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Dynamical studies of gratings formed in polymer-dispersed liquid crystal films

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The use of polymer-dispersed liquid crystal films to fabricate gratings was demonstrated. The written gratings are permanent, but are electrically switchable. In this article, we report the results obtained from the dynamical studies of gratings formed in polymer-dispersed liquid crystal films having various liquid crystal-polymer mixing ratios. The results showed that during the initial phases of formation, a thermal grating effect dominated. Later, it was offset or quenched by the photopolymerization effect which eventually dominated and determined the characteristics of the final grating. © 1998 American Institute of Physics. [S0021-8979(98)03502-6]

I. INTRODUCTION

Liquid crystals in their mesophases have been used extensively in both fundamental and applied situations. Among the three mesophases (nematic, cholesteric, and smectic), nematics have been the most commonly used to date due to their sensitivity to weak perturbation forces induced by electric, magnetic, and optical fields. In fundamental studies, nonlinear optical processes have been one of the key subjects of worldwide study. In the bulk volume of nematics, the second-order optical nonlinearity is usually negligible due to the inversion symmetry of the medium molecular arrangements. The focus, therefore, has been concentrated on the third-order nonlinear processes that result in effects such as degenerate four-wave mixing (DFWM) phase conjugation, self-focusing (or defocusing)...etc. For application-oriented situations, display applications dominate.

Recently, an increasing amount of interest has been shown in liquid crystal polymer dispersions which include both so-called polymer-dispersed liquid crystal (PDLC)^{1,2} and polymer-stabilized cholesteric texture (PSCT) films.³ The former usually has a polymer concentration more than ~20 wt % in the mixture in order to confine liquid crystals (LCs). For PSCT, the polymer concentration is usually low (~1–5 wt %) and is used to stabilize the LC structure in the cell. Since these devices use no polarizers, a high transmission state is obtained. Thus, they show high promise for display applications.

In addition to being useful for displays, PDLC films have also been reported for several other applications. They are variable transmittance windows,^{1,2,4–9} Gaussian filters,¹⁰ and grating/holograms.^{11,12} The formed grating/hologram is permanent, but can be electrically switchable.

In this article, we report the results obtained from the dynamical studies of gratings formed in PDLC films. Bunning *et al.* have also studied the real-time development of a PDLC grating.¹³ Their results show that there is an induction period before the formation of LC droplets or domains due to

phase separation. During this period, no diffraction is observed. However, we found when the intersecting angle between the two pump beams was small (see Fig. 1), diffraction was present within this induction period. The cause of such a diffraction is believed to be associated with a thermal grating.

II. EXPERIMENTS

Figure 1(a) shows the experimental setup for studying the dynamics of the gratings formed on PDLC films. The two writing beams, E_1 and E_2 , derived from an Ar⁺ laser ($\lambda = 514.5$ nm), intersected at an angle θ . They were unfocused, each having a beam diameter of ~4 mm and a power of ~75 mW. Since they were coherent, an intensity interference pattern was created in the intersecting region. The sample was placed in this region. An unpolarized He-Ne laser was introduced in the plane determined by beams E_1 and E_2 to probe the writing region of the sample. One of the first-order diffracted beam intensities was monitored as the grating was being formed.

The liquid crystal and polymer materials employed in this experiment were E7 and NOA65,¹⁴ respectively. A small amount of photoinitiator dye, Rose Bengal (RB), was added to the E7-NOA65 mixture (~1.5 wt % of the E7). The function of this dye, with the presence of a coinitiator in the polymer, is to form free radicals, and then to initiate polymerization of NOA65 with the exposure of the film to green-blue light. Drops of the homogeneously mixed E7-NOA65-dye mixture were then sandwiched between two indium-tin-oxide (ITO) coated glass slides separated by 25 μ m-thick plastic spacers to form a sample.

The variations of the diffracted beam intensity with respect to the intersecting angle θ , and the E7-NOA65 mixture ratio were measured. For a given set of measurements, only one parameter was allowed to vary.

