Microscale Polarization Color Pixels from Liquid Crystal Elastomers

Yubing Guo, Hamed Shahsavan, and Metin Sitti*

1. Introduction

Liquid crystal elastomers (LCEs) attract burgeoning research interests due to their programmable 3D shape transformation and achievable large strain (up to 400%), which allow their diverse applications. One exciting application is soft microrobots towards biomedical applications. Here, it is demonstrated that polarization colors, an intrinsic property from the anisotropic nature of LCEs, can assist LCEs in their diverse applications. Microscale color pixels with sizes as small as 15 μm x 15 μm are obtained with designable colors from precisely controlled thicknesses enabled by two-photon polymerization technique. It is then demonstrated that in-plane rotation of LCE pixels only changes their color brightness instead of color hue and small tilting angle (<15°) causes almost no change of their color. These properties enable high-contrast tracking of LCEs under polarized microscope. Furthermore, it is exhibited that both 2D and 3D microstructures with pre-designed multiple colors can be realized, allowing for LCE applications requiring precise discrimination of different components. Finally, dynamic polarization colors are explored by insertion of waveplates and change of temperature, which allows for either better tracking of LCEs or applications of LCEs in temperature sensing and information encryption. It is expected that polarization colors will assist various LCE applications, especially soft microrobot and art display applications.

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1. Introduction

Liquid crystal elastomers (LCEs) have received an increasing amount of interest due to their large strain and programmable 3D shape transformation with external stimuli, such as temperature and light illumination.[1–10] Based on these properties, LCEs are strong functional material candidates to be used in soft microrobot applications, which would offer disruptive new biomedical applications in targeted drug delivery, biosensing for precise diagnosis of disease, minimally invasive surgery, and detoxification.[11–13] LCEs own these properties ascribed to their anisotropic physical properties resulted from their long-range orientational order. Specifically, LCEs are cross-linked polymeric chains with rod-like mesogenic segments, which are usually aligned along certain direction called the director \( \hat{n} \).[14–16] Typically, refractive index along \( \hat{n} \) and perpendicular to it are different, resulting in the so-called polarization colors,[17–20] which can be treated similar to interference colors from thin plates.[21] Since polarization colors are intrinsic property of LCEs, we can expect that they carry built-in information of LCEs and thus enable LCEs to be used in diverse applications.

Colors are indispensable in the world we are living, assisting, or enabling communication, signaling, camouflage, and many other behaviors of creatures.[22] To date, a great deal of efforts has been devoted to generating colors using a variety of active materials that respond to external stimuli, such as temperature, electric field, and different chemicals.[23–29] As mentioned above, polarization colors originate from the difference between refractive indices and are crucially dependent on the thickness of birefringent materials as indicated in the Michel-Levy chart.[30–33] Thus, LCE colors can be controlled by precisely manipulating the thickness of an LCE layer. Currently, LCE layer thickness is usually controlled with spherically or cylindrically shaped particles or flat films with feature sizes of several micrometers to several hundred micrometers.[1–3] Guo et al. demonstrated sub-micrometer thickness of liquid crystal layer by using reactive ion etching and glass bonding.[34] However, LCEs with locally variant thicknesses are non-trivial and only demonstrated in large scale with a 3D printing technique.[35–37] Therefore, a strategy with high resolution for local thickness control and microscale pixel size is highly desirable to achieve desirable LCE colors on the micron scale.

Here, we show that 15 μm x 15 μm LCE pixels with desirable polarization colors in visible range can be achieved with well-controlled thickness of LCEs enabled by two-photon polymerization (TPP). As an intrinsic property of LCEs, these polarization colors allow for high-contrast tracking of LCEs under polarized microscope based on the following facts: in-plane rotation of LCE films will not change the color hue but only change the color brightness; tilting of LCE films below 15° cause almost no change of colors. We demonstrate that both 2D and 3D microstructures with pre-programmed colors can be realized, which will benefit LCE applications requiring precise discrimination of different components. We further explore the dynamic switching of polarization...
colors with insertion of a waveplate, which enables better tracking of LCEs under polarized microscope. Finally, we exhibit temperature switching of these polarization colors, which permit application of LCEs for temperature sensing and information encryption.

