New Side-Chain Nematic Liquid Crystalline Elastomers Containing Smectic Crosslinking Units

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ABSTRACT: A series of siloxane-based liquid crystalline elastomers containing the smectic crosslinking agent M-1 and nematic monomer M-2 were synthesized by a one-step hydrosilication reaction. The chemical structures of the monomers and polymers obtained were confirmed by FTIR spectroscopy. The mesomorphic properties and phase behavior were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements. The influence of the crosslinking unit on the phase behavior was discussed. The experimental results demonstrated that the glass transition temperatures of elastomers had no remarkable change, and isotropization temperatures decrease with increasing the content of the crosslinking agent M-1. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3755–3760, 2004

Key words: liquid crystalline elastomers; smectic phase; nematic phase

INTRODUCTION

The fact that polymeric systems differ from all other materials makes it possible to form crosslinked systems by binding chains together. A network structure may be formed if a sufficient number of crosslink is available. Crosslinked liquid crystalline elastomers (LCEs) are one of the new supermolecular systems, with material science being directed towards the development of a multifunctional and oriented structure. In the past decade, research into this kind of material with anisotropic properties has expanded rapidly.[1–6] Recently, LCEs have been especially interesting for the investigation of the different orientational tendencies of both the mesogenic groups and the polymer chains and their interaction. Side-chain LCEs are attracting more attention because of their special optical, mechanical, and piezoelectric properties.[7–9] In general, studies have forced on the production of side-chain LCEs in which the perturbation to the mesophase is kept to a minimum. As a consequence, the crosslinking units are usually sited directly onto the polymer backbone. Side-chain LCEs can be achieved by a one-step reaction in which both mesogenic units and crosslinking agent are added to the polymer backbone or by the methods presented by Twomey[10] and Mitchell.[11] Thus, synthesizing various kinds of side-chain LCEs and exploring their potential application are not only necessary but also useful.

In a previous study, we reported synthesis and properties of side-chain cholesteric LCEs.[12–15] In this study, we present the synthesis of side-chain nematic LCEs containing biphenyl 4,4′-bis(10-undecen-1-ylenate) as a crosslinking agent and 4-allyloxybenzoyl-4′-ethoxybenzoyl-*p*-benzenediol bisate as a mesogenic unit. Their liquid crystalline properties were characterized with DSC, POM, and XRD measurement. The effect of the crosslinking unit on phase behavior was discussed.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS, $M_n = 700–800$) was purchased from Jilin Chemical Industry Company (China). Undecanoic acid was purchased from Beijing Jinlong Chemical Reagent Co., Ltd. (China). Antioxidant and *p*-Ethoxybenzoic acid were purchased from Beijing Chemical Industry Company (China). 4-Hydroxybenzoic acid was purchased from Beijing Fuxing Chemical Industry Co. (China). 3-Bromopropene and *p*-Dihydroxybenzene were purchased

Scheme 1 Synthetic routes of monomers.

form Shengyang Xinxi chemical Reagent Company (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 (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). Phase transition temperatures and thermodynamic parameters were determined by using a TA Q100 DSC (TA Instruments, USA) equipped with a liquid nitrogen cooling system. The heating and cooling rates were 20°C min^{-1}. Phase transition temperatures were collected during the second heating and the first cooling scans. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and FP 80 central processor was used to observe phase transition temperatures and analyze mesomorphic properties for liquid crystalline monomers and polymers through observation of optical textures. XRD measurements (Rigaku, Japan) were performed with a nickel-filtered Cu-K$_\alpha$ radiation with a Rigaku powder diffractometer.

Synthesis of monomers

The synthesis of monomers is shown in Scheme 1. 4-Hydroxyphenyl-4'- allyloxybenzoate was synthesized according to a route described by Hu et al.[16]

Biphenyl 4,4'-bis(10-undecen-1-ylenate)

Undecenoyl chloride (0.2 mol) was added dropwise to a solution containing 0.1 mol biphenol in 100 mL dry chloroform. The reaction mixture was refluxed for 3 h after stirring for 3 h at room temperature. The precipitate was removed by filtration and the crude product was purified by recrystallization from ethanol. White

Scheme 2 Synthesis and schematic representation of elastomers.

Figure 1 DSC thermograms of the polymers.

