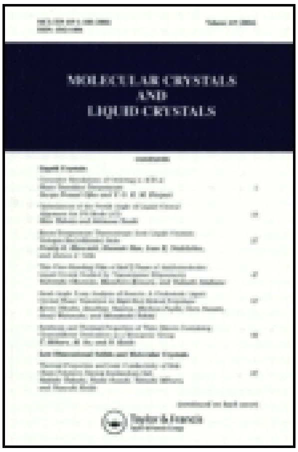

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Inverse Piezoelectric and Electrostrictive Response in Freely Suspended FLC Elastomer Film as Detected by Interferometric Measurements

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We report the electric field induced thickness variations of homeotropically oriented free standing films of a smectic (C* or A*) FLCE prepared from cross - linkable ferroelectric polysiloxanes. The changes in optical path length in free standing ferroelectric liquid crystal elastomer films have been detected by means of interferometric measurements at both the first and second harmonic of the exciting electric field (ω=33Hz). The measured electrostrictive strain is above 2.7% (in the thickness direction) at a electric field around 1.5 MV /m. Our experiment reveal that the inverse piezoelectric and electrostrictive response increases sharply near the Sm-C* - Sm-A* phase transition temperature. Also X-ray reflection measurements on a spin cast FLCE film reveal the constriction of smectic layers.

Keywords: FLCE; piezoelectric; electrostrictive; interferometer; X-ray.

INTRODUCTION

During the last decade ferroelectric liquid crystal elastomers (FLCE) have attracted great deal of attentions as a promising candidate for electro-optic and piezoelectric applications. In FLCE , the properties of

FLC phases are combined with an inherent polymer property, rubber elasticity[1-5]. The formation of network points in the FLC polymers by the thermal[2-3] or photoinduced[4-5] crosslinking hindered flow processes and as a result of that FLCE have a high mechanical stability. The electromechanical effect in freely suspended LC films has been of a special interest. Very recent measurements[6] on ultra-thin FLCE free standing film show a giant electrostrictive strain in the thickness direction which is higher than that of any other commercial piezoceramics like PZT or barium titanate. For practical applications it is important to know the quantitative change of thickness in the film plane. The objective of the present paper is to achieve high electromechanical response in FLCE through the electroclinic effect[7]. In the present study mechanical deformation in FLCE freely suspended film is effectively excited by a lateral alternating electric field and the thickness modulation (optical path-length modulation) perpendicular to the electric field have been measured by means of a Michelson Interferometer. In this paper we report the changes in film thickness at both the first (linear) and second harmonic (quadratic) of the exciting electric field. Additional X-ray reflections measurements have been performed on a spin-cast FLCE film in order to observe the electroclinic layer constriction.

EXPERIMENTAL

Sample

The chemical structure of the polymer used for the experiments is shown in Fig. 1. The polymeric sample was made as a self supported membrane by slowly pulling the molten substance with a razor blade across a hole of 1 mm diameter in a 150 μm thick glass substrate, between two evaporated silver electrodes. The smectic layers are arranged parallel to the plane of the film. The sample preparation is completed by a UV irradiation (Panasol-Elosol UV-P200 lamp) at 75^{0}C in the Sm-A* phase for five minutes to crosslink the FLC polymer. After the crosslinking, the sample is cooled down very slowly to room temperature. This crosslink stabilise the Sm-A* mono-domain structure at lower temperature.

