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This is the author's submitted version of the contribution published as:

Original

Polarization-dependent deformation in light responsive polymers doped by dichroic dyes / Martella, Daniele; Nocentini, Sara; Micheletti, Filippo; Wiersma, Diederik S.; Parmeggiani, Camilla. - In: SOFT MATTER. - ISSN 1744-683X. - 15:6(2019), pp. 1312-1318-1318. [10.1039/c8sm01954a]

Availability:

This version is available at: 11696/66835 since: 2021-02-19T18:51:02Z

Publisher:

ROYAL SOC CHEMISTRY

Published

DOI:10.1039/c8sm01954a

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Polarization-dependent deformation in light responsive polymers doped by dichroic dyes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Light represents a very versatile stimulus and its use to control the deformation in shape-changing polymers can take advantage of multiple parameters (such as wavelength, power and polarization) to be explored in order to obtain differentiated responses. Polymers with selected color responsiveness are commonly prepared by using different dyes, while a polarization-dependent control can be introduced exploiting *trans-cis* isomerization of azobenzenes. As shape-changing polymers driven by a photothermal effect are gaining more and more attention in many application fields, exploring polarization to modulate their response could enlarge the tuning parameter space and provide an insight into the material optical properties. In this work, we demonstrate the effect of light polarization on the deformation of Liquid Crystalline Networks doped by a small amount of a push-pull azobenzene. We demonstrate how enhancing the dye alignment in the polymeric matrix leads to different deformations by orthogonal polarizations. These results demonstrate polarization as a convenient further degree of freedom besides wavelength and intensity of the light stimulus.

Introduction

The ability to control the deformation in shape-changing materials offers many opportunities in different fields, from robotics¹ to biomedicine.² Among the possible different stimuli able to activate smart polymers (e.g. temperature, magnetic and electric fields, pH), light results a wireless and highly selective (both in time and space) energy source. Indeed, it allows for improved resolution with respect to other chemical and physical stimuli, and enables the remote and real time control of miniaturized devices.³ Moreover, electromagnetic waves due to their intrinsic characteristics (e.g., wavelength, polarization and intensity) offer many variables, that can be exploited singularly or convoluted, to investigate polymer optical properties and the related responses. In this sense, a single light beam represents a source of multiple stimuli, to be selectively sensed by the material thanks to the designed chemical structure.

To obtain light sensitive polymers, the mainly explored strategy is based on doping a host matrix with photochromic molecules. Herein, two different behaviours can be distinguished: light can induce both a chemical modification (such as isomerization or ring-opening process) that triggers a molecular rearrangement in the whole system,⁴ or can be absorbed and then dissipated into heat leading to thermal transitions.^{5,6} In this framework, azobenzenes represent the widely employed dopants.⁷ Considering the host matrix, liquid crystalline elastomers (LCE) and networks (LCN) are among the best

candidates to realize artificial muscles thanks to their peculiar properties, such as the ability to reversibly change shape due to a phase transition inside the network.⁸ Interestingly, programming specific molecular alignments during polymer preparation, allows to achieve different deformations by switching in between -at least- two material shapes, corresponding to the liquid crystalline and the isotropic phases, respectively.⁹ The result is a synthetic material able to perform contractions,¹⁰ rotations,¹¹ bending¹² or even more complex movements.

To date, light responsive liquid crystalline networks have been prepared by different substituted azobenzenes sensitive to both UV and visible light.¹³ Playing on the stability of the two azobenzene isomers, it is possible to obtain materials with persistent deformations (a second wavelength is needed to recover the initial shape)¹⁴ or reversible one (the material returns to the original shape once the light is switched off).¹⁵ A wavelength dependent control can be exploited not only by triggering the azobenzene back isomerization but also by a selective colour responsiveness of different parts of the device. Combination of dyes with different absorption properties in the same actuator has been demonstrated in artificial cilia constituted by subunits containing two different azobenzenes, creating a selective actuation in dependence of the wavelength shined on the whole system.¹⁶ More recently, reprogrammable actuators sensitive to two colours were demonstrated by the use of a single formulation containing an azomerocyanine dye, thanks to a selective acid patterning (resulting in the conversion of the dye in its hydroxyazopyridinium form, showing then very different absorption spectra).¹⁷

