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Diffraction from Polymer-Stabilized Cholesteric Texture Films

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We have performed diffraction experiments on polymer-stabilized cholesteric texture (PSCT) films made from E48-BAB6 mixtures cured at various UV intensities. The diffraction observed in these samples is the Qu’etelet-type ring pattern, which is generated from the scattering of light by the clusters of the polymer networks and the focal conic domains of cholesteric liquid crystals in a PSCT cell. We monitored the dynamic change of the intensity of the first ring of a sample during polymerization. After polymerization, both the electro-optical characteristics and the diffracted ring intensities of various orders were measured. The results showed that both the applied voltage and the UV curing intensity affected the diffraction intensity significantly. Furthermore, the results obtained from diffraction measurements correlate with the electro-optical ones. Thus, the diffraction measurements could provide us with another qualitative, nondestructive method to analyze PSCT devices.

KEYWORDS: liquid crystals, polymer network, focal conic domains, diffractions

1. Introduction

Liquid crystal (LC) polymer dispersions have been studied intensively because of their promise for use as displays and light modulating devices.1−7 Usually liquid crystal polymer dispersions can be divided into two types, depending on the polymer concentration in the mixture. One is the so-called polymer-dispersed liquid crystals (PDLCs), in which the polymer concentration is usually high, ranging from 20−80%, to confine LCs. In addition to their use as displays, PDLC films have also found other applications including variable transmission windows, Gaussian filters9 and switchable gratings.9,16 The second type is the polymer-stabilized cholesteric texture (PSCT), in which the polymer concentration is usually below 10%, for use in stabilizing the cholesteric structure in the cell. Because of their haze-free characteristics at wide view angles in the clear mode, PSCT films have shown great promise for display applications.11

Depending on the surface treatment of the substrates and on the pitch length of the cholesteric LC, we can fabricate three types of display devices for the PSCT films. They are normal-mode (opaque in a field-off condition and clear in a field-on condition), reverse-mode (clear in a field-off condition and opaque in a field-on condition) and color-reflective bistable mode.11−13

In this paper, we report the results obtained from the measurements of diffraction from the PSCT normal-mode films. The PSCT cells cured with various UV intensities were fabricated. The diffraction pattern observed in these samples is the Qu’etelet-type (QT) ring,14 which is generated from the light scattering by the cluster parts of the polymer networks and the focal conic liquid crystal domains. We monitored the change of the first-ring intensity of a sample during polymerization. After the sample was polymerized, both the electro-optical characteristics and the ring intensities of various diffraction orders were measured. The results showed that both of the applied voltage and the UV curing intensity affected the ring intensity significantly. We also measured the ring intensities of a PSCT normal-mode cell with the light incident on the sample from the front surface and the back surface in a field-off condition. The front surface is defined as the surface which faces the UV curing light during polymerization (refer to Fig. 7). Slight differences were observed in this case. Finally we measured the variation of the intensity of first ring as a function of the curing UV intensity. The variation of the diffraction ring intensity as a function of the applied voltage correlates with that of the electro-optical characteristics of the PSCT cell. Thus, these measurements provide us with another qualitative, nondestructive method to analyze PSCT films.

2. Experimental

The cholesteric LC used in this experiment was a mixture of nematic E48 with a chiral dopant CB15 (both from E. Merck) at a weight ratio of ~91.5:8.5. A small amount of laboratory synthesized monomer bis[6-(acryloyloxy)hexyloxy]-1,1′ biphenylene (BAB6) at ~2.5 wt% and a photoinitiator were then added to the LC mixture. As seen from its molecular structure given in ref. 15, the monomer BAB6 has a reactive double bond at both ends. Under UV irradiation, it is polymerized to form a cross-linked anisotropic polymer network. In a separate experiment, we have studied the dependence of this PSCT system on the monomer concentration. The result showed that the addition of ~2.5 wt% of monomer gives the best electro-optical characteristics. The photoinitiator used in this experiment is benzoin methyl ether (BME; ~10 wt% of the monomer) purchased from Polyscience.

The fabrication method of a PSCT normal-mode cell was reported in ref. 16. The LC/monomer mixture was sandwiched between two indium-tin-oxide (ITO)-coated glass slides separated by a 12 µm thick plastic spacer; the surface of the ITO glass slides were untreated. The filled cells were polymerized using a Phillips model 400/30 s metal halide lamp. During curing, the cell was aligned homotropically by the application of an AC voltage (~50 V, 1 KHz) across the ITO electrode. The UV curing intensities were 1.3 mW/cm², 2.6 mW/cm², 7.8 mW/cm², 18.8 mW/cm², and 48 mW/cm². Figure 1 shows the schematic diagram of the experimen-

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Fig. 1. Schematic diagram of the experimental setup for studying Qu'etelet-type scattering. PD: photodiode; osci: oscilloscope; Si: silicon wafer.

3. Results and Discussion

Figure 2 shows the observed half diffraction ring pattern on a screen from a normal-mode PSCT cell. The screen was placed just in front of the photodiode. This sample had a monomer concentration of 2.5 wt% and the UV curing power was 2.6 mW/cm². The diffraction pattern is believed to result from the micron-sized scatterers in the PSCT sample. The scatterers are clusters in the polymer networks formed during polymerization and the focal conic LC domains.

Figure 3 shows the variation of the first-ring intensity of the pattern measured from normal-mode PSCT cells as a function of time during polymerization. The UV curing intensities were 1.3 mW/cm², 2.6 mW/cm², 7.8 mW/cm², and 18.8 mW/cm². Notably, the signal began to increase immediately after the UV irradiation. It increased continuously and then saturated. At this stage, the sample was almost fully cured, and monomers were phase-separated from LCs, forming a polymer network dispersed in the LCs.

The polymerization of LC/polymer mixtures involves a sequence of events, i.e. initiation, propagation and termination. During polymerization, polymer networks are formed and separate from the LCs. The polymerization rate increases with the UV curing intensity. The result shown in Fig. 3 that the signal increases initially, then becomes saturated is understandable from the polymerization sequence. It is believed that polymer networks gradually form after the UV irradiation is on, thus producing more scatterers with time. The polymerization continues until it terminates. At this stage the signal is saturated as shown in Fig. 3.

