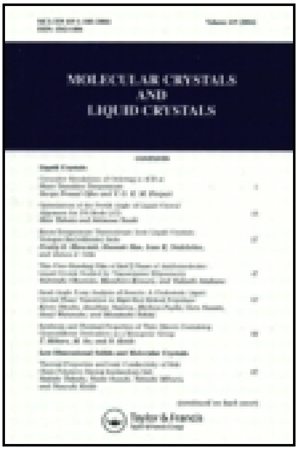

Molecular Crystals and Liquid Crystals

Electromechanical and Electrooptical Effects of Liquid Crystal Elastomers Swollen with a Low Molecular Weight Liquid Crystal

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We experimentally investigated the electromechanical and electrooptical effects in polydomain liquid crystal elastomers (LCEs) swollen with a well known LMWLC, 4-n-pentyl-4-cyanobiphenyl (5CB). The displacement and optical intensity changes

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were measured as a function of the voltage. We found that the threshold value for the onset of electromechanical and electrooptical effects is small, V ~ 1.0 V.

Keywords: electromechanical effects; electrooptical effects; liquid crystal elastomers

1. INTRODUCTION

Liquid crystal elastomers (LCEs) which were first synthesized by Finkelmann *et al.* in 1981 [1] are unusual, complex and fascinating materials obtained by crosslinking polymer liquid crystals, that combine the anisotropic properties of liquid crystalline order of mesogens and the elastic properties of cross-linked polymer networks (Fig. 1a). Due to the coupling between the elastic properties of the polymer

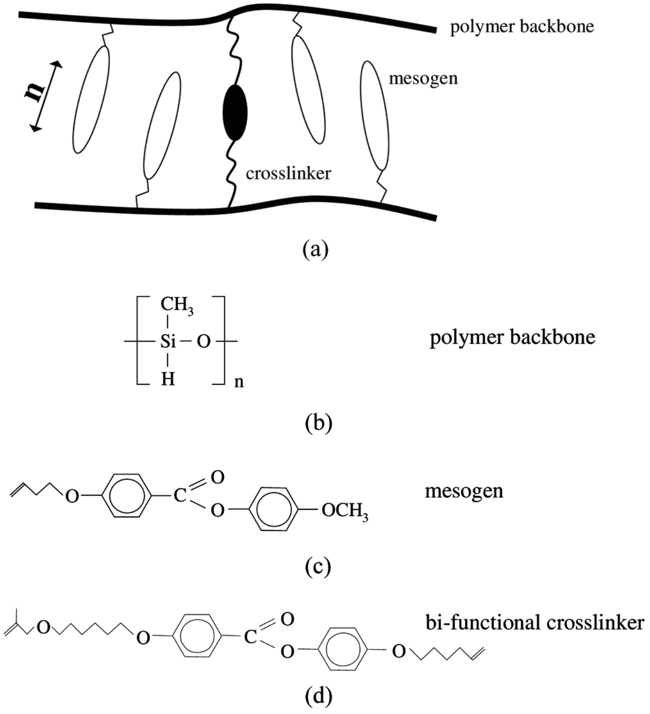


FIGURE 1 Schematic picture for a polydomain LCE structure (a) and the chemical structure of the polymer backbone (b), mesogenic side chain (c) and crosslinker (d).

network and the anisotropy of the mesogenic side chains, the applications of any external stimulus such as mechanical, temperature, magnetic and electric fields, will induce shape and optical birefringence changes. Because of this response to external stimuli, LCEs promise many potential applications such as soft actuators, micro-pumps and artificial muscles [2,3]

Without any special treatment, LCEs always form a highly non-uniform, *i.e.*, polydomain structure, in which there is a distribution of domains with different director orientations, denoted by a unit pseudo-vector **n** (Fig. 1a) [1]. But then it was discovered that applying a large enough strain could reorient the domains giving rise to a uniform director orientation resulting in a LCE with a unique **n**, a so-called monodomain sample, *i.e.*, liquid single crystal elastomers (LSCEs) [4–6]. Polydomain LCEs are prepared by polymer analogue reaction of polymethyl-hydrogen-siloxane with an average degree of polymerization of about 60 (Fig. 1b), the monomeric mesogen 4-butenoxy-4-methyloxy benzoic acid phenylester (CH2=CH−CH2−CH2−O−phenyl−COO−phenyl−OCH3) (Fig. 1c) and the cross-linking agent (H2=CH−O−(Si(CH3)2−O)12−CH=CH2) (Fig. 1d). The cross-linking agent is the mesogen with terminal vinyl groups. The concentration of the cross-linker is about 8%. The procedure of the synthesis is described in [1,4].