Besides such interesting examples, it has to be kept in mind that absorption spectra of azobenzenes are quite broad and the obtainment of materials responsive to more than two colours is difficult to be achieved. Therefore, exploiting other physical properties of light to get independent movements in response to a wider range of parameters is still a hot topic of research, and introducing an actuation dependence on polarisation allows the system control on a further degree of freedom.

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Electronic Supplementary Information (ESI) available: polarized absorption spectra and other images of light-deformation of materials. See DOI: 10.1039/x0xx00000x

The first example exploring the LCN deformation dependence to this parameter was described by Yu *et al.* for a polydomain polymer.¹⁸ They demonstrated the selective activation of different regions of the sample presenting the director parallel to the polarization direction, resulting in the bending toward specific directions. Both the extent of photomechanical bending and the speed of deformation can be enhanced by chemical modification of the polymer (e.g. by choosing appropriate crosslinking degree) leading also to an increased dependence on light polarization.¹⁹

Analysing monodomain LCNs, an interesting example reported the bidirectional movement of a cantilever: it bends towards the laser source when illuminated by light having a polarization parallel to the nematic director, and away from it by using the perpendicular one.²⁰ Exploiting the same principle, White *et al.* demonstrated how, controlling the angle of beam polarization, the bending of a cantilever can be modulated for more than 40°.²¹ The use of monodomain samples, in respect to polydomain ones, enhances the polarization dependence and increases both the deformation speed and induced stress during the deformation.²²

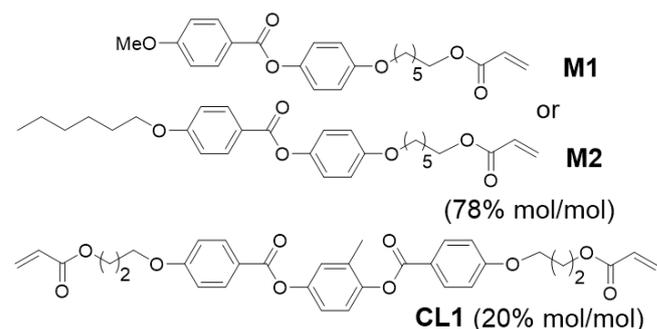
Although all the above presented examples are related to an optical effect (due to azobenzene isomerization), LCNs driven by photoinduced thermal effect are gaining more and more attention allowing for sub millisecond dynamics of light actuation.²³ Following this second approach, in this article we focus on the demonstration of the deformation polarization-dependence in monodomain LCNs doped with small amounts of push-pull azobenzenes. First, we evaluated the dichroic absorption of mixtures containing different liquid crystalline matrixes and azobenzenes characterized by absorption in the visible range. Then, we employed the formulation showing the highest dichroic ratio for light actuation tests by using different power and polarizations. Differently from the previously reported examples, we demonstrated that a good liquid crystalline alignment results fundamental to introduce a polarization-dependent actuation of LCNs driven by photoinduced thermal effect.

Results and discussion

Polarization-dependence of light response arises from the anisotropic absorption properties of dichroic dyes such as azobenzenes. When inserted in liquid crystalline host, they tend to align along the nematic director and, if their dipolar moment is parallel to the long molecular axis, the optical properties of the whole sample present an angular dependence. Enhancing the dye alignment can improve the polarization-dependence response of the final material. To verify this hypothesis, we prepared different liquid crystalline networks by changing both the LC host and the azobenzene guest, and we investigated how different molecular structures create supramolecular interactions that can result in different degrees of alignment.

