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ORIGINAL CONTRIBUTION

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Synthesis and properties of cholesteric liquid crystalline elastomers

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Abstract The synthesis of new side-chain cholesteric liquid crystalline elastomers, containing the flexible non-mesogenic crosslinking agent M-1 and the cholesteric monomer M-2, is described by a one-step hydrosilication reaction. The chemical structures of the monomers and network polymers obtained were confirmed by FT-IR spectroscopy. Their mesogenic 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 network polymers showed elasticity, reversible phase transitions, and cholesteric Grandjean texture. The experimental results demonstrated that the glass transition temperatures and isotropization temperatures of network elastomers decreased as the concentration of crosslinking units was increased, but the cholesteric phase was not disturbed.

Keywords Liquid crystalline · Elastomers · Crosslinking · Polysiloxane

Introduction

Recently, cholesteric liquid crystalline networks (Ch LCNs) have attracted considerable interest because of the special properties of liquid crystalline network polymers and optical characteristics of cholesteric liquid crystals [1, 2, 3, 4]. ChLCNs can be divided into two categories according to their crosslinking density: highly crosslinked cholesteric liquid crystalline thermosets (ChLCTs) and lightly crosslinked liquid crystalline elastomers (ChLCEs). In the last decade, ChLCTs have been extensively investigated because the helical structure of the cholesteric phase is permanently fixed and so its optical properties are temperature independent [5, 6, 7, 8, 9, 10]. Moreover, ChLCTs are capable of forming a stable Grandjean texture with selective reflection of visible light. ChLCTs are prepared by photocrosslinking of cholesteric liquid crystalline polymers [6, 7, 8, 9], and can also be obtained via thermal or chemical crosslinking of cholesteric mixtures containing bifunctional nematic and chiral monomers. At present, polyexpoxides [10, 11], polyacrylates [5], polymethacrylates [6], and polyvinylethers [12] are usually used for ChLCTs.

Contrary to ChLCTs, ChLCEs combine the basic features of elastomers with properties of cholesteric liquid crystals. Therefore, ChLCEs not only show entropic elasticity, but they also show a reversible phase transition during heating and cooling cycles. LCEs exhibit exceptional physical properties, which cannot be observed in isotropic elastomers. Compared to nematic elastomers, networks containing a chiral side group were shown to exhibit piezoelectric and nonlinear optical activity in the cholesteric and smectic C^* phase because of their helicoidal superstructures. Actually, it has been proved that a piezoelectric voltage occurs under deformation of a cholesteric elastomer. The piezoelectricity of LCE occurs in the non-crystalline state, and due to the "soft" Young-modulus of LCEs, a completely new type of piezoelectric sensor may be possible [13]. However, to the best of our knowledge, research on ChLCEs is rarely reported [14, 15, 16, 17, 18]. Therefore, it is both necessary and useful to synthesize various kinds of side chain ChLCEs in order to explore their potential applications.

In this paper, the synthesis of a side chain ChLCE, containing cholesteryl 4-allyloxybenzoate as mesogenic unit M-2 and flexible 1,6-hexanediol diundecylenate M-1 as crosslinking units, was prepared in one step where the mesogenic monomer and crosslinking agent were simultaneously attached to the polysiloxane through hydrosilication reaction. Three aspects of adopting a flexible crosslinking agent were considered: 1) development of networks; 2) the T_g of cholesteric polymers is usually high, so a flexible crosslinking agent and siloxane could lower the T_g; 3) this technique may not disturb the cholesteric liquid crystalline order. The mesogenic 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 crosslinking units on phase behavior and liquid crystalline order is discussed in detail.

Experimental

Materials

Polymethylhydrosiloxane (PMHS, $n = 7$) was purchased from Jilin Chemical Industry Company (China). 1-Bromopropene and undecylenic acid were purchased from Beijing Jinlong Chemical Reagent Co., Ltd. (China). Cholesterol was purchased from Henan Xiayi Medical Co. (China). 4-Hydroxybenzoic acid and 1,6-hexanediol were purchased from Beijing Fuxing Chemical Industry Co. (China). Toluene used in the hydrosilication reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

Characterization

Fourier Transform Infrared (FT-IR) spectra of the synthesized polymers and monomers in the solid state were measured on a Nicolet 510 FT-IR spectrometer via KBr. Phase transition temperatures and thermodynamic parameters were determined using a TA 2910 DSC 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 the 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 source and a Rigaku powder diffractometer.

