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Role of polarization and alignment in photoactuation of nematic elastomers

C.L.M. Harvey and E.M. Terentjev[a]

Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, UK

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Abstract. Changing the orientational order in liquid-crystal elastomers leads to internal stresses and changes of the sample shape. When this effect is induced by light, due to photoisomerization of constituent molecular moieties, the photomechanical actuation results. We investigate quantitatively how the intensity and the polarization of light affect photoactuation. By studying dissolved, as well as covalently bonded azo-dyes, we determine the changes in absorption and the response kinetics. For the first time we compare the response of aligned monodomain, and randomly disordered polydomain nematic elastomers, and demonstrate that both have a comparable photoresponse, strongly dependent on the polarization of light. Polarization-dependent photoactuation in polydomain elastomers gives an unambiguous proof of its mechanism since it is the only experiment that distinguishes from the associated thermal effects.

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Liquid-crystal elastomers (LCE) are remarkable materials that combine physical properties of liquids and solids in a unique way. LCE are rubbers whose constituent molecules are orientationally ordered. The resulting coupling of the elastic medium to magnitude and orientation of the underlying (nematic) order leads to many new effects. One class of such effects is the ability of LCE to change shape, or exert force, when the nematic order is altered. This is the foundation for mechanical actuation, a phenomenon with far-reaching practical applications. Since, unlike in most other shape memory systems, the direct relation between the elastic shape and the underlying order is an equilibrium property of LCE, the resulting actuation is equilibrium too, *i.e.* a fully reversible motion not requiring re-setting the system.

Thermal and solvent-induced actuation of LCE has been widely described in the literature. Although both have merits, it is hard (if not impossible) to apply such stimuli in a controlled way, both in the sense of localization and time. In contrast, the photo-induced actuation is an ideal mechanism for remotely stimulated mechanical response. The mechanism for photoactuation in LCE is the photoisomerization of rod-like dye molecules. The most studied example of such molecules is azobenzene (although a number of other photochromic groups are available, such as stilbenes). After the first reports of mechanical actuation induced by UV-light [1,2], a number of studies have addressed more fine aspects of the effect in different types of materials [3,4].

Although original studies have focused on the linear motion (uniaxial contraction) along the alignment axis of monodomain nematic elastomers, or the corresponding force if the shape change is restricted, it was soon realized that an important aspect of photoactuation is the bending of flat samples [5,6]. Indeed, when light falls on a sample from one side, and the absorption depth is comparable to or smaller than the sample thickness, even a small photo-induced strain gradient would produce very large bending. The bending mode of photoactuation has been investigated in other uniaxial systems combining macroscopic elastic characteristics of a sample with the underlying orientational symmetry breaking, which is affected by photoisomerization (usually with azobenzenes) [7]. Today this is a broad field across chemistry, physics and engineering. In this paper we do not concentrate on absorption depth issues, instead measuring an integrated uniaxial stress exerted on the isostrain sample.

In spite of many exciting and attractive features of photoactuation in nematic elastomers, there is still a question about the true mechanism of the effect. Is it the photoisomerization of rod-like dyes that disrupts the nematic (or other uniaxial) order and leads to the elastic response, or could it be just an effect of local heating? Such heating is impossible to exclude even if a direct infrared radiation from the light source is blocked: the stimulated *trans-cis* reaction, and the subsequent *cis-trans* relaxation, are

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[a] e-mail: `emt1000@cam.ac.uk`

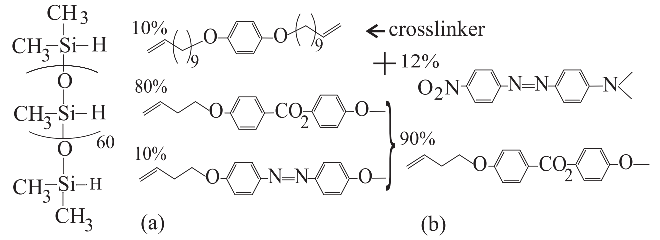

Fig. 1. Polysiloxane nematic elastomers used in the study: (a) Az, with azobenzene moiety attached to the backbone; (b) DO, with Disperse-Orange dye as dopant.

exothermic processes, releasing heat in direct proportion to the light absorption. Since heating also affects nematic order, one might see exactly the same mechanical actuation. Even if one compares the response of aligned monodomain materials to polarized light at different angles to the nematic director (and detects a difference, as we shall demonstrate below), one could still argue that the photon absorption is different at different polarization angles and so the heating is different too. The only unambiguous proof of the mechanism arises from the study of polydomain nematic elastomers.