TABLE I
Phase Transition Temperatures of Monomers

Monomers	Transition temperature in °C (Corresponding enthalpy changes in $J \cdot g^{-1}$) $\frac{\text{Heating}}{\text{Cooling}}$	ΔT_1^a	ΔT_2^b
M-1	$K78.9(41.7)S_A113.3(2.7)I$ $\overline{I108.5(2.0)S_A70.3(39.1)K}$	34.4	38.2
M-2	$K179.9(83.8)N264.5(7.7)I$ $\overline{I261.2(4.6)N172.6(79.9)K}$	84.6	88.6

K = solid, S_A = smectic A, N = nematic, I = isotropic.
[a] Mesophase temperature ranges on heating cycle.
[b] Mesophase temperature ranges on cooling cycle.

scale-shaped crystals were obtained: m.p. = 78–79°C; yield = 93%. IR (KBr) cm^{-1}: 3079 (=CH); 2941, 2860 (CH$_3$, CH$_2$); 1745 (C=O); 1635 (C=C); 1605, 1510 (Ar).

4-Ethoxybenzoyl chloride

4-Ehoxybenzoic acid (42 g, 0.25 mol) was reacted at 45–50°C with 50 mL of thionyl chloride containing a few drops of N,N-dimethylformamide for 10 h, then the excess thionyl chloride was removed under pressure to give the corresponding acid chloride: yield = 81%.

4-Allyloxybenzoyl-4'-ethoxybenzoyl-p-benzenediol bisate

4-Ethoxybenzoyl chloride (0.2 mol) was slowly added dropwise to a solution containing 52 g (0.2 mol) 4-Hydroxyphenyl-4'-allyloxybenzoate and 15 mL of pyridine in 200 mL of dry tetrahydrofuran. The reaction mixture was stirred for 10 h at room temperature. After refluxing for 6 h, the above mixture was then poured into much water, precipitated, filtered, and washed with water. The crude product was purified by recrystallization from ethanol. White solid powers were obtained: m.p. = 178–179°C; yield = 60%. IR

(KBr) cm^{-1}: 3040 (=CH); 2940, 2860 (CH$_3$, CH$_2$); 1731(C=O); 1640(C=C); 1604, 1510 (Ar).

Synthesis of polymers

The synthetic routes of the polymers are outlined in Scheme 2. For the synthesis of polymers P-1–P-10, the same method was adopted. The synthesis of polymer P-4 is given as an example.

The monomers M-1, M-2, and PMHS were dissolved in dry, freshly distilled toluene. The reaction mixture was heated to 60°C under nitrogen and anhydrous conditions, and then the proper amount of THF solution of hexchloroplatinate hydrate catalyst was injected with a syringe. The reaction was kept for 24 h. The polymers were obtained by precipitation in methanol, and then dried under vacuum. IR (KBr) cm^{-1}: 2980–2850 (CH$_3$, CH$_2$); 1736 (C=O); 1020–1150 (Si—O—Si).

## RESULTS AND DISCUSSION

Thermal analysis

The samples of the monomers and polymers obtained were heated to 100°C and cooled to 0°C after 10 min,

TABLE II
Polymerization and Thermal Properties of Polymers

Polymer	Feed (mmol)			M-1[a] (mol %)	DSC		
	PMHS	M-1	M-2		$T_g/°C$	$T_i/°C$	ΔT^b
P-1	1	0.00	7.00	0.0	47.8	251.4	203.6
P-2	1	0.25	6.50	3.7	46.8	245.8	199.0
P-3	1	0.50	6.00	7.7	48.2	240.2	192.0
P-4	1	0.75	5.50	12.0	46.5	222.1	175.5
P-5	1	1.00	5.00	16.7	48.3	214.8	166.5
P-6	1	1.25	4.50	21.7	46.4	195.2	148.8
P-7	1	1.50	4.00	27.3	48.7	187.0	138.3
P-8	1	1.75	3.50	33.3	46.3	171.9	125.6

[a] Molar fraction of monomer M-1 based on (M-1 + M-2).
[b] Mesophase temperature ranges ($T_i - T_g$).
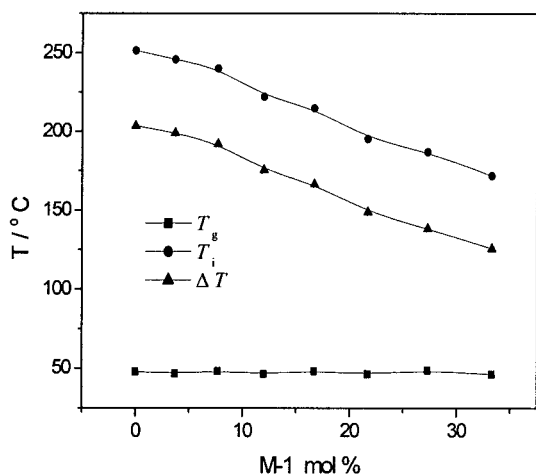
Figure 2 Effect of M-1 contnet on phase transition temperatures of polymers.

then DSC was used to measure the thermal transitions with reheating the samples at 20°C/min to 300°C. Typical DSC curves of the polymers are shown in Figure 1. The phase transition temperatures are listed in Tables I and II.

