation reaction is described. The chemical structures of the monomers and network polymers obtained were confirmed by FTIR and ^{1}H NMR spectroscopy. The mesomorphic properties and phase behaviour were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The influence of the crosslinking units on phase behaviour is discussed. Liquid crystalline elastomers containing less than 15 mol% of the crosslinking units showed elasticity, reversible phase transitions and a threaded texture. The experimental results demonstrated that the glass transition temperature of polymers P-1–7 increased with increasing concentration of crosslinking agent M-1; but the isotropic temperature and liquid crystalline range decreased slightly.

1. Introduction

Liquid crystalline polymers may be lightly crosslinked to form elastomers, called 'liquid crystalline elastomers' (LCEs). These LCEs exhibit both rubber-like elasticity and anisotropic liquid crystalline behaviour between the glass temperature and the liquid crystalline to isotropic phase transition. Since the first synthesis in 1981 [1], LCEs have received much attention in recent years, mainly owing to their special optical, mechanical, ferroelectric and piezoelectric properties [2–11]. One of their most remarkable characteristics is the ability to undergo a polydomain-to-monodomain transition; i.e. stress-induced macroscopic orientation leading to the formation of 'liquid single crystal elastomers' [12–14]. In this case, liquid crystal polymers can exhibit single crystal behaviour in their optical properties. Mesogenic monomers containing two reactive groups, or prepolymers incorporating reactive groups, can be photo or thermally polymerized or crosslinked in one or two steps with the addition of a non-mesogenic crosslinking agent.

At present, the backbone of side chain LCEs is based on polysiloxane [1, 5–9, 13, 15–18], polyacrylate and polymethacrylate [14, 19–26]; in addition, LCEs have been extended to slightly crosslinked main chain polymers and combined polymers [19, 27–30]. The chemical composition of the LCEs, apart from the crosslinking unit, is similar. Up to now, most LCE crosslinking agents have been non-mesogenic flexible chains, which may influence the mesophase properties in two ways. First, crosslinking units may act as non-mesogenic diluents, and bring disturbance to the liquid crystalline phase. Second, in a similar way, copolymerization with a non-mesogenic crosslinking agent leads to a marked downward shift in the clearing point, as increasing crosslinked proportions are added to a liquid crystalline polymer. However, there have been only a few reports of LCE synthesized with rigid rod-like crosslinking agents (mesogenic or non-mesogenic) [5, 6, 18, 26].

In this paper, we report the synthesis of a difunctional liquid crystal monomer as crosslinking agent, which may minimize perturbations to the liquid crystalline behaviour of LCEs. The LCEs were prepared by a one-step process in which monofunctional liquid crystal monomer and a bifunctional mesogenic crosslinking agent were simultaneously attached to the polysiloxane through a hydrosilylation reaction. The mesomorphic properties and phase behaviour were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The effect of

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the concentration of crosslinking units on phase behaviour is discussed.

2. Experimental

2.1. *Materials*

Polymethylhydrosiloxane (PMHS, $n=7$) was purchased from Jilin Chemical Industry Company (China). 1-Bromopropene was purchased from Beijing Jinlong Chemical Reagent Co., Ltd. (China). 4-Hydroxybenzoic acid, *p*-dihydroxybenzene, 4,4′-dihydroxydiphenyl and 4-butylbenzoic acid were purchased from Beijing Fuxing Chemical Industry Co. (China). Toluene used in the hydrosilylation reaction was first heated under reflux over sodium and then distilled. All other solvents and reagents were purified by standard methods.