It is noted from Fig. 3 that the QT scattering signal increases proportionally to the UV curing intensity. This can be understood as follows. When the UV intensity is low, the polymer networks formed are thin and long. On the other hand, when UV curing intensity is high, the polymer networks formed are thick and short. As a result, the micron-sized clusters in the polymer networks formed in the sample that scatter light increase with increasing UV curing intensity. The fluctuation of the signal intensities for the samples cured with 7.8 mW/cm² and 18.8 mW/cm² is quite noticeable as shown in Fig. 3. Since the polymer networks formed for these two samples are thick and short, some of them may not attach to the substrate surfaces (refer to Fig. 7). As a result, they may vibrate during the propagation stage of the polymerization process. The cause of the fluctuation of the signal intensities is believed to be such polymer-network vibrations.

It is also noted from Fig. 3 that the diffraction signal is also
observable before the UV is on. It is believed that this signal comes from the micron-sized domains of the Grandjean and fingerprint textures in the mixture before polymerization.\textsuperscript{19} In this experiment, the amount of monomer added in a PSCT cell was so small (\(\sim 2.5\) wt\%), the mixture remained in the LC phase. Therefore, domains existed with Grandjean and fingerprint textures.\textsuperscript{19} They served as scatterers before polymerization in the normal-mode PSCT cell.

Figures 4(a) and 4(b) show the measured transmission and the first-ring intensity of a PSCT normal mode cell, respectively, as a function of the applied voltage. At low applied voltage, the cell is in the focal conic state, the incident light is scattering randomly, and the transmission is low. As mentioned above, the QT scattering diffraction signal is attributed to the micron-sized scatterers in the PSCT normal-mode cell, and the scatterers are believed to be clusters in the polymer networks and focal conic domains of the cholesteric LC. In a field-off state, the focal conic domains are too dense. They not only generate the QT scattering signal but also scatter the signal strongly. Therefore, the first-ring intensity is low. As the applied voltage is increased to a value above the saturation voltage, the cholesteric LC molecules are unwound and align with their director axes parallel to the applied field. The sample is now in the homeotropical state and the transmission is high. The contribution of the QT scattering ring intensities is due solely to clusters in the polymer networks. Therefore, Fig. 4(b), in which the ring intensity at voltages above saturation becomes smaller than that in the off state, is reasonable.

As mentioned in the previous paragraph, the focal conic domains not only generate the QT scattering signal but also scatter it strongly. When the applied voltage is increased to the value just above the threshold, some focal conic domains are unwound. This reduces the random scattering effect and results in an increase in the QT ring intensity. Upon further increasing the voltage, the signal then decreases again due to the disappearance of the focal conic domains, as shown in Fig. 4(b). Notably, the hysteresis effect that appears in the transmission curves versus the applied voltage of a PSCT normal-mode cell\textsuperscript{17} is also shown in the QT ring intensity versus-applied voltage curve. The correlation between Figs. 4(a) and 4(b) strongly indicates that the focal conic domains and the polymer networks are the key factors affecting the QT ring signals. Figure 5 shows the measured ring intensities of the PSCT normal-mode cell as a function of diffraction angle \(\theta\) at various applied voltages. The angle \(\theta\) is made between the diffracted rings and the undiffracted beam (0-th order) for the rings shown in Fig. 2.

Figure 6 shows the measured intensities of the QT rings of a PSCT normal-mode cell with the light incident from the front surface and from the back surface after curing as a function of the diffraction angle \(\theta\). No voltage was applied to the cell in this case. The result shows that the ring intensities measured from the front surface are slightly greater than those from the back surface. This can be understood as follows. As a film of LC/monomer mixture is cured by UV light, the photoinitiator decomposes into free radicals with absorption of UV light.
hysteresis effect that appears in the transmission curve versus the applied voltage of a PSCT normal-mode cell is also shown in the QT ring intensity-versus-applied voltage curve. This correlation indicates that the QT scattering effect could provide us with another qualitative, nondestructive method to analyze the PSCT films.

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Laser-induced ripple structure of dopant on the substrates in a dye-doped liquid crystal cell and its alignment effect

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Abstract

This letter describes a recording of a holographic grating on a homeotropically aligned dye-doped liquid crystal (DDLC) cell. The photo-excited azo dyes, methyl red (MR), diffuse and adsorb onto the cell substrates, thereby forming a ripple structure. This laser-induced ripple structure then reorients the LC molecules and induces a holographic grating.

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Photo-induced reorientation effects in dye-doped liquid crystals (DDLCs) have received considerable interest recently. Related studies have indicated that several mechanisms contribute to such reorientation effects [1-5]. Janossy et al. [1] observed that photo-excited anthraquinone dye molecules induced a positive torque, thereby facilitating the reduction of the optical Freedericksz transition. Gibbons et al. [2,3] demonstrated that nematic liquid crystals were reoriented perpendicularly to the optical electric field, if the substrate coated with an azo-dye doped polyimide was excited with a linearly polarized light. In other words, the photo-excited azo dyes induce a negative torque in this case. While observing another dye-induced reorientation effect, Khoo et al. [4,5] indicated that the dye-induced space charge field could induce the reorientation of the nematic liquid crystals.

In general, a doping dye could result in one of the above orientational effects. However, some dyes could induce several effects simultaneously. Among these effects one may dominate, depending on the experimental conditions. For example, methyl red (MR) dyes, after photo-excitation, could develop trans-cis isomerization [6], surface alignment effect [7,8], and photorefractive-like effect [4]. During the dynamic measurements, the trans-cis and photorefractive-like
effects dominate in the early time, while the surface alignment effect dominates in the later stage.