In the present study we use polydomain LCE. Picture of a dry polydomain LCE sample in the nematic and in the isotropic phases is shown in Figure 2. At low temperatures, in the nematic phase, the polydomain is optically opaque because of the strong light scattering by random domain (director **n**) orientation. In the isotropic phase, the polydomain sample is clear since there is no scattering. While dry monodomain LCEs exhibit drastic length and shape changes at

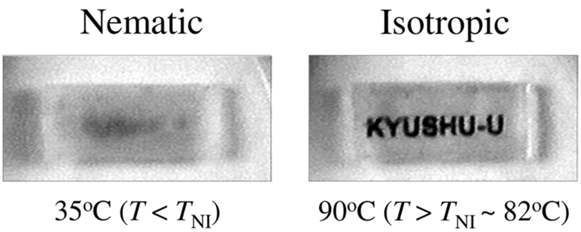


FIGURE 2 Photographs of a polydomain LCE sample in the nematic and the isotropic phases. In the nematic phase a polydomain sample is opaque, while at high temperatures above T_{NI} (~82°C) a polydomain sample is clear.

the nematic-isotropic phase transition, dry polydomain LCEs show no significant shape and volume changes after heating to the isotropic phase. Dry polydomain LCEs behave in this respect like isotropic elastomers. This seems reasonable as the orientational order of side chains in polydomain LCEs is limited to small domains.

The electromechanical and electrooptical effects of anisotropic gels have been studied experimentally by several groups [7–13]. In the first investigation of electromechanical effects in LCEs swollen with low molecular weight liquid crystal (LMWLCs) in 1986, Zentel found [7] tiny changes in large fields. Barnes *et al.* [8] reported their largest field driven shape change to be about 20% contraction of a polydomain elastomer swollen in 6CB (hexyl-cyanohexyl-biphenyl) when both, the elastomer and 6CB, were isotropic. In 1994, Kishi *et al.* [9] reported quantitative results on shape changes of swollen polydomain LCEs under a DC electric field (~0.3 V/μm). Courty *et al.* [10] demonstrated a fairly large electromechanical response for a low concentration of carbon nanotubes embedded in a LCE. They needed a large applied field (order of ~1 V/μm) to generate a strain, ε, of order ~0.1%. Recent papers discussing the experimental results of electromechanical effects of LCEs swollen with LMWLC are by Yusuf *et al.* [11] and Urayama *et al.* [12,13].

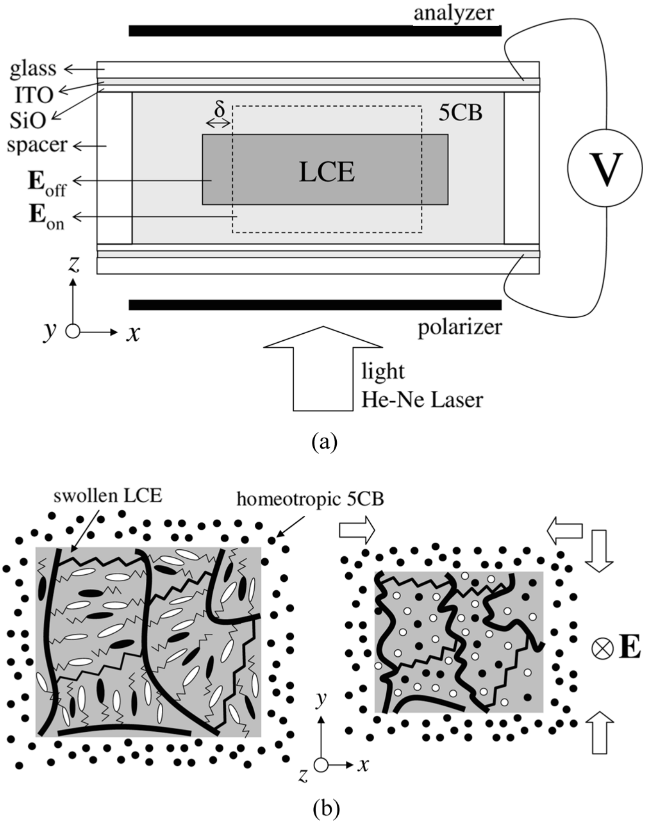
Concerning electrooptical effects, Hikmet *et al.* [14] studied the switching properties of polymer-dispersed liquid crystals (PDLCs) by measuring the transmission and birefringence as a function of voltage. Chang *et al.* [15] studied electro-optic effects in nematic gels obtained by photo-crosslinking a well-oriented LMWLC. They found that relatively high voltages were required to observe a small director reorientation. Recently, Urayama *et al.* [16] studied electro-optical effects in nematic gels obtained by a mixture of side chain nematic polymers and a photoinitiator (Irgacure-784).