This may appear self-contradictory: how can one expect a uniaxial strain (or force) be exerted if the polydomain LCE consists of small (usually $< 1\,\mu$m) domains with randomly aligned director? The answer has been first implicated in [8] when a flat polydomain sample (of nematic glass) was illuminated by polarized light and shown to locally contract along the axis of polarization. Theoretical work [9] has predicted substantial photomechanical response due to preferential contraction of domains aligned along the polarization axis. On averaging over the domain orientation one predicts a uniaxial macroscopic mechanical response along this axis. If this effect were due to the local heating generated by photon absorption, the length scale of temperature gradients would be on the μm scale, which is impossible to sustain for any significant time because of thermal diffusion.

In this work we present the first quantitative study of how the changing polarization affects the magnitude and the speed of photoactuation in nematic elastomers. We use a traditional polysiloxane side-chain nematic polymer system at small (10%) crosslinking density, and compare the effect in i) aligned monodomain and the corresponding polydomain systems, and ii) dye moieties either covalently bonded to the polymer chain or doped into the network. We also compare the plain azobenzene moieties (main absorption at 365 nm) and the donor-acceptor substituted azobenzene dye (absorption at 495 nm). This dye is similar in its properties to a commercial Disperse Orange 1, from Aldrich, and we shall refer to it as "Disperse Orange" hereafter. All chemicals and elastomers were synthesized and aligned in our lab; Figure 1 gives the details of our materials.

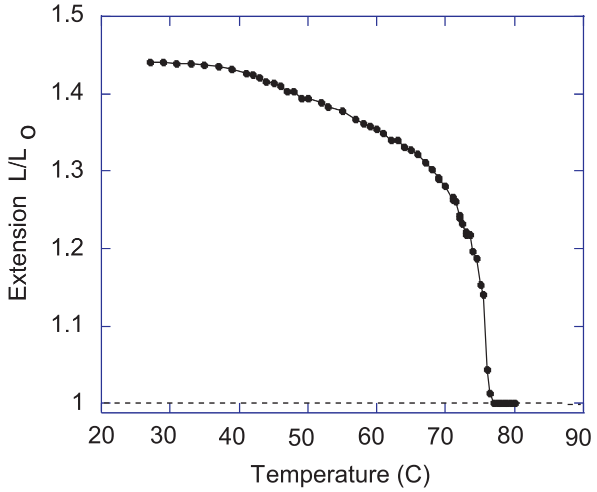

Fig. 2. Uniaxial thermal expansion of a monodomain nematic LCE, which remains unaffected by doping with photochromic molecules.

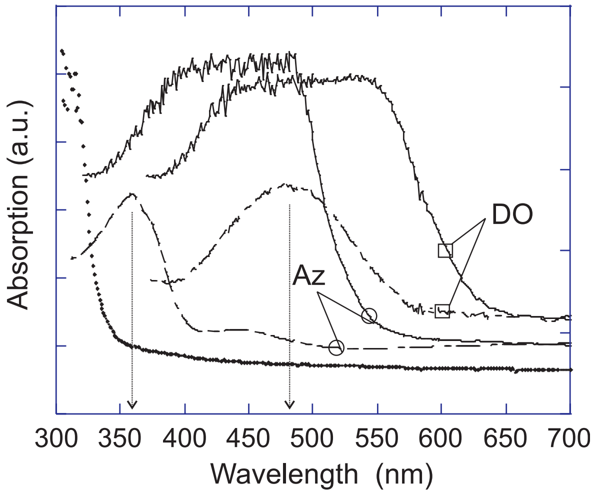

Fig. 3. Absorption spectra of our materials: dashed lines: absorption of the dyes in dilute solution; solid lines: the corresponding elastomers. For comparison, the line of dots represents the absorption of pure nematic LCE.

