Molecular Orientation Change Nearby Topological Defects Observed by Photo-Induced Polarization/Phase Microscopy

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ABSTRACT: Topological defects in liquid crystals (LCs) have been intensively studied and intentionally generated in an organized way recently because they could control the alignment and motion of LCs. We studied how the topological defects could change the molecular orientation/alignment from the observation of photo-induced orientation change of a photo-responsive LC. The photo-induced dynamics was observed by an LED-induced time-resolved polarization/phase microscopy with white light illumination. From the color image sequence, we found that the molecular orientation change started from the topological defects and the orientation change propagated as a pair of defects and was connected, and further disordering was induced as a next step after the initial orientation change finished.

INTRODUCTION

Topological defects for liquid crystals (LCs) are the positions where the molecular orientation cannot be defined and are easily found when LCs are placed in a cell without an alignment layer. There are various types of topological defects, and they are categorized by the topological charge, which is determined by the rotational angle of molecules around each defect. At these positions, elastic energy is higher than those in neat alignment, which could be understood from Frank’s free energy. 1

In recent years, much attention has been given on the topological defects for LCs; they can be intentionally generated by the photoalignment layer and the LC alignment can be controlled. 2,3 Nelson et al. demonstrated LC-made optics on a photoalignment layer and developed various holographic optics. 4,5 Hu et al. developed a photopatterning by using a DMD-based system to demonstrate an optics for optical vortices. 6,7 Orihara et al. demonstrated the pattern of topological defects without using the photoalignment layer and stabilized the pattern by polymerization. 9 The structural control of azobenzene-based LC polymer by light was theoretically studied. 10 Furthermore, the alignment of LC molecules can be utilized for the application of active matter, which means the spontaneous motion of an object due to various physical, chemical, and biological energy sources. 11–13 The motion of self-propelled bacteria was controlled around the topological defects prepared on a patterned LC. 14 A vesicle including active molecules showed a shape change induced by the motion of topological defects. 15 In recent years, it was reported that the growth and collective motion of biological cells is dominated by the property of topological orientation of cells. 16,17 These studies strongly indicate that the motion of LC-like aligned molecules is determined by the properties of topological defects. It is possibly because the topological defects have the origin of the molecular change due to the high cost of their elastic energy and also LC molecules have a long-range molecular interaction.

On the other hand, we have studied the photo-induced change of photo-responsive LCs and could observe the photo-induced change of the topological defects. For double emulsions made of LC as a shell, the photo-induced phase transition was induced, and the phase change always occurred from the center of a topological defect. 18 Also, we have found the photo-induced motion of an LC droplet inside a surfactant solution, where the defect position was oriented toward the light source. 19

In this study, we intentionally generated topological defects inside a planer cell without an alignment layer, and the photo-induced molecular orientation change was observed under the polarization/phase microscope with a millisecond time resolution. By the observation of color image sequences and the analysis of spectral response, we investigated how the molecular orientation change proceeded around the topological defects.

RESULTS AND DISCUSSION

The transmittance spectra for the LC orientation at different angles to the analyzer direction are shown in Figure 1a,
calculated based on the theory section. In this simulation, the wavelength dependences of the extraordinary and ordinary refractive indexes were obtained from the literature.\textsuperscript{20} When the LC orientation angle is larger or smaller than 45 degrees, the transmittance becomes smaller. This is the origin of the pattern formation of topological defects, where the orientation of LC molecules rotates 360 degrees around the topological defects for +1 or $-1$ charge, and the bright and dark regions are repeated as the orientation angle changes. However, the spectral shape does not depend on the LC orientation angle and it depends on the refractive indexes of the LC and the thickness of the LC layer. The large oscillation feature in the spectrum is originated from the optical interference due to the thin LC layer. Typically, the pattern around a defect is formed because the transmittance is modulated as the orientation angle changes around the defect as shown in Figure 1a. Since the transmittance is modulated in a similar way for different wavelengths, the spatial pattern of topological defects should be the same for different colors. The difference of the patterns for different colors indicates that the refractive index and/or the wavelength dependence of the refractive index around defects were different from the values for neat LCs.

Here, we assumed three types of molecular orientation change induced by the photoisomerization: Disordering, rotation, and density change. The disordering indicates that the molecular direction becomes random, meaning the decrease in the order parameter. The rotation indicates that the director axis rotates to the analyzer direction, and the density change indicates the decrease in the molecular density. The rotation indicates that the molecular direction becomes random, meaning the rotation, and density change of a liquid crystal layer. The disordering indicates that the molecular orientation angle becomes random, meaning the rotation, and density change induced by the photoisomerization: Disordering, and it depends on the refractive index and/or the wavelength, while the spectral change showed the same sign for the entire wavelength region for the rotation process, and the density change showed a very little change even for the same order of the refractive index change as the disordering.