In this letter, we report on the formation of laser-induced ripple structure of the adsorbed MR dyes on substrate surfaces in a DDLC cell. Permanent reorientation of the liquid crystal molecules is accompanied with the formation of the ripple pattern. To our knowledge, this study reports on such an effect for the first time. Previous studies have observed laser-induced periodic surface structures (LIPSS) on the surface of metals [9,10], semiconductors [11,12], and dielectrics [13,14], using either the CW or pulsed lasers with the wavelengths ranging from 0.53 \( \mu \text{m} \) to 10.6 \( \mu \text{m} \). Explanations of LIPSS effect were given in terms of the coupling of laser-induced acoustic modes [15], or the driven surface plasmons [16]. Microroughness is crucial in the latter model.

A homeotropical DDLC sample was fabricated by filling a nematic LC, E7 (E. Merck), doped with various concentrations of azo dye, MR, into a 25 \( \mu \text{m} \)-thick indium-tin-oxide (ITO) coated glass cell. The homeotropical alignment was obtained by treating the ITO-coated glass slide surfaces with a solution of DMOAP (N,N-dimethy-N-octadecyl-3-aminopropytrimethoxy-silyl chloride) in distilled water (~0.05 wt%). At room temperature, the refractive indices parallel and perpendicular to the director axis of E7 are \( n_\parallel =1.736 \), \( n_\perp =1.511 \). Figure 1 schematically depicts
the experimental setup. Two linearly polarized (TE-polarized or TM-polarized) writing beams, $\vec{E}_1$ and $\vec{E}_2$ derived from an Kr$^+$ laser ($\lambda = 568.4$ nm) intersected at an angle $\sim \theta = 0.6^\circ$. They were unfocused, each having a beam diameter $\sim 6$ mm and a power of $\sim 10$ mW. An unpolarized He-Ne probe laser ($\sim 1$ mW) was incident normally onto the writing region of the sample through a polarizer during (dynamic measurements) or after the writing of a grating. In addition, the intensity of one of the first-order diffracted beams was measured.

Figures 2(a), 2(b), 2(c) summarize the dynamic measurements of the grating doped with 1 wt%, 1.2 wt%, and 1.5 wt% MR, respectively, written with TE-polarized pump beams. Although an experiment with a sample doped with 0.5 wt% MR was performed, no grating effect was observed. However, once the doping concentration exceeded $\sim 1$ wt%, the grating effect was observable; in addition, the first-order diffracted intensity increased with the MR concentration. Figure 2 clearly reveals that the diffraction of the TM-polarized probe beam is much significantly than that of the TE-polarized one. This finding suggests that the LC molecules are reoriented more along the plane of incidence of the writing beams than out of plane. Recent investigations [7-8,17-18] conferred that photo-excited MR dyes induce a transient three dimensional LC molecular rotation, then diffuse$^\\dagger$ and adsorb$^\\ddagger$ onto the substrates, thereby inducing a torque to reorient LC molecules to form a permanent
grating. The long axes of the absorbed MR dyes are perpendicular to the E-field of the pump beams. The results in Fig. 2 are, thus, satisfactory.

Figure 3(a) plots the measurement results of the variations of the first-order diffracted intensity of a He-Ne probe laser incident normally onto a permanent grating with respect to angle $\varphi$. This grating was generated in a sample doped with 1.2 wt% MR, and written with the TE-polarized pump beams for $\sim 4000$ seconds. Where $\varphi$ represents an angle made between the polarization of the probe beam with the stripes direction of the grating. Figure 3(b) shows the results of the same sample that produces the result of Fig.3(a) except for the polarization of the pump beams, which are TM-polarized. Notably, the diffraction efficiency shown in Figs. 3(a) and 3(b) changes periodically with the angle $\varphi$. These results indicate that the adsorbed MR dyes have their long axes perpendicular to the polarization of the pump beam.

This study also investigated the morphology of the adsorbed MR dyes onto the substrates using a scanning electron microscopy (SEM) and an atomic force microscopy (AFM). The cell was placed in a hexane solvent to remove the liquid crystals. The cell was then placed in a vacuum chamber to evaporate the solvent with the dissolved liquid crystals. Next, the cell was carefully split. One of the slides was coated with a thin film of gold ($\sim 40$ nm) and investigated using SEM. The other was without the gold coating, and investigated using AFM.
Figures 4(a), 4(b) and 4(c), 4(d) present the observed SEM photographs of the adsorbed MR morphology induced by TE-polarized, and TM-polarized pump beams, respectively, for the sample giving the result of Fig. 3. Notably, the pattern (Figs. 4(a), 4(c)) of the adsorbed MR dyes onto the substrates is a print of the interference pattern set up by the two writing beams. The fringe spacing is \( \sim 54 \mu m \), indicating that photo-excited MR dyes diffuse and then adsorb onto the substrates.

Closely examining the MR-rich regions (Figs. 4(b) and 4(d)) reveals a ripple structure with a fringe spacing \( \sim 0.38 \mu m \). According to these figures, the ripple fringes are parallel to the \( \vec E \) field of the writing beams. In a separated experiment, a DDLC sample was irradiated with a single Kr+ laser beam. The results (data not shown) also showed a similar ripple pattern. We therefore believe that the structure is a LIPSS.

Various LIPSS could be generated depending on the illuminated material and the properties of the laser beam used (e.g. wavelength, polarization and the angle of incidence) [19, 20]. The spacing of the ripple fringes whose direction is parallel to the \( \vec E \) field of the writing beam is governed [20] by

\[
\Lambda = \frac{\lambda}{n \cos \theta},
\]

where \( \lambda \) is the wavelength (in air) of the incident light, \( n \) is refractive index of the
liquid crystal, and $\theta$ is the angle of incidence. Taking $\lambda = 0.5684 \mu \text{m}$, $n \approx n_\perp = 1.511$ and $\theta \sim 0^\circ$, $\Lambda$ is calculated to be $\sim 0.38 \mu \text{m}$, and correlates with the observed results.

Figures 5(a) and 5(b) show the AFM images of the same sample that gives the SEM images of Figs. 4(a) and (b). These figures clearly reveal that the pattern of the adsorbed MR dye (Fig. 5(a)) is a print of the interference pattern set up by the two writing beams. Closely examining the MR-rich regions (Fig. 5(b)) reveals a ripple structure as well. Notably, according to Fig. 5(b), the ripple has an average modulation depth $\sim 0.18 \mu \text{m}$, and a spacing $\sim 0.38 \mu \text{m}$.

