



# Birefringence measurement of liquid single crystal elastomer swollen with low molecular weight liquid crystal

Yusril Yusuf<sup>a,\*</sup>, Yusuke Sumisaki<sup>a</sup>, Shoichi Kai<sup>b</sup>

<sup>a</sup> Department of Applied Quantum Physics and Nuclear Engineering, Graduate School of Engineering, Kyushu University, Fukuoka 812-8185, Japan

<sup>b</sup> Department of Applied Quantum Physics and Nuclear Engineering, Graduate School of Engineering, Department of Applied Physics, Faculty of Engineering, and Department of Life Engineering, Graduate School of Systems Life Sciences, Kyushu University, Fukuoka 812-8581, Japan

Received 27 August 2003; in final form 18 September 2003

Published online: 6 November 2003

## Abstract

We experimentally measured the birefringence of a liquid single crystal elastomer (LSCE) swollen with a low molecular weight liquid crystal (LMWLC), 5CB, by polarizing microscopy as a function of temperature. The optical intensity of swollen LSCE shows significant intensity changes at temperatures  $T_{NI}$ ,  $T_A$  and  $T_B$  that indicates a variety of different transitions. A temperature  $T_{NI}$  is known as the apparent nematic-isotropic transition for outside LMWLC,  $T_A$  and  $T_B$  are interpreted as the nematic-isotropic transition for LMWLC inside the LSCE and for the swollen LSCE, respectively.

© 2003 Elsevier B.V. All rights reserved.

## 1. Introduction

Liquid crystalline elastomers, LCEs, and gels presently attract much attention due to volume- and shape-changing properties caused by several environmental factors, such as temperature, compositions, electric fields and so on [1,2]. Recently, the swelling dynamics of anisotropic LCEs swollen with anisotropic solvents, e.g., low molecular weight liquid crystals (LMWLCs), have been extensively investigated [3–5]. Volume change dynamics of

swollen LCEs as a function of temperature show a variety of different transitions [3,5]. These transitions strongly depend on the phase transition of the LMWLC inside and outside the LCE as well as that of the LCE itself.

Dry LCEs exhibit a length and shape change at the nematic-isotropic phase transition that led to the suggestion by de Gennes et al. [6,7] that they may be useful components in artificial muscles. Applying an electric field to LCE swollen with LMWLC, the LMWLC molecules easily reorients parallel to the field, i.e., the electro-mechanical effect, that has been proposed as a soft actuator [3,8,9].

The LCE materials studied here were invented and developed by Finkelmann and co-workers

\* Corresponding author. Fax: +81926423820.

E-mail address: [yusuf@athena.ap.kyushu-u.ac.jp](mailto:yusuf@athena.ap.kyushu-u.ac.jp) (Y. Yusuf).

[10,11]. The macroscopic behavior of these materials arises from the coupling between the elastic properties of the cross-linked siloxane (8%) and liquid crystalline degrees of freedom (polymer backbones and mesogenic units, 92%). At first, only polydomain samples could be produced for which there are domains with highly non-uniform director orientations, denoted by a unit pseudo-vector  $\mathbf{n}$  [10]. It was discovered that applying a large enough strain could reorient the domains giving rise to a uniform director orientation [12,13]. In 1991, Kupfer and Finkelmann [11] succeeded in generating monodomain samples, i.e., liquid single crystal elastomers (LSCEs), by using two cross-linking steps with the second cross-linking step performed on a stretched film. These films turned out to have a spatially uniform  $\mathbf{n}$  parallel to the stretching direction. This anisotropy was optically tested using crossed polarizers to confirm director orientation (Fig. 1) [5]. The optical intensity changes by a rotation of crossed polarizers is shown in Fig. 2.

In the present study, we experimentally measured the birefringence of a LSCE film swollen with a LMWLC as a function of temperature.

## 2. Experimental

The sample cell was observed by a polarizing microscope (Nikon) equipped with a hot stage (Mettler Toledo FP90 Central Processor) as a temperature controller which can be simultaneously used for a photomonitor as well as a differential scanning calorimetry (DSC). The beam of a He–Ne laser has been used as a light source.