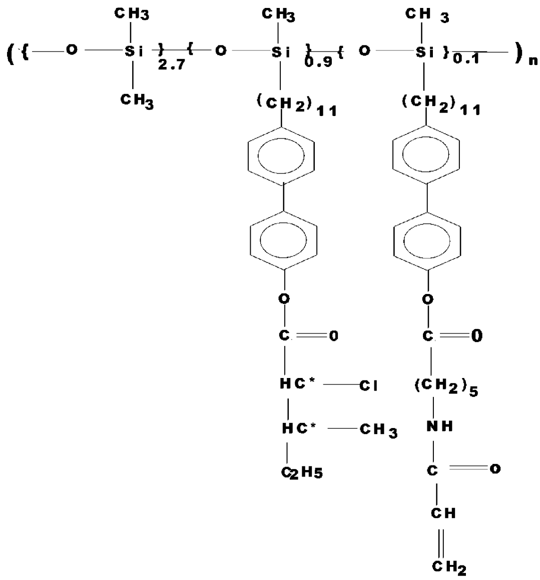

FIGURE 1: Chemical structure of the sample. 10% of the mesogenic sub-units are crosslinkable via UV – irradiation. Phase sequence: Sm-X 30 Sm-C* 61 Sm-A* 86 I.

The reflectivity of the film in the visible spectrum range of light was recorded as a function of wavelength (λ) in order to measure the absolute film thickness (h_0). Fitting the ratio of the reflected and the incident spectral intensities ($I_R(\lambda)/I_O(\lambda)$) with the airy function[8] yielded a film thickness $h_0 = 254 \pm 5$ nm.

The sample geometry for the measurements on free standing films is shown in Fig. 3. The mutual orientation of the electric field and the laser polarization are parallel to each other. In this geometry only the ordinary refractive index n_o is valid when the tilt angle θ of the mesogens is varied via the electronic effect. Details of the optics can be found in the literature[6].

Interferometer Set - Up

The interferometer set-up is depicted in Fig. 2. The sample and the hot stage were mounted at the focus of two long distance microscope objective lenses, which allow a small measurements spot under a negligible aperture angle. The divergence of the focused laser beam is small, because the focal length of the lenses is 20 mm, while the unfocussed beam diameter is 0.8 mm. The piezo actuator with mirror # 1 is used as a reference. Two lock-in amplifiers are employed to detect the photo-current modulations caused by the actuator and sample respectively. The periodic, electric field induced changes in film thickness (Δh) perpendicular to the electric field are measured by the phase sensitive detection as an optical phase shift between a sample beam, passing the film twice (Fig. 2) and a reference beam. The change in film thickness can be calculated from the measured difference in optical path length (Ξ) as follows[6]:

$$\Xi = \Delta h(n_o - 1) \tag{1}$$

In general, the strain ε (t) caused by an electric field $E= E_{AC} \cos(\omega t)$ with amplitude E_{AC} at frequency ω can be described as follows[9].

$$\varepsilon(t) = \frac{\Delta h(E)}{h_0} = \frac{1}{2} a E_{AC}^2 + d(\omega) E_{AC} \cos(\omega t) + \frac{1}{2} a(2\omega) E_{AC}^2 \cos(2\omega t) \tag{2}$$

where Δh is the change in the sample thickness, h_0 is the film thickness without electric field, d is the inverse piezoelectric modulus and a is the electrostriction coefficient. For simplicity Eq. (2) does not account for the tensor properties of the employed physical quantities. The contributions from the 1st harmonic (piezoelectric) and 2nd harmonic (electrostrictive) are easily separated using phase sensitive detection of the interferometer signal. Helium-Neon laser light (λ=632.8 nm) was used to detect the response of the film. The interferometer used in this experiment has a resolution <100 fm. AC electric field with a frequency of 33 Hz has been applied to the sample for the measurements. In order to exclude the effects of scattering, reflections or a modulation of the state of polarization of the laser light which may contribute to the measured signal, an analyzer is placed in front of the photo cell.

