Fabrication of Electrically Switchable Bragg Gratings of The Transmission Mode From Holographic Polymer Dispersed Liquid Crystals

Kyungjin Kim, Byungkyu Kim, Youngsoo Kang and Juseog Jang

Abstract - Holographic transmission gratings were performed by an Ar-laser(λ=514nm) curing of a multifunctional acrylate monomer mixed with the liquid crystal (LC) mixture E7 in addition to octanoic acid, and the surfactant which acted on reducing the surface anchoring of the LC droplet with the polymer surface. Major difference in diffraction efficiency depends on the optimized grating formation caused by the balance between photopolymerization kinetics and phase separation of the LC determined by the change of Ar-laser (λ=514nm) intensity, the ratio of LC contents to the surfactant. The addition of the surfactant to the LC and pre-polymer systems causes the droplet to maintain the ideal size at the high fraction(over 40wt%) of the LC contents that induce the films to be fabricated with high diffraction efficiency than that of no surfactant series. The image of these films was examined using a charge coupled device (CCD). We also studied the angular selectivity plots which support the important role in the multiplexer channel (MUX). Eventually, we showed the reconstructive optical image recorded in this transmission mode of HPDLCs.

Keywords - HPDLC, Bragg grating, Image storage.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are thin composite films composed of micron-sized droplets of low-molecular weight liquid crystals (LCs) of typically positive dielectric anisotropy dispersed on an optically isotropic polymer matrix[1-5]. They have many potential device applications in displays and optical shutters due to their interesting electro-optical properties. A number of important reviews regarding the methods of preparation, materials, modes of operation, device applications, etc., have become available[6-9]. By applying an external electric field, PDLC films can be switched between light scattering in the absence of an external field and light transparent states in the presence of the external field.

Recently, volume holography techniques have been applied to the PDLC and fabricated the controlled architectures of phase separated LC domains[10-16]. This type of PDLCs is called holographic polymer dispersed liquid crystals (HPDLCs) in literature[15]. HPDLCs lead to several interesting potential applications. For example, LC birefringence optical switches and hologram LC combinations have been proposed for reconfigurable optical computing[17], and for beam steering in a laser radar[18]. Also LC dynamic holographic gratings have been explored as an approach to volume optical data storage[19]. This HPDLC has many advantages of modulating the refractive index, competitive price, wavelength selectivity, and ability for external modulation in volume hologram applications. The dispersion of the LC droplets in the polymer matrix is often generated by polymerization induced phase separation (PIPS) where the prepolymer and the LC are mixed together and then polymerization is induced photochemically. At some point in time after illuminating at a sample, the LC molecules are separated as the progressing of polymerization reaction, and diffused out of the polymer lamellae to form LC lamellae. Consequently, periodic lamellae of LC domains separated by polymer walls are fabricated. These periodic structures of multi-layers have very promising optical properties since a specific component of the incident light is refracted by the LC droplets due to the difference in the refractive indices of the polymers and LCs.

The diffraction efficiency of the resulting hologram can be controlled by applying an electric filed across an HPDLC cell. For the lowering of the switching field and improvement in the optical quality, Nartarajan added a surfactant-like long chain alkyl fatty acid in both transmission and reflection gratings[18]. The addition of octanoic acid is likely to reduce the surface anchoring of the nematic droplet with the polymer surface and to

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increase the electrical conductivity of the cell, which favors the lowering of the switching field. The role of the surfactant is the well-dispersion of droplet in the matrix. The spreading coefficient (λ_{31}) (Eq. 1) is given below:.

$$\lambda_{31}=\gamma_{12}-\gamma_{32}-\gamma_{13} \qquad (1)$$

where γ is the anchoring strength between components 1 & 2. When λ_{31} is larger than zero, component 3 spreads on 1 in matrix 2. But, When λ_{31} is smaller than zero, dispersed phases remain separately.

We fabricated the transmission of holographic PDLCs as a function of film composition, surfactant addition and irradiation intensity. We measured the diffraction efficiency and angular selectivity data, that is, the change of the restoration image by rotating the sample per 0.5 (θ) from Bragg' s angle. Three dimensional plots of diffraction efficiency-LC contents-laser intensities are presented showing contours for maximum diffractions. The hologram of a coin recorded in an HPDLC film is shown thorough digital and CCD Cameras.