The LSCE film we prepare is  $\sim 150 \mu\text{m}$  thick and has an area of  $\sim 1.0 \text{ mm} \times 0.5 \text{ mm}$ . The sample is embedded in a well known LMWLC, 4-*n*-pentyl-4-cyanobiphenyl (5CB). As a previous communication [3,5], after swelling the LSCE sample thickness was increased with 1.8 times, i.e.,  $\sim 270 \mu\text{m}$ .

## 3. Results and discussion

The transmitted intensity of light  $I$  after the crossed polarizer is given as a function of the birefringence  $\Delta n$  and the sample thickness  $d$ .

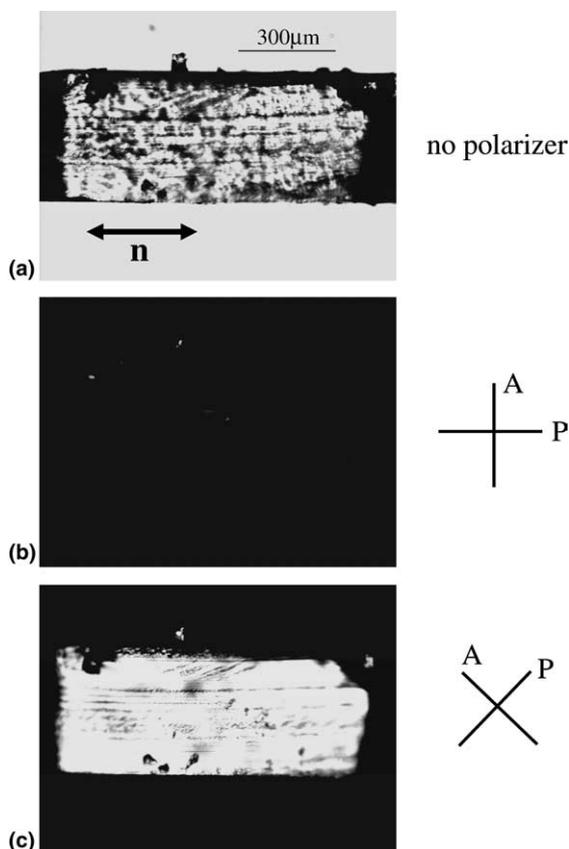


Fig. 1. Optical microscope pictures of dry LSCE: (a) no polarizers; (b) polarizers crossed parallel/perpendicular to director  $\mathbf{n}$  and (c) polarizers rotated  $45^\circ$  to  $\mathbf{n}$ .

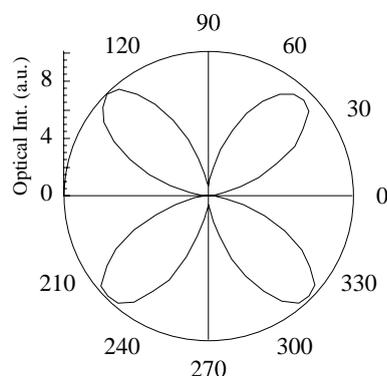


Fig. 2. Optical intensity measurement of in rotation of crossed polarizers.

$$I(\Delta n) = I_0 \sin^2 \left( \frac{\pi d \Delta n}{\lambda} \right), \quad (1)$$

where  $I_0$  is the intensity of the incident light and  $\lambda$  is the wavelength of the laser light (633 nm).  $\Delta n$  depend on the external fields and temperature.