The materials were prepared by in situ photopolymerization of acrylate based mesogens after their alignment in the nematic phase.²⁴ In particular, liquid crystalline compounds used in this study are reported in Figure 1a. Each mixture contains 78% mol/mol of one of the two monoacrylate M1 or M2, 20% of the diacrylate CL1, the photoinitiator Irgacure 369 (1% mol/mol) to induce the polymerization by UV light and one of the azobenzenes (1% mol/mol) reported in Figure 1b. We selected two different monoacrylate (M1 and M2), having a different final alkyl chain, on the basis of the demonstrated improved order parameter in systems containing acrylate mesogens bearing long flexible spacers.²⁵

a) Liquid Crystalline compounds



b) Azobenzene dyes

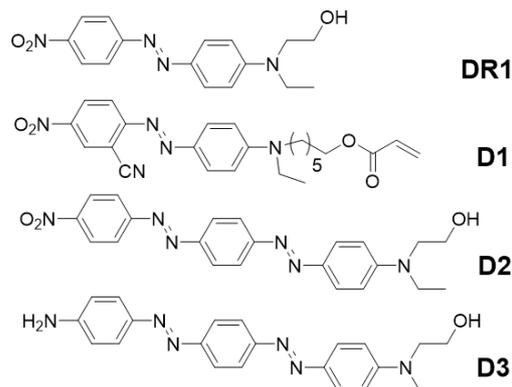


Figure 1 – Molecular structures of liquid crystalline hosts (a) and dyes (b).

All the selected dyes have a maximum of absorption in the visible range. Disperse Red 1 (DR1) is commercially available and presents a linear structure bearing push-pull substituents, while D1 is a customized dye showing a stronger and red-shifted absorption but not presenting a linear molecular structure. Both dyes have been widely used in LCN formulations and many experiments demonstrated that their working mechanism is mainly due to a photoinduced thermal effect.^{26,27} Two more dyes were prepared and used (D2 and D3) presenting a longer linear conjugated core, chosen to yield an increase of the dichroic ratio.²⁸ Moreover, they differ by the electronic nature of the substituent on the aromatic ring (nitro or amino group for D2 and D3, respectively), presenting a diverse host-guest interaction with the LC matrix.

Preparation of the LCNs follows a standard procedure, which comprise the infiltration of the nematic mixture in a LC cell, its alignment and then, the polymerization.²⁹ The mixtures were prepared by combining of one of the two monomers (M1 and M2) with one of the four dyes and the resulting materials are noted as LCNx-y where x indicates the monomer (e.g. x=1 for M1) and y indicates the dye contained in the formulation.

The first simple test performed on the different films consists in the visual observation of the colour change through a linear polarizer, and it highlighted the anisotropic nature of LCN absorbance (Figure 2a). Once fixed the polarization direction, and placing the film LC director parallel or orthogonal to it, the film colour changed. A quantitative analysis of the optical anisotropy of the samples was performed by polarized absorption spectroscopy. Figure 2b reports the spectra for the two more significant formulations recorded using parallel and perpendicular polarization in respect to the rubbing direction, showing a significantly stronger absorption in the first case

(for all the other samples, the spectra are reported in Figure S1 in Supporting Information).