DSC heating thermograms of M-1 and M-2 showed two endothermic peaks, respectively. The first peak represented a melting transition and the other represented mesophase to isotropic phase transition. DSC curves obtained from polymers P-1–P-8 revealed glass transitions at low temperature and nematic-to-isotropic transitions at high temperature. Figure 2 showed the effect of the content of the crosslinking agent M-1 on the phase transition temperatures. As seen from the data in Table II and Figure 2, the glass transition temperatures (T_g) of elastomers P-2–P-8 had no remarkable change compared with the uncrosslinked polymer P-1. The isotropization temperatures (T_i) of P-1–P-8 decreased with increasing the content of the crosslink units.

For side-chain LCEs, T_g was influenced by the polymer backbone, the mesogenic group, the flexible spacer length, and crosslinking density. Generally, crosslinking imposes additional constraints on the segmental motion of polymer chains, and the increase of T_g may be expected. However, the effect is small for lightly crosslinked polymers. Opposing this effect is the influence of the flexible crosslinking
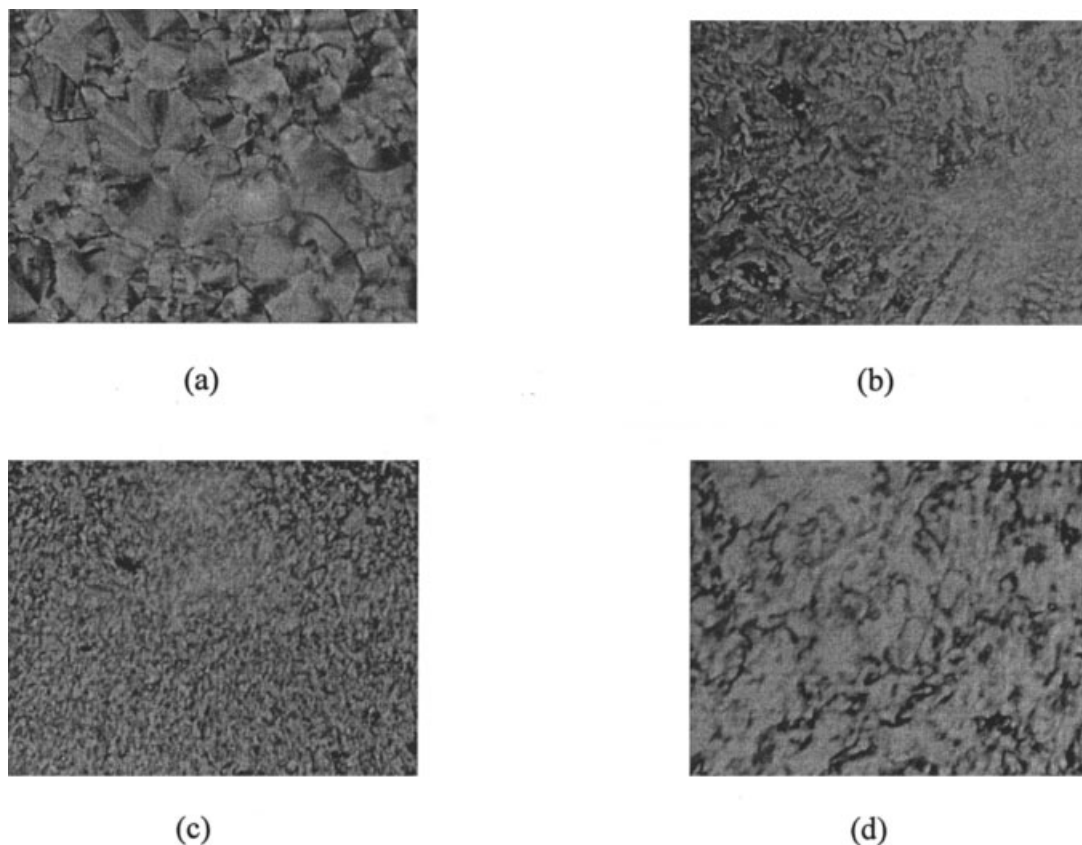
Figure 3 Optical textures of monomers and polymers. (a) Fan-shaped texture of M-1 at 102°C; (b) threaded texture of M-2 at 246°C; (c) threaded texture of P-3 at 214°C; (d) threaded texture of P-5 at 182°C.
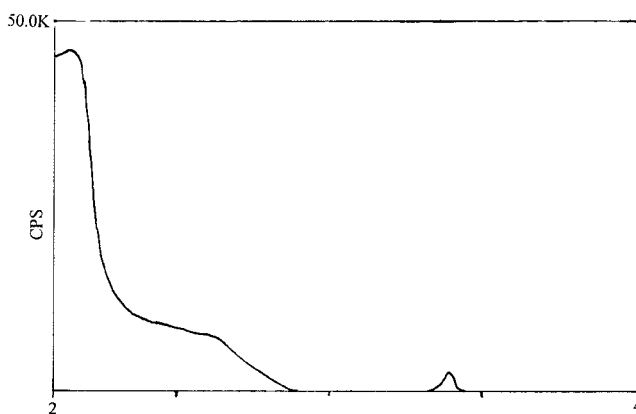
units as a plasticizer.[17] Under the effect of the crosslinking unit M-1, which acted as two controversial roles simultaneously, the reduction of a steric hindrance effect of monomer M-2 with decreasing the concentration of M-2 and the degree of steric regularity of the polymers, T_g of P-2–P-8 undulated compared with the uncrosslinked polymer P-1.