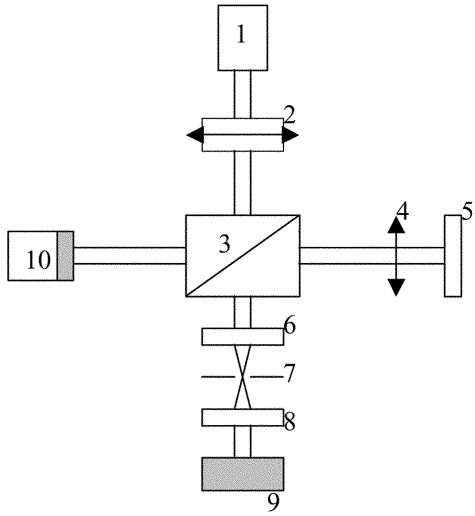

FIGURE 2: Interferometer setup. 1) He-Ne laser 2) Optical isolator with polarizer. 3) Beam splitter 4) Analyzer 5) Photo cell. 6) Lens 7) Sample position. 8) Lens 9) Mirror #2 10) Piezo actuator with Mirror #1.

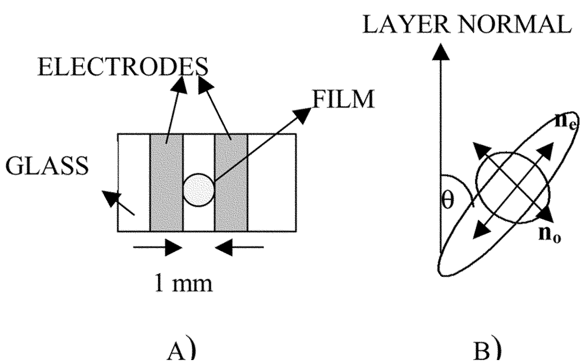

FIGURE 3: Sketch of the sample geometry. A) Top view of the sample. B) Molecular orientation.

X-Ray Geometry

Electroclinic layer constriction of another FLCE sample has been determined by X-ray reflection measurements. Measurement geometry is shown in Fig. 4.

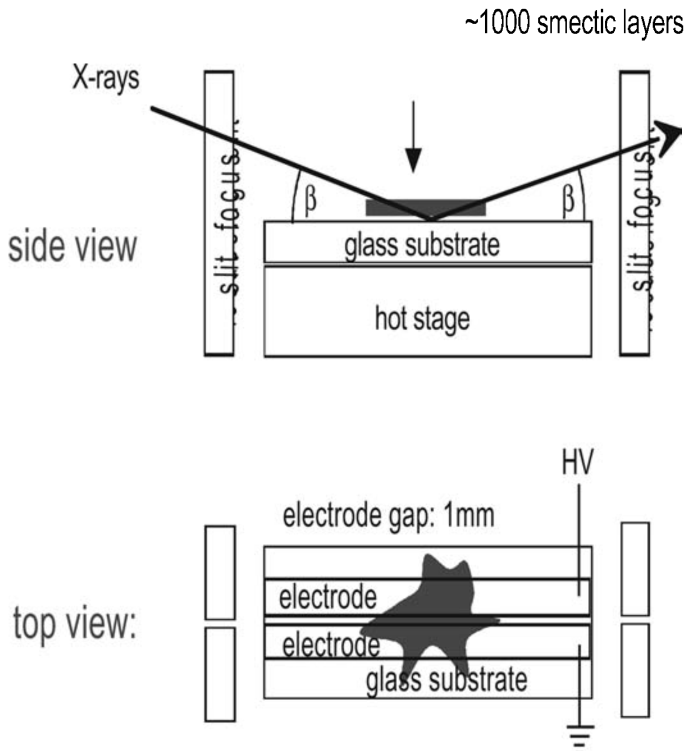

FIGURE 4: Above figure shows side and top view of the sample geometry respectively. At first silver electrodes with a gap of 1mm has been evaporated on the top of a glass substrate. Then a FLCE film has been deposited using spin casting method. The thickness of the sample is 4 μm (around 1000 smectic layers). The smectic layers are parallel to the glass substrate. Two collimating vertical slits ensure, that only the film area between the electrodes contribute to the scattered intensity.

