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Electrooptical Effects of Swollen Polydomain Liquid Crystal Elastomers

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The electrooptical effects of polydomain liquid crystal elastomers (LCEs) swollen with low molecular weight liquid crystals (LMWLCs) have been investigated in detail. A well known LMWLC, 4-*n*-pentyl-4-cyanobiphenyl (5CB), is used as the solvent. The optical intensity of transmittance was measured as a function of voltage. The switching behavior was characterized by the voltage and time dependences of the transmittance on an instantaneous voltage switch. It is found that the threshold for the onset of the electrooptical effects is small ($V \sim 1.0$ V). The measured response time when switching *on* for the electrooptical effects is consistent with the response behavior of ordinary liquid crystals. However, the relaxation time when switching *off* shows a voltage independence and its value is about 4 times smaller than that of the electromechanical effect.

KEYWORDS: liquid crystal elastomer, electrooptical effect
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Liquid crystal gels such as liquid crystal elastomers (LCEs) have recently attracted considerable attention due to their anisotropic properties, which show changes in their shape, size, and optical properties in response to many external stimuli such as temperature and electric fields. The interest in LCEs is generated by a combination of the properties of liquid crystals and the elasticity due to polymer networks.[1,2] Owing to these properties, changing the temperature or applying an electric field induces or leads to anisotropic thermomechanical, electromechanical, and electrooptical effects.[2–15,17–29] In addition to the attractiveness of such properties in fundamental physics, LCEs have many potential applications such as soft actuators and artificial muscles.[12–16]

The electrooptical effects of anisotropic gels have been studied experimentally by several groups.[20,28,30] Hikmet *et al.*[30] studied the switching properties of polymer-dispersed liquid crystals (PDLCs) by measuring the transmission and birefringence as a function of voltage. Chang *et al.*[20] studied the electrooptic effects in nematic gels obtained by photocrosslinking a well-oriented low molecular weight liquid crystal (LMWLC). They found that relatively high voltages were required to observe a small director reorientation. Urayama *et al.*[28] studied the electrooptical effects in nematic gels obtained by a mixture of side chain nematic networks and photoinitiators (Irgacure-784).

In the previous studies, we demonstrated the electromechanical effects in polydomain and monodomain LCEs swollen with LMWLC.[25,26] Changes in shape (~ 1–$20\,\mu$m) are observed with small voltages ($V \sim 0.5$–10 V). In ref. 26, we note the following: (1) As compared to unswollen LCEs, a dramatic decrease of ~200 times in the threshold field was observed for electromechanical effects in swollen LCEs. (2) Field-induced shape changes in swollen monodomain planar LCEs (P-MONO) are observed in the vicinity of the swollen LCE-LMWLC interface where the director of LMWLCs changes its orientation. In the bulk of swollen P-MONO, when a low electric field (below $V \sim 200$ V) is applied, electrooptical effects are not observed. This is because monodomain LCEs have a strong elastic network due to the stretching process during LSCE preparation.

Here, we investigate the low-voltage-driven electrooptical effects in polydomain LCEs swollen with LMWLCs.

Polydomain LCEs are produced in which there are domains with different director orientations, denoted by a unit pseudo-vector, $\hat{n}$.[2] They are prepared by the polymer analog reaction of poly(methyl hydrogen siloxane) with an average degree of polymerization of about 60 and monomeric mesogen 4-butenoxy-4-methyloxy benzoic acid phenylester (CH_2=CH–CH_2–CH_2–O–phenyl–COO–phenyl–OCH_3) and a cross-linking agent (H_2=CH–O–$(Si(CH_3)_2$–$O)_{12}$–CH=CH_2). The cross-linking agent is oligomeric poly(dimethylsiloxane) with terminal vinyl groups. The concentration of the cross-linking (about 8%) agent is related to the reactive vinyl groups. The procedure of synthesis is described in refs. 2 and 3.

The polydomain LCE films that we prepared are $\sim 25.0 \pm 1.0\,\mu$m thick with an area of $\sim 300 \times 150\,\mu m^2$. Samples were embedded in LMWLCs (anisotropic solvents) for swelling between two transparent indium tin oxide (ITO) electrodes with very clean SiO surfaces. The SiO coating was used to avoid complications such as, for example, the hydrodynamic effects arising from a charge injection. We used a well-known nematic LMWLC, 4-*n*-pentyl-4-cyanobiphenyl (5CB), that was homeotropically aligned at the electrode surface. The cell gap was controlled by a $100\,\mu$m polymer (Mylar) spacer. In the experiments, an alternating electric field with frequency $f = 50$ Hz with a rectangular waveform was applied between the electrodes, i.e., $\mathbf{E} =$

