Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Side chain liquid crystalline elastomers II. Thermal properties and orientational behaviour of the LCE based on unsaturated copolyesters

Min Li[a]; Hongjin Qiu[a]; Xinfang Chen[a]
[a] Department of Materials Sciences, Jilin University, Changchun 130023, PR China,

To cite this Article Li, Min , Qiu, Hongjin and Chen, Xinfang(2000) 'Side chain liquid crystalline elastomers II. Thermal properties and orientational behaviour of the LCE based on unsaturated copolyesters', Liquid Crystals, 27: 12, 1641 — 1645

To link to this Article: DOI: 10.1080/026782900750037202

URL: http://dx.doi.org/10.1080/026782900750037202

LIQUID CRYSTALS, 2000, VOL. 27, NO. 12, 1641–1645

Side chain liquid crystalline elastomers II. Thermal properties and orientational behaviour of the LCE based on unsaturated copolyesters†

MIN LI*, HONGJIN QIU and XINFANG CHEN
Department of Materials Sciences, Jilin University, Changchun 130023, PR China

(*Received 17 March 2000; accepted 21 June 2000*)

The effect of crosslinking density on the phase behaviour of smectic liquid crystalline networks was studied; the results showed that crosslinking in their smectic phases can greatly enhance the stability of the liquid crystalline phase. The higher the crosslinking density, the higher the smectic–isotropic transition temperature. The mechanically–induced orientation was studied by polarized FTIR spectroscopy. The smectic liquid crystalline network could be oriented parallel to the mechanical field at higher draw ratio λ, while at lower λ the mesogenic groups are oriented perpendicular to the field for the networks with higher crosslinking density. The observed mechanically–induced orientation is interpreted by a proposed mechanism.

1. Introduction

Liquid crystalline elastomers (LCEs) are known to be a peculiar class of polymer system with coupling between the nematic or smectic field and the backbone conformations. These networks are interesting from both theoretical and practical viewpoints [1–3]. For example, LCEs offer new aspects with respect to technical application, e.g. in non-linear and integrated optics [4]. One of the most important features of LCEs is that they can be macroscopically, uniformly oriented by mechanical deformation; meanwhile the oriented structure can be chemically locked-in by crosslinking, resulting in the so-called liquid single crystalline elastomers [5]. Besides this, crosslinking, and various striking phenomena, such as electrically-induced shape changes can attenuate the interaction between the mesogenic units and the polymer backbone chains. Mechanical and electrical molecular switching, memory effects and variation in phase behaviour are thought to arise directly from these interactions. LCEs provide the best system in which to investigate the coupling between mesogenic units and polymer backbone [6].

Two kinds of liquid crystalline elastomers have been intensively studied: (i) siloxane-based side chain liquid crystalline networks that display rubber-like elasticity at room temperature; (ii) acrylates or methyacrylate-based side chain liquid crystalline networks which have a relatively high T_g due to much higher rigidity of the backbone compared with siloxane-based polymers [6–8]. The common features of these systems are that all the crosslinking reaction took place between the side chains of the precursors, and thus the phase behaviour changed little (only a few degrees) compared with that of the linear precursors.

The crosslinking reaction of the new kind of LC network reported here, which is derived from unsaturated copolyesters [9, 10] with *para*-nitroazobenzene as mesogenic groups, was based on different sites of the polymer backbone instead of the precursor side chains reported in the literature. The main objective of the present work is to investigate the phase behaviour of LC networks and their orientational behaviour under a mechanical field by means of polarized FTIR spectroscopy.

2. Experimental

2.1. *Synthesis of the polymers and elastomers*

A series of side chain liquid crystalline copolyesters whose molecular formulae are given in figure 1 was synthesized [9, 10] through the melt copolycondensation of maleic anhydride, succinic anhydride and *N*-6-[4-(4-nitrophenylazo)phenyoxy]hexyl diethanolamine (C6) at the melting temperature until gel formation occurred. The reaction mixture was dissolved in tetrahydrofuran and then precipitated with petroleum ether. The proposed molecular structure was confirmed by IR and ^{1}H NMR spectroscopy. By changing the molar ratio of maleic anhydride and succinic anhydride, copolyesters with different amounts of double bond in the polymer backbone were obtained.

Side chain liquid crystalline elastomers (SCLCEs) were prepared from a concentrated solution of the

---

* Author for correspondence; e-mail: mat@mail.jlu.edu.cn
† For part I see ref. [10].