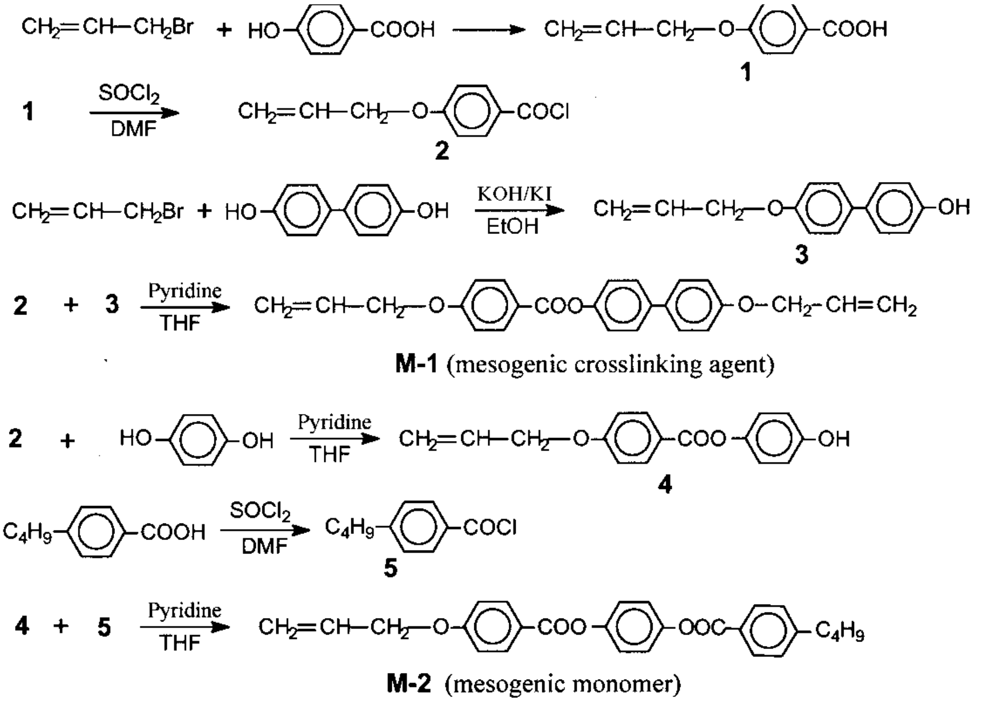
2.2. *Characterization*

Fourier transform infrared (FTIR) spectra of the synthesized polymers and monomers in the solid state were measured on a Nicolet 510 FTIR spectrometer. Phase transition temperatures and thermodynamic parameters were determined using a Netzsch DSC 204 at a heating rate of $20°\text{C}\,\text{min}^{-1}$ under nitrogen. A Leitz Microphot-FX polarizing optical microscope equipped with a Mettler FP 82 hot stage was used to observe visual textures and phase transition temperatures. XRD measurements were performed with a nickel-filtered CuK_α ($\lambda=1.542$ Å) radiation on a Rigaku powder diffractometer.