2. Results

We first explore the capability of generating microscale polarization color pixels with the well-controlled thickness of LCE films. To fabricate LCE films, we assembled a cell with two glass slides coated with polyimide, which was rubbed with velvet cloth in a preferred direction to induce uniform planar alignment. The assembled cell was then filled with a mixture of ST3021 (33 wt%), ST3866 (66 wt%), and Irgacure 369 (1 wt%) at elevated temperatures (Figure 1a). Afterward, microstructures with different geometries, such as arrays of 20 µm × 20 µm squares with different thicknesses, pyramids, and arbitrary alphabetical characters were fabricated by TPP (Nanoscribe GmbH).

Scanning electron microscopy (SEM) images of the fabricated microstructures in Figure 1b–d confirms that the
designed microstructures can be fabricated with minimal structural defect using the TPP technique. We used laser interferometer (Keyence) to measure thickness of the fabricated microstructures (Figure 1e,f). Figure 1e,f and Figure S1. Supporting Information confirm the accuracy of the TPP procedure in the replication of designed graphics files by comparing the measured feature sizes for an array of squares with varying thickness to that of original designs. The designed film thickness varies from 1.1 to 8.2 µm with 0.1 µm increment. The difference between the measured thicknesses and designed thicknesses is mostly within 0.3 µm, which enables one to choose the desired color by using the corresponding thickness of LCE layers. We remark that the thickness accuracy can be further improved by systematic variation of laser writing speed, laser power uniformity, LCE mixture homogeneity, etc. Another choice is to use LCEs with smaller birefringence, which correspond to larger thickness to achieve the same colors, and thus lowering the requirement of thickness control.

The molecular alignment of LCE films was examined by polarized optical microscope (POM) images of the fabricated films. As exhibited in Figure 1g–j, the sharp contrast between transmission of light when LCE director is −45° (transmission) and parallel (extinction) to the polarizers shows the successful alignment of LCEs. Additionally, we can clearly observe the variation of colors with thickness. The film with the smallest thickness shows almost no color, but as the film thickness increases, colors evolve in the sequence of yellow, orange, purple, blue, and red. These colors are polarization colors due to the anisotropic optical property of LCEs. Birefringence (Δn = n⊥ − n∥) is the difference between the refractive indices of light rays propagating through the LC with polarization along, extraordinary ray (n⊥), and perpendicular, ordinary ray (n∥), to the nematic director field. The birefringence of an ordered nematic LC film with a thickness of d results in an optical path difference (OPD = dn) between transmitted ordinary and extraordinary rays, generating polarization colors when sandwiched between two polarizers.

For a film with thickness d, the phase difference between the ordinary and extraordinary rays can be expressed as \( \Gamma = 2\pi(d(n_\perp - n_\parallel))/\lambda = 2\pi(\text{OPD})/\lambda \), where \( \lambda \) is the wavelength of the incident light. In some particular cases, the light after going through the LCE film can be linearly polarized (e.g., \( \Gamma = \pi/2 \)) or circularly polarized (e.g., \( \Gamma = \pi/4 \)). In more general cases, the transmitted light is elliptically polarized. Therefore, for a film with certain thickness \( d \), lights with different wavelength will have different polarization state after transmission, as a result, films with different thickness yield different transmission spectra, which corresponds to different colors exhibited in Figure 1i,j. By comparing these colors to the Michel-Levy chart, we find that the OPD of fabricated films changes slowly from a very small number to \( 1.2 \) µm, which gives LCE birefringence of \( \Delta n = 0.15 \).

To characterize the colors generated from the LCE films, we measured the transmission spectra of each film. Figure 2a represents results for the spectral measurement of LCE films with six representative OPD. The values of OPD are fitted from Equation (1) as shown below. Note that the transmission of light through the parallel polarizer and analyzer is considered as a background \( I_0(\lambda) \). We observe that transmission peak values are close to one, and the number of peaks/dips increases as the film thickness increases. Transmission of light with different wavelength through LCE with its molecular orientation making angle φ relative to x-axis is calculated as \[ T(\lambda) = I_0(\lambda)\sin^2 2\phi \sin^2 \left( \frac{\pi d \Delta n}{\lambda} \right) \]  

The Michel-Levy chart shows that polarization colors from continuously increasing thickness of liquid crystals correspond to different colors. In order to show the achievable color range,
we calculated the corresponding color coordinates based on measured transmission spectra $T(\lambda)$ in Figure 2a, power spectra of light source $I(\lambda)$ (Figure S2a, Supporting Information), and color matching functions $x(\lambda)$, $y(\lambda)$, $z(\lambda)$, which correspond to chromatic response of standard observer (Figure S2b, Supporting Information). Results are presented as black cross on the CIE 1931 chromaticity diagram in Figure 2b,[39] which clearly show that the fabricated LCE films cover a large visible color range with their coordinates relatively close to the center of the diagram. We observe that pure colors close to the edge of the chromaticity diagram cannot be achieved in our microscale pixels, which is due to the broad transmission peak as shown in Figure 2a.