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010002210

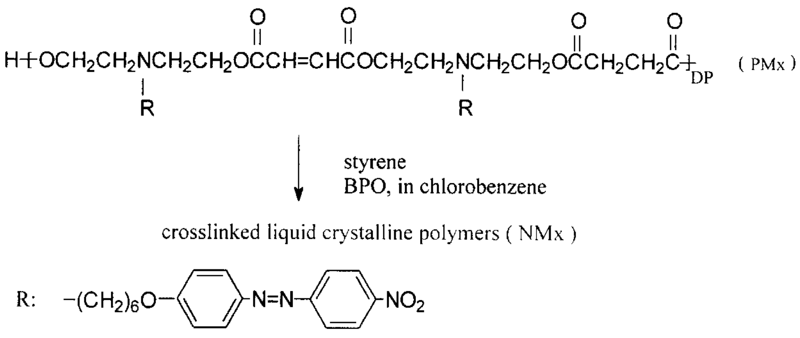

Figure 1. Schematic representation of the synthesis of the LC elastomers.

copolyesters in chlorobenzene containing an equivalent amount of styrene and a small amount of (BPO) as initiator. The reaction mixture was spin-cast onto a supporting polymer film (HDPE), thus the thin films obtained were allowed to react at 60°C for 48 h. The crosslinking reaction was confirmed by FTIR spectroscopy and the swelling test experiment. The degree of network swelling was calculated by the following equation

$$\mathrm{Wt}\,\% = (W_1 - W_0)/W_0 \qquad (1)$$

where, W_1, W_0 are the weights of samples after and before swelling in chlorobenzene for 48 h, respectively.

2.2. *Characterization*

^{1}H NMR spectra were recorded on a Varian Unity 400 spectrometer (400 MHz) using tetramethylsilane (TMS) as an internal chemical shift reference and deuterium chloroform as solvent. IR spectra were recorded on a BIO-RAD FTS-7 Fourier Transform infrared spectrometer. Thermal transitional properties were studied with a Perkin-Elmer DSC-7 differential scanning calorimeter. The calibration was performed with indium. Weights of samples were *c.* 10 mg; the heating and cooling rate were 10°C min^{-1}. Optical textures were obtained by using a Leitz-Welzlar optical microscope equipped with a hot stage on an option R Pol camera. Samples were cast onto the glass slide from a 1% solution in chloroform to form a thin film and were then covered by another glass slide.

2.3. *Mechanical stretching*

Due to the difficulty in preparing the SCLCE films suitable for mechanical stretching and infrared dichroism measurement, we employed the method developed by Zhao [11]. A solution of the copolyesters, mixed with a small amount of BPO as an initiator and styrene as crosslinking agent in chlorobenzene, was cast onto an HDPE film (*c.* 50 μm) and the prepared thin films were allowed to react at 60°C for 48 h. The prepared thin SCLCE film, supported by an HDPE film, was stretched in the LC phase on an Instron 1121 instrument.

2.4. *Measurement of the orientational parameter*

The measurement of IR dichroism was used to characterize the orientational order of the mesogens of the LCE films under a mechanical field. The dichroism absorption of the antisymmetric stretching vibration of $-NO_2$ at 1342 cm^{-1} was used to determine the orientation of mesogens. The order parameter (f) can be evaluated by the following equation [11, 12]:

$$f = (D-1)(D_0+2)/(D+2)(D_0-1) \qquad (2)$$

where $D = A_{\parallel}/A_{\perp}$; $A_{\parallel}$, $A_{\perp}$ are the integral areas of the absorbance bands when the transition axis of the polarization is parallel and perpendicular to the stretching direction, respectively. $D_0 = 2\cot^2\alpha$, α being the angle between the long axis of the mesogenic group and the transition moment of the $-NO_2$ stretching vibration. As a first approximation, α can be taken as 90° and we obtain the order parameter of the mesogens (f_m)

$$f_m = -2(D-1)/(D+2) \qquad (3)$$

3. Results and discussion

3.1. *Thermal properties of the LC network*

The crosslinking of the copolyesters was performed in a concentrated chlorobenzene solution through a radical polymerization procedure. The crosslinking reaction was characterized by FTIR spectroscopic study of the samples before and after crosslinking. The relative intensity of the band at 1300 cm^{-1} attributed to the in-plane bending vibration of the $-C-H$ in the *trans* $-CH{=}CH-$ groups decreased greatly; others at 686 and 1410 cm^{-1}, attributed to the in-plane and out-of-plane bending vibration of the *cis*-isomerization of $-CH{=}CH-$ groups remained almost unchanged during crosslinking. So, it can be concluded that the crosslinking reaction takes place between the *trans*-isomerization of the $-CH{=}CH-$ groups. From the degree of polymerization measured, the monomeric ratio in the copolymers, and the *trans*/*cis* ratio given in [10], the average number of reacted maleic anhydride molecules per polymer chain in the