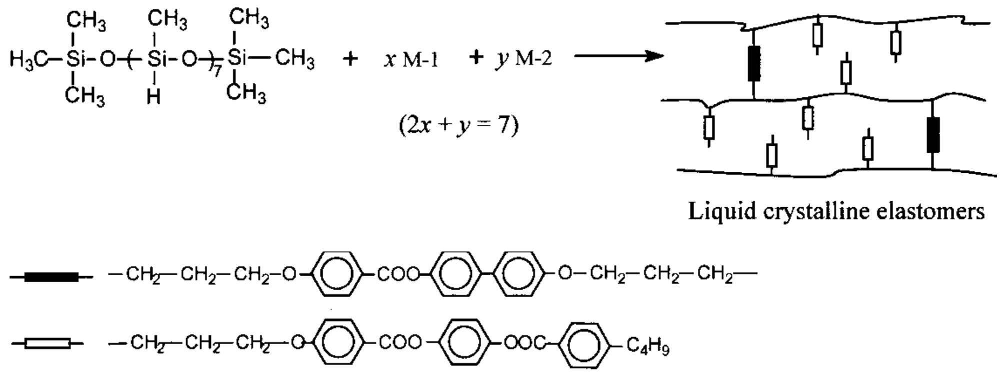
2.3. *Synthesis*

2.3.1. *Monomer synthesis*

The synthesis of liquid crystalline crosslinking agent M-1 and mesogenic monomer M-2 was carried out as shown in scheme 1. The mesogenic crosslinking agent 4-allyloxybenzoyloxy-4′-allyloxybiphenyl (M-1) was synthesized according to our previous paper [17]. The intermediate product of M-2, 4-hydroxy-4′-allyloxybenzoyloxybenzene **4** was prepared as previously reported [31]. The mesogenic monomer M-2 was synthesized as follows. 4-Hydroxy-4′-allyloxybenzoyloxybenzene (13.5 g, 0.05 mol) was dissolved in 30 ml of tetrahydrofuran (THF) containing 10 ml of pyridine; 0.05 mol 4-butylbenzoyl chloride was then added dropwise to the mixture at room temperature. After heating the mixture was at reflux for 4 h, a crude product was precipitated with water. This was purified by recrystallization from ethanol; yield 91%, m.p. 135°C. IR (KBr, ν/cm^{-1}): 3076 (=C–H); 2963, 2856 ($-CH_2-$); 1736 (–ArCOOAr–); 1641 (C=C); 1607, 1581, 1510 (Ar); 1250 (C–O). ^{1}H NMR ($CDCl_3$, δ/ppm): 0.93–0.98 [t, 3H, $-CH_2(CH_2)_2C\underline{H}_3$]; 1.35–1.68 [m, 4H, $-CH_2(C\underline{H}_2)_2CH_3$]; 2.69–2.74 [t, 2H, $-C\underline{H}_2(CH_2)_2CH_3$]; 4.64–4.66 [d, 2H, $CH_2=CHC\underline{H}_2O-$]; 5.33–5.49 [m, 2H,



Scheme 1. Synthetic routes for monomers.



Scheme 2. Synthetic route for liquid crystalline elastomers.

$C\underline{H_2}=CHCH_2O$–]; 6.04–6.11 [m, 1H, $CH_2=C\underline{H}CH_2O$–]; 6.91–8.31 [m, 12H, Ar–H].

2.3.2. *Elastomer synthesis*

The LCEs were prepared by attaching liquid crystal monomer M-2 and the bifunctional mesogenic crosslinking agent M-1 simultaneously to the highly flexible polysiloxane through a hydrosilylation reaction. The synthesis of the polymers was performed as indicated in scheme 2 and the table. The same method was adopted for the synthesis of polymers P-1–8. The synthesis of polymer P-3 is given as an example.

The monomers M-1, M-2, and PMHS were dissolved in dry toluene in the quantities shown in the table. 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 held at 65°C under nitrogen until the Si–H absorption peak of PMHS at 2160 cm^{-1} disappeared. The polymer was obtained by precipitation with methanol, and then dried under vacuum. IR (KBr, ν/cm^{-1}): 2924, 2853 (–CH_2–, –CH_3); 1735 (C=O); 1605, 1581, 1510 (Ar); 1200–1000 (Si–O–Si).

3. Results and discussion

3.1. *FTIR analysis*

The FTIR spectra of mesogenic crosslinking agent M-1, mesogenic monomer M-2 and some elastomers are presented in figure 1. Due to the analogous structure of M-1 and M-2, the monomers show similar characteristic absorption bands, on the whole, which are: ester group near 1730 cm^{-1} (–ArCOOAr–); alkene

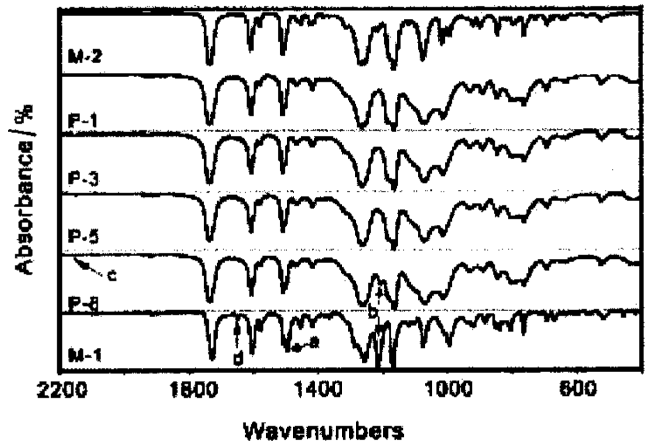


Figure 1. FT-IR spectrum of monomers and elastomers.

