

# Side chain liquid crystalline elastomers I

## Phase behavior of their precursors

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### Summary

Side chain liquid crystalline polyesters (PMx) were synthesized through the melt polymerization between N-6-(4-((4'-nitrophenyl)azo)phenyl)oxy)hexyl diethanolamine (C6), maleic anhydride and succinic anhydride. The effect of the polymer backbone on the phase behavior of PMx was studied by DSC, polarized optical microscopy (POM) and wide angle X-ray diffraction (WAXD) and the results showed that smectic-isotropic transition temperature ( $T_{SI}$ ) increased largely, while melting temperatures ( $T_m$ ) decreased slightly and  $T_g$  increased slightly with the increase of the content of maleic anhydride in the copolymers. The results also indicated that introduction of maleic anhydride to polymer backbone was unfavorable of the molten crystallization of the side chains. The IR-dichroism study on the side chain liquid crystalline elastomers prepared from PMx showed that the elastomers exhibited anisotropic behavior after stretching under the mechanical fields.

### Introduction

Some years ago for the first time liquid crystalline elastomers (LCE) were synthesized on the basis of crosslinked liquid crystalline side chain polysiloxanes (1-2). Since then several other types of liquid crystalline elastomers having different polymer backbones and mesogenic units incorporated in the main chain and side chains have been realized by different groups (3,4). Because of the exceptional physical properties of LCE, this field has attracted increasing attention from theorists (5-8), explaining the physical behavior of the LCE by different phenomenological, or molecular model; also, LCE offer new aspects with respect to technical application, e.g. in nonlinear and integrated optics (9,10).

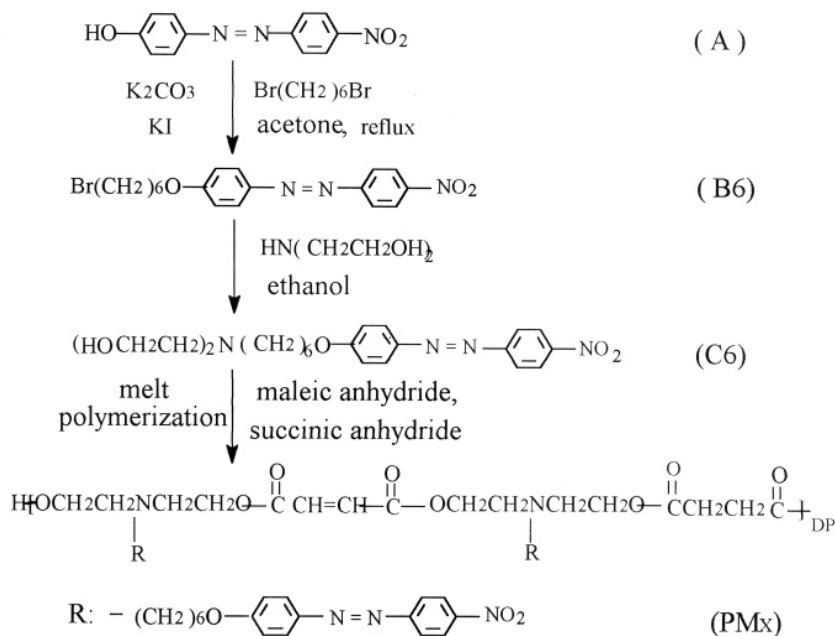
Among the synthesized side chain LCE, most of them were based on the precursors such as, liquid crystalline polysiloxanes, polyacrylates and polymethylacrylates in which functional groups were introduced and used as reactional groups to form LCE. As far as we know, no reports about the side chain LCE based on the unsaturated polyesters as polymer backbones were found. The present paper reports the syntheses and the effect of the polymer backbone on the phase behavior of side chain liquid crystalline polyesters, which were used as precursors to prepare side chain LCE. The unsaturated side chain liquid crystalline copolyesters could be obtained through the melt polycondensation of difunctional diols, N-6-(4-((4'-nitrophenyl)azo)phenyl)oxy)hexyl diethanolamine (C6), maleic anhydride and succinic anhydride. Thus obtained polymers and the resulted elastomers might be used

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as nonlinear optical materials due to the existence of the highly delocalized  $\pi$ -electron system( para-nitro azobenzene ) with a dipolar moment of 4.2 D and a positive dielectric anisotropy ( $\Delta\epsilon > 0$ ). The mechanical properties and the orientational behavior will be reported in a forthcoming paper.