The morphology of cured gratings was also examined using a scanning electron microscopy (SEM). The preparation of SEM samples was reported in Ref. 12.

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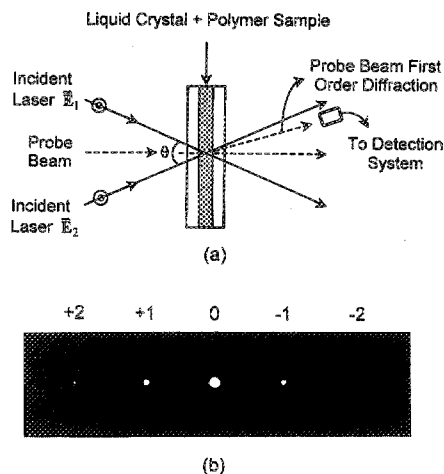


FIG. 1. (a) The experimental setup for studying the dynamical behavior of a grating formed in a PDLC films and (b) the typical diffraction pattern probed by a He-Ne laser in the above grating during writing.

How the structure of an E7/NOA65/dye system develops during the curing process is also important. It helps in understanding the dynamical behavior of the formation of the gratings. A light scattering method was used to determine the onset of phase separation in this PDLC system. This experiment was performed with the application of both an Ar⁺ laser and a He-Ne laser simultaneously. The He-Ne laser was used to probe the transparency of the sample when it was cured by the Ar⁺ laser. The onset of turbidity can be used to set an upper limit for the liquid crystal solubility in the polymer.¹⁵ This has been applied to the determination of solubility limits in PDLC films with apparently good results.^{16,17} In other words, the transmission of the probe beam will be approximately unchanged if no phase separation or no macroscopic phase separation occurs during curing in this case. It should be noted that this method does not apply if the phase separation produces nematic domains much smaller than the wavelength of light.

III. RESULTS AND ANALYSIS

Figure 2 shows the result of the light scattering experiment with the E7/NOA65/dye system. For the samples having LC contents less than ~30 wt %, no phase separation or macroscopic phase separation was observed. Phase separation started to occur for LCs at ~32 wt %. Lovinger *et al.*¹⁸ have reported a detailed phase diagram on the E7/NOA65 (without dye). At room temperature, their result shows that phase separation occurs when the LC content is greater than 30 wt %. This indicates that the addition of the photoinitiator dye does not significantly affect the phase separation.

Figure 1(b) shows the typical diffraction pattern of a PDLC film during the writing of a grating on it. Figure 3(a) shows the side-view SEM image of the grating fabricated from a sample having a LC content of ~40 wt %, and Fig. 3(b) corresponds to the surface view. It was written with the two Ar⁺ laser beams each having a power of ~75 mW, and the angle θ between them of ~3°. It is clear to see that LC droplets were formed in Fig. 3(b). Since the writing beams were incident from the top surface of the sample shown in

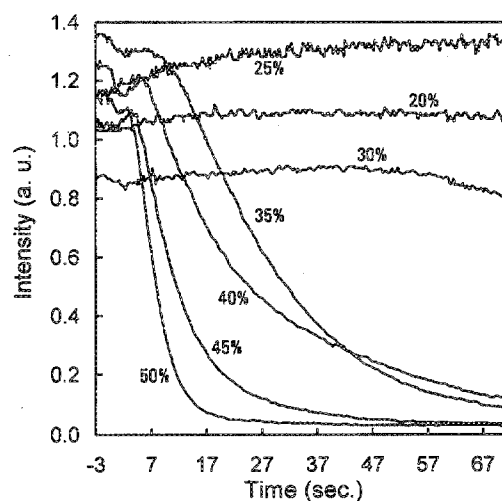


FIG. 2. Results obtained from the light scattering experiment with the E7/NOA5/dye system.