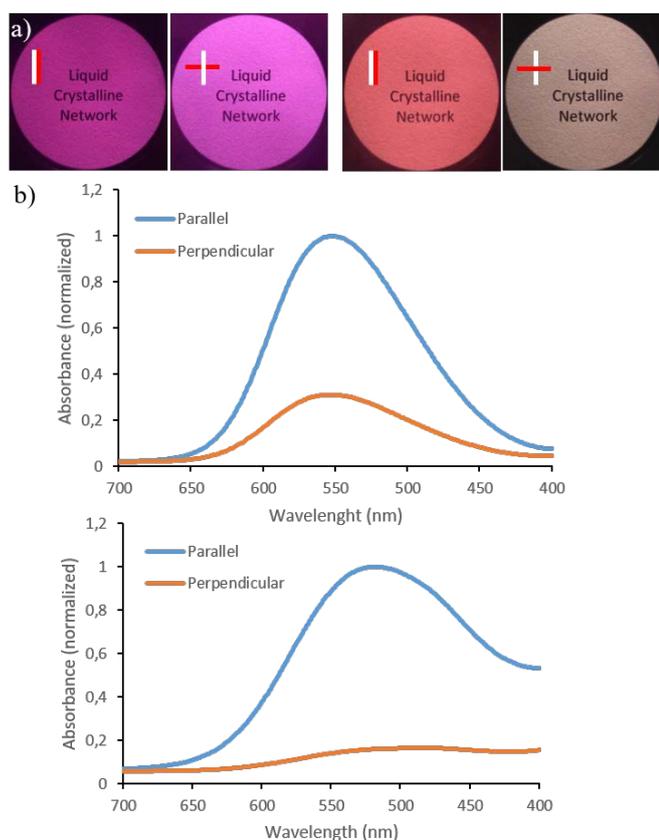


Figure 2 – Dichroic optical properties of selected LCNs. a) Optical images of the films with different director orientation in respect to linearly polarized light. White line indicates the light polarization direction and red line indicates the nematic director. b) Polarized absorption spectra of LCN1_1 and LCN2_2.

Degree of optical anisotropy is estimated by comparison of dichroic ratios (R) and order parameters (S), both calculated from the maximum in the absorbance spectrum of each sample and are summarized in Table 1.

Table 1 – Dichroic ratio (R) and order parameter (S , in bracket) for different LCN compositions. Parameter are calculated on the basis of the maximum in the absorbance spectra of each dye.

Dye / Monomer	M1	M2
DR1	3.83 (0.48)	5.56 (0.60)
D1	3.28 (0.43)	3.88 (0.49)
D2	4.34 (0.53)	6.23 (0.64)
D3	4.31 (0.52)	2.70 (0.36)

As expected, both the liquid crystalline host and the guest chemical structure play a role in the alignment properties. First considering the mixtures containing M1, we observed as both dyes containing 3 aromatic rings in the core (D2 and D3) are able to enhance the dichroic ratio up to a value of 4.3. While analysing the samples containing M2, dichroic ratio values are higher than the samples containing M1 except when D3 is used as dopant. This sample results in the less ordered material of the series. On the other hand, comparing samples containing DR1 and D2, we can observe as the

push-pull system with nitro- and amino- group in para positions leads to the highest degree of molecular alignment. This is particularly evident when D2 is used, thus confirming as longer conjugated systems are able to promote the dye orientation.

Due to the demonstrated improved optical anisotropy, we selected LCN2_2 for further characterization and we compared it with the material with lower alignment degree, LCN1_1, already used by our group in many studies.^{23,26,30}

Because of the enhanced deformations presented by splayed films with respect to planar samples, splayed alignment was chosen for the following analysis. Indeed, the differential strain across the material thickness leads to a well measurable bending towards the homogeneous side as a clear marker of the molecular properties of the system.³¹

From splayed films, thin cantilevers (around 10 mm x 3 mm x 20 μ m in size) were cut with the longer dimension parallel to the LC director of the homogeneous side. Their deformation was characterized by irradiation with a green laser light (continuous wave, 532 nm). The whole setup is depicted in Figure S2 and comprises a ND filter wheel (to control the irradiation power), a linear polarizer (to select only one polarization of the laser beam) and a quarter waveplate to rotate the polarization direction. The effective polarization results not perfectly linear due to experimental setup limitation.

Cantilevers were irradiated increasing the laser power, and bending angles were measured and reported in Figure 3a for both, parallel and perpendicular polarizations (with respect to the LC director of the planar side). In both samples, bending starts around 5 mW and increases with the actuation power. As soon as the irradiation is removed, samples recover the original position in less than 1 second, as expected due to the photoinduced thermal effect.²⁹ Interestingly, the bending angles present different values for the two reported formulations. A larger actuation is detected for LCN1_1 cantilever with a more pronounced effect at higher laser intensity. This behaviour could result from the different absorptions of the two samples: LCN1_1 presents an absorbance 1.6 times higher than LCN2_2 (absolute absorbance values of 1.01 and 0.62 respectively for a 10 μ m thick film measured at 532 nm). An enhanced dye absorption can result in a more efficient energy-into-heat transfer rate that increases, in the LCN1_1 splayed cantilever, the strain gradient and therefore the deformation.

