Fabrication and characterization of imprinted photonic crystalline polymer matrices via multiple UV polymerizations†

Chih-Chieh Chien,a Jui-Hsiang Liu*a and A. V. Emelyanenkob

A photonic polymer network was imprinted using multiple UV-induced polymerizations in the presence of cholesteric liquid crystals (CLCs). Here, the imprinted polymer matrices provided a chiral environment due to the chirality of the polymer networks. The fabricated cell exhibited Bragg reflections even in the absence of anisotropic materials. Moreover, a phototunable liquid crystal cell was fabricated with photosensitive liquid crystalline ethyl 4-[4-(11-acryloyloxy undecyloxy) phenyl azobenzoyl-oxyl] benzoate. The tuning properties of the cells were examined as a function of the irradiation time and concentration of the photosensitive material. Both the tuning rate and dark relaxation of E–Z photoisomerization of the embedded LCs in the polymer network were also examined.

Introduction

Cholesteric liquid crystals (CLCs) are known to exhibit selective reflection due to their periodic helical structures. The maximum reflection of unpolarized light from a CLC is 50% because only circularly polarized light with one handedness is reflected. For example, for a right-handed CLC, right-handed circularly polarized light is reflected and left-handed polarized incident light is transmitted.1–3 The central wavelength ($\lambda_0$) of the reflection can be calculated using the following equation:4

$$\lambda_0 = n_{\text{avg}} \times P,$$

where $P$ is the pitch of the helical structure and $n_{\text{avg}}$ is the average refractive index of the cholesteric phase defined as $n_{\text{avg}} = (n_s + n_o)/2$, where $n_s$ and $n_o$ are the extraordinary and ordinary reflective indices, respectively. CLCs are formed by introducing chiral elements into liquid crystalline molecules or by doping small amounts of chiral dopants into nematic liquid crystalline hosts. The chiral environment induces slight distortions in the molecular alignment, yielding a helical microstructure. The $P$ of a CLC helix is defined as a unit length for a 360° molecular rotation related to the concentration of the chiral dopant and the helical twisting power (HTP) of the chiral compound.5

The $\lambda_0$ of the CLC can be altered by adjusting the refractive index $n$ or the helical pitch $P$ (eqn (1)) under the action of various external forces, such as heat, light, electrical fields, or mechanical stress.5–11 Cholesteric liquid crystalline materials have been extensively studied and many applications, such as reflective liquid crystal displays, optical memory and optical sensors, for these materials have been found.12–14

An increasingly common trend for fabricating tunable CLC devices is the use of light-induced CLC materials. These phototunable CLC devices are demonstrated using photoresponsive chiral dopants or the CLC mixture with chromophores that go through photochemical transitions.5,15 The helical twisting power of these materials changes upon exposure to UV light, resulting in changes in helical pitch; therefore, the CLC reflection band can be adjusted using UV irradiation. Among the chrophore materials, azobenzene derivatives are the most widely used in CLC media due to their thermal stability, easy processability and photo-reversibility.16–18

One approach for the fabrication of phototunable CLC devices is based on the use of azobenzene-based nematic LC (azo-NLC) mixtures that undergo photoisomerization.15,19 Another approach is the introduction of a chiral azobenzene derivative into a nematic LC (NLC). During $E$–$Z$ photoisomerization, the configuration of azobenzene changes, resulting in changes in the twisting power or optical characteristics. A chiral azobenzene derivative dissolved in a host NLC can act as a chiral dopant to induce a CLC phase and to control the helical pitch.20–22

In a series of investigations of phototunable devices on CLCs, the synthesis of highly ordered liquid crystalline polymers and chiral polymers was discussed due to their optical properties and their applications in LC cells and recording films.15,23 These polymers are formed by the UV curing of CLC mixtures...
containing small concentrations of the LC monomer and initiator. Theoretically, an increase in monomer content would create a denser polymeric network. However, an increase in monomer may lead to the loss of the anisotropic properties of the original CLC mixture. In this paper, an improved imprinting method was used, and the memory effects of the helical structure of the polymer network were improved through multiple UV-induced polymerizations. When this technique was used, the imprinted polymer films themselves exhibited Bragg reflection properties without any added liquid crystals or chiral compounds. Moreover, this is the first paper to demonstrate the tuning of the reflective wavelength of the imprinted polymer template by filling the cell with a non-chiral azobenzene derivative via photoirradiation.

