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Photo-induced control of bubble domains in chiral–nematic liquid crystal by a violet laser beam

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The stable bubble domains generated by mixing 10% of chiral molecules into an azobenzene liquid crystal (LC)-doped nematic host can be optically controlled by a violet laser beam (415 nm). The photon-induced reversible *trans–cis* photo-isomerisation of azobenzene changes the helical twisting power (HTP) of LC mixtures in which the HTP of *cis*-azobenzene LC is lower than *trans*-azobenzene LC. Under the irradiation of an optical field (>20 mW cm^{-2}), the helical pitch distance, which is inverted proportional to the HTP, increases and the bubble domains disappear. Immediate obstruction of laser light irradiation initiates cholesteric nucleation, merging of domains and the subsequent generation of stably dispersed bubble domains.

Keywords: liquid crystal; chiral–nematic; photo-induced control; bubble domains

1. Introduction

The cholesteric liquid crystals (CLCs) of twisted helical directors in periodically layered ordering, generated by the addition of chiral molecules to nematic LCs, have demonstrated unique optical properties (*1*). For example, selective Bragg reflection could be achieved by matching the helical pitch (p), special distance of one full turn rotated by the twisted helical director, into the wavelength of light (*2, 3*). The value of p could be passively controlled by the weight concentration of the chiral agent and the helical twisting power (HTP), which depends on the molecular structure of the chiral agent situated in the surrounding nematic host. Short pitch cholesterics ($p < 1$ μm) containing high concentrations of chiral molecules and high HTP value in nematic phase have been widely applied in photonic applications such as colour display (*4–6*), mirrorless lasing (*7, 8*), and switchable Bragg reflectors (*9*). Long-pitch cholesterics ($p > 1$ μm) containing low concentrations of chiral molecules and low HTP value have, however, received minimal attention as the selective wavelengths of reflection reside in the optically hard to observe far-IR. Haas and Adams (*10*) first reported an electrically tunable bubble domain in long-pitch CLCs at the designed concentration of chiral molecules and LC cell thickness. Through utilising the influence of electric fields, the transformations of homeotropics to bubble domains and the corresponding reverse transition have been observed. Their realisation of electro-controllable bubble domains later initiated the potential use of electrically tunable diffractive elements for application in photonic crystals, lens, displays and filters (*11*).

Among those demonstrations of CLCs in photonic applications, the CLCs are confined between two glass substrates treated to make the CLCs pre-aligned in well-defined orientation. Different LC textures derived from the confined cholesterics in varieties of homeotropic boundary conditions could be actively controlled by thermal (*12*), electrical (*13*), or optical fields (*14, 15*). The magnitude of the free energy determined from the competition between elasticity and surface anchoring of confined cholesterics and applied fields results in different shapes of the cholesteric phase, such as loops, fingers and bubbles (*16, 17*). The understanding of those phase transitions and structures under different experimental conditions is of fundamental importance in obtaining unique optical properties from CLC-based photonic devices. In particular, the modulation of the mesophases and optical properties of photoresponsive LCs controlled by photochemical isomerisation of doped azobenzene has been used in all-optical tuning elements in photonic applications (*18–20*).

The *trans–cis* photo-isomerisation of doped azobenzene dissolved in the host of nematic LCs or cholesteric–nematic mixture disorganises the host and modulates the corresponding optical properties of photoresponsive LCs, such as the refractive index, via irradiation with an external light. For the photoresponsive LCs containing a chiral–nematic mixture as host, the photochemical-induced, reversible phase transition between cholesterics and nematics was

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achieved by an optical field of two different wavelengths (*21–23*). For example, Kurihara *et al.* (*22*) reported that a fingerprint texture (long-pitch cholesterics) could be generated by doping chiral azobenzene molecules to the nematic LC host. Under exposure to UV light, the *trans* to *cis* photo-isomerisation of the doped azobenzene increased the helical pitch distance and the fingerprint texture disappeared. The reversal of this transition and the reappearance of the fingerprint texture were achieved by exposure to visible light.

