*Superficies y Vacío **19(3)**, 30-34, septiembre de 2006*

Laser-induced mechanical bending in azo dye-doped liquid-crystal elastomers

M. A. Camacho-Lopez
Coordinacion de Posgrado, Facultad de Medicina, Universidad Autonoma del Estado de Mexico,
Paseo Tollocan s/n esq. Jesus Carranza, Toluca Edo. de Mexico 50120, Mexico.
Liquid Crystal Institute, Kent State University, Kent, OH 44240, USA

P. Palffy-Muhoray
Liquid Crystal Institute, Kent State University, Kent, OH 44240, USA

H. Finkelmann
Institut für Makromolekulare Chemie, Universität Freiburg, D79104 Freiburg, Germany

Laser-induced deformation (bending) in azo dye-doped liquid-crystal elastomer thick films is demonstrated. We directly measure the laser-power-dependent deformation-strength (driving force). The deformation-relaxation time is also measured. We have observed that it recovers within 300 ms after the excitation laser pulse is gone, this gave a constant time of 75 ms. By estimating the optical electric field value of the laser pulses used in our experiments, we can compare our results with those obtained in polyurethane elastomers studied by the electrostriction technique [1,9].

Keywords: Liquid-crystal elastomers; Electrostriction; Opto-mechanical response

1. Introduction

Recently, actuators that generate flexible and soft movements such as bending, expansion and twisting have received attention because these exotic and biomimic motions are required for medical equipment, robotics and human muscle replacement in the future. Various kinds of such actuators have been demonstrated using conducting polymers [2, 3], gels [4], ion-exchange membranes [5] and nanotubes [6], which are operated in electrolyte solutions. In conducting polymers, the driven force is generated by electro-chemomechanical deformation (ECMD) [7]. Bending electrostriction in polyurethane elastomer (PUE) has also been demonstrated [1, 8, 9]. Polyurethane elastomer, was found to be actuated by an applied electric field (~35 KVcm^{-2}). The characteristics of the PUE electrostrictive actuator were studied as functions of molecular structure, electrode material, its thickness, dielectric constant and applied field. The PUE actuator was confirmed to move smoothly like a finger.

Nematic elastomers have the remarkable property of being able to change their shape by up to 400% in a relatively narrow temperature interval straddling their nematic-isotropic (NI) transition temperature T_{ni} [10]. This extreme effect is a reversible elongation (contraction) along the director **n**, on entering (leaving) the nematic state.

Liquid-crystal elastomers (LCEs) are rubbers whose constituent molecules are orientationally ordered. Their salient feature is strong coupling between the orientational order and mechanical strain [11]. For example, changing the orientational order gives rise to internal stresses, which lead to strains and change the shape of a sample. Orientational order can be affected by changes in externally applied stimuli such as light. Rapid light-induced deformations allow LCEs to interact with their environment in new and unexpected ways. When light from above is shone on a dye-doped LCE sample floating on water, the LCE 'swims' away from the light, with an action resembling that of flatfish such as skates or rays [12].

Mesogenic monomers incorporated into main- or side - chains of weakly cross-linked polymers can become orientationally ordered. The resulting LCE material combines the anisotropy and large susceptibility of low molecular weight liquid crystals with rubber elasticity. The possibility of coupling between orientational order and mechanical strain was first raised by de Gennes [15]. Symmetry arguments and free energy considerations indicate [11,16] that in nematic LCEs mechanical strain acts as an external field aligning the liquid crystal, while the orientational order acts as an external body stress, leading to elastic strain. The first LCE was synthesized by one of us [17] (H. F.). Recent interest in LCEs is fuelled both by their potential for device applications as artificial muscles [18] and mechanically tunable optical elements [19], and by curiosity regarding their unusual response to excitations [20, 21].