### Experimental

The synthetic route taken to prepare the polyesters is given in Scheme I



Scheme I

#### 4 -hydroxy-4'-nitro azobenzene (A)

The compound A was synthesized through the coupling of a diazotized aniline with phenol as described in detail elsewhere(11).

#### 6 - bromo-1-((4-(4'-nitrophenyl)azo)phenyl)oxy)hexane (B6)

B6 was synthesized by the Williamson etherification as described elsewhere (12).

#### N-6-((4-nitrophenyl)azophenyl)oxy)hexyl diethanolamine (C6)

C6 was prepared through the reaction between B6 and diethanolamine in ethanol for 10 hr. The detail description of the procedure was given in ref. (12).

#### Polyesters (PM<sub>x</sub>)

The mixture of monomers C6 ( 5 mmol ), 5 mmol of maleic anhydride and succinic anhydride was heated slowly in a four-neck flask under nitrogen, after melting, the mixture was stirred vigorously and maintained at the temperature until gel occurred. Then the reaction mixture was allowed to cool and the polymer was dissolved in tetrahydrofuran ( THF ). The solution was filtered and the polymer was precipitated by the addition of petroleum ether and filtered off. Finally, the polymer was dried under vacuum at room temperature.

IR( KBr, cm<sup>-1</sup>): 3437 ( bd, -OH, vs); 2938, 2857 ( -CH<sub>2</sub>-, vs ); 1725 ( -C=O, vs ); 1600, 1580, 1500, 1453 (aromatic, -C-C, vs ); 1522, 1343 ( -NO<sub>2</sub>, vs, vas ), 1256, 1139 ( -C-O-,vs ); 1106, 1041; 1640 ( -C=C-, vs ); 860 (Ar-H, v);

<sup>1</sup>H NMR spectrum of PM3 and the attributions of the peaks were given in Figure 1.

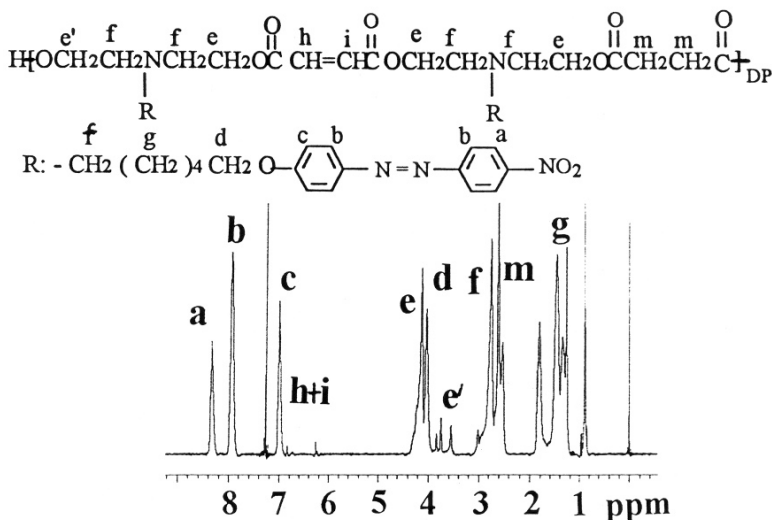


Figure 1 <sup>1</sup>H NMR spectrum of PM2

Figure 1 <sup>1</sup>H NMR spectrum of PM3

## Characterization

<sup>1</sup>H NMR spectra were recorded at room temperature on a Varian Unity 400 spectrometer ( 400 MHz ) using chloroform ( CDCl<sub>3</sub> ) as solvent and tetramethylsilane as an internal chemical shift reference.