To find the LCE birefringence, we fit the transmission spectra (Figure 2a) with Equation (1) with different phase retardation $\Delta n$. The relationship between phase retardation and LCE thickness is presented in Figure S2c, Supporting Information. A linear fitting with $\text{OPD} = 0.145d$ agrees well with the data points. The fitted birefringence 0.145 agrees well with the previous deduced value of 0.15 from the Michel-Levy chart.

These polarization colors allow for high-contrast tracking of LCEs under polarized microscope for various applications. For example, precise manipulation of LCE microrobots requires accurate localization of these robots. From Figure 1i,j we observe that totally different colors can be achieved by adding a 1 µm thickness. If we have several microrobots with similar appearance, by selecting proper thickness of each robot, we can track all of them easily under polarized microscope. Another situation is when we want to track the motion of an LCE object surrounded by large amount of similar LCE objects. We can easily set this LCE object with yellow color (5.7 µm thick) and all other objects with red color (6.7 µm thick). Since we have a large range of colors, we can always choose the most suitable color (LCE thickness) to work with.

For tracking of LCE micro-objects, one important issue is color shifting during their motion, that is, color shifting with respect to azimuthal angle $\phi$ and tilting angle $\theta$. From Equation (1), $\phi$ is not coupled to any other parameters, which means rotation of LCE films in-plane will change transmission of each wavelength by the same ratio. As a result, rotation of LCE films will not change the color hue but change the color brightness, which is verified in Figure S3a–f, Supporting Information. We observed that when LCE director field is very close to polarizer orientation ($\phi < 5^\circ$), the color brightness is too small and colors are difficult to be determined. Conversely, tilting of LCE film with angle $\theta$ will increase the effective thickness to $d/cos\theta$, which shifts the colors to larger thickness. For example, 15° and 20° tilting corresponds to effective thickness of 1.035$d$ and 1.064$d$, respectively. As is presented in Figure S3g,h, 15° tilting of LCE films cause almost no change of their colors; while 20° tilting introduce obvious shifting of some colors. Therefore, LCE birefringence colors can be used to track LCE motion when the tilting is smaller than 15°.

Figure 3. Colors designed from the controlled thickness of the fabricated LCE films. a) POM images of “M”, “P”, “I”, “–”, “I”, “S” with thickness 2.6, 4.0, 5.5, 7.3, 4.9, and 3.5 µm, respectively. b) POM images of “M”, “P”, “I”, “–”, “I”, “S” with thickness 3.3, 4.7, 6.2, 8.0, 5.6, and 4.2 µm, respectively. c) POM images of “M”, “P”, “I”, “–”, “I”, “S” with thickness 4.0, 5.4, 6.9, 8.7, 6.3, and 4.9 µm, respectively. d) POM image of a pyramid with 10 µm height. e) POM image of a pyramid with 20 µm height. f–h) POM image of an LCE microrobot with director field 0°, 22.5°, and 45° relative to polarizer, respectively. i) POM image of the LCE microrobot with director field 45° relative to polarizer and 15° tilting angle. In (a–i) $P$, $A$, and $n$ shows direction of polarizer, analyzer, and LCE director field, respectively.
Since LCE film thickness can be precisely controlled by the TPP process, 2D patterns, and 3D structures with predetermined colors can be designed. Figure 3a–c show the pre-designed variation of colors inside an arbitrary 2D pattern, that is, “MPI – IS”. The color of each letter corresponds to a certain thickness. For instance, the sequence of yellow, blue, green, red, cyan, and orange colors in the POM image shown in Figure 3a correspond to the LCE films with 2.6, 4.0, 5.5, 7.3, 4.9, and 3.5 µm thickness, respectively. It can be expected that any combination of desired colors can be obtained by simply choosing the corresponding thickness of LCE films. Figure 3b and c show the color shift of the original “MPI-1S” pattern to the right side of the Michel-Levy chart by 100 and 200 nm OPD of each letter, respectively.