Table. Polymerization and thermal analysis results for the polymers.

	Feed					DSC			
Polymer	PMHS/mmol	M-1/mmol	M-2/mmol	M-1[a]/mol%	Yield/%	T_g/°C	T_i/°C	ΔH_i/J g^{-1}	ΔT^b/°C
P-1	1	0.00	7.00	0.00	89	38.2	218.4	4.43	180.2
P-2	1	0.125	6.75	1.80	85	37.6	217.5	3.91	179.9
P-3	1	0.25	6.50	3.60	87	39.3	215.2	3.65	175.9
P-4	1	0.375	6.25	5.40	91	40.1	213.8	2.43	173.7
P-5	1	0.50	6.00	7.20	83	41.2	212.8	2.35	171.6
P-6	1	0.75	5.50	10.8	87	42.9	209.7	2.10	166.8
P-7	1	1.00	5.00	14.4	84	46.1	208.1	1.47	162.0
P-8	1	1.50	4.00	21.6	83	53.7	—	—	—

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

[b] Mesomorphic temperature ranges (T_i–T_g).

C=C stretching near 1640 cm^{-1}; C=C aromatic ring vibration near 1605, 1581, 1508 cm^{-1}; and C–H in-plane bending vibrations at 1166, 1074 cm^{-1}. However, for the diphenyl structure of M-1, additional absorbance peaks are observed at 1495 cm^{-1} (a) and 1213 cm^{-1} (b), due to C=C aromatic ring vibration and C–H in-plane bending vibration respectively. The two additional peaks of M-1, as compared with M-2, were used to reflect all these changes with crosslinking agent M-1 increasing from P-1 to P-8, and provide an effective method for verification in the synthesis of all the polymers.

From figure 1, the successful incorporation of the monomers into polysiloxane is indicated by: (i) the disappearance of the peaks for the Si–H stretching at 2160 cm^{-1} (c) and vinyl C=C stretching about 1640 cm^{-1} (d) of the monomers; (ii) the increase of M-1 diphenyl peaks near 1495 cm^{-1} (a) and 1213 cm^{-1} (b), with the increasing content of crosslinking agent M-1 from P-1 to P-8.

3.2. *Liquid crystalline behaviour*

The liquid crystalline properties of monomers M-1, M-2 and polymers P-1–8 were determined by DSC and POM. Thermal behaviour determined by DSC was consistent with POM observations.

Typical DSC curves for M-1 and M-2 are shown in figure 2; the mesogenic properties of crosslinking agent M-1 were discussed in a previous paper [17]. M-1 showed two endothermic peaks on heating, corresponding to a crystal–melting transition at 141.5°C and a mesogenic–isotropic transition at 238.8°C. Monomer M-2 was a typical nematic; it showed two endothermic peaks on heating, a melting transition at 135.4°C and a nematic-to-isotropic transition at 225.6°C. The monomers display reversible phase transitions on heating and cooling. A polarizing micrograph of M-2 at 175°C is shown in figure 3 (*a*), indicating a nematic threaded texture.