IR spectra were recorded with a BIO- RAD FTS-7 spectrometer. Samples were pressed tablets with KBr.

The number-averaged molecular weight (Mn as well as the number-averaged degree of polymerization ( DP) were determined by analysis of the terminal group method based on the results of <sup>1</sup>H NMR spectroscopy.

Thermal transitional properties were studied by a Perkin-Elmer DSC-7 differential scanning calorimeter. The calibration was performed with Indium. Weights of samples were ca. 10 mg. All the samples were treated before measurement. Each sample was heated to liquid crystalline state and maintained at that temperature for 10 min. and then quenched to 0 °C, thus obtained sample were then studied by DSC at a heating and cooling rate of 10 °C/ min.

Optical textures, were obtained by using a Leitz-welzlar optical polarizing microscope equipped with a hot stage and an Option R Pol camera. Samples were casted on the glass slide from a 1% solution of chloroform to form a thin film and then were covered by another glass slide.

Wide angle X-ray diffraction spectra were recorded on a Rigaku D/MAX-rA (Rigaku Co., Japan ) X-ray diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation at room temperature.

IR-dichroism measurement for the side chain liquid crystalline elastomers, which was prepared by crosslinking the side chain liquid crystalline polyester precursor using styrene as crosslinking reagent, BPO as initiator, stretched in their liquid crystalline phase were performed with a BIO-RAD FTS-7 Fourier Transform infrared spectrometer. Dichroism absorption of antisymmetric stretching vibration of  $-\text{NO}_2$  at  $1343\text{ cm}^{-1}$  was used to determine the orientation of mesogens in LCE. The order parameter ( $f$ ) can be evaluated by the following equation(13, 14).

$$f = -2(D - I)/(D + 2)$$

Where  $D = A_{\parallel} / A_{\perp}$ ,  $A_{\parallel}$ ,  $A_{\perp}$ , the integral areas of the absorbance bands when the transmission axis of the polarizer is parallel and perpendicular to the stretching direction, respectively.

## Results and Discussion

### Syntheses

Copolycondensation of difunctional diols C6 and maleic anhydride, succinic anhydride was carried out in melt under a nitrogen atmosphere. IR spectroscopic study on PM3 showed that there appeared absorption bands at  $1725\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$ ;  $1601$ ,  $1580$ ,  $1445$ ,  $830\text{ cm}^{-1}$ ;  $1521$ ,  $1345\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$ ; indicating the existence of  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{C}-$ , and 1,4 -substituent aromatic rings,  $\text{NO}_2$ , and C-N, respectively. The  $^1\text{H}$  NMR spectrum of PM3 as well as the attributions of the peaks were given in Figure 1. The existence of chemical shifts at  $\delta = 6.22\text{ ppm}$  (protons of cis-  $\text{CH}=\text{CH}-$ ) and  $\delta = 6.82\text{ ppm}$  (protons of trans-  $\text{CH}=\text{CH}-$ ) indicated the existence of cis and trans -configuration of  $-\text{CH}=\text{CH}-$  in the polymer backbone. Chemical shift at  $\delta = 3.60\text{ ppm}$  was attributed to the absorption of protons of  $-\text{CH}_2$  groups neighboring to  $-\text{OH}$  terminal group at each end of macromolecular chain ends and  $\delta = 2.50\text{ ppm}$ , the absorption of proton of  $-\text{CH}_2$  group of succinic anhydride unit in the polymer backbone. According to the definition of number averaged degree of polymerization ( $DP$ ),  $DP$  can be determined by the following equation based on the analysis of terminal groups:

$$DP = \frac{(Ac + Ah + Ai + Am/2) / 2}{Ae' / 4}$$

Where  $Ac$ ,  $Ah$ ,  $Ai$ ,  $Am$  and  $Ae'$  are the integral areas of protons c, h, i, m and e', respectively,  $(Ac + Ah + Ai + Am/2) / 2$ , the total moles of monomeric units;  $Ae'/4$ , total moles of the polymers. Number averaged degree of polymerization, compositions and ratios of trans- to cis- configuration of  $-\text{CH}=\text{CH}-$  groups in the polymer backbone were given in Table I