2. Experimental

We used the following materials for this experiment[20, 21]. An eutectic mixture of four cyanobiphenyl and cyanoterphenyl mixtures with T_{KN}=-10℃, T_{NI}=60.5℃, $\varepsilon_{\parallel}$ =19.0, and $\varepsilon_{\perp}$=4.2 (E7, Merck) was used as the LC. Two types of photopolymerizable monomers (Fig. 1), viz., trimethylol propane triacrylate (TMPTA, f=3) and N-vinylpyrrollidone (NVP, f=1), have been used, in appropriate combinations, to prepare the host polymers upon laser irradiation. TMPTA has high reactivity as well as high viscosity due to its high molecular weight and provides the polymers with extensive crosslinkings, whereas monofunctional NVP simply extends the chains at a much lower rate. However, the use of monofunctional monomers is often essential to reduce the viscosity of the LC/monomer mixture and make the starting mixture homogeneous. Otherwise, polymerization induced phase separation starts with a heterogeneous reaction mixture and the morphology of the composite film becomes out of control. A dye, Rose Bengal, was used as a photo initiator for holographic recording with the Ar-ion laser, as it displays a broad absorption spectrum with a peak molar extension coefficient of ~$10^4M^{-1}cm^{-1}$ at about 490nm[11]. To this, a millimolar amount of N-phenyl-gycine (NPG) was added as coinitiator. In this experiment 3×10^{-6}M of RB and 1.2×10^{-4}M of NPG were used. Basic formulations of our binary (TMPTA/NVP) system is given in Table 1.

Gratings were formulated with different film compositions (monomers/LC) which were irradiated at various laser intensity. Monomer composition was fixed at TMPTA/NVP=8/1 by weight and the effects of film composition and irradiation intensity were examined.

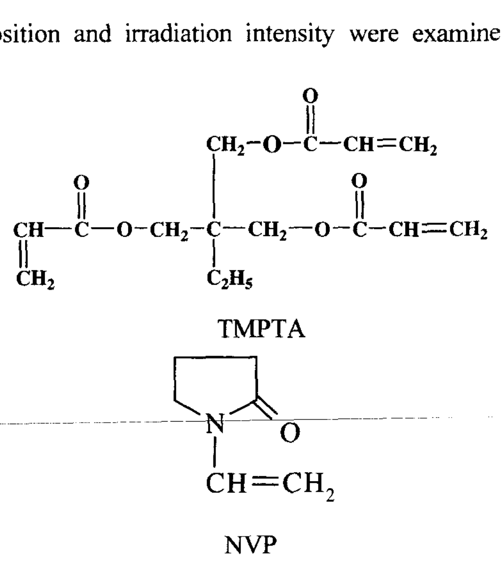


Fig. 1 Chemical structures of photopolymerizable monomers.

The holographic recording system is schematically shown in Fig. 2. An Ar-ion laser (λ=514nm) was used as a light source. Beams passe through a spatial filter, a beam expander, and are splitted in two beams of identical intensity. These two beams are subsequently passed through a collimator and only the central portion was reflected from the mirrors and impinged normally on the cell from the same sides. The cell was constructed by sandwiching the monomers/LC mixture between two indium tin-oxide (ITO) coated glass plates, with a gap of 10㎛ adjusted by a bead spacer. The interference of the two beams established the periodic interference pattern according to Bragg's law, which is approximately 514nm in our case. Laser intensity varied from 30 to 70mW/cm^2, with exposure times of typically 30s to 120s.

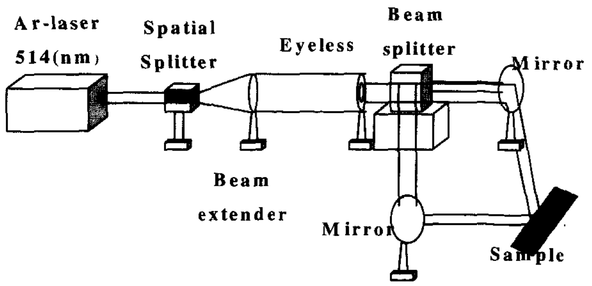


Fig. 2 Experimental setup for transmission mode HPDLCs.