Moreover, when polarization rotates of 90°, the two samples behave differently. Keeping the laser light intensity fixed and changing the polarization, LCN1_1 shows a negligible bending angle variation, presenting comparable deformations by parallel and perpendicular polarization. Instead, a moderate polarization-dependence can be observed for LCN2_2, presenting a 15° bending angle difference (inset in Figure 3a) by switching among the two orthogonal polarizations. Representative optical images showing the deformation of the two materials under an actuation power of 17 mW, are reported in Figure 3b.

Material deformation is the result of a complex interplay among many parameters (such as crosslinking density, alignments, internal strain, etc.), and a simple tuning mechanism to control it consists in playing on geometrical parameters, such as the arbitrary selection of the cantilever long axis with respect to the LC director.^{32,33} We thus prepared a cantilever by cutting it off at 45° in respect to the rubbing direction of the LCN2_2 splayed film. This alignment tilting introduces larger bending angles and an improved polarization-dependence. As expected, an out of plane deformation appeared in the system.³³ The comparison among the bending angles obtained at different irradiation conditions for stripes cut parallel or at 45° in respect to rubbing direction is reported in Figure 3c. It is immediately

clear as larger deformations are obtained for the new sample independently on the polarization direction of the actuating light. This effect can be attributed to an increased internal stress inside the molecular network. For an illuminating power of 17 mW, the more selective polarization response has been recorded showing a 40° bending angle difference for the two orthogonal polarizations (Figure 3c).