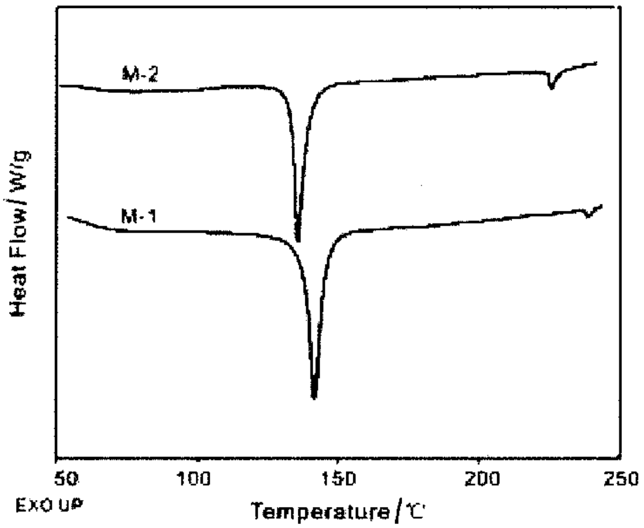
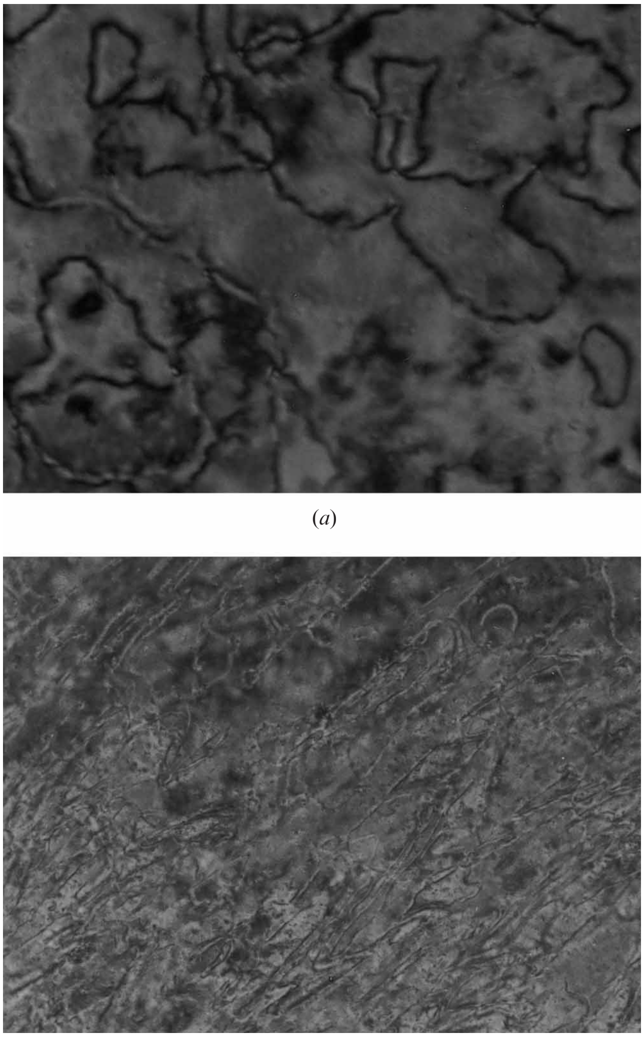


Figure 2. DSC thermograms of monomers M-1 and M-2.



(*a*)

(*b*)

Figure 3. Polarizing optical micrographs: (*a*) threaded texture of M-2 at 175°C; (*b*) threaded texture of P-3 at 202°C (200 ×).

DSC thermograms for polymers P-1–8 are shown in figure 4, and thermal results of the synthesized polymers are summarized in the table. The liquid crystalline polymers show LC behaviour only over a restricted temperature range, with an upper limit set by the mesogenic–isotropic transition temperature (T_{i}) and a lower limit set by the glass transition (T_{g}). As can be seen from the table and figure 4, light crosslinking has no remarkable influence on the phase behaviour of the liquid crystalline elastomers; no difference is observed

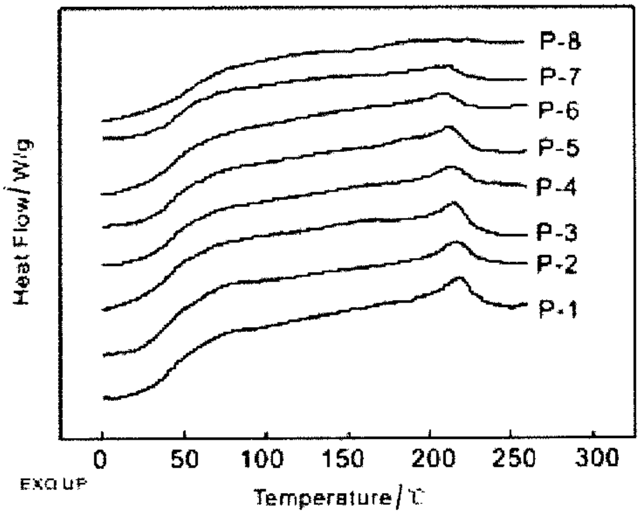


Figure 4. DSC thermograms for the liquid crystalline elastomers.