Experimental

Materials

Nematic LC HSG-22200 was purchased from Fusol Material Co., LTD. The LC exhibits a nematic phase over a wide range of temperatures, up to 114.5 °C. The chiral dopant CB15 was purchased from Merck and used at a concentration of 38.3%; it induces a left-handed helical structure in the host nematic LC. The photoinitiator Irgacure-184 was obtained from Ciba Specialty Chemicals. The bifunctional monomer BAHB (4,4'-bis-(6-(acryloyloxy)-hexyloxy)biphenyl) was synthesized following the processes described previously. The azobenzene chromophore A11AEt (ethyl 4-[(11-acryloyloxyundecyloxy) phenyl azobenzoyl-oxyl] benzoate) was synthesized according to a previously reported method. The chemical structures of CB15, Irgacure-184, BAHB and A11AEt are shown in Fig. 1. Details of the synthesis of BAHB and A11AEt are given in the ESI.

Analysis apparatus

Chemicals used in this investigation were all confirmed using a spectrophotometer, although the spectra are not shown. 1H NMR spectra were analyzed on a Bruker 200 MHz FT-NMR. The FT-IR spectra were recorded with a Jasco 410. Scanning electron microscope (SEM) microphotographs were measured with a JEOL HR-FESEM JSM-6700F (Osaka, Japan) instrument. UV spectroscopy measurements were carried out with a Jasco V-550 UV-VIS spectrophotometer. The birefringence of the materials was analyzed using polarized optical microscopy (POM).

Polymeric network preparation

The sample cells were fabricated following typical procedures. Two ITO (Indium tin oxide) glasses coated with polyvinyl alcohol (Mw = 20 000) were parallel rubbed after washing. The two glass plates were then separated by 12 µm spacers and sealed with epoxy resin on two sides of the cell. The cell was filled with a homogeneous mixture containing achiral nematic LC HSG-22200 (48.3%), chiral dopant CB15 (38.3%), bifunctional monomer BAHB (13.3%) and photoinitiator Irgacure-184 (0.1%) by capillarity. To improve the memory effect, a new approach for preparing a high-density imprinted polymer template via multiple UV-induced polymerizations was used. The cell was fabricated through a circle mask with a diameter of 6 mm (Fig. 2) and irradiated with 254 nm UV light several times. After 1 hour of photopolymerization, the cell was kept in the dark for 1 day. During this period, unreacted monomers from the surrounding region diffused into the UV-irradiated area. The photopolymerization/diffusion process was repeated five times. After the photopolymerization was complete, the LC mixture and unpolymerized monomer were extracted by immersing the sample cell in acetone and CHCl3 for 2 days. The sample cell was then dried in a vacuum at 40 °C.

UV-tunable color cell fabrication

After the liquid crystals were removed from the sample cell, the empty cell was refilled with an achiral mixture of nematic LC HSG-22200 and azobenzene chromophore A11AEt in a range of concentrations from 0.1 to 6% (Fig. 3(d)). The phototuning was
performed with UV light (365 nm) at an intensity of 0.6 mW. The reflection spectra of the fabricated sample cells were then estimated using an optical probe.\textsuperscript{24}

**Results and discussion**

**Multiple UV-induced polymerizations**

The spectra presented in Fig. 4 shows the selective Bragg reflections of the LC cell before and after the photopolymerization and after washing out the LC mixture. Different photopolymerization/diffusion times led to different performances of the imprinted polymer network. Fig. 4a and b show the spectra obtained when the polymer cell was irradiated one time and five times, respectively. A slight blue shift was observed after UV polymerization due to crosslinking-induced volume shrinkage.\textsuperscript{5,24,30} After the LC mixture and unreacted monomers were washed out, the reflection band of the cell irradiated five times shows a much higher response than the cell irradiated one time. This difference is ascribed to the higher degree of polymerization. During the multiple photopolymerization/diffusion procedures, the density of the polymer structure is changed via multiple photopolymerizations of the monomer \textit{BAHB} had well-established helical structures. After washing, even though the system did not contain any chiral compounds, the cell exhibited a clear Bragg reflection. This result is further evidence of the existence of imprinted helical polymer matrices. The Bragg reflection indicates the presence of photonic crystalline structures.

The reflection spectra of LC cells in Fig. 4 were measured under normal lab conditions. The non-zero base line is due to the refraction of surrounding light.

**UV-tunable selective reflection light**

Azobenzene derivatives are well-known photochromic materials that exhibit light-induced \textit{E–Z} photochemical isomerization.\textsuperscript{11,12} As shown in Fig. 5(a), UV irradiation caused a configurational change of \textit{A11AEt} from \textit{E} to \textit{Z}, leading to a decrease in UV absorption to approximately 362 nm and an increase in UV absorption to approximately 444 nm. \textit{A11AEt} showed a strong absorption band at 362 nm in the \textit{E}-form. This absorption is attributed to the \textit{π–π*} transition. A weak absorption band at 444 nm due to the \textit{n–π*} transition was also observed. This absorption was much weaker than that due to the \textit{π–π*} transition because the \textit{n–π*} transition corresponds to a “forbidden” electronic transition with a low probability of occurrence. As shown in Fig. 5(b), after 45 hours in the dark, the absorption returned to its original level. This result suggests that \textit{A11AEt} gradually changed from \textit{Z} to \textit{E} thermally, without any light exposure. Theoretically, the photo-induced configurational isomerization from \textit{Z} to \textit{E} is expected to alter the helical pitch of cholesteric liquid crystals. Of course, the average refractive indices of anisotropic materials can be different due to variations in molecular arrangements. Depending on orientation, configurational isomerization may increase or decrease the average refractive index of anisotropic materials. Accordingly, adding \textit{A11AEt} into the photonic cells is expected to reveal the photo-tunable phenomena.