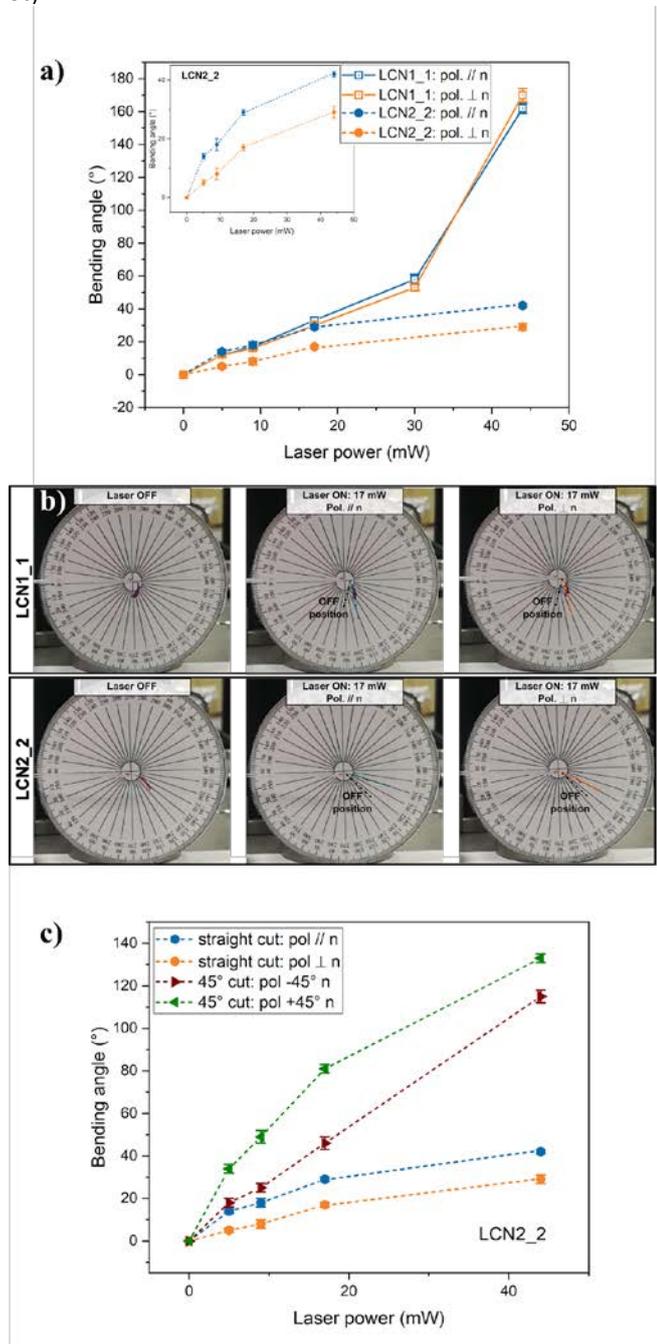


Figure 3 – Light response of LCNs to irradiation with different powers and polarizations. a) Bending angles for stripes cut along the rubbing direction; b) optical images of deformation obtained in LCN stripes under a 17 mW irradiation; c) comparison of bending angles obtained in two stripe of LCN2_2 cut respectively parallel and at 45° in respect to the rubbing direction.

Interestingly, common LCNs responding to light by an optical effect (derived from the azobenzene isomerization), are able to deform in a controlled way also in case of polydomain alignments.¹⁸ This behaviour is not reproduced by our materials, as shown in Figure S4, reporting how the light irradiation on a polydomain LCN2_2 cantilever results in its permanent droop due to the material softening - induced by the increased sample temperature. The inhibited recovering of the original position indicates the needing, in our system, of a well-engineered molecular alignment to ensure the shape-change control. Moreover, in LCNs based on an optical effect, light polarization can be exploited to select the direction of out of plane deformation (e.g. for material cut oblique to rubbing in splayed arrangement).³³ On the other hand, in systems driven by photothermal effect, the handedness of material torsion can be defined only during the material processing, e.g. by set an appropriate cutting angle (Figure S5).

Two main effects emerged during the preparation and the characterization of the here presented photothermally driven networks. On one side, the improved guest-host alignment strongly affects the material responsiveness, while, on the other side, the internal strain - induced in our case by tilting the cantilever long axis with respect to its LC director in the planar homogeneous side - enhances the deformation and the polarization-dependent response. Combining such main properties, in Figure 4, we compared LCN1_1 and LCN2_2 cantilevers both cut from splayed film choosing the stripe long axis at 45° with respect to the molecular alignment of the planar homogeneous side. Stripe deformation during irradiation with different polarizations is also shown in Movie S1 and S2. For LCN1_1, the material with the lower degree of alignment, the control of the bending degree can be achieved only by modulation of the irradiation laser power, while a selective polarization behaviour was not observed. On the other hand, for LCN2_2, orthogonal polarized light creates a difference in the bending angle of around 40° offering a further parameter to tune the material deformation, in addition to the irradiation power.

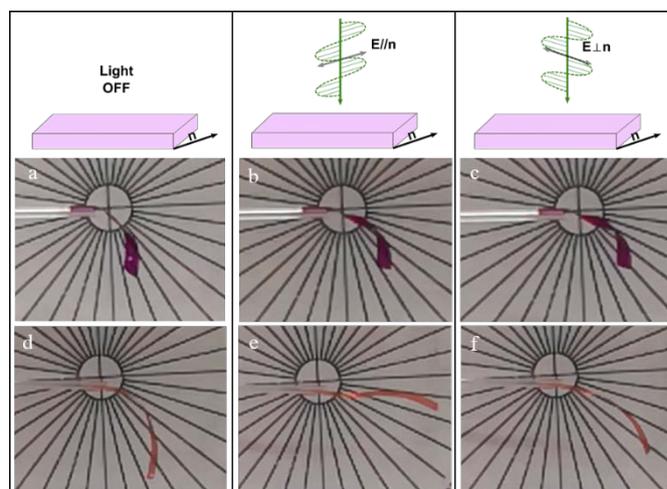


Figure 4– Control of LCN deformation by orthogonal polarization of light. Stripes of LCN1_1 and LCN2_2 are cut at 45° with respect to the rubbing direction (a and d, respectively) and then, irradiated by a green laser with parallel (b and e) and perpendicular (c and f) polarization.