Table. Phase behaviour of the LC elastomers and their precursors. M = averaged number of maleic anhydride molecules in each polymer chain; wt % = degree of swelling calculated from equation (1); MA = averaged number of reacted maleic anhydride molecules per polymer backbone in LCE assuming that all the *trans*-isomerization is consumed; Cr = crystalline, SmA = smectic A, I = isotropic; transition temperatures in °C

Precursors	M	Phase behaviour	Network	Wt %	MA	Phase behaviour
PM2	2.9	Cr 48.6 SmA 78.4 I	NM2	—	2.00	Cr 45 SmA 92 I
PM3	4.6	Cr 49 SmA 96.4 I	NM3	10.5	2.58	Cr 45 SmA 138 I
PM4	11	Cr 43 SmA 108.7 I	NM4	8.64	7.92	Cr 43 SmA 146 I
PM5	14.8	T_g 35.6 K 48.7 SmA 118.6 I	NM5	3.16	10.58	Cr 45 SmA 160 I

LCE, which reflects the difference of the crosslinking density of the LCE, was calculated; results are given in the table. The results of swelling test experiments are also listed in the table. The FTIR study on the crosslinking sample showed that the LC networks had been prepared successfully.

Figure 2 shows the DSC curves of the liquid crystalline networks NM*x* with different crosslinking densities in the cooling cycles. These results indicate the effect of the crosslinking density on the phase behaviour of the liquid crystalline network. The exothermic peak, assigned to the liquid crystalline–isotropic transition, was shifted to higher temperatures and broadened with the increase of the crosslinking density. The liquid crystalline behaviour was also studied by polarized optical microscopy: on cooling a sample from its isotropic phase, bâtonnet texture first appeared, followed by a broken fan-like texture. The liquid crystalline–isotropic transition on the DSC curves was thus due to a smectic-isotropic transition. The photomicrograph of NM3 at its liquid crystalline phase is given in figure 3. The effect of crosslinking density is interpreted in terms of reduction in the molecular motion of the polymer segments in the polymer network. The higher the crosslinking density, the less the molecular motion. Similar results of stabilization of liquid crystalline phase by crosslinking have been reported in other systems [13].

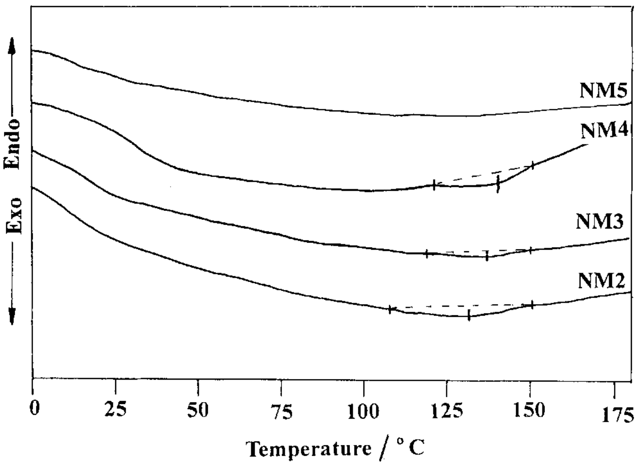

Figure 2. DSC curves of the liquid crystalline networks NM*x* in the cooling cycles.

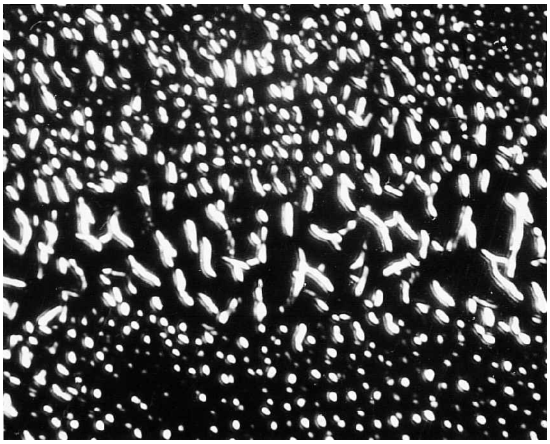

Figure 3. Polarized optical microscopy photomicrograph of NM3 at 75°C (× 600).