RESULTS AND DISCUSSION

Interferometer Measurements

The copolymer film was crosslinked in the Sm-A* phase by irradiation with ultraviolet light[10] in order to obtain homeotropically aligned elastomer film. This exposure in UV light results in a pure elastic membrane[11] and the electromechanical behaviour of this membrane has been studied quantitatively. In our interferometric experiments we measured the thickness variation of (Δh) of thin FLCE films by the application of AC electric fields. The intensity modulations at the photo cells caused by the 254 nm FLCE film in response to the AC field are shown in Fig. 5. The measurements were performed at the 63^0 C in the Sm - A* phase of the elastomer. The main panel in Fig. 6 and Fig. 7 show the thickness variation (Δh) of the film with the amplitude of applied voltage (U_{AC}) at the first harmonic (33 Hz) and at the second harmonic respectively. From the interferometric measurements we obtained the Ξ values and if the effective refractive index (n_0 in our geometry) does not change due to tilt angle variations, Δh can be calculated simply using Eq. 1[6]. As expected, the data show a linear relationship (Fig. 6) between the Δh and the applied voltage U_{AC} and a square dependence at the second harmonic (Fig. 7). The linear relationship is due to the inverse piezoelectric behaviour and the quadratic is due to the electrostriction of the membrane. The linear effects are found to be small. It may be due to small angular mismatch in the set-up (i.e. laser beam not perfectly perpendicular to the film plane or due to a residual ferroelectric properties). On the other hand, the electrostrictions are found to be large.

In our measurement geometry smectic layers are arranged parallel to the plane of the film. In the simple model the smectic layer constriction i.e. thickness modulation can be written as $\Delta h/h_0 = 1\text{-}cos\theta$. The modulation will appear at the second harmonic of the electric field, because the upright position of the mesogens (θ=0) will passed twice during one period of the electric field as a consequence of electroclinic effect (in which $\theta \propto E$). We have found maximum 2.7 % thickness modulation at the lateral electric field of 1.5 kV/mm. The film thickness constriction of 2.7 % corresponds to an electrically induced tilt angle θ = 13.3^0 (obtained from the above simple cosine model).

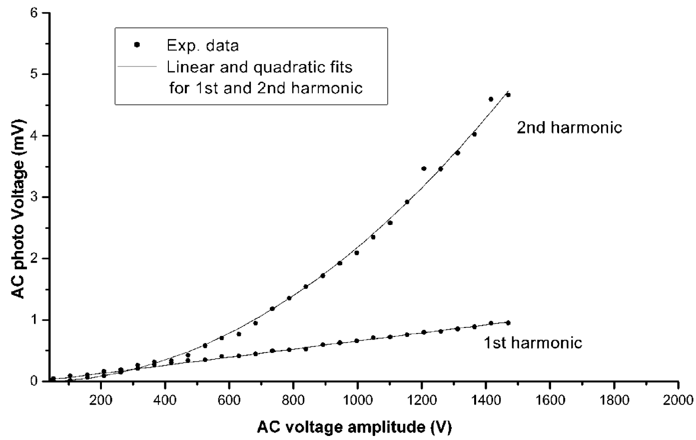

FIGURE 5: Intensity modulation at the photo cell at the 1st and 2nd harmonic of the AC field, at the temperature 63^0C.