If no special precautions are taken at the crosslinking stage, liquid-crystalline elastomers are always in the equilibrium polydomain state (see [10] and references therein). In order to prepare aligned monodomain nematic elastomers, we followed the two-step crosslinking procedure first introduced in [11]. The material with azobenzene groups incorporated into the chain, Figure 1(a), is denoted Az hereafter, while the ordinary nematic elastomer doped with the dye, Figure 1(b) is called DO. We intentionally kept the dye concentration low to ensure the sufficient penetration depth of light into our samples. Az and DO are very similar in their thermal and mechanical properties. The Young modulus was relatively low (at only 10% crosslinking), determined as $E \approx 3.8 \cdot 10^4$ Pa. Doping with small concentration of rod-like molecules did not affect the nematic transition point, $T_{\mathrm{ni}} \approx 76\,^{\circ}$C. Figure 2 shows a typical thermal actuation effect in monodomain nematic elastomers [12], practically indistinguishable between the two materials and reaching a maximal extension of about 45%.

Contrary to our expectations, we found a significant change in absorption spectra when the photochromic dye was incorporated into LCE matrix. Figure 3 shows the data both for pure azobenzene and Disperse-Orange dyes in dilute solution, and for their corresponding elastomers (Az and DO). In the first case we confirm the absorption bands of the *trans-cis* transition: 365 nm and 480 nm, respectively (marked by arrows in the plot). When the same dyes are immersed in the LCE environment, in both cases the absorption band becomes much broader and with its low-energy edge shifted to the red. We could speculate about the reasons for such a change, but this is not the focus of the present study. The measured absorption spectra are important for us in order to accurately determine the intensity of light that is absorbed in each experiment, by convoluting the data from Figure 3 with the emission spectra of our light sources.

In order to irradiate the Az materials a Merck-4.L Mercury lamp was used; we shall label it "HG" below. The DO elastomers were expected to absorb in the visible and so we used two additional sources: a bright blue Luxeon Star light emitting diode from Philips Lumileds (San Jose, CA), labelled as "LED" below, and the powerful Ar ion laser (488 nm), from Newport Spectra-Physics Ltd. (Newbury, UK), labelled "ArL". The light sources were coupled to a 10 mm diameter optic fiber to minimize direct heating of the sample. Measuring the intensity of absorbed light is not a trivial matter, involving first calibrating the overall intensity detected with a photodiode, then determining the spectral density of each source at the given distance to the sample (including the losses in fiber optic and polarizer) and then convoluting it with the independently measured absorption spectrum. We thus obtained the absorbed intensity of Az from HG source to be $\sim 7\,\mathrm{mW/cm^2}$ without a polarizer. The efficiency of a UV-polarizer was so low that we could not use this sample/source for the measurement of the effects of polarization angle. The absorbed intensity of DO from LED source was $\sim 4\,\mathrm{mW/cm^2}$ without a polarizer; from HG source $\sim 10\,\mathrm{mW/cm^2}$ without a polarizer. The defocused beam from the ArL source provided $\sim 13\,\mathrm{mW/cm^2}$ with the polarizer; this was the experimental system used in the polarization study. We remark as an aside that a very high local intensity of light is required to produce a significant photoactuation.

In all experiments we kept the samples ($10 \times 5 \times 0.3$ mm) at room temperature fixed in the dynamometer frame, Figure 4, measuring force with an accuracy of $\pm 4 \cdot 10^{-5}$ N and then converting it to engineering stress. This isostrain configuration has an advantage in that it avoids the need for the polymer chains to move and thus face complications due to entanglements and other viscoelastic phenomena.

The experimental sequence was as follows: The mechanical history of the sample was eliminated by annealing at $\sim 100\,^{\circ}\mathrm{C}$, to start all experiments from the same conditions. The sample was clamped in the dynamometer and a small pre-strain ($\sim 0.5\%$) was imposed, allowing the stress to fully relax; this achieves a starting level of force above noise. The samples were then exposed to light via the shutter, through the plane polarizer when appropriate, with the exerted force constantly logged. The light source was shut off and the force relaxation to its initial value recorded. The polarizer was rotated (by 30° each time) and the light on/off sequence repeated, until the full range of rotation had been covered. To ensure that any effects seen were not the result of degradation of photobleaching, before each sequence the samples were illuminated 5 times in succession without the polarization being changed, confirming the height of the peaks and the response time remained the same.