In this work, we focus on investigating the mechanical response of dye-doped nematic LCE samples (molecular weight ~ 4000 gr mol^{-1}) to visible light. When azo dyes and other photoisomerizable molecular rods absorb light, they suffer a *trans* → *cis* isomerization whereupon they are bent (until undergoing the reverse *cis* → *trans* reaction, whereupon the rods are restored) [10]. One effect is dye mediated heating due to absorption; the change in the degree of order caused by the change in temperature can lead to strain and shape change. Another is the reduction in the degree of orientational order due to photoisomerization of the dissolved dye. Liquid crystals can also be reoriented by light, with the required intensity dramatically reduced in dye-doped samples [22]. This anomalous reduction in the threshold intensity, the so-called Janossy effect, can be

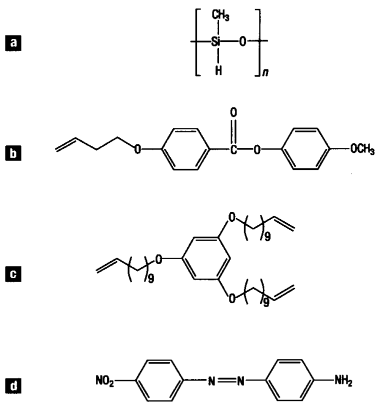

Figure 1. The chemical structures of the nematic LCE and dye. a) The methylsiloxane monomer backbone; b) the mesogenic biphenyl sidechain; c) the tri-functional crosslinker; d) the azo dye Disperse Orange I.

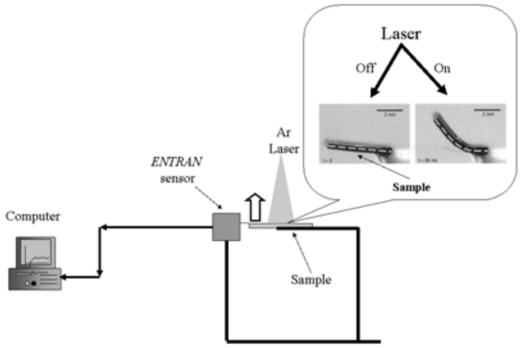

Figure 2. Experimental setup diagram. The light at 514 nm from a continuous-wave argon-ion laser is chopped and used to pump the LCE sample. A computer-controlled ultra-sensitive *Entran* sensor is used to measure the bending driving force. The inset shows; Left figure: a dye-doped LCE sample of dimensions 5 mm ×5 mm× 0.32 mm anchored at one end illuminated from above for 60 ms by argon-ion laser (600 mW) with a 3-mm beam waist (full-width at half-maximum). Right figure: the sample about 80 ms after onset of illumination.

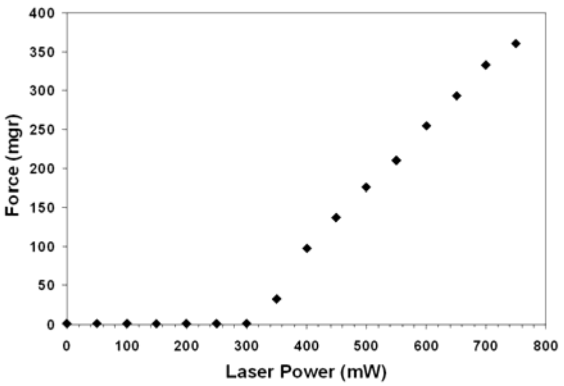

Figure 3. Laser power-dependent driving force measured in the azo dye-doped LCE sample. The laser (at 514 nm) was chopped to deliver pulses at 1 Hz (Rep. Rate) and 60 ms of duration. The threshold of the bending occurs around 300 mW. Each measurement is the result of averaging 15 movements, corresponding to 15 laser shots.

understood in terms of a Brownian ratchet mechanism, where the dye molecules in the nematic field are rotors of light-driven Brownian motors [23]. The optomechanical response of nematic LCEs with covalently bonded azo dyes has been studied recently [10]. These materials showed large isochoric contraction (by more than 20% of their original length) when irradiated with UV light, with relaxation times of the order of one hour.

Here we demonstrate that by dissolving—rather than covalently bonding—azo dyes into an LCE sample, its mechanical deformation in response to non-uniform illumination by a pulse of visible light becomes very large (more than 60° bending) and is more than two orders of magnitude faster than previously reported [10, 13-14]. We measured the magnitude of the bending and its driving force. The mechanical relaxation time (full recovery) of our LCE takes no longer than 350 ms.

In order to compare the magnitude of the photo-induced mechanical response measured in our LCE with that of the electrical-induced mechanical (electrostriction) response in a polyurethane sample [9], we estimated the electric field (optical) produced by the laser pulses. Our results show that the mechanical response (driving force) in our LCE is larger than the response induced in the polyurethane sample when electric fields of equal magnitude are applied, optically and electrically, respectively.