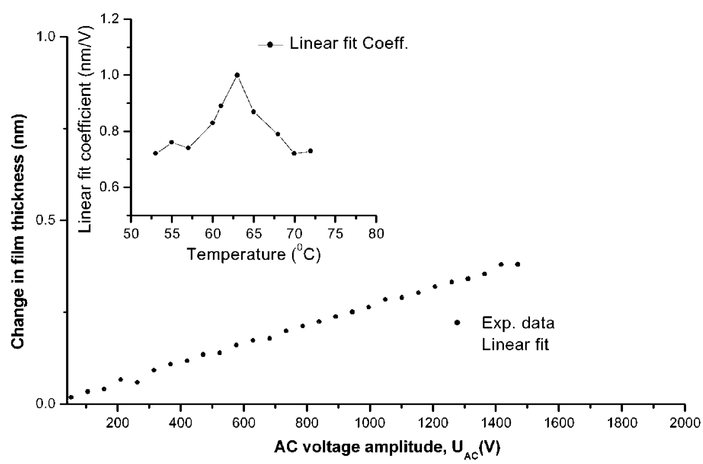

FIGURE 6: Main panel show the change of film thickness (Δh) as a function of applied AC voltage with amplitude U_{AC}(ω=33Hz) at the first harmonic, as determined in the interferometer at T= 63^0C. Inset shows the temperature dependent of linear fit coefficients.

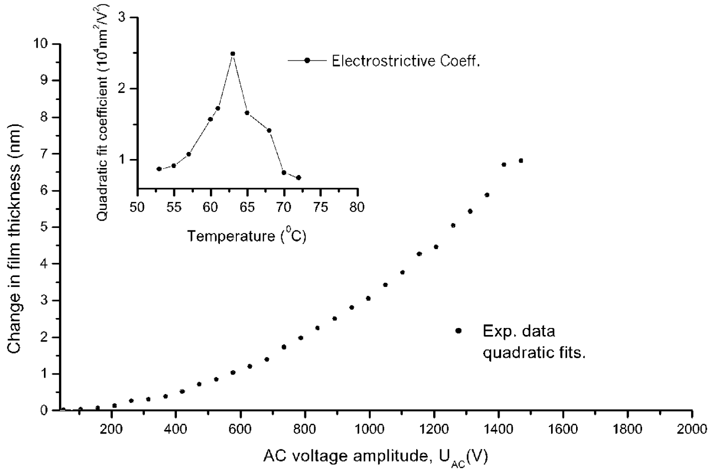

FIGURE 7: Main panel show the change of film thickness (Δh) as a function of applied AC voltage with amplitude U_{AC}(ω=33Hz) at the first harmonic, as determined in the interferometer at T= 63^{0}C. Inset shows the temperature dependent of the quadratic fit coefficients.

This is a quite acceptable number, as comparable θ values has already been reported for a FLC- polysiloxane in a commercial, 4 μm thick sample cell [12]. Electroclinic tilt angle of this sort of structurally similar copolymers were measured [2,13] by FTIR in 2 μm thick cells and which show that a 25 times stronger electric field was necessary to induce such a tilt. This is essentially due to the strong anchoring effects in the rather thin cells compared to the self supported film having no surface effect. Recently 4% lateral strain has been reported for this sample[8] of 70 nm thin film and which is highest strain observed in any material. In the present study we have found 2.7% strain at the same lateral electric field of a 254 nm thin film. The lower response may be due to the relatively thick film. The collective layer constriction in the thicker FLCE film may be slower than that of thinner film. Another reason may be the crosslinking time. In the present study crosslinking time is three minutes higher than in ref [6]. The higher crosslinking time may hindered the movement of the chiral liquid crystalline moieties in the elastomer, which turn the lower electrostrictive value. Nevertheless, this value in the present study is also huge compare to other electrostrictive materials. The inset of Fig. 6 shows the inverse piezoelectric coefficient (*d*) as derived from the linear fits (defined by $\Delta h/h_0 = d\, E_{AC}$, where $E_{AC}=U_{AC}/1mm$) to the first harmonic data at different temperatures. The inset of Fig. 7 shows the electrostriction coefficient *a* as derived from square fits (defined by ($\Delta h/h_0 = (1/2)a\, E^2_{AC}$) to the second harmonic data at different temperatures. Both the linear and quadratic response have sharp maxima close to the phase transition (Sm-C* - Sm-A*) temperature and that is two degrees higher than given in literature. This shift is most likely due to the fact that there is a temperature gradient between the hot stage and sample. For the small linear effect an increase (of coefficient *d*) of about 30 % is observed at the phase transition (Sm-C*- Sm-A*) temperature, whereas the quadratic effect (coefficient *a*) increases by about 175% near the transition (Sm-C* - Sm-A*) temperature. The above results can easily be explained by the electroclinic effects, as θ becomes softer near the phase transition temperature. All the above responses are reversible as expected from a pure elastic material.