To understand whether to know if the ripple structure plays an important role in reorienting the LC molecules, this work conducted further SEM studies on DDLC samples written at various time intervals. According to those results, the induction of a ripple structure is crucial in the formation of a permanent grating in the present case. Consider the samples that give the dynamic measurements shown in Fig. 2. The ripple structure is found after being illuminated for $\sim 1800$ seconds in a DDLC cell doped with 1.2 wt% MR (Fig. 2(b)), and $\sim 600$ seconds for a 1.5 wt% MR sample. (For the sample doped with 1wt% MR, no ripple structure is found even when it is irradiated over 5000 s). Restated, if the writing beams are stopped at (or after) this crucial time, the sample forms a permanent grating.
In conclusion, this study has demonstrated the formation of laser-induce ripple structure of the dopant in glass surfaces of a DDLC cell doped with MR having a concentration above 1.2wt%. The induction of the ripple structure is accompanied with the formation of the permanent reorientation of liquid crystals. Moreover, the director axis of LC is reoriented perpendicularly to polarization of the writing beam.

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References


Figure Captions

Fig.1: Schematic diagram of the experimental setup.

Fig.2: Dynamic measurements of the first-order diffracted intensity of both the TE-polarized and TM-polarized He-Ne probe laser incident normally onto the a sample doped with (a) 1 wt%, (b) 1.2 wt%, (c) 1.5 wt% MR, written with the setup shown in Fig.1 with the TE-polarized pump beams.

Fig.3: Measurements of the variation of the first-order diffracted intensity of the probe laser incident normally onto a grating with respect to the polarization angle $\varphi$ of the probe beam. The grating was written using (a) TE-polarized, (b) TM-polarized pump beams in a sample doped with 1.2wt% MR, and illuminated for $\sim$4000 s.

Fig.4: SEM images of the adsorbed MR dyes on the substrates for a sample written with (a) TE-polarized, (c) TM-polarized pump beams. The images (c) and (d) are a close inspection of the shown area in (a) and (c).

Fig.5: (a) AFM images of the sample that gives the SEM image of Fig.4(a), (b) Close inspection of the area shown.
Incident laser E1

probe beam

Incident laser E2

First order

To Detection system

Sample

Polarizer

Fig. 1 Fuh et al.
Fig. 2  Fuh et al.
Fig. 3 Fuh et al.
Fig. 4  Fuh et al.
Fig. 5  Fuh et al.
Study of a Holographic Grating based on Dye-Doped Polymer-Ball-Type Polymer-Dispersed Liquid Crystal Films

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This study investigates the characteristics of the holographic grating formed in polymer-ball-type polymer-dispersed-liquid crystal (PBT-PDLC) films, doped with a diazo dye (G206). A dye-doped PBT-PDLC sample was fabricated, and used to write a holographic grating. Experimental results indicate that the grating had memory of the polarization of the writing beams. This memory effect was reversible if the sample was heated to the isotropic phase, and then cooled down to room temperature. Based on these observations, we believe that the memory of the grating effect does not relate to the memory in the transmission versus applied voltage curve of PBT-PDLC films. Rather, the effect is due to an intrinsic feature of the grating, resulting from the reorientation of the liquid crystals through their interaction with the photo-induced adsorption of the doped dyes on the surface of the polymer balls.

**KEYWORDS:** photopolymerization, polymer-ball-type PDLC, dye adsorption, molecular reorientation, polarization-dependent grating

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1. Introduction

Recording holographic gratings in films of inorganic\textsuperscript{13} and organic materials\textsuperscript{2-18} has received considerable attention recently. The latter includes polymers\textsuperscript{23}, liquid crystals (LCs)\textsuperscript{4-9}, polymeric liquid crystals\textsuperscript{10,11}, and PDLCs\textsuperscript{11-18}. The use of PDLCs for recording holographic gratings is particularly interesting since the grating can be formed in a single-step process relatively fast. Although permanent, the formed grating can be electrically\textsuperscript{12,13,17,18} and optically\textsuperscript{16} switchable.

PDLCs have also been reported for their potential use in displays\textsuperscript{19} and other light control applications.\textsuperscript{20} PDLCs exist the so-called LC-droplet-type\textsuperscript{19} and the polymer-ball-type (PBT) PDLC\textsuperscript{21} films. The former contains micro-sized LC droplets in a polymer matrix, and the latter involves polymer balls in the LC matrix. In addition to scattering light and appearing opaque in the off-state, they can be switched electrically into a transparent-state. These two types differ mainly in the intrinsic memory (hysteresis) effect in the transmission versus applied voltage curve. The memory is highly pronounced only in the PBT-PDLC films\textsuperscript{21}.

The organic materials mentioned above, doped with different sensitizing dyes, have also researched extensively to developing means of recording holographic gratings. Ref. [22] reviews mechanisms for grating formations. Generally, a doping dye can result in photoalignment, photoisomerization or photorefractivity. However, some
dyes (e.g. methyl red) can simultaneously induce several of these effects. One of these effects may dominate, however, depending on the experimental conditions.

This study reports the results obtained from studying holographic gratings based on PBT-PDLC films doped with a diazo dye (G206). PBT-PDLC samples were first prepared using the photopolymerization-induced phase separation method (PIPS). Holographic gratings were then written on these samples. Experimental results indicate that the formed grating had memory of the polarization of the writing beams. This memory was reversible when the sample was heated to the isotropic phase, and then cooled down to room temperature. Accordingly, we conclude that the grating is formed due to the reorientation effect of the liquid crystals through their interaction with the photo-induced adsorption of the doped dyes on the surface of polymer balls.