Fig. 3 shows dramatic differences in the optical intensity changes between dry (Fig. 3a) and swollen (Fig. 3b) LSCE as a function of temperature. Increasing temperature at the elevation rate of temperature about 0.7 K/min, the intensity for a dry LSCE changes significantly in the vicinity of  $T_c \sim 80$  °C, i.e., the nematic-isotropic phase transition temperature of dry LSCE. According to the DSC measurement, a broad and small bump is observed at vicinity of  $T_c$ . Above  $T_c$ , LSCE film is still birefringent that is known as a typical feature

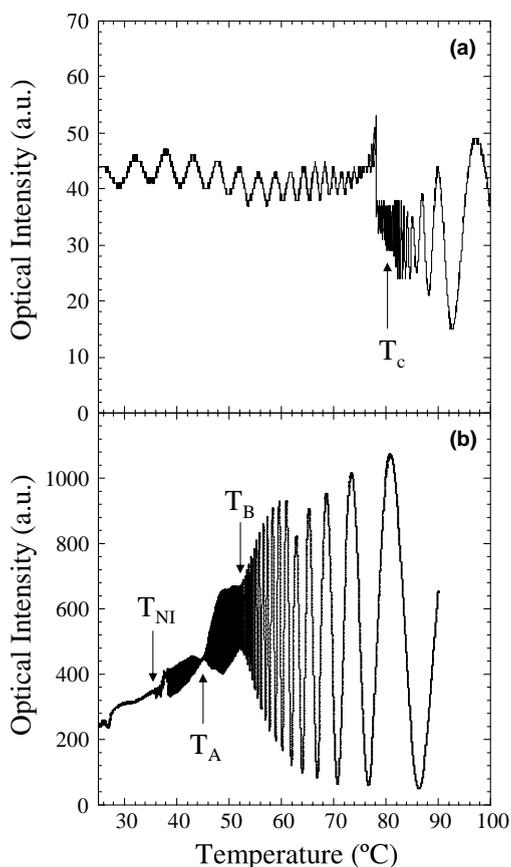


Fig. 3. Optical intensity changes for dry (a) and swollen LSCE (b) as a function of temperature.

of LSCE as being a consequence of ‘frozen-in’ nematic order (short range effects) in LSCE [14]. Black area in the graph of Fig. 3 is induced by very short of the period of sinusoidal modulated intensity which was analyzed by expanding data.

In the swollen LSCE, three dramatic optical intensity changes are observed at temperatures  $T_{NI}$  ( $\sim 34.5$  °C),  $T_A$  ( $\sim 45.0$  °C) and  $T_B$  ( $\sim 52.0$  °C). According to Eq. (1), these dramatic intensity changes indicate a variety of induced birefringences on the swollen LSCE system as a function of temperature. These transition temperatures are also observed in the volume transition measurement [3,5], also in DSC as well, where  $T_{NI}$  is the apparent nematic-isotropic transition for the outside LMWLC,  $T_A$  and  $T_B$  are interpreted as the nematic-isotropic transition for LMWLC inside the LSCE and for the swollen LSCE network, respectively. Above  $T_B$ , the swollen LSCE sample is still birefringent, i.e., not perfectly isotropic.

The birefringence  $\Delta n$  can be calculated from sinusoidal modulated intensity  $I$  in Eq. (1):

$$\frac{\pi d \Delta n}{\lambda} = \frac{\pi}{2} (2N - 1), \quad (2)$$

$$\Delta n = \frac{\lambda}{2d} (2N - 1), \quad (3)$$

with  $N$  is the peak number of sinusoidal intensity in Fig. 3. Notes that  $N$  should be counted from the peak at sufficiently high temperature in the isotropic phase.

Fig. 4 shows the temperature dependence of the birefringence  $\Delta n$  for dry (Fig. 4a) and swollen (Fig. 4b) LSCE. In the dry sample (Fig. 4a),  $\Delta n_{dry}$  has maximum value  $\sim 0.11$  at low temperature (in nematic phase). The continuous nematic-isotropic phase transition at  $T_c$  in dry LSCE indicates smooth transition without any jump.  $\Delta n_{dry}$  changes significantly at about 80 °C ( $T_c$ ). Above this temperature, there is remain a valuable  $\Delta n_{dry}$  because of a consequence of ‘frozen-in’ nematic order in LSCE [14]. Due to short range effects, we expected that  $\Delta n_{dry}$  can be approximated by a power law at above 80 °C

$$\Delta n_{dry} = a(T - T^*)^{-1}, \quad (4)$$

where  $T^*$  is known as a temperature slightly smaller than  $T_c$  [15]. Fit of the insertion in Fig. 4a