Most of the defects in the samples showed a pattern with four brushes, indicating that they had $+1$ or $-1$ charge before the light irradiation. However, various different patterns were found when the multiple defects were nearby. An example is shown in Figure 2. There was a strong transmittance between two defects in the red image, and bright double spots were observed near each defect for the green image, and another connected region became brighter in the blue image. Unexpectedly, the patterns were different for the observed colors. As mentioned in the Theory and Method section, the patterns should be same for different colors if the refractive indexes around the defects do not have different values from those for the neat LC. The difference from the typical four- brush pattern indicates that the refractive indexes were varied in space around the topological defects. Furthermore, the pattern difference for different colors (wavelengths) means that the refractive index nearby the topological defects had different spatial dependences on the wavelength. The detailed analyses

**Figure 1.** (a) Transmittance spectra for different angles to the analyzer are shown. (b) Spectral change was calculated for disorder, rotation, and density change of a liquid crystal layer.
on the refractive indexes on the wavelength and the position for the static conditions are necessary in the near future.

To observe the photo-induced image change around the topological defects, several experimental parameters were optimized for observation: The temperature, the pump light intensity, and the duration, etc. When the pump light was turned on, the image changed to a small extent for several hundred milliseconds and returned to the original image on the similar timescale when the pump light was turned off. By the illumination of the pump light for 2000 ms with an interval of 5000 ms, this pattern change was repeated. In this study, the image change during the pump illumination was discussed in detail.

One of the typical responses is shown in Figure 2 for the wavelength regions of red, green, and blue from the top to the bottom, respectively. In these image sequences, two topological defects were recognized, which correspond to +1 and −1 topological charge. When the pump light was irradiated, a slight change of the intensity and pattern was observed.

To visualize the weak change, the initial image before the pump irradiation was subtracted from each image of the sequence. Hereinafter, the image is called a “subtraction image.” Figure 3 shows the subtraction images corresponding to Figure 2. In the image sequence for red and green, a connection line between the two defects appeared around 20 ms at first, (Figure 2, dotted regions at 20 ms) the other lines outside the initial line gradually grew and connected the two defects in a few hundred milliseconds. However, it is noted that the bright line connecting two defects for the shortest distance was bright for both red and green images but the outer region showed the opposite change in sign. In the image sequence for green, the bright and dark parts appeared around the defects and they were connected. In the image sequence for blue, the change was weaker than the others.

Another typical example is shown in Figure 4 (Top: original, Bottom: subtraction). In the sequence for the red subtraction images, a bright line connecting between two defects appeared at 50 ms, as was similar in Figure 3. (Figure 4b, dotted regions at 50 ms), and the lines outside the initial line grew to connect the two defects in the red and blue images indicated in the dotted regions at 200 ms of Figure 4b. Again, the color contrast of the secondary connecting lines was opposite for the red and blue images, while the initial connecting lines were bright for the red and blue images. In the sequence for the green subtraction images, a local change was observed only around defects. The flip of the color contrast indicates that disordering is involved in the photo-induced process, as was explained in the theory section. The minor difference of the color contrast dependence of Figures 3 and 4 is possibly due to the local thickness difference, which causes the shift in the spectra shown in Figure 1.

From these results, it was revealed that the change of molecular alignment occurred from the defect positions and spread out to connect defects. The proposed scheme is shown in Figure 5. The UV irradiation caused photoisomerization of MBBA (a,b) and the molecular alignment became unstable around the defects due to the unstable points of elastic energy.
Therefore, change in molecular orientation started from the center of defects and it extended between defects in the shortest connecting region. (c,d) Further light illumination induced the disorder in the outer connecting region around the initially disordered region. (e,f) Thus, molecular orientational change and the following disordering occurred in two steps between two defects.

Other examples when multiple defects were involved are shown in Figures 6 and 7, and the corresponding subtraction image sequences are also shown. In the original images, the bright connection between defects was observed in red and blue images, but the bright regions were different for colors. For green, the defect positions showed bright spots. In the sequence of the subtraction images, bright connecting lines initially appeared in the red images (Figures 6b and 7b at 50 ms), and gradually the secondary changes connecting two defects were observed in the green images a few hundred milliseconds in the green images (Figures 6b and 7b at 200 ms) but the secondary change showed an opposite contrast with red images.

The proposed scheme is shown in Figure 8. When there were multiple defects, the molecular orientation change occurred by connecting pairs of defects. The UV irradiation caused photoisomerization of MBBA, causing an orientation change between the defects with a pair of defects (in c), which was connected. When the pump light was kept irradiated, the disorder expanded in the outer region similar to the two-defects type (d−f).

**CONCLUSIONS**

The molecular alignment change nearby the topological defects was observed by the photo-induced phase/polarization microscopy. We could observe the molecular alignment change from the subtraction image sequences and revealed the dynamic processes. From the theoretical analysis of the spectral response, the orientational change between the topological defects proceeded. The UV light irradiation caused the isomerization of MBBA at first, and the molecular alignment became unstable at the defect positions, from which the molecular orientation was changed between the...
defects. This orientation change induced the disordering by irradiating the light in multisteps. This observation of the defect-related molecular disordering will deepen the understanding of the molecular alignment change. Furthermore, various photomechanical motion and shape change have been demonstrated for photo-responsive LC systems, and this methodology would help in understanding the mechanism of the macroscopic shape/order change of LCs based on the observation and simulation.