2. Experimental

The liquid crystal, monomer, crosslinking agent, coinitiator, photoinitiator and diazo dye used in our experiment were E7 (Merk), di-pentaerythritol pentaacrylate (DPPA; Polysciences), 1-vinyl-2-pyrrolidinone (NVP; Aldrich), N-phenylglycine (NPG; Aldrich), Rose Bengal (RB) and G206 (Nippon Kankoh-Shikiso Kenkyusho), respectively. The mixing ratio of the above components was 50 wt% of E7, 41 wt% of DPPA, 8 wt% of NVP, 0.5 wt% of NPG, 0.7 wt% of RB, and 0.3 wt% of G206. The
homogeneously mixed compounds were then sandwiched between two indium-tin-oxide (ITO) coated glass slides separated by a 38-μm-thick plastic spacer, to form a sample. The sample was polymerized over 60 minutes using a UV light with an intensity of \( \sim 2.2 \text{ mW/cm}^2 \) to form a PBT-PDLC film.

Figure 1 shows the setup for the experiment. The two writing beams, \( E_1 \) and \( E_2 \), derived from an Ar\(^+\) laser (\( \lambda = 514.5 \text{ nm} \)), intersected at an angle \( \theta \sim 1^\circ \). They were unfocused, having a beam diameter of \( \sim 3.5 \text{ mm} \), and an intensity of \( \sim 2.2 \text{ W/cm}^2 \). Since they were coherent, an intensity interference pattern was created in the intersecting region. The sample was placed in this region. After the grating was formed, an unpolarized He-Ne probe laser (\( \lambda = 632.8 \text{ nm} \)) was normally incident onto the sample through a polarizer.

The morphology of a UV cured PBT-PDLC film was also examined using scanning electron microscopy (SEM). Ref. [13] describes the preparation of SEM samples.

3. Results and Discussion

Figure 2 depicts the top-view SEM image of the PBT-PDLC sample doped with G206 cured with UV light with an intensity of \( \sim 2.2 \text{ mW/cm}^2 \) for \( \sim 60 \) minutes. The figure clearly shows that polymer balls have been formed. Ref. [16] presents the absorption spectrum of G206 dissolved in a PDLC sample. Briefly, it exhibits a peak
at $\lambda \sim 432\text{nm}$. The spectrum is relatively broad and covers the $\text{Ar}^+$ lasing at 514.5nm (at which wavelength, the absorption is about a quarter of that at peak). However, the He-Ne laser ($\lambda \sim 632.8\text{nm}$) is not absorbed by G206.

After the grating had been written using s-polarized pump beams for 60s, the diffraction patterns in Fig. 3 were obtained. Figures 3(a) and 3(b) were for a s-polarized and p-polarized probe beam, respectively. The diffraction of the grating is clearly polarization-dependent. Namely, the diffraction can be seen only when the probe beam has the same polarization as the pump beams. Figure 4 shows the grating image observed under an optical microscope with a polarizer placed in front of the sample. Figures 4(a) and 4(b) are the images of grating corresponding to the polarizer’s being placed with its transmission axis parallel and perpendicular to the grating stripes direction, respectively. These images are consistent with the results in Figs. 3(a) and (b), and are therefore reasonable. Similar results were obtained using p-polarized pump beams. Notably, even the zeroth-order diffracted beam of the p-polarized probe beam (refer to Fig. 3(b)) can not be seen, indicating that the sample is at the scattering state both in high- and low-intensity regions of the interference pattern for the p-polarized probe beam.

An experiment using a modified setup shown in Fig. 1 was performed to understand the mechanism that gives rise to the grating characteristics shown in Figs.
2 and 3. The PDLC sample was illuminated by a single s-polarized Ar\(^+\) laser with an intensity of \(~2.2\ \text{W/cm}^2\) for around 5 minutes. The variation of the transmission of the sample with respect to the polarization of the probe beam was then measured. Let \(\phi\) be the polarization angle between the polarization of the probe beam and the direction of the stripes in the grating. Figure 5 presents the measurements. The transmission of an unpumped sample is included for comparison. Figure 5 reveals that the transmission of the s-polarized pumped sample changes periodically with the angle, \(\phi\). It peaks at 0\(^\circ\), 180\(^\circ\), and 360\(^\circ\), which angles correspond to the s-polarized probe beam. The transmission of an unpumped sample, however, shows no change. We believe that the transmission of the s-polarized pumped sample changes periodically with the angle, \(\phi\) is caused by the adsorbed dyes. The photo-excited dyes diffused and then adsorbed loosely in a direction perpendicular to the polarization and the propagation directions of the pump beam (s-polarized). The adsorbed dyes then reoriented LC molecules. As a result, the s-polarized (p-polarized) probe beam “sees” the ordinary refractive index \(n_o\) (the extraordinary index \(n_e\)) of the liquid crystal, which matches (mismatches) the index of the polymer \(n_p\). The pumped sample is, thus, partially transparent for the s-polarized probe beam, but is opaque (scattering state) for the p-polarized probe beam. The unpumped sample is in scattering state for both s- and p-polarized probe beams. These findings indicate that the transmission of the
sample in the high-intensity regions of the interference pattern (similar to the above pumped sample) is partially transparent for the s-polarized probe but opaque (scattering state) for the p-polarized probe beam, if the grating is written by s-polarized pump beams. The low-intensity regions, however, are opaque to both the s- and p-polarized probe beams. Thus, the sample is a grating (amplitude grating) for an s-polarized probe beam only. The observed grating features shown in Figs. 3 and 4 are, thus, reasonable.

The variation of the first-order diffraction efficiency of the grating shown in Fig. 3(a) was also measured with respect to temperature. The result (not shown) shows that the variation is reversible when the sample is heated to 65°C (at which E7 is in the isotropic state), and then cooled back down to the normal temperature.

In conclusion, this study has demonstrated that a holographic grating can be written on a cured PBT-PDLC film doped with a diazo dye. The formed grating is polarization-dependent, and diffracts a probe beam with the same polarization as the writing beams. This memory effect is not due to the memory effect of transmission versus applied voltage in a typical PBT-PDLC film, which is generally irreversible \cite{21} when the sample is heated above the nematic-isotropic transition temperature, and then cooled down. Rather, the memory effect discussed here is due to the photoalignment of the adsorbed dyes on the polymer balls.
Acknowledgments

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References


Figure Captions

Fig. 1: Schematic diagram of the experimental setup.