Table 1 Formulation to prepare HPDLCs

TMPTA: NVP(wt%)	LC Contents (wt%)	RB (wt%)	NPG (wt%)	Cell Gap (㎛)	Surfactant (wt%)	Intensity (mW/cm^2)
8:1	25	0.3	1.8	10	4	30
	30					50
	35					70
	40					
	45					
	50					

We have briefly studied the image storage of these HPDLC gratings. For the reconstruction of virtual images, we used a digital camera. The holographic image of a coin was captured with a CCD camera and digititalized. We have also shown the change of the restoration image in proportion to mismatches of Bragg's angles.

3. Results and Discussion

Examples of peak diffraction efficiency and angular selectivity obtained with these transmission type HPDLC gratings are shown in Fig. 3. It shows the angular selectivity of the composite film having the ratio of 35% LC in syrup. According to Kogelnik's couple wave theory[22], diffraction efficiency is given by:

$$\eta = \sin^2(\nu^2+\xi^2)^{1/2}/(1+\xi^2+\nu^2) \qquad (2)$$

where $\nu = \pi n_1 L/\lambda \cos\theta$ and $\xi = \pi L \Delta\theta \sin^2\theta_B/\lambda \cos\theta$. L is the physical thickness of the grating, n is an average refractive index, n_1 is the amplitude of the index modulation, λ is wavelength, θ is the angle of incidence in the sample, and $\Delta\theta = \theta - \theta_B$ is the deviation from the Bragg angle θ_B. The line in Fig. 3 is a curve fit of the data to Eq.(2), assuming n=1.4388 and using Snell's law to correct for the angle of incidence in the sample. We note that the agreement between theory and experiment is remarkably good even though the index modulation is not strictly matched. A small deviation from the couple-wave theory is probably due to the Fresnel reflection at the cell. The sample thickness L was 10㎛, and the index modulation fit parameter n_1 for λ=514nm is 2.82×10^{-3} are shown in Fig. 3. Hence, there is relatively good numerical agreement between independent measurements of the samples, and we conclude that these ratings are well described by the couple-wave theory.

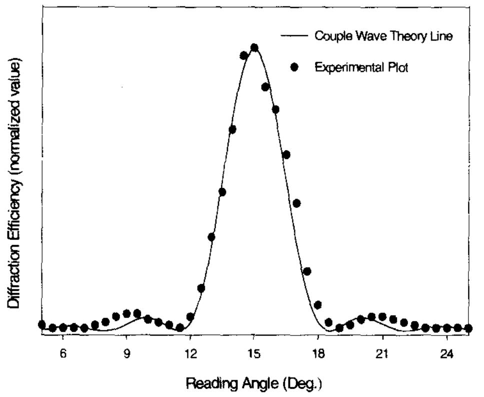
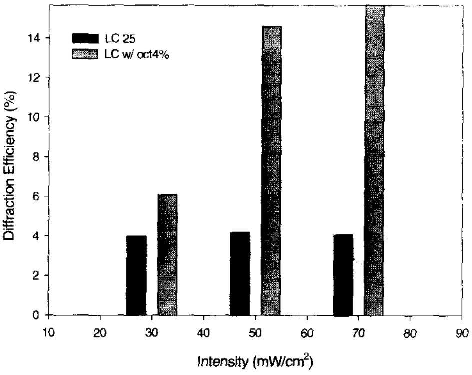
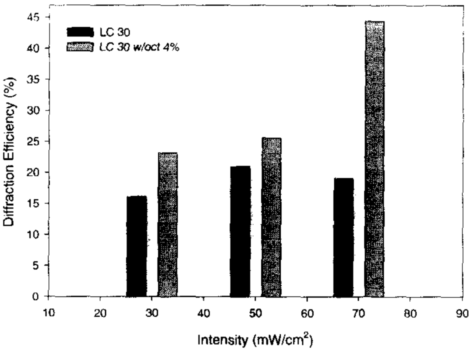


Fig. 3 Angular selectivity plots for HPDLCs written at 514nm.