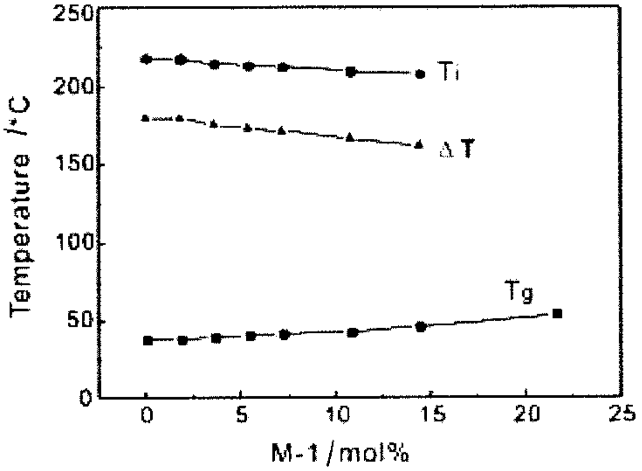


Figure 5. Effect of M-1 concentration on the phase transition temperatures of the elastomers.

in the shapes of DSC curves of linear and crosslinked polymers, and the phase transition temperature of lightly crosslinked LC polymers is shifted by only $\pm 10°C$. However, higher crosslinking has a stronger effect on the phase behaviour of the LCEs; this could cause the mesophase to disappear due to the inhibiting effect of high crosslinking on the liquid crystalline order. Thus, for network polymer P-8 only the glass transition is observed in the DSC curve, and no liquid crystal–isotropic phase transition.

The glass transition temperature (T_g) is affected by polymer backbone, the length of flexible chain of the monomer and the crosslinking density. In general, crosslinking imposes additional constraints on the motion of chain segments, which causes T_g to increase; but this effect is small for the lightly crosslinked elastomers. On the other hand, the flexible chain of the crosslinking agent, similar to plasticization, will cause a decrease in T_g. Because of the short flexible chain at both ends of M-1, the plasticization effect is minor. So, this effect leads to a T_g of polymer P-2 lower than precursor polymer P-1. With the increase in crosslinking agent M-1, the influence of crosslinking becomes more significant than plasticization by the flexible chain, and T_g of the elastomers rises. For P-2–8, when the concentration of the crosslinking agent M-1 increased from 1.8 to 21.6 mol%, T_g increased from 37.6 to 53.7°C. Figure 5 shows the effect of the concentration of crosslinking agent on phase behaviour of the LCEs.

The crosslinking agent also influences the isotropic temperature of LCEs in two respects. On the one hand, the flexible crosslinking chains act as a diluent, leading to a decrease of T_i. On the other hand, the crosslinking agent containing a rigid core may either promote the formation of a mesophase or produce a perturbation in the arrangement of liquid crystalline order; as a result, the former will make T_i increase, but the latter causes a reverse effect. For the short flexible chain of the mesogenic crosslinking agent M-1 the effect of diluent on T_i is small, but it limits the orientation of the mesogenic core of M-1 and at the same time affects the orientation of the mesogenic unit of M-2. As seen in figure 5, T_i of elastomers P-1–7 reveals a downtrend. As the mesogenic crosslinking agent M-1 increases from 0 to 14.4 mol%, T_i of the elastomers decreases from 218.4 to 208.1°C and the enthalpy changes (ΔH_i) decrease from 4.43 J g^{-1} for P-1 to 1.47 J g^{-1} for P-7. When the crosslinking density reaches 21.6 mol%, T_i of P-8 disappears due to the inhibiting effect of high crosslinking on the liquid crystalline order. As for the influence of crosslinking density on the downtrend of T_i, the mesogenic crosslinking agent is much smaller than the non-mesogenic crosslinking agent. In addition, as the concentration of the crosslinking agent M-1 increases, the mesomorphic temperature range (ΔT) of the LCEs also decreases slightly.