We also demonstrated the variation of colors within a single 3D microstructure. Figure 3d,e show the variation of colors along with the height of two pyramids with a height of 10 and 20 µm, respectively. As expected, both patterns show four-fold symmetry of colors, which indicates the accuracy in the control of the thickness of fabricated pyramids. For each pyramid, the colors evolve continuously from side to the center according to the Michel-Levy chart. In addition, the change of colors for the pyramid with 20 µm height is more pronounced than that of 10 µm height.

Designable colors in 2D and 3D are extremely convenient for LCE applications, especially for applications requiring precise discrimination of different components. We present an LCE microrobot with its body and four legs designed into different colors. We verify that rotation of this microrobot only change its color brightness (Figure 3f–i) and tilting of this microrobot by 15° introduces almost no color shifting.

Dynamic colors have important applications in various fields, such as animal camouflage and color display industry. Here, we show that the fabricated LCE films in our work have potential in switching colors. We have used two different mechanisms to realize color switchability in our microstructures: color switching with waveplates and temperature change. In the first method, we used waveplates to achieve color changes based on 1) the phase retardation of waveplates and 2) angles between slow axis of waveplates and LCE director. Figure 4a–c show an example of color change, when a 532 nm waveplate is inserted between the films and the analyzer with its slow axis parallel to the analyzer, along the LCE director field, and 45° to the analyzer, respectively. In Figure 4a, no extra OPD is added and colors are exactly the same as those without waveplate (Figure 3a). In Figure 4b, OPD of 532 nm added to LCE films, thus all colors should change. However, adding 532 nm OPD results in shifting the colors to similar colors but in the next order according to the Michel-Levy chart. Therefore, the overall color change is rather trivial. In contrast, adding 532 nm OPD to the axis perpendicular to the slow axis of LCE films leads to shifting of all colors to the left on the Michel-Levy chart. In this case, the color change is more pronounced as can be seen in Figure 4c. Likewise, insertion of half-waveplate (266 nm OPD), and quarter-waveplate (133 nm OPD) creates vivid color changes as shown in Figure 4d–i, respectively. We expect that these switchable colors can be used in tracking of LCEs under some extreme conditions. For example, if a fixed thickness with less recognizable color is required, we can insert a certain waveplate to switch this color into a distinct one.

It is well known that high temperature causes reduction of order in liquid crystals, which results in decrease of birefringence and thus introduces color shifting of LCE films. Based on this phenomenon, one can judiciously manipulate the color of LCE films by varying the temperature. In Figure 5a,b and Figures S4, Supporting Information, we show that the color of LCEs can reversibly change by increasing and decreasing the temperature, both in 2D and 3D structures. The heating and cooling rate is set to be 10 °C min⁻¹. Due to the small thickness of LCE films, the temperature response of these films can be very fast. Indeed, sequential heating and cooling process lead to the appearance of almost identical colors at the same temperature. In this case, LCE temperature is encoded into its colors, very fast. Indeed, sequential heating and cooling process lead to the appearance of almost identical colors at the same temperature. The appearance of almost identical colors at the same temperature.
Based on the color switching with temperature in Figure 5b and Figure S4, Supporting Information, we anticipate having different thermal color shifting response from films with similar colors but with different thickness. For example, films with 2.6 and 5.8 \( \mu m \) thickness both show yellow colors at room temperature, which shift into light yellow and green colors at 130 °C, respectively. Similarly, films with 5.0 and 8.2 \( \mu m \) show green colors at room temperature, whereas they shift into blue and red colors at 130 °C, respectively. We employed such property to create thermally switchable patterns, such as “MPI”, which are invisible at low and visible at high temperatures. Our pattern is formed by an array of pixels with 10 \( \mu m \times 10 \mu m \) size and 5 \( \mu m \) distance. The “MPI” patterns are composed of films with 5.8 (Figure 5c) and 8.2 \( \mu m \) (Figure 5d) thickness, while the surrounding pixels have films with 2.6 (Figure 5c) and 5.0 \( \mu m \) (Figure 5d) thickness. At room temperature, “MPI” pattern is invisible since it has the same color as the surrounding pixels. When temperature increases, pixels in “MPI” pattern and surrounding pixels undergo a different thermal color shift, therefore, “MPI” patterns start to appear at 70 °C and become high-contrast at 130 °C (Figure 5c,d and Figure S6, Supporting Information). This temperature switchable hide-and-show behavior can be used as temperature sensor with higher contrast. Another application is information encryption, that is, information encoded in selected pixels, invisible under optical microscope and SEM (Figure S5, Supporting Information), can only be decoded with high temperature as a key.