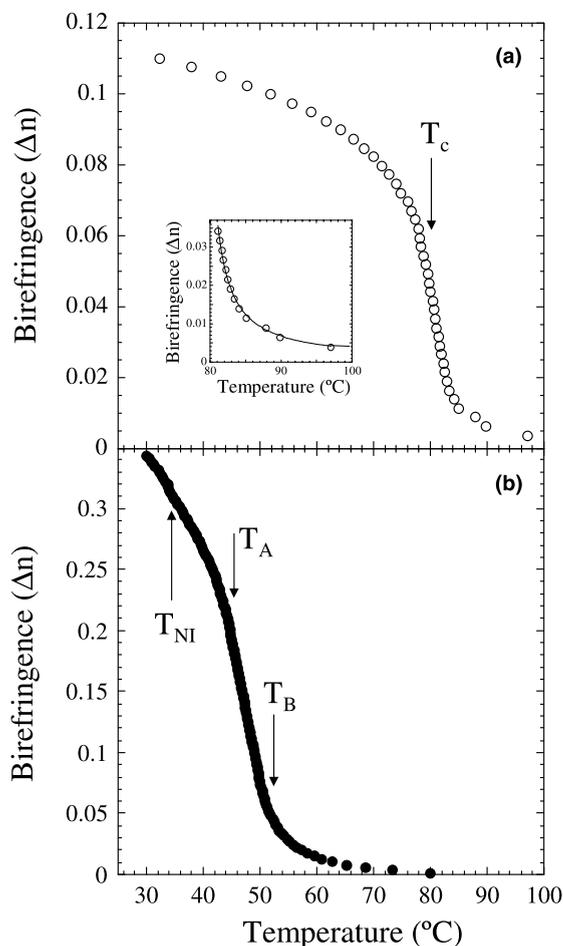


Fig. 4. Measured birefringence  $\Delta n$  for dry (a) and swollen LSCE (b) as a function of temperature.

and the extrapolation of the curve in Fig. 5 give  $a = 0.07897$  and  $T^* = 78.99$  °C. Temperature  $T^*$  is slightly below the expected  $T_c = 80$  °C which was determined from DSC measurement simultaneously done. Above  $T > T_c$ ,  $\Delta n_{\text{dry}}$  decreases smoothly with increasing temperature.

In the swollen LSCE cell (Fig. 4b), the birefringence  $\Delta n_{\text{swell}}$  has a maximum value  $\sim 0.35$  at low temperature (in nematic phase) and much larger than that of dry LSCE. In this graph, temperature dependence of  $\Delta n_{\text{swell}}$  shows that the apparent nematic-isotropic transition ( $T_B \sim 52.0$  °C) is lower than dry LSCE. No dramatic change of  $\Delta n_{\text{swell}}$  is observed at  $T_{\text{NI}}$ ,  $T_A$  and  $T_B$ . An important evidence in swollen LSCE is a large shift of tran-

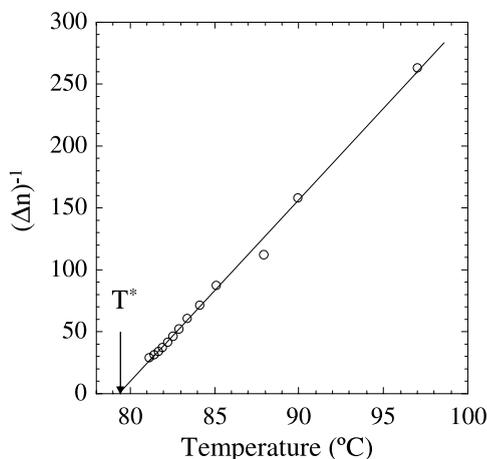


Fig. 5. Inverse of the birefringence  $\Delta n$  for dry LSCE plotted as a function of temperature.

sition temperature for a large change of birefringence.