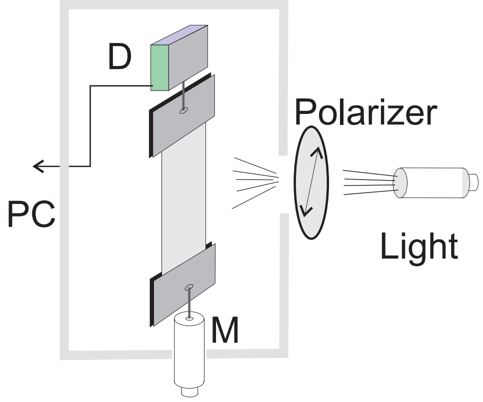

Fig. 4. The scheme of photoactuation experiment, with the sample length controlled by a *M*icrometer and the exerted force recorded by *D*ynamometer.

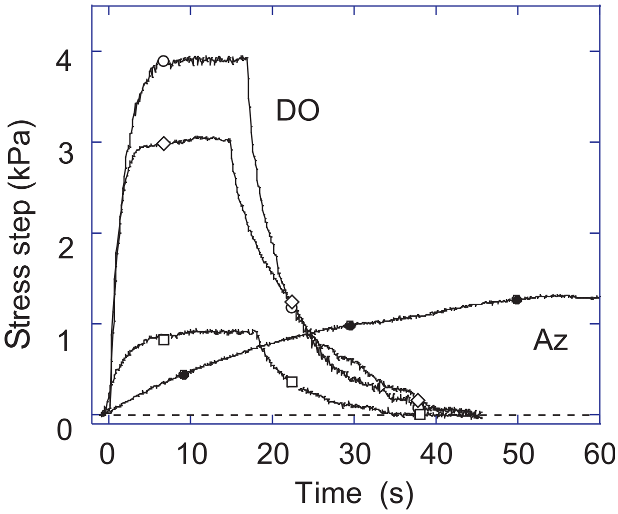

Fig. 5. The typical actuation stress of Az (●) and DO materials to light of different intensity (□ LED, ◇ HG lamp, ○ ArL laser).

In many previous reports [1,2] the response time has been found to be quite slow, between several minutes and an hour. In contrast, the use of a dissolved dye in [5] resulted in much faster response, on the order of seconds (although saturation was never reached in [5]). Figure 5 gives our results and allows comparison. Here monodomain LCE samples were used in all four experiments, with the uniform director axis aligned with the force measurement direction, and the polarization axis of the ArL

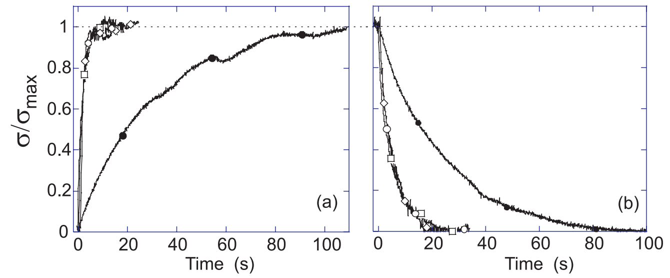

Fig. 6. The normalized stress response and relaxation: (a) light-on; (b) light-off. Data sets are labelled as in Figure 5: Az- (●), and DO-doped LCE illuminated with: □ LED, ◇ HG lamp, ○ ArL laser.

source. We must again emphasize that we are not analyzing absorption depth here (in a separate study of bending of free-standing samples we obtained this length not small, comparable with sample thickness). Bending of photoelastomers has been qualitatively demonstrated before [5,7] and is not our aim here.