Electro-optic Study

In order to confirm that there is tilt variation by the application of an electric field and the state of polarization of laser light does not change after passing through the film, a simple electro-optic study has been carried out. To do so the reference beam of the interferometer (Fig. 3) was blocked out and the signal from the photo cell was recorded by a Keithley multi-meter, instead of a lock-in amplifier. For a membrane having a thickness h_0 and an effective refractive index n, the transmission coefficient (T) at normal incidence depends on the wavelength λ as follows[14]:

$$T = \frac{I_t}{I_i} = \frac{1}{1 + ((n^2 - 1)/2n)^2 \sin^2(2\pi n h_0 \cos(\theta)/\lambda)} \quad (3)$$

where I_i and I_t are the incident and transmitted intensity of laser light through the films. θ is the tilt of the smectic phases. As we crosslinked the film at the Sm-A* phase, θ in above Eq. 3 becomes 0, when there is no external perturbation. Also in our measurement geometry n has to be replaced by n_0 of the medium.

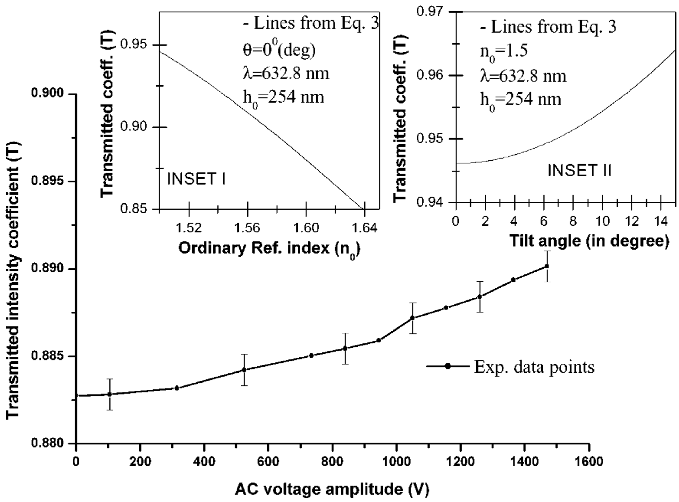

FIGURE 8: Main panel show the change of transmission coefficient as a function of applied AC voltage with amplitude $U_{AC}(\omega=33Hz)$ at temperature T= 63^0C. Inset I and II show the simulation curves as derived from Eq. (3).

It is observed experimentally from the main panel of Fig. 8 that the transmitted intensity coefficient (T) increases with the increase of applied AC voltage. In order to explain this behaviour two simulation curves of Eq. 3 have been depicted in the inset of Fig. 8. Inset I is the plot of Eq 3 considering n_0 is dependent on an external electric field. The initial value of n_0 is chosen 1.5 which is quite common for LC materials and θ considered to be 0^0. Inset II represents the plot of Eq. 3 considering θ as dependent under the application of an external electric field. In both cases h_0 and λ are chosen 254 nm and 632.8 nm respectively as these values are used in experiment. It is clear from inset I if n_0 would changed only we could expect a decrease of T for the particular above parameters but that did not happen in the electro-optic experiment. On the other hand if the induced tilt increases keeping the n_o fixed then the transmission coefficient increases. As $\theta \propto E$ we also found T increased with the increase of Voltage. The nature of variation of T of Inset II is not exactly similar with that of the main panel but quite comparable and clearly indicates that there is an induced tilt by the application of electric field. The magnitude of T in the main panel is few % smaller than that of Inset II. It may be attributed to the scattering of light from film plane, due to angular mismatch.