A maximum value of the birefringence of swollen LSCE,  $\Delta n_{\text{swell}}$ , is achieved when both LMWLC and LSCE are nematic ordering ( $T < T_{\text{NI}}$ ). Above  $T > T_{\text{NI}}$ , both inside LMWLC and LSCE network are still nematic. The isotropic outside LMWLC induces the nematic-isotropic phase transition in the inside LMWLC which is completed at  $T_A$  ( $\Delta n_{\text{swell}} \sim 0.2$ ), i.e., the birefringence due to the inside LMWLC vanishes. As already explained that the LSCE have 92% mesogenics (side chains and backbone) and only 8% the crosslinkers, we expected that the liquid crystalline features dominate the swollen LSCE system in between  $T_A$  and  $T_B$ . In this temperature range the birefringence of LSCE take place. At  $T_B$  ( $\Delta n_{\text{swell}} \sim 0.02$ ),  $\Delta n_{\text{swell}}$  vanishes, then whole systems becomes isotropic (except short range effects).

According to the DSC measurements for swollen LSCEs performed simultaneously with optical measurements, a sharp peak is observed at  $T_{\text{NI}}$  and two broad small bumps are observed at  $T_A$  and  $T_B$ .

#### 4. Conclusion

It has been discussed that the birefringence dynamics of LSCE swollen with LMWLC as a

function temperature induce the dramatic optical intensity changes at different temperatures that indicate a variety of different transitions. These transition temperatures strongly depend on the phase transition of the LMWLC molecules inside and outside the LSCE and the LSCE networks.

### Acknowledgements

This work is partially supported by the Grant for Scientific Research sponsored by the Japan Society for the Promotion of Science. We hearty thank P. E. Cladis, H. R. Brand and H. Finkelmann for supplying us the samples and for valuable suggestions and comments.

### References

- [1] M. Shibamaya, T. Tanaka, in: *Responsive Gels: Volume Transition I*, 109, Springer-Verlag, Berlin, 1993, p. 1.
- [2] H.R. Brand, H. Finkelmann, *Physical Properties of Liquid Crystalline Elastomers*, in: D. Demus et al. (Eds.), *Handbook of Liquid Crystals Vol. 3: High Molecular Weight Liquid Crystals*, Wiley-VCH, Weinheim, 1998, p. 277.
- [3] Y. Yusuf, Y. Ono, Y. Sumisaki, S. Kai, 'Mathematical Aspects of Complex Fluids III', Research Institute for Mathematical Science (RIMS) report, vol. 1305, Kyoto University, Feb. 2003 p. 139.
- [4] K. Uruyama, Y. Okuno, T. Nakao, S. Kohjiya, *J. Chem. Phys.* 118 (2003) 2903.
- [5] Y. Yusuf, P.E. Cladis, H.R. Brand, H. Finkelmann, Y. Ono, Y. Sumisaki, S. Kai, to be published.
- [6] P.G. de Gennes, M. Hubert, R. Kant, *Macromol. Symp.* 113 (1997) 39.
- [7] M. Hubert, R. Kant, P.G. de Gennes, *J. Phy. I France* 7 (1997) 909.
- [8] R. Zentel, *Liq. Cryst.* 1 (1986) 589.
- [9] R. Kishi, Y. Suzuki, H. Ichijo, O. Hirasa, *Chem. Lett. Japan* (1994) 2257.
- [10] H. Finkelmann, H.-J. Kock, G. Rehage, *Makromol. Chem. Rapid Commun.* 2 (1981) 317.
- [11] J. Küpfer, H. Finkelmann, *Makromol. Chem. Rapid Commun.* 12 (1991) 717.
- [12] S. Disch, C. Schmidt, H. Finkelmann, *Makromol. Chem. Rapid Commun.* 15 (1994) 303.
- [13] S. Disch, C. Schmidt, H. Finkelmann, *Liquid Single Crystal Elastomers*, in: *Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, 1996.
- [14] H.R. Brand, K. Kawasaki, *Macromol. Rapid Commun.* 15 (1994) 251.
- [15] W. Kaufhold, H. Finkelmann, H.R. Brand, *Makromol. Chem.* 92 (1991) 2555.