Fig. 3(a) during the writing of this grating, its morphology is seen to vary as a function of depth. Due to the overshadowing effect from the writing beams which propagated through the sample, the polymer-rich regions appear coneshaped. Figure 3(b) is a SEM image viewed from the bottom surface of the grating shown in Fig. 3(a). The presence of cone-shaped LC-rich lamellae through the thickness of the film makes the film diffract light in a slightly different manner if it is flipped over. Experimentally, it shows that the diffraction is stronger when the narrow ends of the cones face the incident light.

The regions having LC droplets shown in Fig. 3 correspond to the interference minima. In other words, high-intensity regions are polymer rich. These results can be understood by considering the chemical potential.¹³ Ignoring

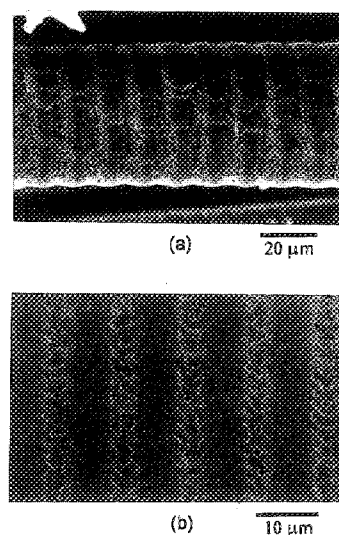


FIG. 3. (a) A "side-view" SEM image of a typical grating formed in a PDLC film. The writing beams were incident from the top during the writing of this grating and (b) a SEM image viewed from the bottom surface of the above grating.

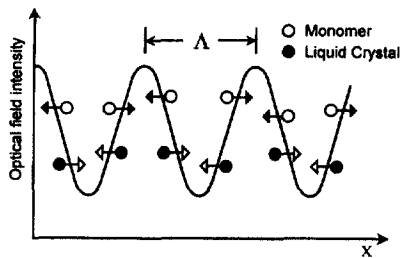


FIG. 4. Direction of molecular diffusions for liquid crystal and monomer molecules during the phase separation process in an optical interference pattern.

interactions between various components, we can write the chemical potential μ_i of the i th component of mixture as

$$\mu_i = \mu_i^0 + kT \ln \left(\frac{N_i}{\sum_j N_j} \right), \quad (1)$$

where N_i is the number of molecules of the i th component, j is the number of components, k is Boltzmann's constant, and T is the absolute temperature. Referring to Fig. 4 which shows the intensity profile resulting from the interference of E_1 and E_2 . The polymerization preferentially initiates in the high-intensity regions. The consumption of monomers in these regions thus lowers their chemical potential. This gives rise to the diffusion of monomers towards the higher-intensity regions from the lower-intensity ones. On the other hand, as liquid crystal molecules are not consumed, their chemical potential increases in the higher-intensity regions over that in the lower-intensity regions due to the consumption of the NOA65 monomers. Hence, there was a diffusion of LC molecules from higher-intensity regions towards the lower-intensity ones to equalize the chemical potential everywhere in the writing area.

Figure 5 shows the measured curves of the dynamical changes of the first-order diffraction efficiency (which is defined as the intensity of the diffracted beam divided by that of the probing beam) for a sample having ~ 20 wt % E7 as a function of time at various angles θ .

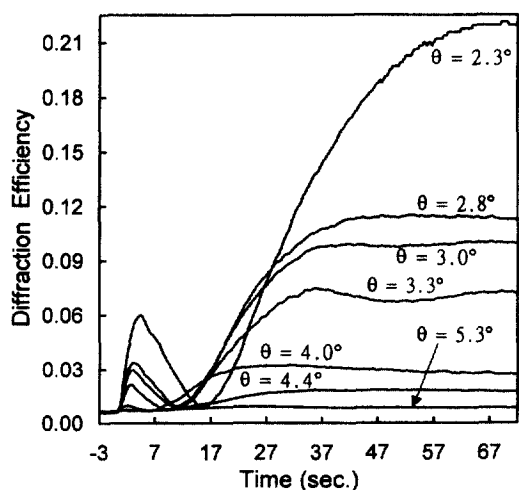


FIG. 5. Dynamical changes of the first-order diffraction efficiency for a PDLC sample having ~ 20 wt % E7 as a function of time at various angles θ .