To study the chiral efficiencies of the imprinted polymer matrices, the imprinted polymer cell was filled with an achiral mixture containing 95% nematic LC HSG-22200 and 5% azobenzene chromophore \textit{A11AEt}. As shown in Fig. 6, a reflection band at 450 nm was observed. Theoretically, a red shift and a broadened reflection band should be observed due to higher refractive index of the cell filled with liquid crystalline material compared to that of the empty imprinted cell (the refractive index of air is 1) based on eqn (1). However, as shown in Fig. 6, a narrow band with no significant shift was observed after the refilling of the cell with the azobenzene/LC mixture. This result suggests that the filled liquid crystal molecules arranged in a specific order, decreasing the imprinted birefringence (\textit{Δn}) of the imprinted matrices. However, the average value of the refractive

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Fig. 4  Reflection spectra of the LC cells with (a) one-time and (b) five-time photopolymerization/diffusion processes before and after photopolymerization and after removing the LC mixture.

![Reflection Spectra of the LC Cells](image)

Fig. 5  Dependence of reflection spectra of the fabricated cell on (a) UV-irradiation time and (b) recovering in the dark.

![Reflection Spectra vs Time](image)

Fig. 6  Reflection spectra of (a) the imprinted empty cell, (b) the cell after being refilled with the LC mixture (95% HSG22200 + 5% \textit{A11AEt}) and the LC cell after UV irradiation for (c) 1 h, (d) 2 h, (e) 3 h and (f) 4 h.

![Reflection Spectra vs UV Irradiation](image)
index was kept, maintaining the reflection central wavelength. A decrease in the birefringence narrows the band width of the reflection light.

The $E$- and $Z$-form isomers have different physical and chemical properties due to the different spatial arrangements of their aromatic moieties; the $E$-form is nearly planar, while the $Z$-form has a three-dimensional (3D) conformation.\textsuperscript{33} To elucidate the photo-induced changes in the Bragg reflection of the photosensitive azobenzene, the cell was exposed to UV light (0.6 mW at 365 nm) for several hours.

Initially, the refilled imprinted cell had a selective reflection band at 450 nm. After UV irradiation at 365 nm for 1 hour, the reflection band changed from 450 nm to 525 nm. Further UV light exposure (for a total of 4 hours) drove the red-shift reflection wavelength to 560 nm, as shown in Fig. 6. The textures of both the empty film and the LC film before and after photol­irradiation with 365 nm light were investigated using both transmittance and reflectance polarized optical microscopy (POM). Fig. 7 shows the color-tuning properties of the imprinted films. The typical liquid crystalline POM textures were observed, as were the birefringences of the imprinted matrices.

**Mechanisms of the phototunable behaviors**

Fig. 8 presents a schematic representation of the pitch tuning of the imprinted cells containing photochromic A11AEt. Based on eqn (1), change of both the pitch ($P$) and the refractive index ($n_{avg}$) causes variations in the reflection central wavelength. After UV irradiation at 365 nm, the molecular structure of azobenzene A11AEt changed from the linear $E$-form to the 3D $Z$-form. The 3D $Z$-form may disturb the arrangement order of the liquid crystal molecules, leading to an increase in the refractive index of the imprinted polymer network. Theoretically, the molecular arrangement inside the polymer matrices has a specific birefringence value that may increase or decrease the birefringence of the imprinted matrices. Similar phenomena in CLC cells were reported by Bunning et al.\textsuperscript{23} A red-shift in the reflection wavelength of a CLC film based on the photosensitive chiral dopant QL-76 upon UV irradiation due to a UV-induced change in the HTP value was reported.