We report here the first demonstration of photo-induced control of bubble domains in a chiral–nematic LC doped with azobenzene LCs only by a laser beam. Prior to applying the optical field, the bubble domains ranging from 1 to 5 μm were well dispersed throughout the nematic phase. Light scattering was observed owing to the formation of slightly ordered bubble domains in the LC film. Application of a violet laser increased p of the CLC phase due to the *trans* to *cis* deformation of the doped azobenzene LC. Since the HTP of *cis*-azobenzene LC is lower than *trans*-azobenzene LC, the increase in p (inverted proportionally to HTP) (*22*) shrank the size of the bubble domains. The LC phase transformation from cholesteric bubble to homeotropic state caused an increase in the overall transmittance (70% maximum) of the mixed LC cell at an applied optical field larger than 20 mW cm^{-2}. The response time between the high and low transmittance at the on-off state of LC cell was 4 seconds and 14 seconds, respectively. The removal of the applied light instantly initiated seeding, merging and growth of the cholesteric phase and finally the reappearance of stable bubble domains in homeotropic nematics.

2. Experimental

The chiral–nematic LC was prepared by doping a commercial room temperature multi-component nematic LC (TL213, Merck, Whitehouse Station, NJ, USA) with 10 wt% of chiral dopant (ZLI 811, Merck). The azobenzene LC (4-butyl-4́-methyl-azobenzene) of 10 wt% was added to the chiral–nematic mixture to prepare the mixed LC cell. A cell gap of 25 μm was achieved by using a PEN spacer (Kou Ryou Enterprise Corp., Taipei, Taiwan). The mixed LC sample was prepared by capillary action without any pre-alignment. The cell was heated to 100°Celsius and cooled to room temperature before characterisation. The optical micrograph of bubble domains was observed at room temperature using a polarised microscope and the irradiation was generated with an unpolarised violet laser diode (415 nm peak wavelength). The transmission measurements of the LC film and the response times of the photo-induced tuning bubble domains were recorded using a He-Ne laser as a probe light source and a detection system consisting of a photodiode, chopper and lock-in amplifier. The switching behaviour of the LC film was observed by manually blocking the irradiation of light and recording the transmitted signal from the He-Ne laser.

3. Results and discussion

Figure 1 shows the polarised optical micrographs that demonstrate the photo-induced control of bubble domains generated in an azobenzene LC-doped chiral–nematic mixture. Before application of the optical field the cholesteric bubble phase ranging from 1 to 5 μm in size was stably dispersed in the homeotropic phase, which is the dark region between cholesteric domains (Figure 1(a)). The bubble domain boundary was very sensitive to the external optical fields and under the irradiation of 10 mW cm^{-2} of a violet laser the size of the bubble domains decreased (Figure 1(b)). Almost 30% shrinkage of the bubble domains was observed. The dispersed bubble domains in the homeotropic sea returned to their original size immediately (<1 second) after the removal of the external optical field. For the generation of the cholesteric phase in the chiral–nematic mixture, a chiral twisting agent has to be added to the nematic LC host. The p distance determines the formation of the bubble domains (*10, 15*). Since the p

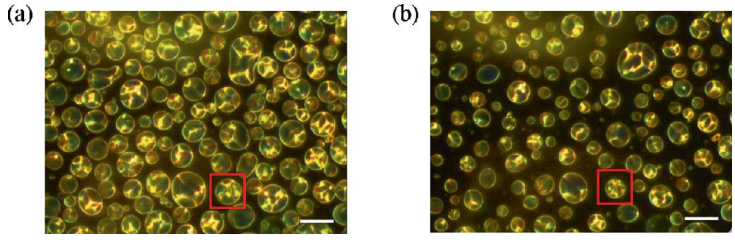

Figure 1. Optical micrograph of the bubble domains in the chiral-nematic mixture doped with azobenzene LCs between crossed polarisers at room temperature (a) before applying an optical field and (b) after applying an optical field of 10 mW cm^{-2}. The scale bar in the micrograph is 5 μm.

