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Multifunctional liquid crystal elastomers: Large electromechanical and electro-optical effects

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A multifunctional main chain liquid crystal elastomer (MCLCE) with large mechanical and optical effects in applied electric fields is investigated, when MCLCE is swollen in a low molecular weight liquid crystal, 4-*n*-pentyl-4-cyanobiphenyl, a nematic solvent. The size change by the field effects is linearly proportional to the transmittancy change. This suggests the possibility of broad application as a field-induced-optical actuator device. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2917465]

Liquid crystal elastomers (LCEs) exhibit a number of interesting physical effects and have recently attracted considerable attention due to their anisotropic mechanical and optical properties in response to many external stimuli such as temperature and electric fields.[1–26] The interest in LCEs is generated by a combination of the orientational properties of liquid crystals and the elastic properties of conventional cross-linked polymer networks.[1–3] As a result, the thermomechanical and electromechanical effects have many potential applications as soft actuators and artificial muscles.[10–18,21–26] In addition to their attractive mechanical properties, LCEs also exhibit electro-optical properties due to changing the orientation of the director.

LCE polydomains are usually opaque due to strong light scattering by random director orientation of domains. However, when a large enough uniaxial extension is applied, they undergo a polydomain-monodomain (*P*-*M*) transition and the opaque polydomain LCE becomes a transparent monodomain LCE.

Experimental and theoretical studies of *P*-*M* transition have been discussed in detail in Refs. 2–4, 27, and 28. During the *P*-*M* transition, the macroscopic nematic alignment of domains takes place giving rise to a large elastic response for small changes of the elastic stress leading to a plateau-type behavior on the stress-strain curve. In addition, such LCEs couple to electric fields: the director orientation associated with the mesogens aligns parallel to the field in the case of positive dielectric anisotropy of the material ($\Delta\epsilon$). In dry LCEs, large electric fields are required for a director rotation, although no report has been published. In unconstrained systems such as swollen polydomain LCEs with nematic solvent,[21,22] it is expected that LCEs can also undergo such a *P*-*M* transition. In the swollen case, a low electric field should be sufficient to change the director orientation and large macroscopic shape changes are expected. However, so far, no experimental work discussed this phenomenon, although some papers examined the electric field effects in swollen LCEs.[14–18,21–26]

In previous studies, we demonstrated electromechanical and electrooptical effects in polydomain and monodomain side-chain LCEs (SCLCEs) swollen with a low molecular weight liquid crystal (LMWLC).[21,22,29] Swollen SCLCEs are used to achieve low driving voltages and fast response times for electromechanical and electro-optical properties, contrary to dry LCEs in which very high fields are required to induce electromechanical effects.[30] Substantial changes in shape ($\sim 1-20$ μm) due to electromechanical effects are observed for voltages in the range of $V \sim 0.5-10$ V applied across a sample of thickness 100 μm.[22] Summarizing the results for them (Refs. 22 and 29), we note the following facts. (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 SCLCEs were observed but remarkable electro-optical effects were not observed. This is because monodomain LCEs are under a strong elastic tension due to the stretching process during LSCE preparation. Even if there was a reorientation of the director in the bulk of the swollen polydomain SCLCE to be parallel to a relatively high electric field ($V \sim 80$ V applied across a sample thickness of 100 μm), the optical change is relatively small; it does not induce a sufficiently large electro-optical effect[29] for a trifunctionally cross-linked LCE. This is due to its attached mesogen side chains and its high cross-linker concentration ($\sim 8\%$). Most experimental work thus, up until now, has focused on SCLCEs.

In this paper, we report on a study of the electromechanical and electro-optical effects carried out on polydomain main chain LCEs (MCLCEs) swollen with

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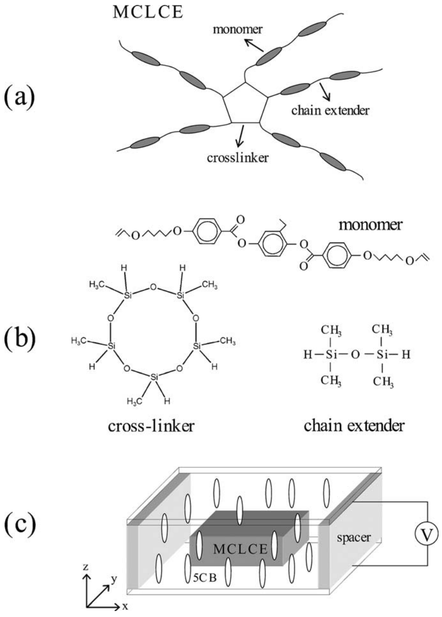

FIG. 1. Schematic picture of (a) a MCLCE and (b) its chemical composition. (c) Schematic of experiment.