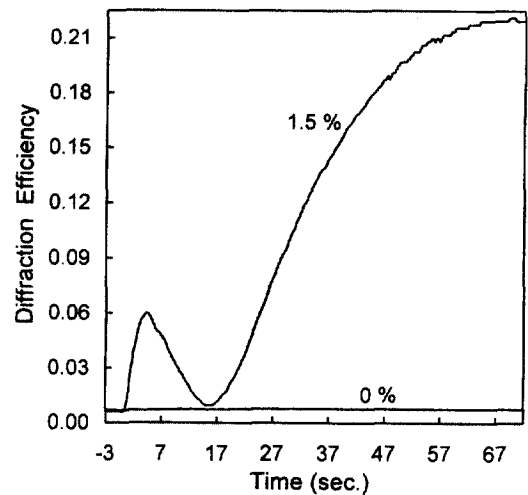


FIG. 6. Dynamical changes of the first-order diffraction efficiency for a PDLC sample having ~ 20 wt % E7 with (~ 1.5 wt %) and without the addition of the RB dye. The angle θ is $\sim 2.3^\circ$.

function of time at various angles θ . It is noted from Fig. 2 that no phase separation happened in this case. The He-Ne probing laser was diffracted almost immediately after the Ar^+ laser beams were turned on at $t=0$. This is believed to be due to the laser-induced thermal grating. In order to confirm that the thermal grating is due to the photoabsorption of the dye, a control experiment was performed. The result is shown in Fig. 6. It is seen that no grating effect was observed in the sample without addition of the RB dye. In a separate experiment, the refractive index of the prepolymer NOA65 as a function of temperature was measured. The result (not shown) showed that the refractive index decreased linearly with an increase in temperature. The intensity interference pattern produced by the two Ar^+ laser beams then sets up a thermal grating due to the photoabsorption of the dye molecules. Mathematically, it can be written as

$$n = n_0 + n_2 I, \quad (2)$$

where n_0 is the linear (under zero optical field) refractive index, n_2 is the Kerr coefficient which is negative in the present case, and I is the light irradiance.

The other contribution to the grating is from the photopolymerization effect. Photopolymerization preferentially initiates in the high-intensity regions. This gives rise to a spatial pattern of monomer concentration across the film. Consequently, there is a diffusion of monomer molecules towards the high-intensity regions. The molecular weight of polymers in the high-intensity regions increases from crosslinking to a much greater extent than that of polymers in the low-intensity regions. Therefore, the intensity interference pattern produced a refractive index grating that can be associated with the spatially varying molecular weight of polymer molecules. This photopolymerization grating grows slower than that of the thermal grating, and they are 180° out of phase with each other. As a result, the diffracted intensity was observed to initially increase because of the rapid formation of the thermal grating as shown in Fig. 5. The intensity then decreased as the photopolymerization grating began

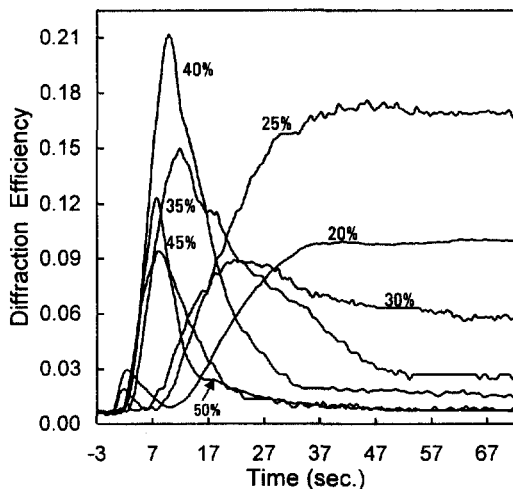


FIG. 7. The diffraction efficiency as a function of the curing time for samples having various LC contents (shown in wt %).

to grow. When the gratings were equal in amplitude and opposite in phase, the diffracted intensity became zero. Finally, the diffracted intensity increased again, and eventually became saturated when the photopolymerization process was complete.