The chemical crosslinking also affected the mesophase-to-isotropic phase transition. The flexible crosslinking units acted as a diluent; this caused a decrease in the T_i-value. According to Table II, it could be clearly seen that T_i decreased from 251.4°C of P-1 to 171.9°C of P-8 when the content of the crosslinking units ranged from 0 to 33.3 mol %. In addition, the mesomorphic temperature ranges (ΔT) of P-1–P-8 decreased from 203.6 to 125.6°C because T_i decreased more than T_g.

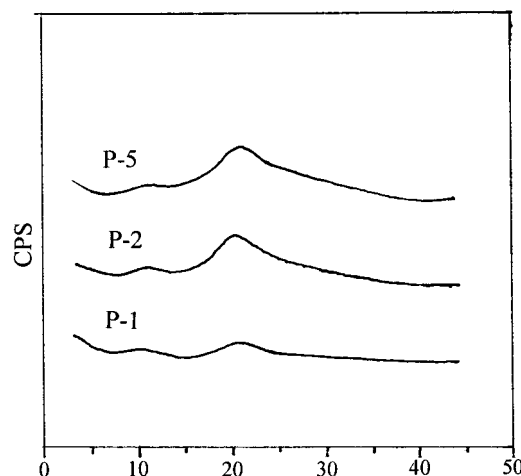**Figure 5** X-ray diffraction patterns of quenched samples of polymers.

Optical micrograph analysis

POM observation results revealed that M-1 exhibited a smectic phase, and M-2 displayed a nematic phase in both its heating and cooling cycles. When M-1 was heated to about 78°C, fan-shaped texture appeared. The texture did not disappear until the sample was heated to 114°C. When M-2 was heated to 178°C, the sample melted and showed the threaded texture, which is a typical nematic phase, and the texture disappeared at 264°C. Photomicrographs of M-1 and M-2 are shown in Figure 3(a) and (b).

Polymers P-1–P-8 exhibited a nematic threaded texture. Photomicrographs of P-3 and P-5 are shown in Figure 3(c) and (d) as examples. The textures of highly crosslinked polymers P-4–P-8 were observed under an additional force because they exhibited obvious elasticity.

X-ray diffraction analysis

XRD measurements could provide more detailed information on the liquid crystalline phase structures. Figure 4 showed typical small-angle X-ray scattering (SAXS) patterns of the quenched sample of M-1. The wide-angle X-ray diffraction (WAXD) patterns of samples of the polymers are shown in Figure 5. The samples of M-1 and polymers were respectively quenched at 100 and 140°C, then measured by WAXD and SAXS. A strong small-angle reflection associated with the smectic layers was observed at $2\theta = 2.74°$, corresponding to d-spacing of $d = 3.2$ nm, which is the evidence to show that M-1 was a smectic liquid crystal. P-1–P-8 exhibited a broad peak at approximate 17° in WAXD curves, and no sharp peak in SAXS curves. It was evident that they all exhibited only the nematic phase, which is consistent with optical textures.

CONCLUSIONS

A series of side-chain nematic LCEs containing a smectic crosslinking agent were synthesized and characterized. The monomers and polymers obtained were all thermotrophic liquid crystals. M-1 exhibited a smectic fan-shaped texture and M-2 displayed a nematic threaded texture. The elastomers P-2–P-8 revealed elasticity, reversible phase transitions, and a nematic threaded texture in the heating and cooling cycles. The glass transition temperatures undulated, and isotropization temperatures and the mesomorphic temperature ranges decreased with increasing the content of the crosslinking unit M-1.

Figure 4 X-ray diffraction patterns of quenched sample of M-1.

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