**THEORY AND METHOD**

An optical configuration of the equipment for this experiment is shown in Figure 9. This consists of a phase microscope (BX50, Olympus) with a polarization dependent detection, where the direction-dependent refractive index was imaged for a sample by the illumination of a white LED (Thorlabs, SOLIS-3C) from the bottom side under the cross-Nicole condition. Another pump light with a wavelength of 365 nm (Thorlabs, SOLIS-365C) was illuminated from the top side to the sample after being reflected by a dichroic mirror, the sample absorbed the pump light, causing the molecular orientation change due to the photoisomerization reaction of photo-responsive LC molecules. Since this change caused the direction-dependent refractive index change in the sample, the refractive index change could be obtained as a contrasted image by the polarization/phase microscopy under the cross-Nicole condition. The pump light was illuminated to a sample for 200 or 2000 ms and turned off. The photo-induced molecular orientation change and its recovery was observed during and after the light illumination. Acquisition of an image sequence was started 20 ms before the illumination of the pump light and the sequence of images was acquired at a constant interval, 10 ms. Typically, 100 images (1000 ms) were stored for each cycle. After the LC recovered to the original condition, this process was repeated and the image sequence was stored and averaged for several times.

**Figure 7.** (a) Photo-induced change of the image sequences are shown. The “R”, “G”, and “B” indicates the red, green, and blue image sequences, respectively. The pump light was illuminated from 0 to 200 ms, and the bottom number corresponds to the time after the pump light was illuminated. The temperature of the sample was set at 35.0 °C. The scale bar corresponds to 50 μm. (b) Subtraction images for (a) is shown. The images were obtained by subtracting the image intensity before the pump light illumination from the images corresponding to (a). The disordered region is indicated in yellow. The dotted regions were highlighted because of the characteristic changes, as described in the text.

**Figure 8.** Schematic drawing is shown to describe the mechanism of the photo-induced molecular alignment change in MBBA by irradiation of the pump light: (a) before light irradiation, (b) photoisomerization of molecules, (c) propagation of molecular orientation change, (d) connection of the regions with orientation change, (e) secondary disordering, and (f) formed disordered region.

\[ N-(4\text{-methoxybenzylidene})-4\text{-butylaniline} \] (MBBA, Tokyo Kasei) was used as purchased. The sample was put into an LC cell (EHC Co.) with a sample thickness of 3 μm, with a nonrubbed polyimide film inside. The pump light was UV-LED (SOLIS-365C, Thorlabs; wavelength: 365 nm, intensity: 1.12 mW/cm²) and the illumination light was white LED (SOLIS-3C, Thorlabs: intensity: 0.29 mW/cm²). A color CMOS camera (VCXU-23C, Baumer) was used for measurements and a color image sequence was obtained, which was separated into color image sequences: red (610 ≈ 750 nm), green (500 ≈ 560 nm), and blue (435 ≈ 480 nm). The
Refractive index change was imaged by a CMOS camera.

Under the cross-Nicole condition, the transmittance spectrum can be calculated as:

\[
I = \frac{n_3}{n_1} \cos^2 \alpha \sin^2 \alpha (t_{\parallel} - t_{\perp})^2
\]

(1)

where \( n_1 \) and \( n_3 \) are the refractive index of the top and bottom layers for an LC cell, \( \alpha \) is the angle of the LC director to the analyzer direction, and \( t_{\parallel} \) and \( t_{\perp} \) correspond to the Fresnel transmittance coefficients for the light field directions parallel and perpendicular to the molecular axis, respectively. The wavelength dependence comes from the Fresnel transmittance coefficient for a multilayer system. Under our experimental condition, a thin layer of an LC with a thickness of 3 \( \mu \)m is sandwiched between two glass layers. In this case, the Fresnel transmittance coefficients are given as:

for \( t_{\parallel} \) or \( t_{\perp} \) = \[
\frac{t_{12}t_{23} \exp(i\beta)}{1 + r_{23}^2 \exp(2i\beta)}
\]

(2)

where \( t_{12}, t_{23}, r_{23} \), and \( r_{31} \) are the Fresnel transmittance and reflectance coefficients at the interfaces between 1 and 2, 2 and 3, respectively, and \( \lambda \) is the wavelength, \( n_{1e}(\lambda) \) and \( n_{2e}(\lambda) \) are the wavelength-dependent extraordinary and ordinary refractive indexes for the LC respectively, and \( d \) is the thickness of the LC layer. This transmittance coefficient, \( t_{\parallel} \) and \( t_{\perp} \) are obtained for the light field parallel and perpendicular to the LC director.

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