The table 1 gives an overview of the achievable strains and the required electric field strengths in FLCE.

TABLE 1

Material	Electrostrictive strain	Piezoelectric strain	Reference
Self Supported FLCE film	4% lateral strain at 1.5 MV/m	0.004% at 1.5 MV/m	Ref. 6
Self supported FLCE film	2.7% lateral strain at 1.5 MV/m	0.0015% at 1.5 MV/m	This work
Spin cast FLCE film on glass substrate	1% lateral layer constriction at 2MV/m		This work

X-Ray Study

In order to confirm the electrostrictive layer constriction by an independent method, X-ray reflections measurements on spin-cast FLCE films have been performed. The thickness of the films were measured using the alpha-step surface profilometer. X-ray reflections characterization of the films were carried out using a reflectometer operating with Copper Kα radiation (wavelength 0.1541 nm). The core of the butterfly-type reflectrometer - devised to measure small angle scattering from a horizontal surface – consists of three goniometers (Model No. 420, Huber, Garching, Germany) carrying the sample stage, the X-ray tube and detector pivot towers. The instrument has a precision of determining the scattering angle (called β here to avoid confusion with the tilt angle θ) of 5×10^{-3} deg (^{0}). Details of the X-ray set - up can be found in the literature[15].

Earlier, the electroclinic layer constriction of smectic layers is conclusively demonstrated by X-ray scattering on low molecular weight ferroelectric liquid crystals by other group[16]. The Bragg reflections from the smectic layers of a similar FLCE with 20% of crosslinkable mesogens [10] , that showed a stronger response on the substrate are displayed in Fig. 9 . The spin casting process leads to an arrangement of the smectic layers parallel to the plane of the film (and of the substrate), similar to that of free standing film. Likewise, the 4 μm thick, cast film was crosslinked in the Sm-A* phase. Measurements as a function of temperature have been performed without electric field and with 2kV applied across a 1 mm gap between evaporated silver electrodes on the glass substrate. During the measurements, the sample is not moved. Instead, the angular position of both, the X-ray source and the detector are simultaneously varied by the same angle β. The moving direction of the goniometer arms was the same.

The electroclinic effect is observed 10 degrees below the phase transition temperature (Sm-C*- Sm-A*) and vanishes 10 degrees above. It was always measured several times with electric field on/off to make sure that other effects (e.g. evaporation of a rest of solvent or so) do not influence the data[17]. The respective curves with electric field on or off were easily reproduced within the error bars given in Fig. 9.

Fig 9 shows that near the Curie temperature of this sample, at T = 95^{0}C, the Bragg peak maximum of the smectic layers maximum is shifted by about +0.01^0 due to an electric field of 2kV/mm. This corresponds to a constriction for a 4.5 nm thick smectic layer by about 1% and an induced tilt angle of θ ~8^0.

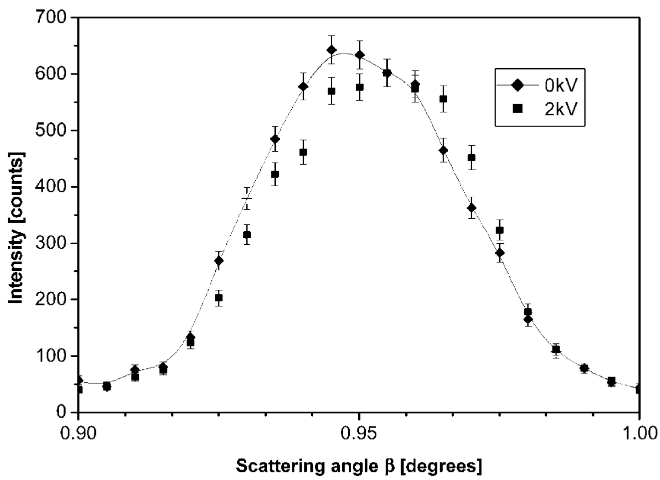

FIGURE 9: The first order Bragg reflections of a spin cast FLCE film are shown without electric field and with the electric field of 2kV/mm at the temperature 95^{0}C.