We can thus envision as using highly ordered liquid crystalline matrix, e.g. by photo-crosslinking of smectic guest,²⁵ could lead to an

increased polarization-dependence on the light-induced deformation in LCNs. Moreover, this concept could be extended for other dyes or nanoparticles (e.g. gold nanorods) presenting dichroic shape already employed in light responsive LCNs.³⁴

Experimental section

Materials and methods.

Liquid crystalline monomers (M1, M2 and CL1) were purchased by Synthron Chemical, Irgacure 369 and Disperse Red 1 were purchased from Sigma Aldrich. D1, D2 and D3 were prepared as previously described.^{28,30} Polarized optical microscopy (POM) was performed using the inverted microscope Zeiss, Axio Observer A1 with cross polarizers to check the liquid crystalline alignment inside the sample.

Liquid crystalline polymer preparation.

The LC mixtures were melted on a hot plate at 75°C and infiltrated by capillarity in appropriate polymerization cells. Cells were prepared by two coated glasses with a 20 µm spacer. Splayed cells were prepared by a PI1211 (Nissan Chemicals) coated glass and a PVA coated glass (after rubbing with a velvet cloth), while homogeneous cells were prepared by the use of two rubbed PVA glasses. Polydomain samples were prepared using untreated glasses. After infiltration, cells were cooled down to 45 °C and the resulting nematic alignment was checked by POM. Aligned cells were irradiated for 10 minutes with an UV LED lamp (Thorlabs M385L2-C4, 385 nm, I: 4 mWcm⁻²) then, heated to 65°C and irradiated for further 10 minutes to complete the polymerization process. LCN films were manually removed from the cell and the cantilever have been cut out for the different experiments.

Optical properties of LC films.

Absorption spectra of homogeneous LCN films were recorded on a Varian Cary 400 instrument equipped with a linear polarizer. The dichroic ratio (R) was evaluated at the absorption maximum for the different dyes according to equation 1:

$$R = (A_{\parallel}) / (A_{\perp}) \quad (1)$$

where A_{\parallel} and A_{\perp} represent the parallel and perpendicular absorbance in respect to the rubbing direction.

The order parameter (S) was defined by equation 2:

$$S = (R - 1) / (R + 2) \quad (2)$$

Light induced deformation.

Cantilever specimens (10 × 3 × 0.02 mm³) were prepared by cutting splayed films and tested by illumination with a DPSS 532 nm laser from the top. Only a part of the actuator was illuminated due to the laser spot dimension (5 mm of diameter) and the movement was recorded with an optical camera. Light intensity was varied using a neutral density wheel-filter while, polarization was selected by a linear polarizer and quarter waveplate filter. The not perfect extinction ratio of linear polarizer alters the working mechanism of the waveplate creating an elliptical polarization more than a perfectly linear one. For a non-filtered measured power of 50 mW, 35 mW constitute the parallel polarized component, while the orthogonal one is 1.5 µW creating an extinction ratio of around 10⁴:1. A scheme of the setup is reported in Supporting Information (Figure S2).

Conclusions

Light-driven liquid crystalline networks based on photoinduced thermal activation are gaining more and more attention thanks to their sub millisecond time performances, which open to real time control on micro robotic and photonic systems. However, inducing their shape-change by different light polarization is not trivial. This study demonstrates that only by enhancing the alignment of the guest dye in the host polymeric matrix leads to different deformations by using two orthogonal polarisation of light without changing neither the wavelength nor the intensity of the stimulus. Further improvements both in material composition (to achieve higher order parameter) and illumination apparatus (by using perfectly linear polarization) can be envisaged to obtain a total decoupling in the material deformation induced by orthogonal polarizations.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

The research leading to these results has received funding from Laserlab-Europe EU-H2020 654148; from Ente Cassa di Risparmio di Firenze (grant 2015/0781) and Fondazione Telethon (grant GGP16191). This research project has been also supported by FAS-Salute ToRSADE project.

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