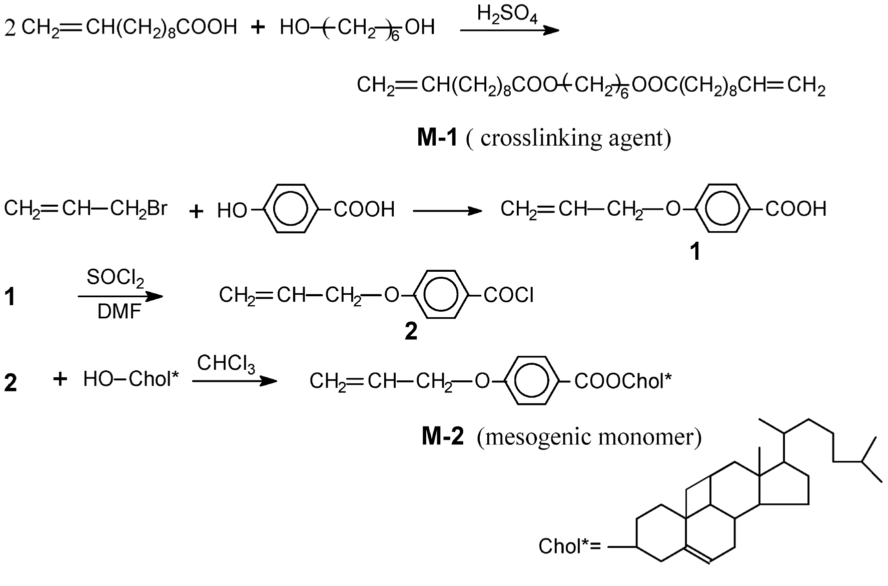
Synthesis of monomers

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

Synthesis of 1,6-hexanediol diundecylenate (M-1)

Undecylenic acid 22.08 g (0.12 mol) and 5.9 g (0.05 mol) of 1,6-hexanediol were dissolved in 30 ml benzene, and then 1 ml concentrated sulfuric acid was added. After the mixture was mixed uniformly, it was refluxed for 8 h, and the mixture was poured into 200 ml of water. After removing the water layer, the oil layer was neutralized with 2% $NaHCO_3$ to pH 7, washed several times with distilled water, and dried with Na_2SO_4. Then the distillate of crude product was collected at 175 °C under 3 mm Hg pressure. Transparent liquid was obtained (yield: 79%). IR (KBr, ν/cm^{-1}): 3076 (=C–H); 2928, 2854 (-CH$_2$-); 1742 (-COOC-); 1640 (C=C); 1237, 1163 (C–O).

Scheme 1 Synthetic routes for monomers



Synthesis of cholesteryl 4-allyloxybenzoate (M-2)

4-Allyloxybenzoic acid and 4-allyloxybenzoyl chloride were prepared according to our previous paper [19]. And 19.3 g (0.05 mol) cholesterol was dissolved in 80 ml of chloroform, and then 0.05 mol 4-allyloxybenzoyl chloride 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 cool ethanol, and filtered. The crude product was purified by recrystallization from ethanol. White crystalline was obtained (mp: 107 °C, yield: 90%). IR (KBr, ν/cm^{-1}): 3086 (=C–H); 2931, 2884, 2867 (-CH$_2$-); 1706 (-COO-); 1641 (C=C); 1608, 1580, 1511 (Ar); 1277, 1258 (C–O).

Synthesis of the elastomers

LCEs were prepared by a graft reaction, in which the crosslinking agent M-1 and the mesogenic monomer M-2 were simultaneously attached to the highly flexible polysiloxane via a hydrosilication reaction.

The synthesis of the polymers was performed according to Scheme 2 and Table 1. For the synthesis of polymers P-1~P-8, the same method was adopted. The synthesis of polymer P-3 is 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_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 elastomers were carefully deswollen with methanol, and then dried under vacuum. IR (KBr, ν/ cm^{-1}): 2934, 2866 (-CH$_2$-, -CH$_3$); 1736, 1712 (C=O); 1607, 1581, 1510 (Ar); 1273, 1254 (C–O); 1200~1000 (Si–O–Si).