2. Experimental

2.1 Sample preparation

Our monodomain LCE samples consist of siloxane main-chain and mesogenic benzoic acid phenyl ester side-chain units (Fig. 1). Using a tri-functional cross-linker, samples under preparation are first weakly cross-linked, then stretched unidirectionally to align the mesogens and establish nematic order, and then finally fully cross-linked to form a transparent birefringent monodomain [24]. The alignment direction can be determined from the orientation of the principal optical axes. In order to retain high orientational mobility in our samples, the azo dye Disperse Orange I was dissolved (rather than functionalized as in References [10, 13]) into the network. To accomplish this, nematic LCE samples were swollen with toluene in which the dye had been dissolved; the toluene was subsequently removed through evaporation in a vacuum oven. The concentration of the dye remaining in the samples, estimated from absorptivity measurements, was 0.1 wt%. The density of our samples is 0.973 gr cm^{-3}, and the thickness of the undeformed LCE films is 0.32 mm. Disperse Orange I molecules are known to align with the nematic director in liquid crystals. In our samples, we observed a broad absorption peak whose amplitude was strongly polarization dependent, with an absorption maximum at $\lambda_M = 495$ nm.

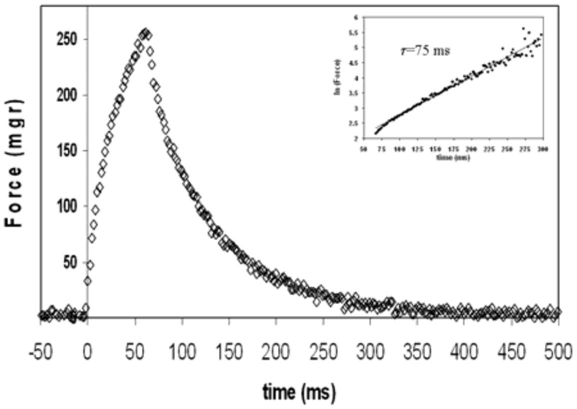

Figure 4: Opto-mechanical response of an LCE sample. Graph of the dynamics of force produced by the sample on and after illumination for 60 ms. The rise time of 20 ms is determined by fitting the increasing part of the force curve to an exponential function describing the approach to saturation. The inset shows the logarithm of the measured force after illumination is removed (60 ms after onset).This reveals a clear exponential relaxation back to the rest state. The linear fit shows the relaxation time to be 75 ms.

2.2 Opto-mechanical response measurements

We illuminated our dye-doped LCE samples by green light at λ = 514 nm from a CW Coherent (model Innova 100) Argon Ion Laser. The output beam was chopped by using a Uniblitz (model T-132) electro-magnetic shutter. The shutter was set to work at 1 Hz (rep. rate) and deliver pulses with a duration of 60 ms. A dye-doped LCE sample of dimensions 5 mm ×5 mm×0.32 mm anchored at one end was illuminated from above for 60 ms by the argon-ion laser (600 mW) with a 3-mm beam waist (full-width at half-maximum). A ultra-high sensitive *Entran* force-sensor controlled by a computer was used to measure the driving force and the recovering time of the LCE sample deformation. The free end of the sample was held in place and prevented from bending by the needle arm of the *Entran* load sensor measuring the force. Each measurement is the result of averaging 15 movements, corresponding to 15 laser shots. Figure 2 shows in detail the experimental setup.

3. Results and Discussion

3.1 Light induced bending

For 5 mm x 5 mm x 0.32 mm samples anchored at one end (Fig. 2), the dominant effect is a large and fast light induced bend deformation (>45^o bend angle after illumination for 60 ms at 600 mW). The axis of the cylindrical bend is parallel to the sample surface and perpendicular to the nematic director whose direction in the sample is known.