DSC curves of the copolymers in the course of heating and cooling cycles were shown in Figure 2. It can be seen that in the course of heating, all the polymers studied showed three transitions corresponding to glass transition ( $T_g$ ), crystalline -liquid crystalline transition ( $T_m$ ) and liquid crystalline-isotropic transitions ( $T_i$ ), respectively. So PMx showed enantiotropic liquid crystalline behavior. WAXD and optical texture observation also confirmed the liquid crystalline behavior of

Table I Molecular structure of the copolyesters PMx

PMx	DP	Molar percentage of the monomers			trans./cis-
		M%	S%	D%	
PM1	27.5	0.8	47.2	52	2:1
PM2	24.6	12	36	52	2.4:1
PM3	25.6	18	30	52	1.27:1
PM4	40	37	12	51	2.58:1
PM5	24	46	0	54	2.53:1

Key: M%, S%, D% represent the molar percentages of the maleic anhydride, succinic anhydride and difunctional diols (C6) in the polymers, DP: number-averaged degree of polymerization. trans./cis-: molar ratios of trans. to cis-configurations of -CH=CH-.

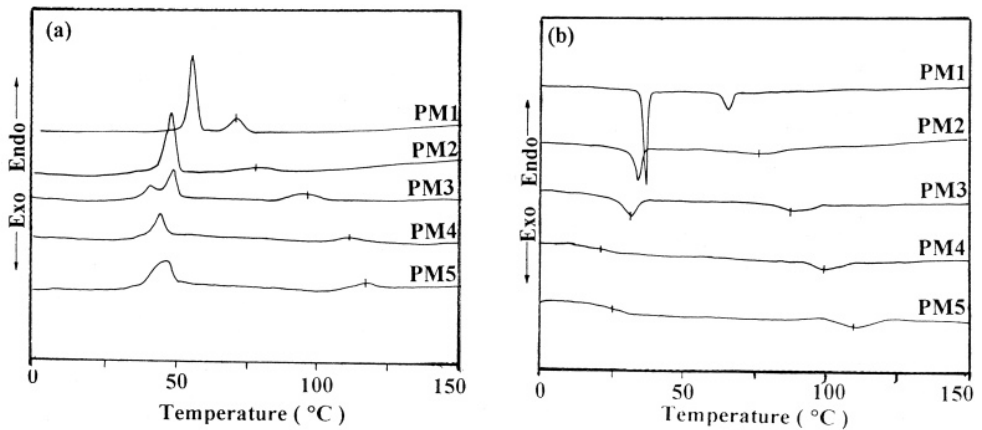


Figure 2 DSC curves of PMx in the course of heating (a) and cooling (b) cycles.

PMx. All the polymers studied showed a diffraction peak at lower diffraction angles corresponding to d-spacing of 1.670 nm which was shorter than the calculated length of the side chains ( $L = 2.09$  nm) containing the flexible spacers according to the standard bond length and bond angles assuming that the spacers are in all-trans configuration. Figure 3 showed the optical texture of PM3 which showing the smectic phase.

Their thermal transitional properties were summarized in Table II. The number-averaged degree of polymerization of PMx was all larger than 10, so the phase transitional properties are in the molar mass independent region. Neglecting the effect of molar mass on the phase behavior it can be seen that  $T_g$  increased slightly and  $T_m$  decreased slightly with the increase of content of maleic anhydride; on the contrary,  $T_{si}$  increased largely with increase of maleic anhydride. Also, when the content of maleic anhydride is larger than 37%, no crystallization peak could be observed in the course of cooling cycle, whose results indicated that introduction of maleic anhydride was unfavorable for the molten crystallization of the mesogenic groups. The above phase behavior of PMx can be

understood that the increase of maleic anhydride cause the increasement of stiffness of polymer backbone which resulted in the increase of  $T_{si}$  and  $T_b$ .