Fig. 2: "Top-view" SEM morphology of a polymer-ball-type PDLC film.

Fig. 3: Diffraction images for a PBT-PDLC grating with (a) the s-polarized probe beam, (b) the p-polarized probe beam. The grating is written using the s-polarized pump beams.

Fig. 4: Grating images (spacing ~ 29.5μm) observed under an optical microscope with a polarizer placed in front of the sample. The transmission axis of the polarizer is (a) parallel, (b) perpendicular to the direction of the stripes in the grating.

Fig. 5: Variations in the transmission of a PBT-PDLC film doped with G206 dye after being pumped by a single s-polarized Ar+ laser for 5 minutes at a polarization angle ϕ made between the polarization of the probe beam and the direction of the stripes in the grating.
PBT PDLC grating

Probe beam first order diffraction to detection system

Fig. 1  Fuh et al.
Fig. 2  Fuh et al.
Fig. 3  Fuh et al.
Fig. 5  Fuh et al.
Studies of the formation of a cholesteric grating and its electro-optical characteristics

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We studied the formation of cholesteric gratings and their electro-optical characteristics. Films of planar cholesteric texture having different thickness to pitch length ratios \(d/p\) were fabricated. Using an optical microscope, we observed the formation of the cholesteric grating with the film under the application of an AC voltage. The micrographs showed that the cholesteric grating formed via two different ways for different \(d/p\) ratios. For a film having \(1/2 < d/p \leq 1.0\), the grating stripes appeared simultaneously and the contrast of stripes was increasing with time during formation. For films having \(d/p \geq 1.3\), the stripes nucleated near edges, and extended along the rubbing direction. The diffraction measurements showed that the diffracted beams could be steered only for the latter type. These results can be explained with the calculated threshold fields of periodic deformation and untwisting of the helical axis.

KEYWORDS: cholesteric grating, beam steering, Fréedericksz transition

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1. Introduction

It is known that cholesteric liquid crystals exhibit highly specific optical properties. In the absence of an electric field or other perturbing forces, the director can be made uniformly twisted along a helical axis. The distance along the helical axis for the director to twist $2\pi$ is called the pitch length, denoted by $p$. When the director of a cholesteric liquid crystal is oriented along the surface of a cell, the helix is perpendicular to the glass surface. In this case, a planar texture is obtained. Cholesteric liquid crystals have been utilized in many applications, such as low-voltage light-modulators,$^{1-3}$ backlight-free displays,$^4$ and smart reflectors.$^5$

The distortions of a planar cholesteric structure induced by an external field have been studied theoretically and experimentally.$^6,7$ Subacius et al.$^8$ recently reported cholesteric diffraction grating in a fingerprint texture. This texture was obtained by applying an electric field parallel to the helical axis of a planar texture film. They further demonstrated the control of the grating spacing using an electric field.$^9$ The structure of cholesteric gratings was also analyzed theoretically by the same group.$^10$ They classified the fingerprint textures into two different types according to the formation of grating. One is the so-called developable modulation type. The stripes appear in a way similar to a photographic image being developed, i.e. the contrast of stripes increases with time during formation. The other is called the growing
modulation type whose stripes nucleate near edges, and then slowly extended along the rubbing direction. Recently we have demonstrated that the grating spacing and diffracted-beam intensities can be controlled by laser heating with the film doped with a dichroic dye.\textsuperscript{10} The fingerprint gratings are not stable at field-off condition. The use of a low concentration polymer network to stabilize cholesteric grating was made by Lee et al.\textsuperscript{13} The director configuration of fingerprint texture was also studied by Kang et al.\textsuperscript{13} They reported that the cholesteric twist in the cell interior with optical pitch $p$ is complemented by twisted surface regions with optical pitch $2p$.

In this paper, we firstly study the effect of the cell thickness to pitch length ($d/p$) on the formation of a cholesteric grating. We observe the cholesteric gratings having various pitch lengths by using an optical microscope during formation. Then, we evaluate the beam-steering capability of the formed cholesteric grating. Finally we study the diffraction characteristics of cholesteric gratings doped with a dichroic guest-host dye by using the pump-probe technique. The results show that the cholesteric gratings form via two distinct scenarios depending on the ratio $d/p$. For $d/p$ between 0.5 and 1, the cholesteric gratings belong to the developable modulation type. For ratio $d/p \geq 1.3$, both the developable and growing modulation types appear simultaneously, but the latter dominates. For ratio $d/p$ between 1 and 1.3, the fingerprint texture is not uniform. Therefore, experiments with sample having a ratio
d/p between 1 and 1.3 are not performed in the present case. From beam-steering experiment, it is found that only the growing modulation type has beam-steering capability. These results could be explained well with theory.

2. Experiments

In the experiment we used a nematic liquid crystal E7 (E. Merck) with a positive dielectric anisotropy $\Delta \varepsilon = 13.8$, elastic constants $K_{11} = 11.7 \times 10^{-12}$ N, $K_{22} = 6.5 \times 10^{-12}$ N, $K_{33} = 17.1 \times 10^{-12}$ N at 20 °C for splay, twist and bend deformations, respectively. The refractive indices are $n_o = 1.52$, $n_e = 1.74$ at 20 °C for ordinary and extraordinary waves, respectively. The nematic material was doped with a chiral agent CB15 (E. Merck) to yield a cholesteric. Adjusting the concentration of the chiral dopant, cholesteric with pitch lengths ranging from 4 to 15 µm were prepared. Finally, a dichroic guest-host dye G206 (Nippon Kankoh-Shikiso Kenkyusho), ~ 2 wt%, was added into the prepared cholesterial material. The function of G206 dye is to absorb the pump beam, and to induce a temperature change. The liquid crystal solutions were vacuum filled into cells of 8 µm gap with rubbed polyimide which induce ordering of the adjacent liquid crystal molecules parallel to the rubbing direction, thus promoting the formation of the planar state.