Results and discussion

FT-IR analysis

The FT-IR spectra of crosslinking agent M-1, mesogenic monomer M-2 and some elastomers are shown in Fig. 1. The FT-IR spectra of M-1 showed the characteristic absorption peaks as follows: 3076 cm^{-1} (=C–H); 2928 cm^{-1}, 2854 cm^{-1} (-CH$_2$-); 1742 cm^{-1} (-COOC-); 1640 cm^{-1} (C=C); 1495 cm^{-1} C–H bending vibration of CH$_2$; 1237, 1163 (C–O). In addition, except for similar absorption at 3086, 2931, 2884, 2867 cm^{-1} due to alkenyl and methylene, the FT-IR spectra of M-2 shows characteristic absorption at 1706 cm^{-1} from the ester group (-ArCOOC), and at 1608, 1580, 1511 cm^{-1} due to absorption from benzene.

FT-IR can provide an effective method of verification during the synthesis of all compounds, and it can be used to monitor changes with the increase of crosslinking agent M-1 from P-1 to P-8. As seen in Fig. 1, the polymers show characteristic absorption at 1736 cm^{-1} and 1712 cm^{-1} from the ester group, at 1608, 1580, 1511 cm^{-1} from benzene, and at 1200~1000 cm^{-1} from the Si–O–Si group. Noting the increasing content of crosslinking agent M-1 from P-1 to P-8, then from the disappearance of the peaks due to Si–H stretching at 2160 cm^{-1} (a), C–H at 3076 cm^{-1} (b) and C=C of the vinyl group of the monomers at 1640 cm^{-1} (c), as well as

Scheme 2 Synthetic routes for network liquid crystalline polymers

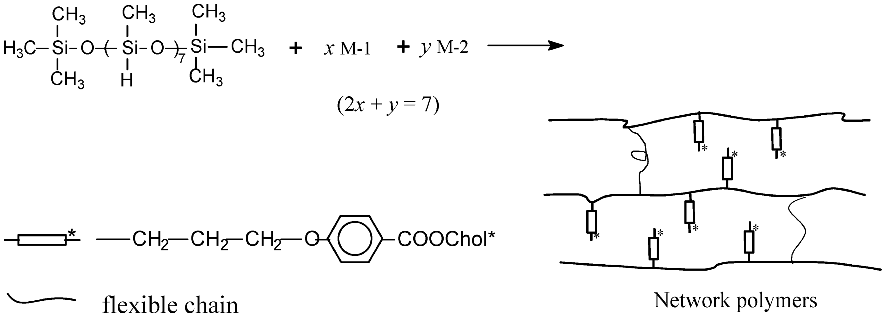


Table 1 Polymerization and thermal analysis results for polymers

Polymer	Feed			M-1[a] (mol%)	Yield (%)	DSC[b]			
	PMHS (mmol)	M-1 (mmol)	M-2 (mmol)			T_g (°C)	T_i (°C)	ΔT (°C)	T_d (°C)
P-1	1	0.00	7.00	0.00	89	73.05	276.07	203.02	323.97
P-2	1	0.125	6.75	1.80	85	62.86	268.59	205.73	327.50
P-3	1	0.25	6.50	3.60	87	59.59	251.01	191.42	324.79
P-4	1	0.375	6.25	5.40	91	58.78	247.00	188.22	324.87
P-5	1	0.50	6.00	7.20	83	57.37	239.21	181.84	330.24
P-6	1	0.75	5.50	10.8	87	54.97	227.68	172.71	326.12
P-7	1	1.00	5.00	14.4	84	50.34	211.09	160.75	326.53
P-8	1	1.50	4.00	21.6	83	40.95	171.82	130.87	325.71

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

[b] T_g: glass-transition temperature; T_i: mesogenic-to-isotropic temperature; $\Delta T = T_i - T_g$; T_d: the temperature at which 5% mass loss occurred