The action of an electric field on the director orientation is another well-known cooperative effect in nematic LMWLCs [17]. Only a small voltage (~1 V) is required to change the orientation of nematic LMWLCs giving a large electrooptic response. In contrast, dry LCEs require a large voltage to obtain any electro-optic response as well as electrooptical effects. Therefore, LCEs swollen with nematic LMWLC could be a good candidate to observe shape and optical birefringence changes at low voltages.

In this article, we investigate electromechanical and electrooptical effects of polydomain LCEs after swelling in a well known nematic LMWLC, 4-n-pentyl-4-cyanobiphenyl (5CB). Previously [18] we investigated the swelling behavior of thin film LCEs by 5CB. We found that polydomain LCEs swell isotropically as expected for isotropic gels.

2. THE EXPERIMENT

The polydomain LCE films we prepare are ~25.0 ± 1.0 μm thick with area ~300 μm × 150 μm. The samples are embedded in 5CB for swelling between two transparent indium tin oxide (ITO) electrodes with very clean SiO surfaces (Fig. 3a). The SiO coating is used to avoid complications such as e.g. hydrodynamic effects arising from charge



(a)

(b)

FIGURE 3 Experimental sample cell and schematic picture for field effects in swollen polydomains. A polydomain sample is embedded in homeotropically oriented 5CB for swelling between two transparent indium tin oxide (ITO) electrodes with very clean SiO surface. An alternating electric field, $\mathbf{E} = (0, 0, E_z)$, is applied to the sample cell (a). The displacement δ is measured at the top of the edge of swollen LCEs from their equilibrium state, at V = 0 V. In (b), a schematic picture is shown for field effects of swollen polydomain sample without voltage (left) and with a voltage (right). The dark and open ellipses inside the swollen LCE indicate 5CB and the mesogenic side chains.

injection. 5CB was homeotropically aligned at the electrode surface. The cell gap was controlled by a 100 µm polymer (Mylar) spacer. In the experiments, an alternating electric field with rectangular waveform is applied between the electrodes, *i.e.*, $\mathbf{E} = (0, 0, E_z)$ at room temperature. The electrooptical measurements were carried out using a He-Ne laser ($\lambda = 633\,\mathrm{nm}$) and a photodetector (Mettler Toledo FP90 Central Processor) with a polarizing optical microscope (Nikon E600WPOL).

To quantify the shape changes as a function of applied voltage, we defined the displacement δ, the displacement at the top of the curved edge of the swollen LCEs from its equilibrium state, at $\mathrm{V} = 0\,\mathrm{V}$ (Fig. 3a).

Figure 3b shows a schematic picture for the electromechanical effects of swollen polydomain LCE. Applying an electric field to LCEs swollen with 5CB, the LMWLC director easily reorients parallel to the field. This electro-mechanical effect is mediated by the cooperative effect typical of LMWLC. The mesogenic side chains can thus communicate with each other on length scales extending beyond a typical mesh size of the cross-linked polymer network. Therefore a relatively weak electric field can also trigger a shape change.

3. RESULTS AND DISCUSSION

Figure 4 shows the voltage dependence of the displacement δ (a) and of the normalized intensity I_{nlz}. The solid lines are fits to

$$\delta(V) = 14.36 - 15.25\exp(-V/3.05) \tag{1}$$

for the displacement and

$$I_{\mathrm{nlz}}(V) = 0.40 + 0.55\exp(-V/13.5) \tag{2}$$

for the normalized intensity, as a guide to the eye. $I_{\mathrm{nlz}}(V)$ monotonically decreases in voltage and is nearly saturated at $\mathrm{V} \sim 100\,\mathrm{V}$, while δ (V) is nearly saturated already at $\mathrm{V} \sim 20\,\mathrm{V}$.