The initial texture of the filled cholesteric cell at field-off was planar, and had the helical axis oriented perpendicular to the cell substrates. When an appropriate AC
voltage was applied to the cell, it transited into a fingerprint texture.

The images of gratings during formation were observed using an optical microscope (Olympus BH2) with an AC voltage (1 kHz) being applied to the samples. The capability of the grating for steering its diffracted beams was then studied. In this part of experiment, an unpolarized He-Ne aser (~3 mW) was used as a probe. The angle of the second-order diffracted beam was measured as a function of the applied AC (1kHz) voltage. Finally, the experimental setup reported in Ref. 11 was used. Basically, it is the pump-probe technique. An Ar+ laser was used as a pump, while a He-Ne laser was used as a probe. Both lasers were linearly polarized, and their polarization were parallel to the stripes' direction. The pump beam was incident normally to the sample, and the probe beam made an angle of ~ 0.1° with the pump beam. The diffracted beams were recorded using a CCD (Charge Couple Device). The signal was fed to a PC for analysis. A color filter was placed in front of the CCD detector to prevent the pump beam from reaching the detector. In this part of experiment, we varied the pump-beam power. The measurement were carried out in an air-conditioned ambient, so that the temperature of the sample would be stable.

3. Results and Discussion

Figure 1 shows the micrographs of the cholesteric gratings during formation with various d/p ratios. As can be seen from Fig. 1, the formation of cholesteric gratings is
completely different for different $d/p$ ratio. For $d/p$ ratio between 0.5 and 1, the planar texture tends to form the cholesteric grating with the developable modulation. The stripes develop like a photographic picture being developed, i.e. the contrast of stripes is increasing during formation. The stripes' direction of developable-modulation gratings is parallel and perpendicular to the rubbing direction for $d/p \sim 0.5$ and $d/p = 1$, respectively. For larger $d/p$ ratios ($\approx 1.3$), two types of modulations appear almost simultaneously, but the modulation of the grating that nucleates near spacers or defects and elongates along rubbing direction dominates. The stripes' direction of the grating with growing modulations is parallel to rubbing direction.

The behavior of nematic and cholesteric liquid crystals under the application of an external electric or magnetic field has been studied extensively.\textsuperscript{6} Due to the dielectric (diamagnetic) anisotropy of liquid crystals, an applied electric (magnetic) field can reorient LC director. For a planar cholesteric film having $d \sim p$, when an external field applied parallel to helical axis of a planar texture reaches the $E_{th}$, where the planar texture changes from uniform to periodic distortion,\textsuperscript{14, 15, 16} namely, the developable modulation type. The plane of planar layers are deformed periodically for developable modulation type, and the stripes' direction is perpendicular to the direction of middle layer.\textsuperscript{10, 17} When the external field is still increased the structure changes from developable modulation type to the homeotropic texture.\textsuperscript{16} Therefore,
for $1/2 < d/p \leq 1$ (belonged to $d \sim p$ range), when the applied field reaches $E_{th}$, the planar textures transit into developable modulations type. As we mention above, the stripes' direction of developable modulation type is always perpendicular to the director in the middle of the cell. Therefore, this is why the stripes' direction of ratio $d/p$ near $1/2$ is parallel to rubbing's direction in Fig. 1(a) and the stripes' direction is perpendicular to rubbing's direction for $d/p = 1$ in Fig. 1(b). The helix must adjust its pitch slightly in order to satisfy surface's condition. Therefore, the stripes' direction for ratio $d/p$ around $1/2$ (ranging from $8/15$ to $8/11$) is the same, and the stripes' direction for ratio $d/p$ around $1$ (ranging from $8/10$ to $8/8$) is the same with $d/p = 1$ in our experiment.

For $d > p$, when the external field reaches the $E_{th}$, the planar texture changes from uniform to developable modulation type. When the external field is still increased above $E_{th}$, the structure changes from developable modulation type to the helical axis is rotated as a whole by $90^\circ$, namely, growing modulation type. Above $E_{th}$ the cholesteric texture is progressively unwound to homeotropic state at $E_{un}$.\textsuperscript{17} Therefore, for $d/p > 1.3$, when the applied field reaches $E_{th}$, the planar texture will transit into developable modulation type. When the external field is still increased above threshold field $E_{th}$, the structure then changes from developable modulations to growing modulations. For growing modulation type, from Fig. 1(c), we can see $E_{th}$ is
near $E_b$, two types of grating appear simultaneously, and we can see the process that growing modulations replace developable modulations gradually. Because the helical axis is parallel to the substrate for growing modulation type, to minimize free energy of system, the stripes' direction of growing modulation type in Figure 1 is always parallel to the rubbing direction.

According to the Figure 1, we conclude that it forms developable modulation type for $d/p$ between $1/2$ and $1$, and forms growing modulation type for $d/p \geq 1.3$ in our experiment. The largest ratio $d/p$ that can form uniform fingerprint texture in our experiment is about 2.5.

Figure 2 presents the angle of the second-order diffracted beam as a function of the applied voltage to the cell for various $d/p$ ratios. It can be seen from Figure 2 that the diffracted beams for a cholesteric grating of developable modulation type cannot be steered by an electric field.