This effect is fully reversible. However the layer constriction of ~1% in the substrate bonded FLCE is significantly smaller than that of 2.7% observed in the freely standing film in the interferometric measurements. This is attributed to anchoring effects on the substrate, that do not occur in freely suspended films.

SUMARRY

The present experimental study on freestanding films of FLCE can be summarized as follows:

i) Freely standing thin films of FLCE were prepared by a photo (UV) induced crosslinking reaction.

ii) Lateral electric field (direction of electric field perpendicular to the layer normal) was applied to the FLCE films and the resulting inverse piezoelectric and electrostrictive response was measured by an interferometer. The constriction is based on an electrically induced tilt of the chiral liquid crystal moieties in the elastomer.

iii) The inverse piezoelectric coefficient (*d*) and the electrostrictive coefficients (*a*) increase sharply at the Sm-C* - Sm-A* transition temperature, which is consistent with the electroclinic effect.

iv) Electro-optic studies indicate clearly that there is a change in the tilt by the application of electric field and also suggest that there is no significant change of effective refractive index (n_0 in our case) .

v) The electroclinic origin of the effect was also proved by X-ray reflections measurements on FLCE films that were spin cast on a glass substrate.

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References

[1] F. Kremer, W. Lehmann, H. Skupin, L. Hartmann, P. Stein, H. Finkelmann, *Poly. Adv. Technol.* . **9**, 672 (1998).

[2] H. Skupin, F. Kremer, S.V. Shilov, P. Stein , H. Finkelmann, *Macromolecules*, **32**,3746, (1999).

[3] T. Eckert, H. Finkelmann, M. Keck, W. Lehmann, F. Kremer, *Macromol. Rapid. Commun*. **17,** 767 (1996).
[4] S.V. Shilov, E. Gebhard, H. Skupin, F. Kremer, R. Zentel, *Macromolecules*, **32**, 1570 (1999).
[5] H. M. Brodowsky, U.-C. Boehnke, F. Kremer, E. Gebhard, R. Zentel, *Langmuir,* **15,** 274 (1999).
[6] W. Lehmann, H. Skupin, E. Gebhard, C. Tolksdorf, R Zentel, P Kruger, M. Losche, F. Kremer, *Nature*, **410,** 447(2001).
[7] S, Garoff and R. B Meyer, *Phys., Rev. Lett*, **38**, 848(1977).
[8] E. Hecht, *Optik*, Addison-Wesley, Bonn, 387 (1989).
[9] T. Jaworek, D. Neher, G. Wenger, R.H. Wieringa, A. J. Schouten, *Science*, **279**, 57, (1998).
[10] E. Gebhard and R. Zentel, *Macromol. Chem Phys*. **201** 902(2000).
[11] H. Schuring, R. Stannarius, C. Tolksdorf, R. Zentel, *Macromolecules,* **34**, 3962(2001).
[12] H. Poths, G. Anderson, K. Skarp, R. Zentel, *Adv. Mat*, **4**, 792, (1992).
[13] S.V. Shilov, H. Skupin, F. Kremer, T. Wittig, R. Zentel, *Phys. Rev. Lett*., **79**, **No.9**, 1686, (1997).
[14] R. Stannarius, C. Cramer, H, Schüring, *Mol. Cryst. Liq. Cryst*, **329,** 423, (1999).
[15] P. Krüger, M. Schalke, J. Linderholm, M. Lösche, *Rev. Sci. Instrum*., **72,** (2001).
[16] A. G. Rappaport, P. A. Williams, B. N. Thomas, N. A. Clark, M. B. Ross, D. M. Walba, *Appl. Phys. Lett*., **67**, 362, (1995).
[17] W. Lehmann*, Ph. D. thesis*, Leipzig University, in preparation.