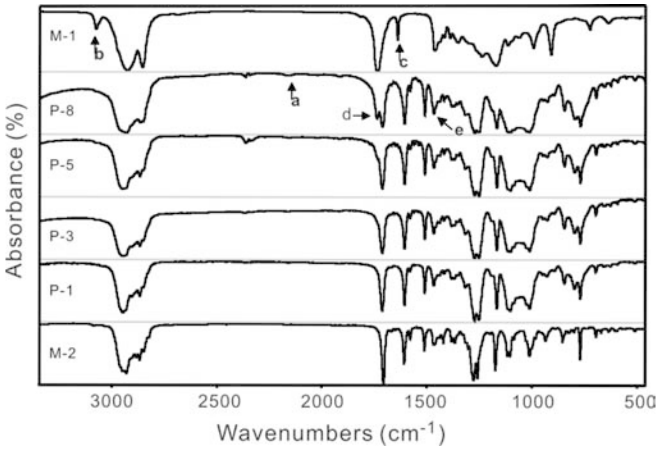


Fig. 1 FT-IR spectrum of monomers and polymers

the appearance of an obvious new peak at 1736 cm^{-1} (d) of ester group of M-1 and the increase of the C–H bending vibration of M-2 at 1467 cm^{-1} (e), we can conclude that we have successful incorporation of the monomers into polysiloxane as we expected.

Liquid crystalline behavior

Liquid crystalline properties of the monomer M-2 and polymers P-1 to P-8 were determined by DSC and POM. The thermal behavior determined by DSC was consistent with POM observation results.

Typical DSC curves of cholesteric mesogenic monomer M-2 are shown in Fig. 2. M-2 showed two endothermic peaks on the heating course, which correspond to the crystal-to-melting transition at 107.1 °C and the mesogenic-to-isotropic phase transition at 225.3 °C. The liquid crystalline range is therefore 118.2 °C. By observation with POM, the monomer M-2 revealed an oily streak texture in its cholesteric phase and the birefringence totally disappeared at 226 °C. However, over the whole cooling course M-2 showed focal conic texture of cholesteric liquid crystals. The photomicrographs of M-2 are shown in Fig. 3a and b; Fig. 3a is an oily streak at 173 °C on the heating course, and Fig. 3b is focal conic at 190 °C on the cooling course.

DSC thermograms of polymers P-1 to P-8 are shown in Fig. 4, and the thermal results of synthesized polymers are summarized in Table 1. Apart from some shift in the phase-transition temperatures, all curves are similar, showing a glass transition (T_g) at low temperature and a mesogenic-isotropic transition (T_i) at higher temperatures. Figure 5 shows the effect of the concentration of crosslinking units on the phase behavior of networks.

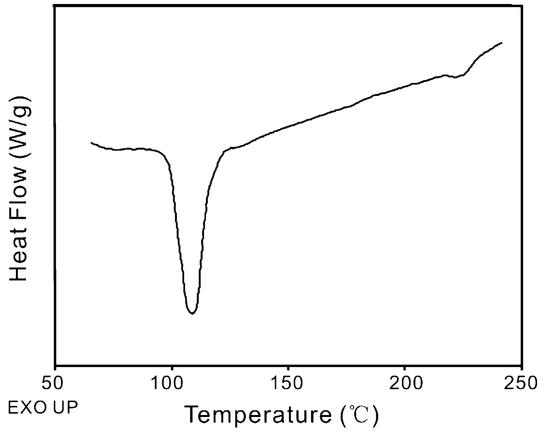


Fig. 2 DSC thermograms of mesogenic monomer M-2

For side-chain ChLCEs, the glass transition temperature (T_g) is influenced by the polymer backbone, mesogenic group, flexible spacer length and crosslinking density. In general, chemical crosslinking imposes additional constraints on the motion of chain segments, and makes T_g increase. However, for the homopolymer with a rigid mesogenic unit in the side-chain, the flexible crosslinking chain is similar to the plasticizer, and this will lead to a decrease in T_g. So, as the crosslinking agent of M-1 increases from P-1 to P-8, the T_g of network polymers decreases, and when the concentration of crosslinking M-1 units increases from 0 to 21 mol%, T_g drops from 73.05 to 40.95 °C.