From these results, we can see that the saturation stress $\sigma_{\max}$ depends on the intensity of absorbed light. It is also evident that the response of the Az material, where the dye moieties are covalently bonded to the chains, is much slower. In order to investigate the kinetics more accurately, we plot the normalized actuation stress $\sigma(t)/\sigma_{\max}$ for each system, Figure 6

These graphs clearly demonstrate the significant difference in response kinetics between Az and DO materials, both in the light-on (stimulated *trans-cis* isomerization) transition and in the light-off (thermal *cis-trans* relaxation) conditions. As was first noted in [5], the ability of the dye molecule to freely diffuse has this effect on photoactuation rates. There is also a very well-known effect of faster reaction rates in chromophores with more pronounced donor-acceptor characteristics, such as in the DO molecule. However, we also reach a very unambiguous conclusion, that the transition rates do not depend on the light intensity. One perhaps could expect that for the "off"-relaxation rates, Figure 6(b), since in all cases the same DO material is being examined. The fact that the "on"-transition rates in Figure 6(a) are also evidently the same, in spite of a great variation of intensity of the absorbed light, may appear surprising. First of all we need to emphasize that the results presented in Figures 5 and 6 are for the actuation stress, *i.e.* the increment due to irradiation (hence the initial value is zero). This allows normalizing the data, which then reveals the kinetics that might otherwise be masked by the variation in amplitudes.

An approximately linear dependence of saturation stress $\sigma_{\max}$ on intensity, as well as the independence of observed transition rates of intensity, are in agreement with the basic theory of photoactuation [1,3]. If one reasonably assumes that the bare *trans-cis* transition rate is a linear function of intensity $1/\tau_{tc} \propto I$, then the population of *cis*-isomers is determined by the balance of that and the *cis-trans* reaction with the constant rate $1/\tau_{ct}$:

$$\phi_{cis} = \phi_0 \frac{\tau_{ct}/\tau_{tc}}{1+\tau_{ct}/\tau_{tc}} \left(1 - e^{-t/\tau_{\mathrm{eff}}}\right), \qquad (1)$$

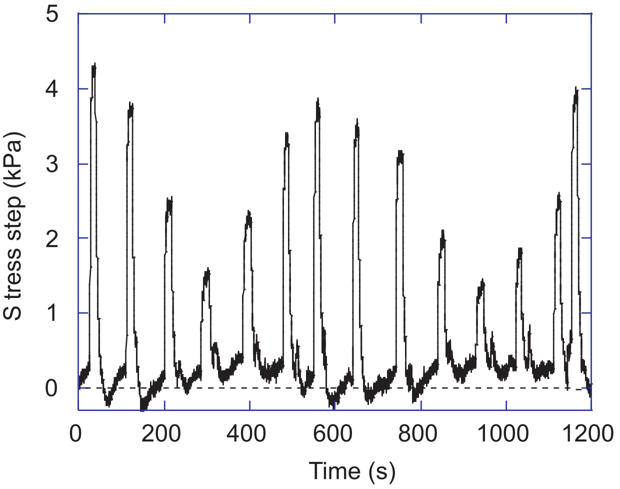

Fig. 7. Effect of polarization: illumination sequence, with polarization rotated by 30° on each cycle.

where ϕ_0 is the concentration of photoreactive groups in the medium and the effective relaxation time $\tau_{\mathrm{eff}} = \tau_{ct}/[1 + \tau_{ct}/\tau_{tc}]$. Far from the critical nematic-isotropic transition (cf. Fig. 2) one expects a linear dependence of actuation stress σ on $\phi_{cis}(t)$. Therefore, in the limit of low intensity, we have $\tau_{\mathrm{eff}} \approx \tau_{ct}$ and $\sigma_{\max} \propto \phi_{cis}|_{t\to\infty} \approx \phi_0(\tau_{\mathrm{eff}}/\tau_{tc}) \propto I$.

All responses has been fitted with a simple exponential function in agreement with equation (1). The effective response time for the Az material was 29.1 s, and for the DO material 1.9 s with LED, 2.0 s with HG and 1.8 s with ArL. The relaxation times in Figure 6(b) were 23.7 s for Az and in the range 4.7–5.0 s for DO in various experiments. The order of magnitude agreement $\tau_{\mathrm{eff}} \approx \tau_{ct}$ is observed, although the slightly longer *cis-trans* relaxation times in DO indicate some deviations from the basic model.