To clarify the effect of chirality on the reflection band, the phototuning of an azobenzene mixed cholesteric liquid crystal (azo-CLC) containing N-LC HSG-2200 (54%), CB15 (41%) and A11AEt (5%) was studied. When exposed to 365 nm UV light, the reflection band decreased in intensity but did not undergo any obvious change, as shown in Fig. 9. The decrease in reflection is due to the destruction of the helical structure caused by the $E$-$Z$ photoisomerization of the azobenzene. In the case of the...
phototuning of the achiral azo-LC mixture in the polymer matrices, shown in Fig. 6, the central wavelength was maintained within 20 nm. This result suggests that the additional chirality improved the efficiency of the imprinted matrices. The reflection wavelength of the azo-CLC mixture did not shift during UV irradiation. This result is ascribed to the high concentration of chiral dopant, which decreases the configurational effect of the \( E \rightarrow Z \) transition. In the case of the phototuning of the achiral azo-LC mixture in polymer matrices (Fig. 6), the chirality was due only to the imprinted polymer matrices. The molecular arrangement in the polymer matrices is more easily affected by the \( E \rightarrow Z \) transition, leading to a clear red-shift in the reflection central wavelength. From Bragg theory, the band width can be expressed by \( \Delta \lambda = \Delta n p \). After UV irradiation, the randomness of LC molecules was increased due to the \( E \rightarrow Z \) transition leading to the decrease of \( \Delta n \). For an isotropic material, \( \Delta n = 0 \). Accordingly, in Fig. 9, some peak narrowing upon irradiation was observed.

**Effect of the concentration of A11AEt on phototuning**

Several azo-NLC mixtures with various concentrations of A11AEt (0.1–6%) were filled through capillarity into the imprinted polymer cell. Upon UV irradiation at 365 nm, the reflection wavelength of the 0.1% cell changed from 450 to 472 nm after UV irradiation. For those cells containing 0.5, 1, 3, 5, 5.5 and 6% of photoisomerizable A11AEt, the reflection wavelength shifted from 450 nm to 507, 519, 543, 560, 563 and 564 nm, respectively. According to the explanations in the mechanism section, the red-shift of the reflection wavelength is based on the photoisomerization of azobenzene from \( E \) to \( Z \). Theoretically, 3D structured molecules usually reveal higher free volumes, resulting in variations in the birefringences of their molecular arrangements. As shown in Fig. 10, an increase in the azo-NLC concentration caused an increase in the red-shift of the reflection wavelength. At lower concentrations of azo-NLC, the shift in wavelength is proportional to the concentration. With increases in the concentration of azo-NLC, the shift reaches a steady-state. This result suggests that, by controlling the azo-NLC concentration, the reflection band can be continuously adjusted and the color of the thin film is tunable.

![Fig. 10](image_url)

**Fig. 10** Dependence of the reflected central wavelength of the fabricated LC cell on the concentration of A11AEt.

The system reported here is distinguished from other reported work in that the chiral environment in this work comes from imprinted polymer matrices without any added chiral dopant. In this study, the polymer density was much higher due to the multiple UV-induced polymerizations. As shown in Fig. 6, the helical pitch was well established. Filling the cell with solvent increased the refractive index of the polymer matrices, leading to red shifts in the reflection band.

Theoretically, the photoisomerization between the \( E \) and \( Z \)-forms is a reversible photoreaction. The photostationary state spontaneously returns to the initial state through back-isomerization from \( Z \) to \( E \). However, in our case, spontaneous \( Z \rightarrow E \) photoisomerization was not observed during the long-term dark relaxation. A possible explanation is that the \( Z \)-form isomer was trapped in the “confined space”. Due to the high density of the polymer network, the dark relaxation from the 3D \( Z \)-form azobenzene was restricted.

In order to provide evidence of the imprinting of the polymer network, a cross section of a sample cell was analyzed. Fig. 11(a) shows the SEM image of the cross-section of the fabricated sample cell. Fig. 11(b) shows the real image of the imprinted liquid crystal cell. Abbreviation of National Cheng Kung University “NCKU” was imprinted on a glass cell via multiple-UV-irradiation through a mask. Fig. 11(a) shows the existence of the porous structure of the fabricated polymer matrix after removing of LC. Furthermore, Fig. 11(b) shows the real image of the reflection color of the LC cell. The results suggest that with a mask, colorful patterns with various colors are available by using this method.

**Conclusions**

By using multiple UV-induced polymerizations, a helical polymer matrix was imprinted in the presence of a cholesteric liquid crystal (CLC). This polymer template was found to exhibit a Bragg reflection (~450 nm), even after the CLC mixture was washed out, due to the memory effects of the high density polymer network. Refilling the imprinted cell with photosensitive azo-NLC material resulted in phototuning through UV irradiation. The original reflection wavelength underwent a red-shift to 560 nm after 4 hours of UV irradiation (5 wt% A11AEt). The reflection shifts increased with increasing concentrations of azo-NLC. Comparatively, the CLC mixture decreased in reflection and a slight red-shift in wavelength was observed due to UV irradiation. However, when the imprinted polymer was refilled with azo-NLC, a clear red-shift and a fixed reflection were...
observed. The contribution of polymers to phototuning is a promising means for maintaining helical structures. Moreover, the slow tuning rate and the irreversible dark relaxation of the fabricated cells based on photoisomerization are due to the high densities of the polymer matrices.

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Notes and references