4-*n*-pentyl-4-cyanobiphenyl (5CB) consisting of many domains with different main chain director orientations. The anisotropic response in MCLCE is much greater than that in SCLCEs due to the direct coupling of the mesogen units into the polymer backbone. As a result, the nematic effect on the macroscopic (mechanical and optical) properties is more pronounced in MCLCEs than in SCLCEs.[31–34] The related swelling dynamics with LMWLC will be reported elsewhere.[35]

Figures 1(a) and 1(b) show the schematic structure of polydomain MCLCE and its chemical compositions. The polydomain MCLCE was synthesised in a one-step reaction,[31–34] by dissolving the monomer 2-ethyl-1,4-phenylen bis [4-[4-(vinyloxi)buboxy] benzoate] ($C_{34}H_{38}O_6$), the chain extender 1,1,3,3,-tetramethyldisiloxane ($C_4H_{14}OSi_2$) and 2.5 mol % of the cross-linking agent pentamethylcyclopentasiloxane ($C_5H_{20}O_5Si_5$) in toluene, adding a Pt catalyst and reacting in a centrifuge cell at 5000 rpm and 70 °C for about 4.5 h to form a film. The polydomain MCLCE was obtained by deswelling the film on a water surface to avoid any orientation. The cross-linking process was completed at 60 °C for 4 days. In order to remove any soluble part, the sample was extracted with toluene. The glass transition T_g is about $-10°$ and the clearing temperature T_c is about 64°.

The main chain LCE samples we prepare are $\sim 20.0 \pm 1.0$ μm thick with an area of $\sim 800 \times 300$ μm^2. The samples are embedded in LMWLCs for swelling between two transparent indium tin oxide electrodes with very clean SiO surfaces, as shown in Fig. 1(c). The SiO coating is applied to avoid complications such as hydrodynamic effects arising from charge injection. We used the well-known nematic LMWLC, 5CB that was homeotropically aligned at the electrode surface by coating. The cell gap between both electrodes was controlled by a 100 μm polymer (Mylar) spacer. In the experiments, an alternating electric field of frequency $f = 100$ Hz with rectangular waveform is applied between the electrodes, i.e., $\mathbf{E} = (0, 0, E_z)$ at $T = 26 \pm 0.2$ °C. The measurements of the electromechanical effect were made by using a polarizing optical microscope (Nikon E600WPOL) on which a charge-coupled-device camera (SONY XC-75) was mounted. The mechanical deformation and temporal changes of the electromechanical effect were captured by a computer. The electro-optical measurements were carried out by using a halogen lamp (12 V, 100 W) and photomonitor (Mettler Toledo FP90 Central Processor) with a polarizing optical microscope.

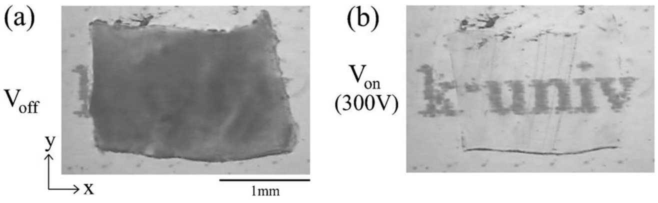

FIG. 2. (a) Swollen polydomain MCLCE. (b) Electromechanical and electro-optical effects are simultaneously observed in swollen polydomain MCLCE after applying a voltage of 300 V across 100 μm.

The polydomain MCLCE isotropically swells in three dimensions by a factor of about 2.3 (corresponding to a volume change by about a factor 12) and the equilibrium swollen state is achieved after about 17 h.[35] After fully swollen in LMWLC [Fig. 2(a)], applying an electric field, the electromechanical and the electro-optical effects are simultaneously observed for the swollen polydomain MCLCE, as shown in Fig. 2(b) (the movie is available on the web[36]).