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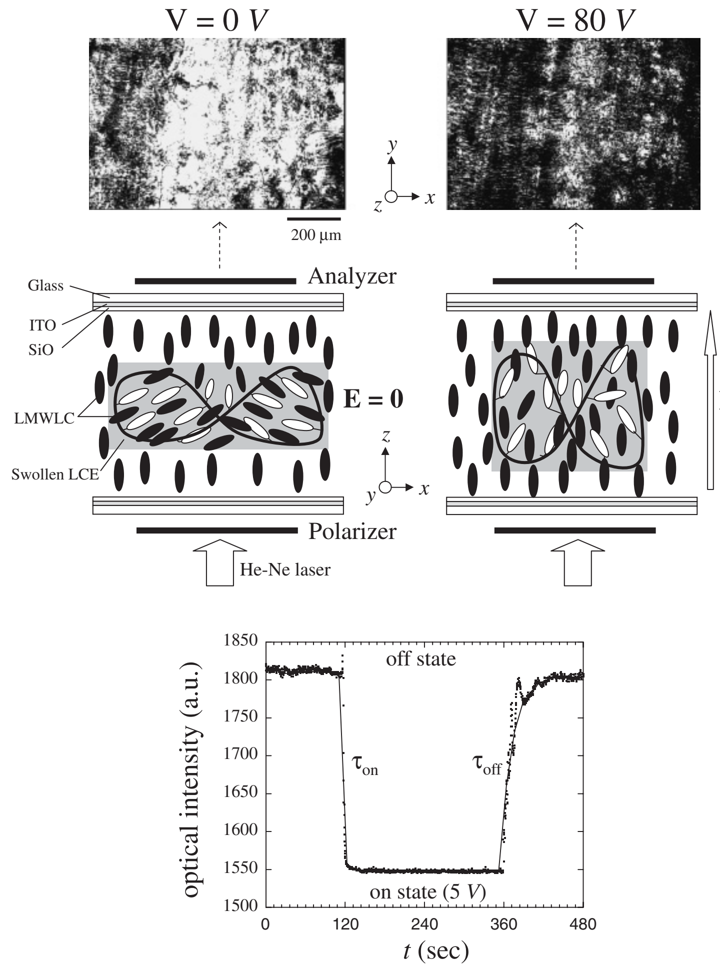

Fig. 1. Schematic picture of the mechanism and polarized optical photomicrographs of the electro-optical effect of a swollen polydomain LCE without (left) and with the application of an electric field ($V = 80$ V, right). The gray region between the two glasses indicates the swollen polydomain that changes its shape under the application of the electric field **E** (see also refs. 25 and 26). Bottom: dynamic response to the application of a voltage ($V = 5$ V).

$(0, 0, E_z)$ at room temperature. Electrooptical measurements were carried out using a He–Ne laser ($\lambda = 633$ nm) and a photomonitor (Mettler Toledo FP90 Central Processor) with a polarizing optical microscope (Nikon E600WPOL).

Figure 1 shows the optical micrographs of a swollen polydomain LCE and the schematic picture of the mechanism of the electrooptical effects and the dynamic response to applied voltage in the swollen polydomain LCE. We note that a polydomain has small domains with different local director orientations. Observing the sample through crossed polarizers, in the initial state at $V = 0$ V, different domains in a swollen sample give different optical birefringence values that are shown as bright and dark regions in Fig. 1. A further increase in the voltage, for example $V = 80$ V, leads to the reorientation of the director of LMWLCs along the electric field, i.e., normal to the glass plane, $\mathbf{E} = (0, 0, E_z)$. This induces the reorientation of many mesogenic side chains inside the LCEs. In this state, the optical intensity of the transmittance reaches a minimum. Applying a very high voltage to the sample leads to the complete reorientation of the mesogenic side chains; the whole sample will then be optically dark. We conclude that the electrooptical effects of polydomain LCEs can be increased by swelling with LMWLCs.

The relationships between the normalized intensity $I_{\rm nlz}$ and applied voltage for the swollen polydomain sample through the crossed polarizers are shown in Fig. 2. $I_{\rm nlz}(V)$ monotonically decreases with voltage and has a tendency to almost saturate at $V \sim 100$ V while in the electromechanical effect, it comes to almost saturate at $V \sim 20$ V [see Fig. 2(b)]. This result indicates that LMWLCs and mesogenic molecules reorient their direction to be parallel to the electric field when sufficient voltage is applied.