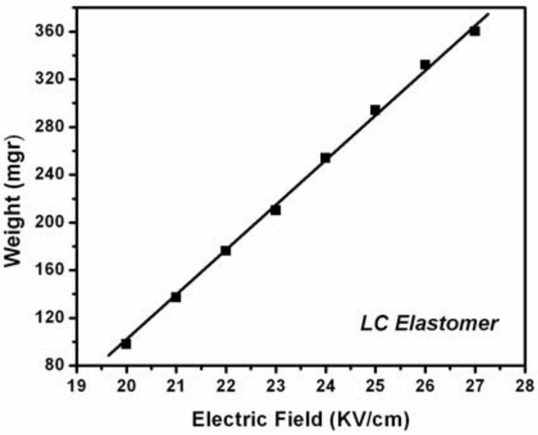

Figure 5: Electric field dependence of the driving force measured in the LCE sample when mechanical deformation is induced optically (Ar Ion Laser).

3.2 Dynamics of the opto-mechanical response

When the elastomer is shinned by a laser pulse, it responds mechanically giving rise to a rapid up and down movement (inset of figure 2). Figure 3 shows the power-dependent driving force. As we can see, up to a laser power of 300 mW the LCE sample does not respond to the laser pulse. However, around 350 mW the elastomer starts responding. Then the sensor detects the elastomer movement and the force is measured. The driving force shows a linear response with the laser power. The driving force values range from 30 mgr for a laser power of 350 mW to 370 mgr for a laser power of 750 mW.

It was noted that illumination causes the flat sample to change shape and to adopt a more compact, bent, configuration. On the cessation of illumination, the sample unbends to resume its original flat shape; it is capable of doing work in this process. As the elastic energy of a bent elastic sheet is $(1/24)Y(d^3/R^2)A$, where Y is Young's modulus, R is the radius of curvature, d is the thickness and A is the area, a crude estimate of the energy stored in the bent sample is ~10 nJ [12]. Because the sample shape depends on illumination that is localized, the sample shape, and hence the potential energy of the system, is a function of position.

3.3 Time response and relaxation time

The force developed by the LCE samples when prevented from bending was measured. Remarkably fast response times, with a rise time of 20 ms at 600 mW and a relaxation time of 75 ms were observed. These times were determined from the measured exponential approach to saturation, and the likewise measured exponential decay after cessation of illumination.

The size of deformation and its time-scales are also power dependent with more rapid onset to larger deformation with increased power (e.g. a 67^o bend angle after irradiation for 60 ms at 1.3 W). Figure 4 shows the dynamics of force produced by the sample on and after illumination for a

Table 1. Comparison of the driving force measured in LCE samples and polyurethane elastomers, induced by an electrical and an optical field, respectively.

Dye-doped LCE		**Polyurethane elastomer** [9]	
Electric Field (kV cm-1)	**Force** (mgr)	**Electric Field** (kV cm-1)	**Force** (mgr)
20	98	35	50
21	137	40	100
22	176	50	200
23	210	60	300
24	254	70	400
25	294	80	500
26	332		
27	360		

pulse of 60 ms. As we can see the full-recovering time occurs within 300 ms after the laser pulse is switched off. It gives evidence that the effect is reversible. Although the curve shown in Figure 4 is the result of averaging 15 elastomer movements, even the single shot measurements gave the same results. This indicates that the mechanical response is stable with respect to the laser power.

The observed bending is consistent with a rapid material contraction along the nematic director at the irradiated surface. This contraction is apparently volume conserving as it is accompanied by an expansion (small, given the aspect ratio of the sample) in the orthogonal direction. The contraction is consistent with decreased orientational order at the surface, relative to the anisotropically ordered rest state, which could lead to the observed material strains. Plausible candidate mechanisms underlying this effect are laser heating by linear absorption and the reduction of orientational order by photoisomerization of the dye. Direct and indirect optical torques may also contribute. We are presently conducting further experimental and modeling studies to identify the salient mechanisms.

3.4 A comparison of the electric field dependence of the driving force measured in LCE to that measured in polyurethane elastomers

As it was mention earlier, mechanical deformation induced by electrostriction has been reported to occur in polyurethane elatomers [8, 9]. Very thin electrodes are deposited on both sides of a polyurethane elastomer film [1]. When a high voltage (some KV/cm) is applied between the electrodes, the polyurethane elastomer film is bent. By switching the voltage off, the elastomer recovers its original shape. The inset of Figure 5 shows the electric field dependence of the driving force and the recovering time measured in a polyurethane elastomer by J. Kiokane *et. al*. [8]. Once the electric field is switched off, the mechanical response (strain) takes around 15 seconds to recover. This time is two orders of magnitude longer than that measured in our elastomer. Figure 5 shows the electric field (produced by the laser pulse at the sample) dependence of the driving force measured in our LCE sample. If we compare the electric field necessarily to induce the same driving force in both, the LCE sample and the polyurethane elastomer [9], we obtain lower values in our material (LCE). Table 1 summarizes the results of the driving force and the electric field measured in both materials.