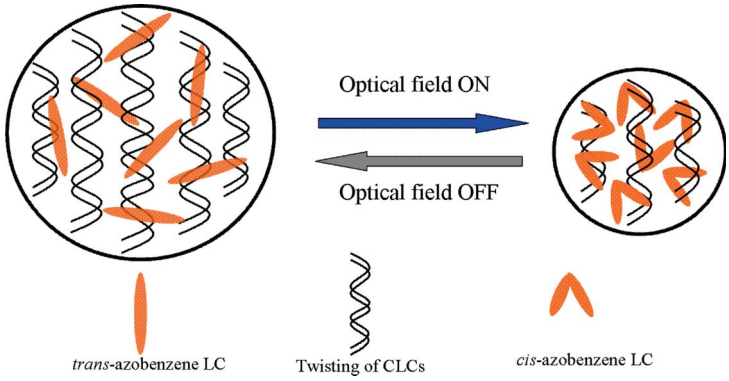

Figure 2. Schematic of tunable bubble domains manipulated by *trans–cis* photo-isomerisation of azobenzene LC-doped in the chiral-nematic mixture.

distance is inverted proportionally to the HTP at fixed concentration of chiral dopant, the manipulation of bubble domains can be approached by controlling the HTP.

The schematic of the photo-induced tuning mechanism of bubble domains generated in azobenzene LC-doped chiral–nematic mixture is shown in Figure 2. Prior to the application of the optical field, the bubble domains were stably generated in the homeotropic nematics at the specific chiral concentration and LC cell thickness. Under the irradiation of an optical field, the decrease of bubble size is due to the increased value of the *p* distance, which is the result of the formation of *cis*-azobenzene in which the HTP of the *cis*-azobenzene (bent shape) is less than the *trans*-azobenzene (rod shape). The size of the bubble domains determined by the *p* distance of the cholesteric–nematic mixture could be optically manipulated by the reversible *trans–cis* isomerisation of doped azobenzene LCs.

The light scattering behaviour of the chiral–nematic mixture doped with azobenzene LC was measured by use of an unpolarised He-Ne laser as probe light. Figure 3 shows the changes of the transmittance of LC mixtures sandwiched in a 25 μm hemeotropic glass cell under different optical powers of a violet laser. Before light irradiation, the transmittance of the LC cell was constant at approximately 40%. The transmittance increased linearly with increases in the irradiation power of the violet laser light in the range 5–20 mW cm^{-2}. The high twisting ability of the *trans*-azobenzene LC forms and stabilises the bubble domains, which is the reason for the low transmittance (high scattering) of the LC cell. Under violet laser exposure, the *trans* to *cis* isomerisation of azobenzene LC shrinks the size of the bubble domains and increases the transmittance (decreases the scattering) of the LC film. The transmittance does not follow the

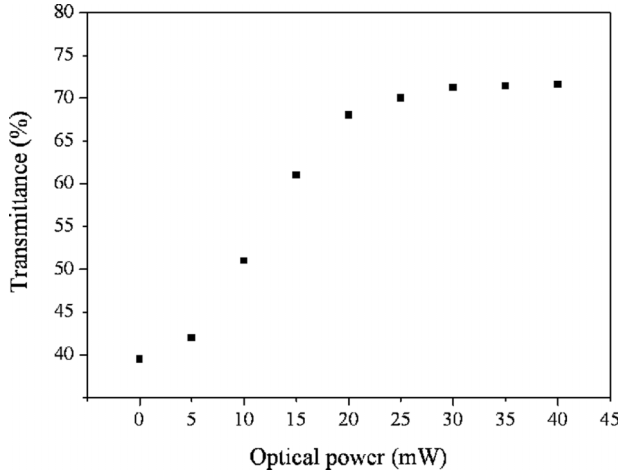

Figure 3. The characteristics of light transmittance of an LC cell dependent on irradiation at different optical power from a violet laser.

linearity when the power of the violet laser is greater than 20 mW cm^{-2} (threshold).