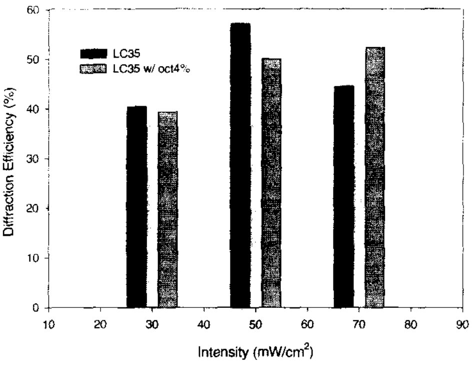
Fig. 4 shows the diffraction efficiency of composite films having various LC contents which were irradiated at various laser powers with or without the surfactant (octanoic acid 4wt%). Before analyzing the data, we should refer to the spreading coefficient (λ_{31}) which determines the morphology in the 3 component system (Eq. 1). When λ_{31} is larger than zero, component 3 spreads on 1 in matrix 2. But, when λ_{31} is negative, dispersed phases remain separately. The surface anchoring strengths play an important role in determining droplet sizes and driving voltage as well as diffraction efficiency in HPDLC films. In our system, component 1 is the LC (E7), component 2 is TMPTA, and component 3 is octanoic acid (OA). When OA is added to the mixture of TMPTA and E7, it is distributed between the monomer and the LC mixture (OA would be equally immmisible with E7 and TMPTA). As polymerization proceeds, the relative miscibility of OA with E7 increases compared to that with TMPTA, thereby OA molecules encapsulate the LC droplets. As OA acts as a surfactant, even the addition of a small fraction of OA can lead to a significant change in the electro-optical properties[23]. Generally, the diffraction efficiency with OA is higher than other. This implies that the decrease in droplet sizes would account for a decrease in scattering as is observed in volume holograms[24]. These facts shows a positive proof over 40wt% of the LC. The addition of the surfactant to the LC and prepolymer systems causes the droplet to maintain the ideal size at high fraction (over 40wt%) of the LC



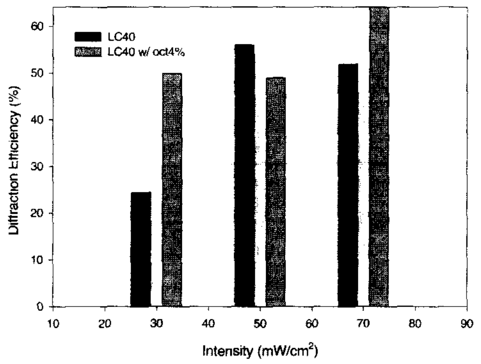
(a) LC 25wt%



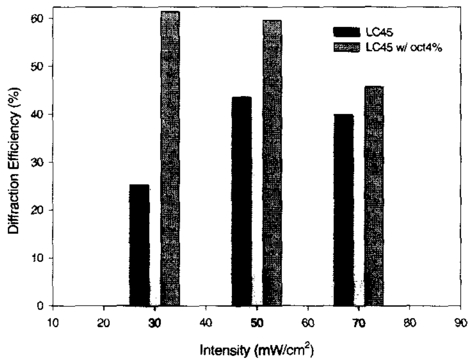
(b) LC 30wt%



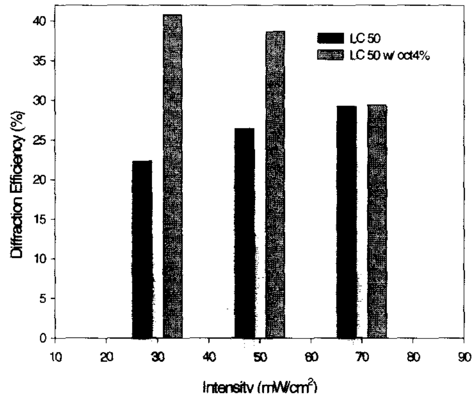
(c) LC 35wt%



(d) LC 40wt%



(e) LC 45wt%

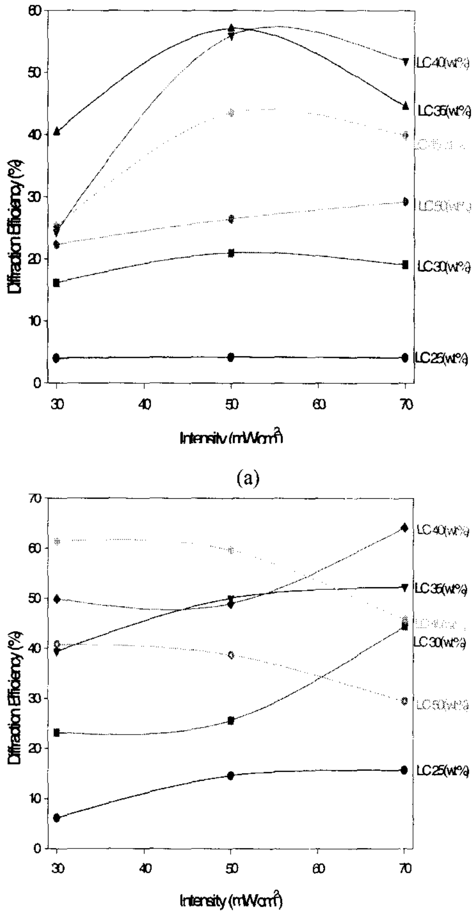


(f) LC 50wt%

Fig. 4 Diffraction efficiency vs. laser intensity of HPDLC films prepared with various LC ratios.