It is also noted in Fig. 5 that the dynamical change of the first-order diffraction efficiency is affected by the angle θ which the two writing Ar^+ lasers make. As the angle becomes smaller, the diffraction efficiency has a higher initial maximum peak at ~ 3 s. Then it takes a longer time to go down to zero, and finally it increases and saturates at the value determined by the photopolymerization grating. This can be understood as follows. For a given θ , the grating spacing is determined by the following equation,

$$\Lambda = \lambda / 2 \sin\left(\frac{\theta}{2}\right), \quad (3)$$

where λ is the wavelength of the writing beam ($\lambda = 514.5$ nm). As a result, the grating spacing increases as the angle θ decreases. It is well known that the fringe visibility of an interference pattern is higher for a larger spacing. Consequently, the results shown in Fig. 5 that the diffraction efficiency has a higher peak (at ~ 3 s), and a higher saturation value after the photopolymerization has cured is reasonable. Furthermore, with a higher peak, we should expect that the time required for the thermal grating to be offset by the photopolymerization grating would be longer. It is reasonable, since the samples were cured under the same intensity. The polymerization rate is assumed to be constant.

Figure 7 shows the variation of the diffraction efficiency with respect to the curing time for various LC contents. Films having LC contents less than 30 wt % resulted in no phase separation and the features of the dynamical diffraction are similar to those shown in Fig. 5. However, once the LC content is higher than 35 wt %, the thermal grating effect is rapidly quenched by the diffusions of both LC and monomer molecules as explained above in Fig. 4 due to phase separation. It is seen, therefore, that the peak appearing in the early time of Fig. 5 is not evident for these films. Formation

of liquid crystal domains begins during this period. It causes the rapid increase of the diffraction efficiency starting at $\sim t = 3$ s. When the domains grow to have diameters comparable to the probing light wavelength, they scatter light effectively. The diffraction efficiency starts to decrease at this moment. This can be understood by comparing Fig. 7 with Fig. 2. The onset for the transmission to decrease in Fig. 2 occurs at the same time as when the LC droplets have formed and start to scatter light effectively. Qualitatively, the onset time for a sample having the same LC concentration shown in Fig. 2 is comparable to that shown in Fig. 7 at which the diffraction efficiency starts to decrease.

Although the observed thermal grating is dominant in nonphase separated structures as in the present system shown in Fig. 7, it would not be the case if the used LC-polymer mixture were too viscous. In such a case, the thermal grating effect would not be rapidly quenched by the diffusions of both LC and monomer molecules even if the mixture had enough LC to impart macrophase separation. As a result, the thermal grating would still be observable in phase-separated structures. The observation of the thermal grating implies that the separation of the mixture into periodic LC domains between polymer planes would be poor. The final grating would, thus, diffract poorly.

In conclusion, we have studied both the phase separation and dynamical behavior of the gratings formed in E7/NOA65/Rose Bengal dispersion films. The results show that phase separation occurs in films having a LC content greater than ~ 32 wt %. The dynamical change of the first-order diffraction efficiency for films having LC contents below the value (32 wt %) can be appropriately explained by competition between the thermal grating and the grating due to photopolymerization. The thermal grating is quenched by the diffusive motion of both LC and monomer molecules in films having LC contents above ~ 32 wt % due to the equalization of their chemical potentials over the writing area. The diffraction efficiency of these films increases rapidly after a short induction period, and then decreases. The cause of the decrease is due to strong light scattering from the LC domains which have formed. This result is supported by the phase separation processes observed in the sample.

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