Figure 4(a) is the polarised optical micrograph of the azobenzene LC-doped cholesteric–nematic mixture under the exposure of a violet laser of 40 mW cm^{-2}. The LC cell shows high transmittance (Figure 3) and only a few bubble domains can be observed at this moment. It seems as though the phase transformation of cholesterics to nematic in which the *p* distance becomes infinite was completely achieved by the application of a high-powered optical field. Hence, the increase in external optical power facilitates the phase transformation from bubble domains to a homeotropic nematic phase. Figure 4(b) is the polarised optical micrograph of azobenzene LC-doped chiral–nematic cell recorded at 1 second after the release of an applied optical field of 40 mW cm^{-2}. The vanished bubble domains were first observed by the application of an optical field larger than

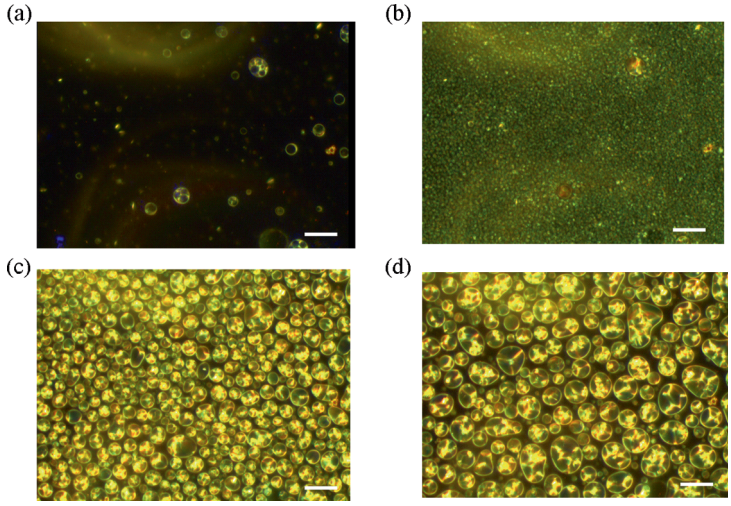

Figure 4. Real-time optical micrographs of the chiral–nematic mixture doped with azobenzene LCs between crossed polarisers at room temperature. In (a) the violet laser intensity is on, while going from (a) to (d) the light is switched off. (a) A few bubble domains were observed under the application of an optical field of 40 mW cm^{-2}; (b) nucleation of cholesterics recorded at $t = 1$ second; (c) growth of bubble domains recorded at $t = 3$ seconds; and (d) the generation of stable bubble domains recorded at $t =$ 5 minutes after taking off the external optical field. The scale bar in the micrograph is 5 μm. (See supporting information available via the multimedia link on the online article webpage for the details.)

threshold, and the bubbles reappeared by nucleating (Figure 4(b), supporting information is available via the multimedia link on the online article webpage), growing (Figure 4(c), supporting information is available via the multimedia link on the online article webpage), merging into one another, and finally forming stable, separate bubble domains dispersed in the nematic phase again (Figure 4(b)).