We now turn to the main focus of this work —the effect of polarization. In a monodomain material, the dye molecules are aligned with the nematic director. This means contraction can only occur in one direction. When the plane of polarization is aligned with the director we expect maximum contraction and when the polarization is at 90°, we expect no or minimal contraction. The situation is much more delicate in a corresponding polydomain nematic LCE where the different parts of the sample are aligned randomly [9]. An average macroscopic contraction is expected parallel to the plane of polarization, as illustrated in [8]. However since our dynamometer only measures the force in one direction, we expect a pattern similar to that of a monodomain material as the angle of polarization changes. Figure 7 demonstrates the effect in the polydomain DO elastomer (the result for the monodomain LCE is qualitatively the same). The plot shows a continuous logging of actuation stress during a sequence of cycles of 20 s illumination and 80 s relaxation (in each case reaching a reliable plateau), with the angle of polarization incremented by 30° after each cycle. The sinusoidal variation of $\sigma_{\max}$ across 360° rotation is apparent, as well as the good reproducibility of the effect.

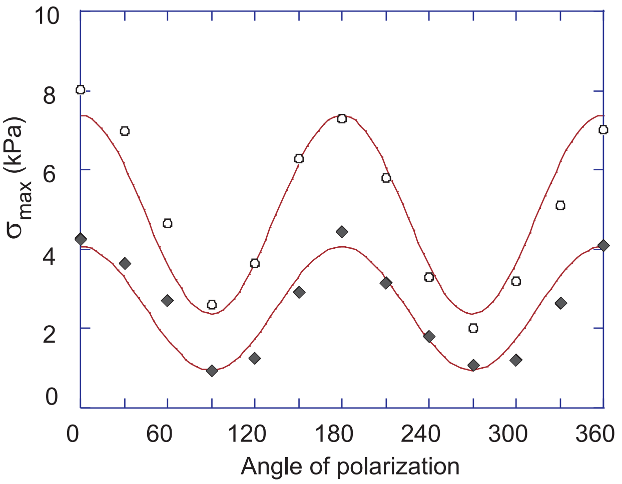

Fig. 8. Effect of polarization: saturation amplitudes $\sigma_{\max}$ plotted against the polarization angle, for (○) monodomain and (♦) polydomain DO nematic elastomers (solid lines are fits with $\cos 2\theta$).

Let us compare the results for the mono- and polydomain samples of DO by plotting the saturation value $\sigma_{\max}$, obtained with the same intensity but at different polarization angles, Figure 8. Importantly, the amplitude of photoactuation does not drop to zero at 90° polarization. For monodomain materials this is not unexpected, simply because the polarizer efficiency is far from 100% and also because the nematic order is not perfect. However, consider the photoactuation in polydomain LCE: at 90° polarization the domains perpendicular to the axis of measured force are contracted, while the ones along this axis affected much less. In this case, due to incompressibility, one could expect an average *expansion* of the sample length along the measurement axis, *i.e.* a negative stress step. We do not see that, although the amplitude in the troughs in Figure 8 is much smaller for polydomain LCE. Presumably the fraction of non-polarized light falling on the sample in our experiments was sufficient to mask the pure effect.

We also determined the effective response times τ_{eff} for the monodomain and polydomain LCE at different polarizations by expanding and fitting the data of each illumination cycle in Figure 7. We found that the different polarizations had no effect, nor did the alignment of the material. All τ_{eff} values were within the range 2 ± 0.5 s for the "on"-transitions; the "off"-relaxation is characterized by 5 ± 0.4 s in monodomain and 7.2 ± 0.5 s in polydomain materials. The order of magnitude is consistent with the earlier results on response times, independent of light intensity and slightly longer in relaxation. The longer still relaxation of polydomain LCE would be an expected feature since many internal defects and domain walls are involved in macroscopic response.

Photoactuation in nematic LCE shows how light energy can be directly converted into mechanical work. Polarization of light allows fine control over the response. However, fundamental problems remain unresolved in detailed understanding of the process kinetics, especially in polydomain materials.

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