3. Discussion

The proposed LCE polarization color pixels can be improved from several aspects. First, LCE materials with lower nematic-to-isotropic phase transition temperatures can be used, which will provide larger color shifting corresponding to temperature change and thus enabling more precise temperature sensing of LCEs. Next, LCE films can be attached to other microscale objects for detecting their motions, temperatures or other properties, such as strain. Finally, large-scale color pixels require new fabrication techniques. We remark that as a series process, two-photon polymerization is not suitable for large-scale area. We expect polymerization with programmable light intensity, similar to gray-scale photolithography can be explored to overcome this challenge.

Figure 5. Switching of the LCE colors with temperature. a) POM images of a LCE pyramid with 10 \( \mu m \) height in a heating process. b) POM images of the LCE films with designed thicknesses from 4.7 to 8.2 \( \mu m \) during a heating process. c,d) Hide-and-show demonstration of “MPI” patterns based on original c) yellow and d) green colors during a heating and cooling process. In each figure, \( P \), \( A \), and \( n \) show direction of polarizer, analyzer, and LCE director field, respectively.
The LCE polarization color pixels demonstrated above is also a potential color display strategy, which allows for color filter-free transmissive display. Compared with liquid crystal displays with multi-step microfabrication, the LCE color pixels are straightforward to be fabricated. As shown in Figures 1 and 2, a large range of colors are generated with precisely controlled LCE film thickness. The smallest pixel size is 15 μm × 15 μm, allowing for 1500 dots per inch (dpi) display, which is around one order of magnitude higher than traditional liquid crystal displays. Due to higher transmission (Figure 2a) and lack of extra color filters, this strategy is much more energy efficient than traditional liquid crystal displays. The obvious disadvantage of this strategy is its slow color switching speed and its small tunable color range. We can expect these polarization color pixels to be used in static displays, such as art exhibitions or displays.

4. Conclusions

In conclusion, we fabricate 15 μm × 15 μm LCE pixels with designable colors in visible range from well-controlled thickness of LCE, which is enabled by two-photon polymerization. We demonstrate that rotation of LCE films will not change the color hue but change the color brightness, while tilting of LCE films below 15° cause almost no color shifting. As a result, these polarization colors permit high-contrast tracking of LCES under polarized optical microscope. We then show both 2D and 3D microstructures with pre-programmed colors, which will benefit LCE applications requiring precise discrimination of different components. We further explore the dynamic switching of colors with insertion of waveplates and change of temperature. These dynamic colors enable better tracking of LCES under polarized microscope, and allow LCE applications in temperature sensing, information encryption, etc. Based on our demonstrated results, LCE microscale polarization color pixels show potential applications in microrobot tracking, temperature sensing, and information encryption, while we also expect other applications of the LCE polarization color on the micron scale.

5. Experimental Section

Materials: 4-methoxybenzoic acid 4-(6-acryloyloxyhexyloxy) phenyl ester (ST3866) and 1,4-Bis[4-(3-acryloyloxypropoxy)benzoyloxy]-2-methylbenzene (ST3021) were purchased from Synthon Chemicals. Irgacure 369 was purchased from Sigma-Aldrich. All the materials are used as received.

Liquid Crystal Cells: Glass substrates were cleaned with acetone and isopropanol, and then spin-coated with polyimide (PI2555) at a speed of 3000 rpm for 30 s. The substrates were then baked at 180 °C for 30 min. The PI layer was then rubbed uni-directionally with a cloth for uniform alignment of LCES. Two glass substrates were assembled to form a liquid crystal cell with 40 μm spacers to maintain the gap size. A mixture of 66 wt% ST3866, 33 wt% ST3021, and 1 wt% of Irgacure 369 was filled into a cell with capillary force at 100 °C hot stage. The cell is then cooled slowly to room temperature.

Two-Photon Polymerization: The LCE films and structures were fabricated with a direct laser writing system (Nanoscribe GmbH) equipped with a 63X oil-immersion objective (NA = 1.4). Films and pyramid structures were designed with SolidWorks and written into LCE cells from the TPP process. Then, the cell was separated and the glass substrate with written films and/or pyramid structures was dipped in toluene for 30 min to remove the unexposed photoresist.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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