The table shows the phase behaviour of the LC networks. For comparison, the phase behaviour of their corresponding precursors is also listed. Crystalline–smectic transition temperatures changed little compared with those of their precursors, indicating that the crystalline regions formed by the regular arrangement of mesogenic groups are not disturbed by the introduction of crosslinking. However the smectic–isotropic transition temperature of the networks are 35 ~ 40 degrees higher than that of their precursors; the larger the amount of the $-C{=}C-$ groups, the higher the transition temperature. It has been reported that the clearing points usually decrease a few degrees in lightly crosslinked LC system. The surprisingly large increase of T_{SI} in our case can be understood as follows: (1) most of the LCEs reported in the literature were prepared by crosslinking of side chains leaving the polymer backbone unchanged, while the LC networks reported here were synthesized through crosslinking of the sites of the polymer backbone, thus rigidity of the polymer backbone increased due to the introduction of the large side chain and T_{SI} increased; (2) crosslinking in the smectic phase also stabilizes the molecular arrangement and thus the T_{SI} is increased.

3.2. *Orientation behaviour*

Polarized FTIR spectra of the NM5 network supported on an HDPE film stretched at 85°C with a draw ratio of 3 are given in figure 4. It can be seen that some of the bands are due to the vibration of groups of the support film, while those at 1342 and 1521 cm^{-1} (indicated by arrows) and 1600, 1580 cm^{-1} are attributed to the antisymmetric and symmetric stretching vibration of NO_2 group and aromatic vibration, respectively. The intensities of the absorption bands of both support film and LCE film, with the transmission axis of the polarizer perpendicular and parallel to the stretching direction in the range of 2000–1000 cm^{-1}, are different; indicating that both the elastomer and HDPE supported film can be oriented by a mechanical field. According to equation (1), the orientational order of the mesogens of NM5 stretched under the above conditions is 0.56.

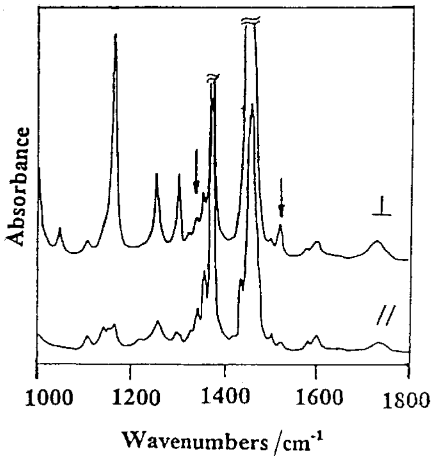

Figure 4. FTIR spectra of NM5 supported by an HDPE film (*c*. 50 µm) stretched under a mechanical field at 85°C with a draw ratio of 3: parallel and perpendicular to the stretching field.

The orientational order–strain curves of the liquid crystalline networks NM*x* are shown in figure 5. Clearly, the orientational parameter of the mesogenic groups of the network with lower crosslinking density fluctuated around zero at lower draw ratio, and then turned to positive and increased slightly to 0.22 with strain; this indicated that there was no preferred orientation at low draw ratio, while with the increase of strain ($\lambda > 1.5$), the mesogenic groups oriented parallel to the stretching field. Quite different behaviour was observed for liquid crystalline networks with higher crosslinking density; negative orientation of the mesogenic groups is observed up to $\lambda = 1.75$ and then it became positive and increased to 0.4 with strain when $\lambda > 1.75$. The same kind of mechanically induced orientation was reported in some types of polyurethane block copolymers in which negative orientation of the hard mesogenic groups is observed up to 400% strain [14, 15].

Up to now, there have been two theories to account for the orientational behaviour of LCEs under a mechanical field. One is that proposed by Micheal and coworkers [6, 7, 16], which is the most prominent interpretation for stress-induced orientation. They interpreted the experimental results from the molecular level by considering the coupling between the polymer backbone and the mesogenic groups. They presume that the mechanical forces always align the polymer backbone along the field direction and as a consequence of coupling, the mesogens orient due to the hinge effect imposed between the polymer backbone and the mesogenic groups through the spacer. Zhao *et al.* [17] recently proposed a new mechanism to interpret the observed results. Instead of emphasizing the orientation by virtue of a hinge effect through the spacer, they suggest that the observed