As for the mesogenic to isotropic phase transition (T_i), in a similar way to T_g, chemical crosslinking with the non-mesogenic crosslinking agent may act as a diluent, which makes T_i fall as increasing proportions of non-mesogenic crosslinker are added to the liquid-crystalline polymers [20]. As shown in Figs. 4 and 5, as crosslinking density increases from P-1 to P-8, the T_i of the elastomers becomes unclear, and when the density of crosslinking M-1 units increases from 0 to 21 mol%, the T_i of the elastomers drops from 276.07 °C to 171.82 °C.

The temperature between the glass transition temperature (T_g) and liquid-crystalline to isotropic phase transformation (T_i) is the mesogenic range (ΔT), which is therefore determined by T_g and T_i. ΔT of the elastomers decreases from 203 °C for P-1 to 130 °C for P-8. In the liquid crystal range the liquid crystalline polymers P-2 to P-8 exhibit both elasticity and anisotropic liquid-crystalline behavior; moreover, with density increasing, the network polymers become more elastic. In addition, by the POM analysis, the homopolymer P-1 and the network elastomers P-2 to P-8 exhibited cholesteric Grandjean texture, but as crosslinking degree increased, the Grandjean texture became more unclear. A photo-

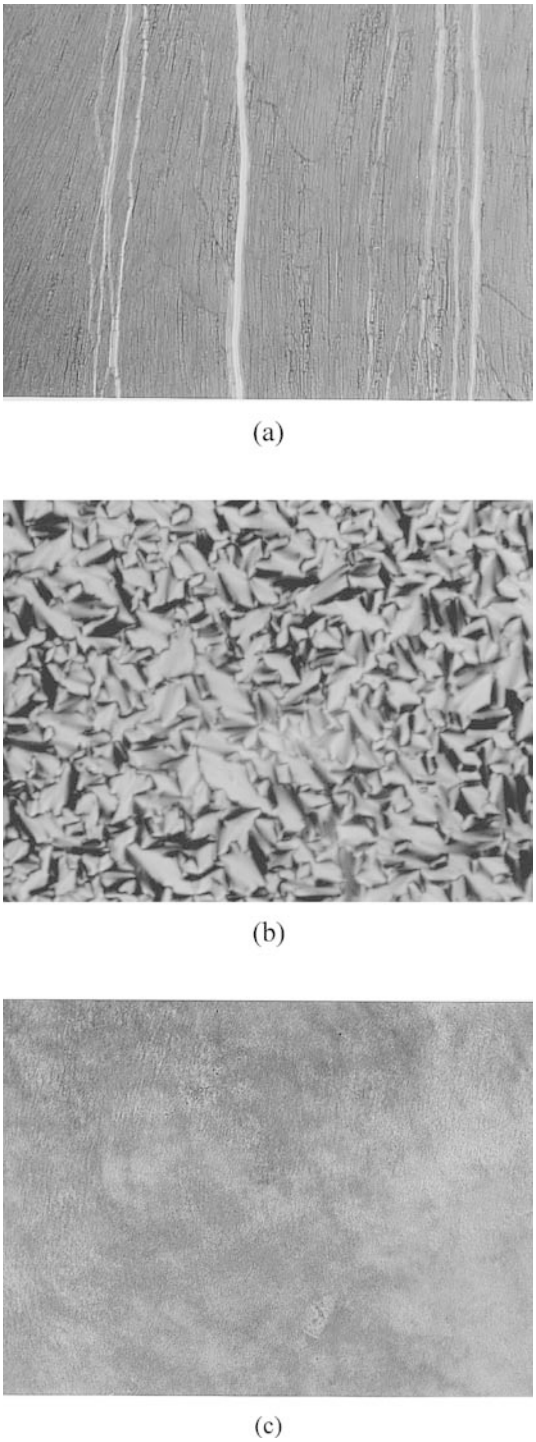


Fig. 3 Polarizing optical micrographs of samples (200×): **a** M-2 at 173 °C **b** M-2 at 190 °C **c** P-2 at 152 °C

micrograph of P-2 at 152 °C is shown in Fig. 3c as an example.