Quantitatively, we can explain why the diffracted beams for a cholesteric grating of developable modulation type cannot be steered by an electric field in Fig. 2 by theoretically calculation. For planar texture, when electric field applied parallel to the helical axis (i.e., $E//h$, where $h$ is helical axis), the formula for threshold field of developable modulations is given as\(^{16}\)

$$E_{th} = \left[ \frac{8\pi^2 (6K_{22}K_{23})^{1/2}}{(\Delta \varepsilon \rho d)^{1/2}} \right]^{1/2}$$  \hspace{1cm} (1)
where \( p \) is pitch length in the absence of a field. When electric field applied perpendicular to the helical axis \((E \perp \mathbf{h})\), there exists the critical field of the cholesteric-nematic transition, and is given as\(^9\)

\[
E_{nw} = (\pi^2/p)(4\pi K_{22}/\Delta \varepsilon)^{1/2}
\]

(2)

Using Eq. (1) and Eq. (2) we can write explicitly

\[
E_{nw}/E_{th} = \alpha[K_{22}/2(6K_{22}K_{33})^{1/2}]^{1/2}(d/p)^{1/2}
\]

(3)

Substituting \( d/p \) from 1/2 to 1, \( K_{22} = 6.5 \times 10^{-12} \) N and \( K_{33} = 10^{-11} \) N into Eq. (3),

we can get \( 0.90 \leq E_{nw}/E_{th} \leq 1.28 \) for \( d/p \) from 1/2 to 1. That is \( E_{nw} \) closes to or less than the threshold voltage of developable modulation type for \( d/p \) from 1/2 to 1. When the applied voltage is still increased until the helical axis is rotated 90° become \( E \perp \mathbf{h} \), the cholesteric-nematic transition occurs. This can explain why the developable modulation type cannot be steered in Fig. 2. This also explains that why ratio \( d/p \) from 1/2 to 1 cannot form the growing modulation type.

For growing modulation type, we substitute \( d/p > 1.3 \) into Eq. (3), we can get \( E_{nw}/E_{th} \gg 1 \). As we mention above, the critical field of growing modulation type \( E_{b} \) is higher than \( E_{th} \). But from Fig. 1(c), we know that \( E_{b} \) is near \( E_{th} \) in our experiment. Thus, we can know that even when the external field above \( E_{b} \), growing modulation type can be unwound progressively to homeotropic state. This explains why the diffracted beams could be steered for the growing modulation type in Fig. 2.
Physically, the large pitch corresponds to low $E_{nw}$. Thus, for small $d/p$, the $E_{nw}$ will be near or less than $E_{th}$. That is when the external field up to the threshold of the helical axis is rotated as a whole by 90°, the cholesteric-nematic transition occurs for developable modulation type. Similarly, the small pitch corresponds to high $E_{nw}$. For large $d/p$, the $E_{nw}$ will much more than $E_{th}$. Thus, when the external field above $E_{B}$, $E_{a}$ is a bit higher than $E_{th}$, the growing modulation type can be unwound progressively to homeotropic state.

Figure 3 shows the variation of the angle of the second-order diffracted beam for various $d/p$ ratios after the sample being pumped by an Ar+ laser having powers ranging from 0 to 300mW. It is clearly seen that the diffracted beam of a cholesteric grating of developable modulation type cannot be controlled by laser heating.

Growing modulation type doped with a dichroic guest-host dye and its pitch can be controlled by pumping various laser powers has been studied by Fuh et al.11 The pitch of growing modulation type increases by increasing laser power. On the other hand, the threshold of developable modulation type is given in Eq. (1). And we know that the physical properties of the parameters $K_{11}$, and $\Delta \varepsilon$ of typical nematic liquid crystals are strongly dependent on temperature. According to the mean-field Maier-Saupe theory,18-20 $\Delta \varepsilon$ is proportional to the order parameter $S$ and the elastic constants are proportional to $S^2$. Furthermore, the order parameter $S$ is approximately
proportional to \((T/T_c)^\gamma\) where \(\gamma \sim 0.7\) to \(0.8\).\(^{21-23}\) And the pitch of cholesteric liquid crystals is also dependent on temperature. But for \(d \sim p\), that is \(1/2 < d/p \leq 1\) in our experiment, due to the strong anchoring force at two substrates, the temperature dependence of cholesteric pitch should be weak. Based on the above facts, the threshold field of developable modulation type \(E_{th}\) given in Eq. (1) can be understood to have \(dE_{th}/dT < 0\). But we apply fixed external field to the developable modulation type during pump-probe process. Thus, the threshold field of developable modulation type is below external field with temperature increases during pumping high power pump beam. But for developable modulation type, we can know from Fig. 2, the field of the developable modulation type transit into the homeotropic texture is near the threshold field of developable modulation type \(E_{th}\). Therefore, the developable modulation type transit into homeotropic state rapidly with temperature increases. Thus, the disappearance of developable modulation type with increasing pump-beam power agrees qualitatively with theory.

Finally, we observe the diffraction pattern of cholesteric grating. From Figure 4 we find that the shapes of diffraction pattern of growing modulation type are different from developable modulation type. For developable modulation type, is like other gratings, the shape of diffraction pattern is near circular. But for growing modulation type, the shape of diffraction pattern is an arc. This can be understandable from their
micrographs. From Figure 5 we can see that lots of the stripes of growing modulation type become deformed near spacer or defect. On the contrary, the stripes of developable growing type are straighter than growing modulation type. This result in the shape of diffraction pattern is an arc for growing modulation type but circular for developable modulation type.

In conclusion, we have showed that formation of cholesteric grating by micrograph. We also demonstrated that not all the cholesteric grating can be changed electrically and optically. These results agree well with theoretical calculation.

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Fig. 2: The final diffraction angle of the second order as a function of the voltage applied to the planar texture for different pitch lengths (cell gap = 8 μm).

Fig. 3: The final diffraction angle of the second order after the sample was pumped by an Ar+ laser for different d/p ratios: (a) 8/15, (b) 8/14, (c) 8/13, (d) 8/8, (e) 8/5, (f) 8/8, (g) 8/8, (h) 8/8, (i) 8/8, (j) 8/8, (k) 8/8, (l) 8/8, (m) 8/8.

Fig. 4: The shape of diffraction patterns of cholesteric grating for different d/p ratios: (a) 8/15, (b) 8/14, (c) 8/13, (d) 8/8, (e) 8/5, (f) 8/8, (g) 8/8, (h) 8/8, (i) 8/8, (j) 8/8, (k) 8/8, (l) 8/8, (m) 8/8, (n) 8/8, (o) 8/8, (p) 8/8, (q) 8/8, (r) 8/8, (s) 8/8, (t) 8/8, (u) 8/8, (v) 8/8, (w) 8/8, (x) 8/8, (y) 8/8, (z) 8/8.