During the heating and cooling cycles, homopolymer P-1 and elastomers P-2–7 show a nematic-threaded texture, but with an increasing crosslinking degree this threaded texture became unclear. A photomicrograph of P-3 at 202°C is shown in Figure 3(*b*) as an example. P-8 only showed elasticity and no texture was observed; this is consistent with the DSC results. Thus, from DSC and POM observations, when the concentration of the crosslinking agent is less than 15 mol% for P-1–7, the liquid crystalline phase type did not change and the phase transition temperature was shifted only slightly.

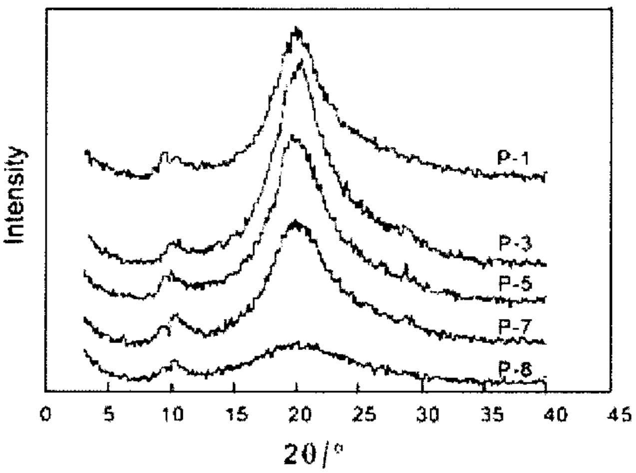


Figure 6. Wide-angle X-ray diffraction patterns of network polymers.

3.3. *X-ray diffraction*

X-ray scattering has been used extensively to determine the structural features of liquid crystalline materials. In general, sharp and strong peaks at low angle ($1° < 2\theta < 3°$) appear in the small angle X-ray scattering (SAXS) region only for smectic LC phases, revealing long-range order or a laminated structure of the molecules. In addition, a broad peak at wide angle ($16° < 2\theta < 21°$) is observed for nematic, smectic and cholesteric liquid crystalline phases, revealing short-range or lateral packing order of the molecules. A sharp peak associated with smectic layers in the small angle region was not observed for the precursor P-1 or the elastomers. In the wide angle scattering region, the polymers show two amorphous diffractive peaks, at 20° ($d_1 \approx 4.4$ Å) and 11° ($d_2 \approx 9$ Å, $2d_1$), which could be attributed to the lateral spacing between the liquid crystalline molecules. Figure 6 shows X-ray scattering curves of elastomers at the wide angle. With increasing content of crosslinking agent M-1, polymer P-8 indicates a low intensity broad peak at 20° due to the inhibiting effect of high crosslinking on the lateral packing order of the molecules. Thus, the nematic phase structure of P-1–7 was confirmed by X-ray scattering, DSC and POM results.

4. Conclusion

This paper describes the preparation of side chain liquid crystalline elastomers containing liquid crystalline crosslinking agent M-1 and mesomorphic monomer M-2. Light crosslinking has no remarkable effect on the phase behaviour of the LCEs, and no difference is observed in the shapes of DSC curves of the linear and the crosslinked polymers; the phase transition temperature of lightly crosslinked liquid crystal polymers is shifted by ±10°C. LCEs P-2–7 containing less than 15 mol% of crosslinking agent exhibited reversible phase transitions and nematic textures on heating or cooling. Compared with LCEs containing non-mesogenic crosslinking agents, the liquid crystalline crosslinking agent only causes a perturbation of the mesophase arrangement. For elastomers P-2–7, the isotropic temperature and liquid crystalline range decrease slightly with increasing concentration of the mesogenic crosslinking agent. The nematic phase structure of P-1–7 was confirmed by XRD, DSC and POM.

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