Thermogravimetric analyses (TGA) in Table 1 show that the temperatures at which 5% mass loss occurred (T_d), for all of the polymers, are above 320 °C, which

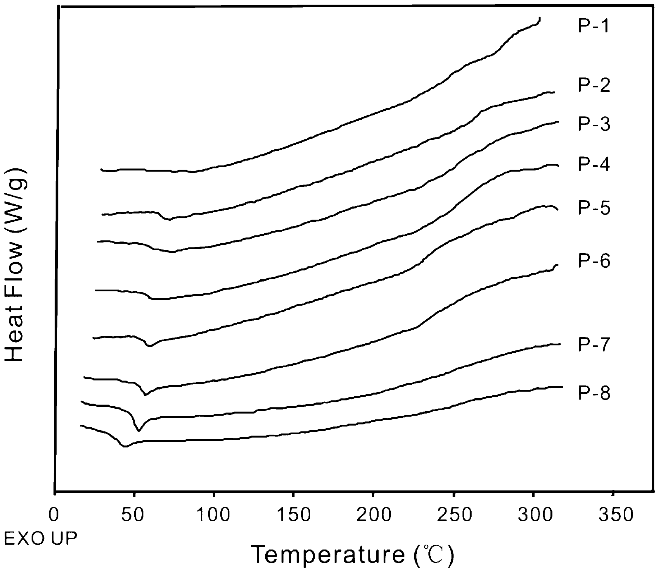


Fig. 4 DSC thermograms of polymers

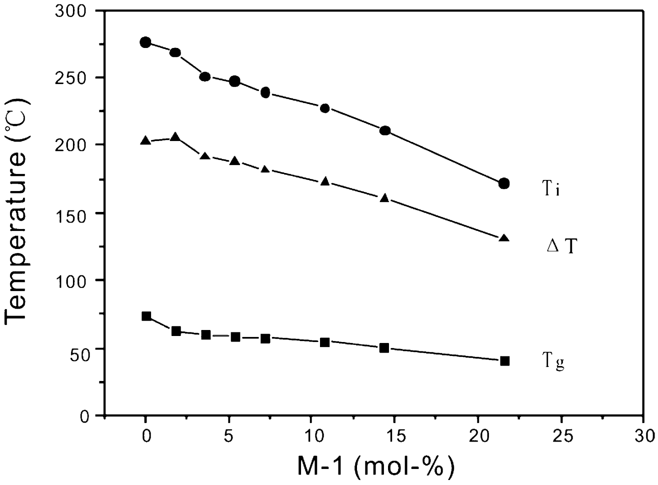


Fig. 5 Effect of M-1 concentration on phase transition temperatures of network polymers

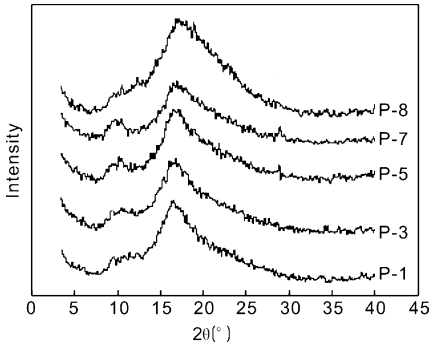


Fig. 6 Wide-angle X-ray diffraction patterns of network polymers

shows that the network elastomers have good thermal stability.

X-ray diffraction analysis

X-ray diffraction studies were carried out to obtain more detailed information on the mesophase structure. For network polymers, a sharp peak associated with the smectic layers at low angle did not appear in small-angle x-ray scattering curves, and a broad peak associated with the lateral packing at wide angle occurred at about 17° in the wide-angle x-ray diffraction curves. Therefore, the cholesteric phase structure of P-1 to P-8 was confirmed by x-ray diffraction, which agrees with DSC and POM results. Figure 6 presents representative x-ray diffraction curves of quenched samples. Moreover, the peak intensity of the polymers stays almost the same as the density of crosslinking units in network polymers is increased, which suggests that the non-mesogenic crosslinking agent does not disturb the liquid crystalline order from P-1 to P-8.

Conclusions

In this study, we synthesized a series of side-chain liquid crystalline network polymers containing both 1,6-hexanediol diundecylenate (M-1) and cholesteryl 4-allyloxybenzoate (M-2). As crosslinking density increases from P-1 to P-8, T_g and T_i of the elastomers decrease because of the incorporation of a flexible crosslinking agent. In the mesogenic range, the network polymers revealed elasticity and reversible phase transitions in heating and cooling cycles, and exhibited cholesteric Grandjean texture. X-ray analyses also reveal that the crosslinking agent does not disturb liquid crystalline order.

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