The insets in Figure 4 show a relatively small threshold value, V_{th}, for the onset of the electromechanical and electrooptical effects: $V_{\mathrm{th}} \sim 1.0\,\mathrm{V}$. Even though both effects show a similar threshold value for the onset, the saturation values as a function of applied voltage for the displacement δ and the normalized intensity I_{nlz} differ by about a factor of 5. This is related to the fact that the electrooptical effect in swollen polydomain samples is associated with the reorientation of LMWLC and mesogenic side chains due to the application of the electric field. This seems reasonable as $\sim$400% LMWLC entered the polydomain sample during the swelling process [18]. The dynamics

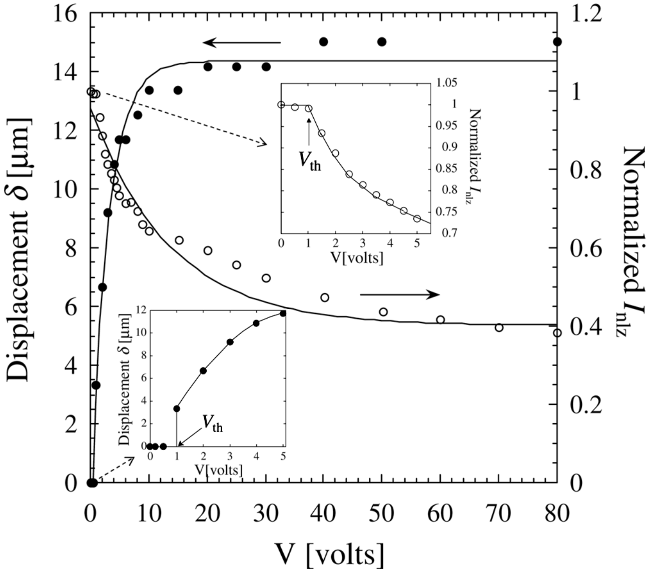
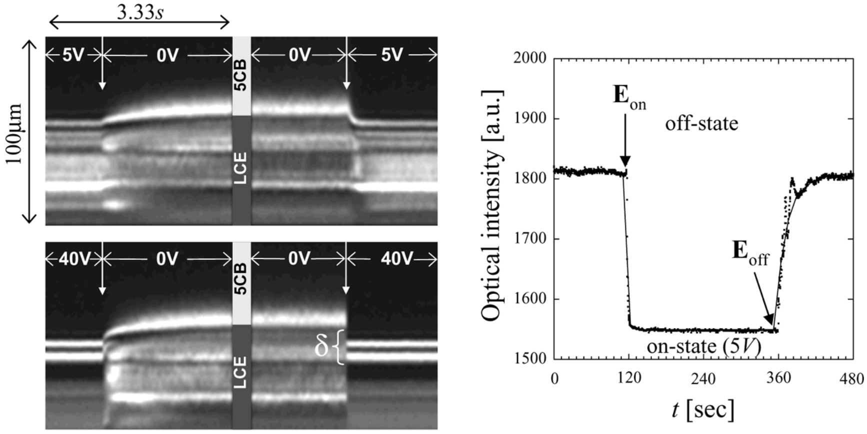


FIGURE 4 Voltage dependence of the displacement δ and the normalized intensity I_{nlz} of a swollen polydomain LCE at room temperature. The solid lines are $\delta(V) = 14.36 - 15.25\exp(-V/3.05)$ and $I_{\mathrm{nlz}}(V) = 0.40 + 0.55\exp(-V/13.5)$. Insets: expanded version of the graph to show the threshold for the shape and optical intensity changes, $V_{\mathrm{th}} \sim 1.0\,\mathrm{V}$.



(a) (b)

FIGURE 5 Dynamics of shape (a) and optical intensity (b) changes of a swollen polydomain LCE after applying a voltage.

of the cross-linked polymer networks coupling to the director reorientation of the LMWLC and to the mesogenic side chains contributes to the electromechanical effect.

The dynamic response for electromechanical and electrooptical effects under crossed polarizers is shown in Figure 5. Figure 5a show s-t plots made at one of the LCE-5CB edges after applying voltages of V = 5 V and V = 40 V. The black region is homeotropically oriented 5CB. The displacement δ is the displacement at the edge from its equilibrium state (V = 0 V). The bright region on the edge is a result of 5CB̀s increasing birefringence as its extraordinary optic axis changes to meet that of the LCE.

The optical intensity change dynamics through crossed polarizers is shown in Figure 5b. The optical intensity decreases very rapidly when the field is switched *on*, *e. g.*, V = 5 V, and increases exponentially after switching *off*.

4. CONCLUSION

We have investigated the electromechanical and electrooptical effects of a thin film polydomain LCE swollen in a nematic LMWLC (5CB) and we observed a relative small threshold value ($V_{\text{th}} \sim 1.0\,\text{V}$) for the onset of electromechanical and electrooptical effects. We conclude that the electromechanical effect is due to the coupling between the elastic properties of the polymer network and the LMWLC and the mesogenic side chains attached to the polymeric backbones. The electrooptical effects arise from the director reorientation of LMWLC and mesogenic side chains due to the application of the electric field.

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