4. Conclusions

Laser-induced bending in azo dye-doped liquid-crystal elastomers (LCEs) has been demonstrated. The bending driving force was measured and values ranging from 30 to 370 mgr, were obtained. The force of the LCE sample increased in proportion to the laser power. The mechanical recovering time of our LCE showed to be faster than that measured in other materials such as polyurethane elastomer (bending electrostriction), in which the mechanical relaxation takes some tens of milliseconds [8]. We have shown that the bending driving force measured in our material is larger than that measured in a polyurethane elastomer when the electrical field applied to it is of the same magnitude of the optical electric field that is applied by the laser to the azo dye-doped LCE sample. As far as we know, we have measured the laser-induced driving force in this azo dye elastomer for the first time. LCEs offer interesting possibilities as actuators and other potential device applications, which can be used to generate mechanical work.

References

[1] T. Ueda, T. Kasazaki, N. Kunitake, T. Hirai, T. Kyokane and K. Yoshino, Synthetic Metals, **85**, 1415 (1997).

[2] X. Chen and O. Inganas, Synthetic Metals, **74**, 159 (1995).

[3] K. Kaneto, M. Kaneko, Y. Min, and A. MacDiarmid, Synthetic Metals, **71**, 2211 (1995).

[4] Y. Osada, H. Okuzaki, and H. Hori, Nature, **355**, 142 (1992).

[5] K. Oguro, Y. Kawami, and H. Takenaka, J. Micromach. Soc., **5**, 27 (1992).

[6] B. Baughman, Science, **284**, 1340 (1999).

[7] K. Kaneto, Y. Sonda, and W. Takashima, Jpn. Appl. Phys., **39**, 5918 (2000).

[8] J. Kyokane, H. Ishimoto, H. Yugen, T. Hirai, T. Ueda, and K. Yoshino, Synthetic Metals, **103**, 2636 (1999).

[9] J Kyokane, K Tokugi, D Uranishi, M Miyata, T Ueda, and K Yoshino, Synthetic Metals, **121**, 1129 (2001).

[10] H. Finkelmann, E. Nishikawa, G. Pereira, and M. Warner, Phys. Rev. Lett., 87 (2001).

[11] P. G. de Gennes, C. R. Acad. Sci. Ser. B, **281,** 101 (1975).

[12] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray and M. Shelley, Nature Materials **3¸** 307 (2004).

[13] J. Cviklinski, A. R. Tajbakhsh and E. M. Terentjev, Eur. Phys. J. E **9,** 427 (2002).

[14] Y. Yu, M. Nakano and T. Ikeda, Nature **425¸** 145 (2003).

[15] P. G. de Gennes, Phys. Lett. A **28,** 725 (1969).

[16] M. Warner and E. M. Terentjev, Liquid Crystal Elastomers (Clarendon, Oxford, 2003).

[17] H. Finkelmann, H. Kock and G. Rehage, Makromol. Chem. Rapid Commun. **2,** 317 (1981).

[18] D. K. Shenoy, D. L. Thomsen, A. Srinivasan, P. Keller and B. R. Ratna, Sensors Actuators A **96,** 184 (2002).

[19] S. Courty, J. Mine, A. R. Tajbakhsh and E. M. Terentjev, Europhys. Lett. **64,** 654 (2003).

[20] H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray, and B. Taheri, Adv. Mater. **13,** 1069 (2001).

[21] S. M. Clarke, A. R. Tajbakhsh, E. M. Terentjev and M. Warner, Phys. Rev. Lett. **86,** 4044 (2001).

[22] E. M. Terentjev, S. Hotta, M. Clarke and M. Warner, Phil. Trans. R. Soc. Lond. A **361,** 1 (2003).

[23] I. Janossy, A. D. Lloyd, and B. S. Wherrett, Mol. Cryst. Liq. Cryst. **179,** 1 (1990).

[24] P. Palffy-Muhoray and T. Kosa, Appl. Phys. A **75,** 293–300 (2002).