The solid line in Fig. 2(a) is a fit to

$$I(V) = 0.04 + 0.55 \exp(-V/13.50). \qquad (1)$$

guide the eye. It is considered that the characteristic voltage, $V = 13.5$ V, in eq. (1) is attributed to the contributions of both the typical threshold voltages for LMWLCs and for mesogenic side chains in the swollen polydomain system. The inset in Fig. 2(a) shows a relatively small threshold value, $V_{\rm th}$, for the onset of the electrooptical effect: $V_{\rm th} \sim 1.0$ V. This threshold value agrees with that for the onset of the electromechanical effect ($V_{\rm th} \sim 0.6$ V).[25,26] However, the saturation value of the applied voltage dependence shows a big difference between the electromechanical and the electrooptical effect. This is related to the fact that the electrooptical effect in the swollen polydomain sample is mainly associated with the reorientation of LMWLCs and mesogenic molecules due to the application of the electric field. This seems reasonable as ~400% LMWLCs entered the polydomain sample after the swelling process.[23] However, the dynamics of the cross-linked polymer networks coupled with the director reorientation of LMWLCs and mesogenic molecules contributes to the electromechanical effect.

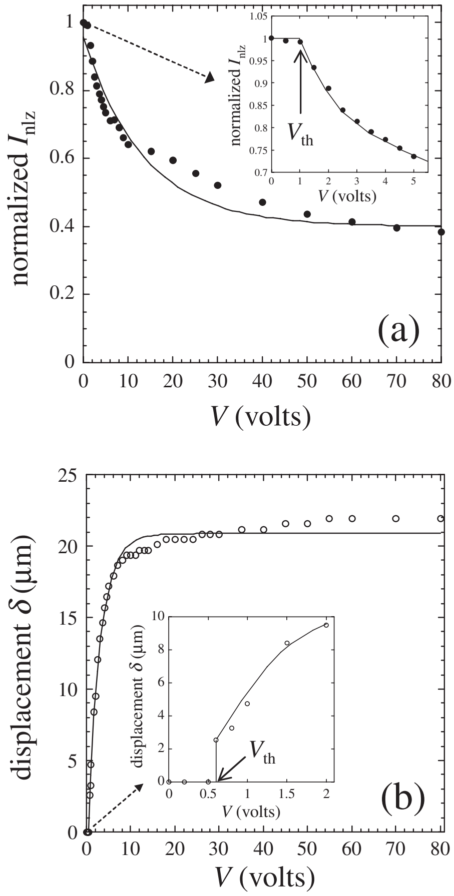

Fig. 2. Voltage dependence of the normalized intensity I_{nlz} through crossed polarizers (a) and of the displacement δ (b).[26] $I_{nlz}(V) = (0.40 \pm 0.01) + (0.55 \pm 0.02)\exp(-V/13.50 \pm 1.57)$ and $\delta = (20.87 \pm 0.16) - (22.38 \pm 0.43)\exp(-V/2.88 \pm 0.17)$. Insets in (a) and (b): expanded version of the graph to show the threshold for the observed electrooptical ($V_{th} \sim 1.0$ V) and electromechanical ($V_{th} \sim 0.6$ V) effects, respectively.

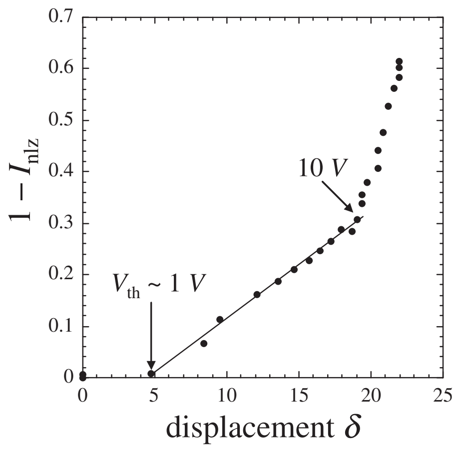

Fig. 3. Intensity change $(1 - I_{nlz})$ is plotted as a function of displacement δ.

In Fig. 3, the intensity change $(1 - I_{nlz})$ is plotted as a function of displacement δ. We can see that there is a linear relation between the electrooptical effects (intensity change) and the electromechanical effects (displacement) between $V_{th} \sim 1.0$ V and $V = 10$ V. Above 10 V, after a sharp change in the slope, this relation still remains linear and only a small displacement change, i.e., change in network shape, is observed, while the intensity (optical birefringence) change is quite large.