Table II Thermal transitional properties of PM3

PMx	Thermal transitional properties			
	heating		cooling	
PM1	K 51.4 (15.3)	S 70 (4.87)	I	1 64.9 (-4.87) S 36.7 (-14.9) K
PM2	Tg 33.1 K 48.6 (15.7)	S 78.4 (2.57)	I	1 76.6 (-7.24) S 34.4 (-11.0) K
PM3	Tg 34.3 K 49.1 (15.6)	S 96.4 (4.29)	I	1 87.6 (-5.69) S 31.8 (-6.95) K
PM4	Tg 35 K 43.3 (11.0)	S 108.7 (4.15)	I	1 98.7 (-5.86) S 22 Tg
PM5	Tg 35.6 K 48.7 (12.8)	S 118.6 (4.09)	I	1 108 (-6.94) S 25 Tg

Key: K, crystalline; S, smectic; I, isotropic; Tg, glass transition; temperatures in °C and enthalpies in J/g (in parentheses).

Study on the thermal transitional behavior of PMx told us that, on the one hand, by introducing maleic anhydride as one comonomer to a side chain liquid crystalline unsaturated polyester, precursors with different double bond content can be obtained and thus the crosslinking density of the resulted side chain liquid crystalline elastomers can be controlled; on the other hand, the phase transitional properties can be changed,  $T_{si}$  increased and thus the temperature range of LC phase widened by introducing a stiff polymer backbone, vice versa.

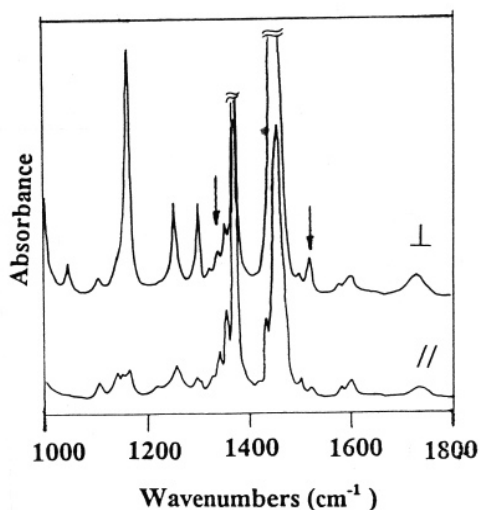


Figure 3 POM photograph of PM3 at its LC phase

Figure 4 FTIR spectra of PM5 stretched under mechanical field

### Crystalline Behavior

WAXD study on PMx with different content of maleic anhydride showed that they showed almost the same WAXD spectra which exhibited diffractions at d-spacings of 0.52 nm, 0.35 nm and 0.30 nm as observed in other side chain polyacrylates, polymethylacrylates with the same mesogenic groups. The results again indicated that for this kind of polyesters with the same mesogenic group, different length of spacer and different polymer backbone, the crystalline region is all formed by the regular arrangement of the mesogens.

## IR-dichroism

Figure 4 showed the polarized FTIR spectra of crosslinked PM5 with a draw ratio of 3. Obviously, the intensity of the absorption band with the transmission axis of the polarizer perpendicular and parallel to the stretching direction in the region of 2000-1000  $\text{cm}^{-1}$  are different indicating that the elastomer can be oriented by mechanical field and for PM5 drawn at 85 °C and with a draw ratio of 3, the order parameter calculated by the IR-dichroism method is 0.56.

Study on the orientational behavior of crosslinked PMx under mechanical field is in progress and the results will be given in a forthcoming paper.

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