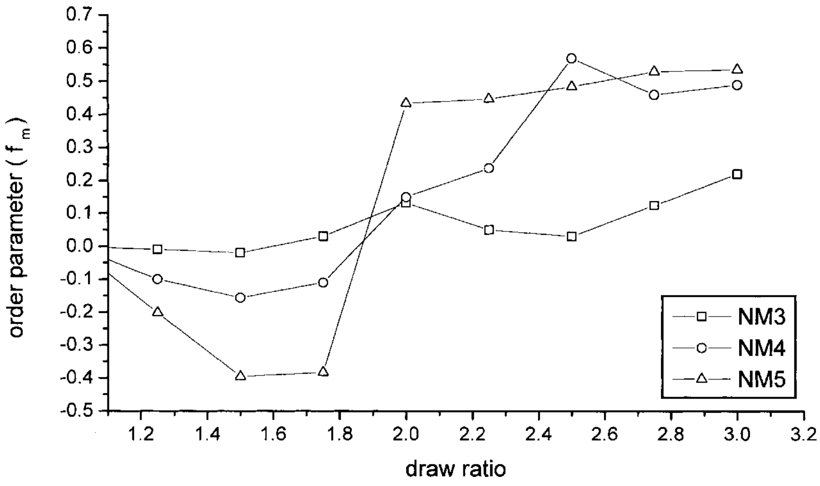

Figure 5. Draw ratio versus order parameter for the mesogenic groups of NM3, NM4 and NM5 stretched at 85, 100 and 110°C, respectively.

macroscopic orientation be mainly related to a direct alignment of mesogenic domains.

In our case, neither of the above theories can interpret the phenomena. Considering the unique chemical structure of our system, we propose that the liquid crystalline network reported here be considered as a crosslinked graft copolymer consisting of liquid crystalline domains and amorphous polystyrene domains; thus a microphase separation would occur. The liquid crystalline domains would tend to become macroscopically anisotropic during elongation. The liquid crystalline domains were oriented perpendicular to the longer axis of the domains and the amorphous domains are envisaged to be stretched initially to different extents, giving rise to local torques. These twist the liquid crystalline domains preferentially transverse to the stretching direction and eventually lead to parallel alignments at higher draw ratio.

4. Conclusion

Smectic side chain liquid crystalline elastomers, based on unsaturated copolyester as precursors with *para*-nitroazobenzene as mesogenic group, have been synthesized and characterized. Their thermal properties were studied with results showing that crosslinking can enhance the stability of the mesophase. A polarized FTIR study on the orientational behaviour of the elastomers under a mechanical field showed that the mesogens orient perpendicular to the stress field at low draw ratio and parallel to it at high draw ratio, for networks with higher crosslinking density; no negative orientation of the mesogenic groups was observed with lower crosslinking density. This phenomenon is interpreted by a proposed mechanism.

The authors would like to express their thanks to the National Natural Science Foundation of China for financial support of this work.

References

[1] Finkelmann, H., Kock, H., and Rehage, G., 1981, *Macromol. Chem. Rapid Commun.*, **2,** 317.

[2] Kock, H., Finkelmann, H., Gleim, W., and Rehage, G., 1984, *Macromol. Chem. Rapid Commun.*, **5,** 287.

[3] Bladon, P., Terentjev, E. M., and Warner, M., 1993, *Phys. Rev. E*, **47,** 3838.

[4] Benne, I., Semmler, K., and Finkelmann, H., 1995, *Macromolecules*, **28,** 1854.

[5] Kupfer, J., and Finkelmann, H., 1991, *Macromol. Chem. Rapid Commun.*, **12,** 717.

[6] Michael, G. R., Davis, F. J., Guo, W., and Cywinski, G., 1991, *Polymer*, **32,** 1347.

[7] Guo, W., Davis, F. J., and Michael, G. R., 1994, *Polymer*, **35,** 2952.

[8] Leedeva, T. L., Zenbarev, E. R., Rogovoi, V. N., and Talroze, R. V., 1998, *Macromolecules*, **31,** 3081.

[9] Li, M., Qiu, H., and Chen, X., 1999, *Macromol. Chem. Phys.*, **200,** 876.

[10] Li, M., Qiu, H., and Chen, X., 1999, *Polym. Bull.*, **42,** 77.

[11] Zhao, Y., and Lei, H., 1994, *Polymer*, **35,** 1419.

[12] Zhao, Y., Roche, P., and Yuan, G., 1996, *Macromolecules*, **29,** 4619.

[13] Kurihara, S., Sakamoto, A., and Nonaka, T., 1999, *Macromolecules*, **32,** 3150.

[14] Seymour, R. W., Allegrezza, A. E., and Cooper, S. L., 1973, *Macromolecules*, **6,** 896.

[15] Bonart, R., and Hoffman, R., 1982, *Colloid Polym. Sci.*, **260,** 268.

[16] Michael, G. R., Coulter, M., Davis, F. J., and Guo, W., 1992, *J. Phys. II Fr.*, **2,** 1121.

[17] Zhao, Y., Roche, P., and Yuan, G., 1996, *Macromolecules*, **29,** 4619.