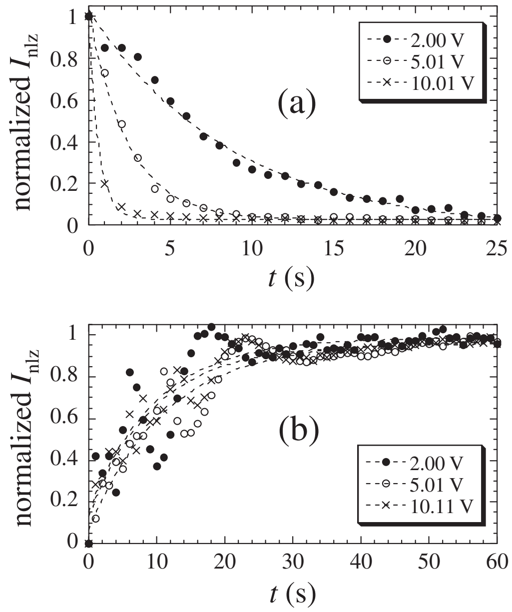

Fig. 4. Dynamic responses of the normalized intensity $I_{nlz}(t, V)$ in the switching *on* (a) and switching *off* processes (b). The dotted lines are the best fits to $I_{nlz}(t, V) = I_0 \exp(-t/\tau_{on})$ (a) and $I_{nlz}(t, V) = I_\infty + I_0 \exp(-t/\tau_{off})$.

Figure 4 shows the dynamic responses of the normalized intensity $I_{nlz}(t, V)$ to the applied voltages in the switching *on* [Fig. 4(a)] and switching *off* [Fig. 4(b)] processes with frequency $f = 50$ Hz. In Fig. 4(a), when the applied voltage is increased, the normalized optical intensity I_{nlz} decreases more rapidly. The dotted line in this figure [Fig. 4(a)] is the best fit to $I_{nlz}(t, V) = I_0 \exp(-t/\tau_{on})$. In Fig. 4(b), when the voltage is switched *off*, I_{nlz} increases rapidly when the initial voltages are below 9 V. The dotted line is the best fit to $I_{nlz}(t, V) = I_\infty + I_0 \exp(-t/\tau_{off})$.

Figure 5 shows the voltage dependence of the inverse of the response times $1/\tau_{on}$ [Fig. 5(a)] when the field is switched *on* and the inverse of the relaxation times $1/\tau_{off}$ [Fig. 5(b)] when the field is switched *off*. In Fig. 5(a), $1/\tau_{on}$ is clearly proportional to V^2. The solid line in Fig. 5(a) is a fit to $1/\tau_{on} = 0.088 + 0.013V^2$. This is consistent with the response behavior of ordinary liquid crystals. We note that $1/\tau_{on}$ in the electrooptical effect is about 8 times larger than that in the electromechanical one.[26] This means that the response for the electrooptical effect for the swollen polydomain sample is faster than that for the electromechanical one by about 8 times. This is because the optical effects are only due to the reorientation of the mesogenic molecules and LMWLCs.

Figure 5(b) shows the voltage dependence of the inverse of the relaxation times $(1/\tau_{off})$; $1/\tau_{off}$ is almost constant. That is, $1/\tau_{off}$ for the electrooptical effect is about 4 times smaller than that for the electromechanical effect.[26] In the former case, τ_{off} is only determined by the rotation of the LMWLCs and the mesogenic side chains, while in the latter case, it is mainly contributed from the elastic properties of the polymer networks.

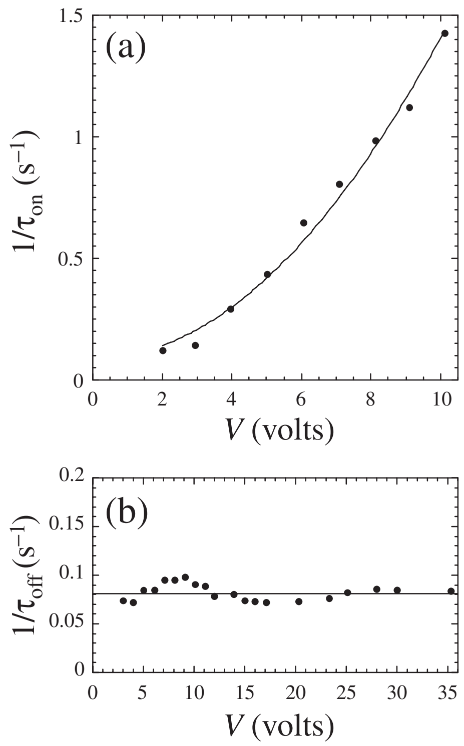

Fig. 5. Voltage dependence of the inverse response time τ_{on} and inverse relaxation time τ_{off} when the field is switched *on* (a) and switched *off* (b), respectively.

We have shown experimentally that the electrooptical effects, as well as the electromechanical effects, of a polydomain LCE is increased by swelling with nematic LMWLCs (5CB). An important finding is that the electro-optical effects arise from the director reorientation of LMWLCs and mesogenic molecules due to the application of the electric field. Due to the mechanical and optical effects arising simultaneously under the application of an electric field, swollen LCEs are promising for application such as soft actuators with electrooptical effects.

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