Kurahara *et al.* (*22*) have reported a reversible photochemical phase transformation between a cholesteric phase of fingerprint texture and a nematic phase of an azobenzene-doped chiral–nematic mixture upon UV and visible light irradiation. From their observation, the distance between each fingerprint texture increases at low applied UV irradiation, indicating that p increases and approaches infinity. The fingerprint texture appeared again with further UV irradiation. No detailed explanation of the reappearance of the fingerprint texture was discussed in the paper. Our experimental results reveal, however, that further increases in the power of the irradiated violet laser (>20 m Wcm^{-2}) do not make the bubble domain reappear. The bubble domains reappear only when the applied optical field is blocked. Usually the absorption spectrum of azobenzene shows two distinct bands: (1) π–π^* transition of azobenzene, which is induced by the shorter wavelength of light (365 nm) (*21–23*); and (2) n–π^* transition of azobenzene (*cis*- and *trans*-form), which is induced by the longer wavelength of light (440 nm) (*24*). In our case, the n–π^* transition of azobenzene LCs should be the explanation for why no bubble domains reappear with further optical field (>20 m Wcm^{-2}). Since the optical field of longer wavelength (415 nm) was used, we expect a small amount of *cis*-azobenzene LC is produced as a result of the n–π^* transition of azobenzene LCs (*25*). Such small amounts of *cis*-azobenzene LCs are sufficient to modulate the bubble domains in a chiral–nematic host due to the low HTP of low concentrated chiral molecules. Further increase of the optical field of a 415 nm violet laser could not provide enough energy to change the LC texture. The use of a violet laser of longer wavelength may also explain why very fast (<1 second) nucleation of cholesterics was observed (Figure 4(b)) when taking off the laser light. Since the 415 nm laser light falls within the weak n–π^* band of azobenzene LCs (*25*), the *cis* to *trans* photo-isomerisation is much easier than that in the strong π–π^* band of azobenzene LCs.

Figure 5 shows the reversible tuning of the transmittance of the LC cell between 40% and 70% achieved by manually blocking the irradiating laser light and switching illumination between the on-off states at the optical power of 40 mW cm^{-2}. The response times for the reversible modulation of transmittance generated by the phase transformation of bubble domains to homeotropic nematics were estimated to be 4 seconds and 14 seconds, respectively. Even though we observed different numbers of bubble domains before applying the optical field (Figure 1(a)) and switching back after applying the optical power of 40 mW cm^{-2} (Figure 4(d)),

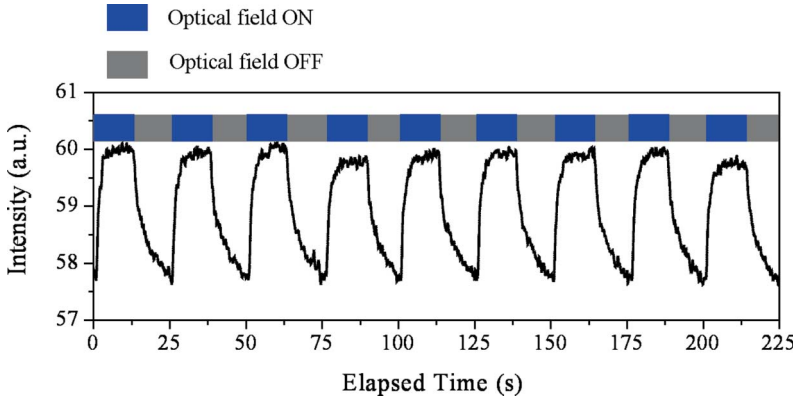

Figure 5. Temporal observation of the transmittance of the LC cell under alternate changes in violet laser irradiation of 40 mW cm^{-2}.

the overall transmittance of the LC cell does not show much difference between the on–off states through the use of optical power greater than threshold.

4. Conclusion

In conclusion, we have demonstrated the photo-induced control of bubble domains generated by the *trans–cis* photo-isomerisation of azobenzene LC-doped chiral–nematic LC. Initially, stable bubble domains are well dispersed in a homeotropic nematic phase before the irradiation of a violet laser. After subsequent irradiation of the violet laser, the generation of *cis*-azobenzene LCs increases the *p* distance (inversely proportional to HTP) of cholesterics in which the HTP of *cis*-azobenzene LCs is lower than the *trans*-azobenzene LCs. The transmittance of the mixed LC cell is increased owing to the decrease in size of the bubble domains. The size of bubble domains is tunable without changing the number of cholesteric domains when the applied irradiation is lower than the threshold of 20 mW cm^{-2}. When the applied optical power is greater than threshold, *p* becomes infinite and all bubble domains disappear. Immediate obstruction of laser light irradiation initiates cholesteric nucleation, merging of domains, and the subsequent generation of stably dispersed bubble domains.

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