The shape changes occur normal to the applied field direction in the *x*-*y* plane. $\lambda = L(V)/L_0$, i.e., the ratio of the length with the applied voltage in the *x* direction (as well as in the *y* direction) to the initial length without the field continuously decreases with increasing applied voltages (Fig. 3). The threshold for shape changes V_{th} is about 10 V across 100 μm and the maximum contraction is about 19%, the largest electric field induced contraction reported so far for main chain LCEs, and thus, comparable to the maximum change observed for nematic gels.[24]

The voltage dependence of the transmittance $I(V)/I_0$ is shown in Fig. 3. The measured transmittance here is only the transmittance for the swollen polydomain sample excluding the contribution from other parts, e.g., LMWLC transmittance and glass substrates. In the present study, for the first time, the features of the *P*-*M* transition in voltage-

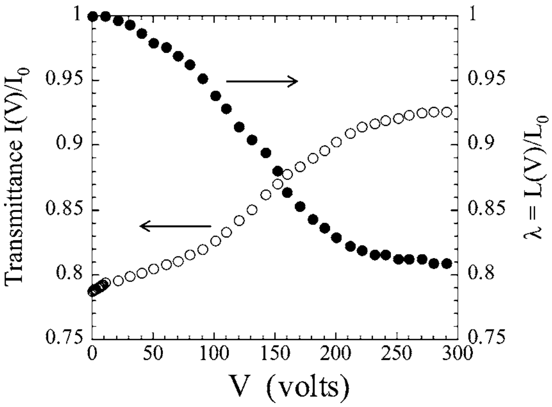

FIG. 3. Voltage dependence of shape changes $\lambda = L(V)/L_0$ and transmittance $I(V)/I_0$ in swollen polydomain MCLCE. Large electromechanical and electro-optical effects are measured after applying the electric field. Voltage-transmittance curve shows the *P*-*M* transition features. The sample thickness *d* was fixed: $d = 100$ μm.

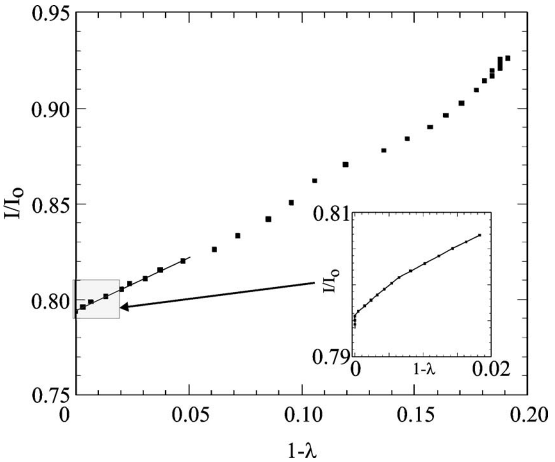

FIG. 4. Transmittance is plotted as a function of contraction change $(1-\lambda)$. The behavior for small voltage is shown in the inset.

transmittance curve in swollen MCLCE was observed. The beginning of the transmittance region with small slope (~10 V) indicates the change of the director reorientation of the domains toward the direction of the applied low electric field. At the end of this region with a smaller slope (~100 V), a rapid increase in the macroscopic nematic alignment of domains arises and then the average director orientation of the domains is mostly parallel to the field direction resulting in a transparent MCLCE, that is an electric field induced *P-M* transition has occured. The waiting times used to obtain the data shown in Fig. 3 are as follows. For the changes of transmittance, we waited up to 10 min—in particular, for smaller fields—and for the contraction measurements the minimum waiting time was 10 min.

In Fig. 4, we have plotted the transmittance as a function of the shape changes $(1-\lambda)$. We can see that there is a linear relation between the electro-optical effect (transmittance) and the electromechanical effect (shape change) in a swollen polydomain MCLCE. This means that (1) both changes in the transmittance and the shape are caused by director rotation and (2) a uniform director orientation in the bulk is the result of the *P-M* transition.

In this paper, we have studied the electromechanical and electro-optical effects of polydomain MCLCE with positive dielectric anisotropy of the material swollen with 5CB. We have observed an electric-field-induced *P-M* transition in swollen polydomain MCLCE for the first time. The director orientation of the domains undergoes a rotation aligning their directions with the electric field inducing large shape and birefringence changes. To sum up, large mechanical and optical effects simultaneously arise in an applied electric field connected to the *P-M* transition. The observed effects are much larger than for the polydomain-monodomain transition in polydomain SCLCEs. These effects show that multifunctional swollen polydomain MCLCE are promising as soft actuators with electrooptical effects and for a broad range of expected applications.

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