that induces the films to be fabricated with higher diffraction efficiency as compared with no surfactant.

The diffraction efficiency-irradiation power relationships are shown in Fig. 5. From the plot, it is visualized that the contour for the maximum refraction efficiency is generally shown at 50mW/cm^2. This implies that polymerization rate should be neither too high nor too low to augment the diffraction efficiency. Only at controllable polymerization rate, rate of phase separation is comparable with rate of polymerization and hence the domain size is appropriately small and its density is high enough to give the diffraction maximum. Also, as LC contents are increased by 40wt%, droplet coalescence forms larger domains allowing scatterings, instead of regular diffraction by gratings. Fig. 5 (b) shows monotonic increase of diffraction with irradiation power. The surfactant helps the droplet maintain the ideal size by protecting droplet coalescence at the high fraction of LC, leading to high diffraction efficiency at high LC fraction and small size of the LC. So this system gives high diffraction efficiency compared with no surfactant series (Fig. 5 (a)) at the high LC fraction (over 40wt%).

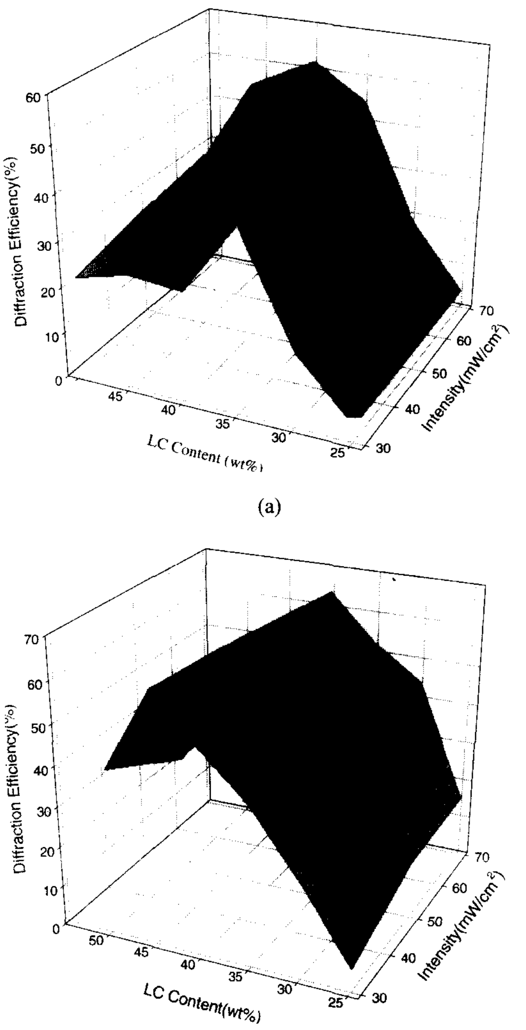


(a)

(b)

Fig. 5 Diffraction efficiency vs. LC ratio of HPDLC films irradiated at various laser intensity and octanoic acid added or not.

The diffraction efficiency-LC ratio-irradiation intensity relationships are plotted in three dimensional forms in Fig. 6. This plot shows that maximum diffraction efficiency depends on film composition and laser intensity. In Fig. 6 (a), maximum diffraction efficiency moves from low LC contents (25wt%) at low irradiation efficiency (30mW/cm^2) to high LC contents (40wt%) at intermediate adequate efficiency (50mW/cm^2). At Fig. 6 (b), the maximum diffraction efficiency moves from low LC contents (25wt%) at low irradiation efficiency (30mW/cm^2) to high LC contents (40wt%) at high irradiation efficiency (70mW/cm^2). Only at a controllable polymerization rate, the rate of phase separation and the adaptable surfactant make domain sizes maintain an appropriately small and high density state.

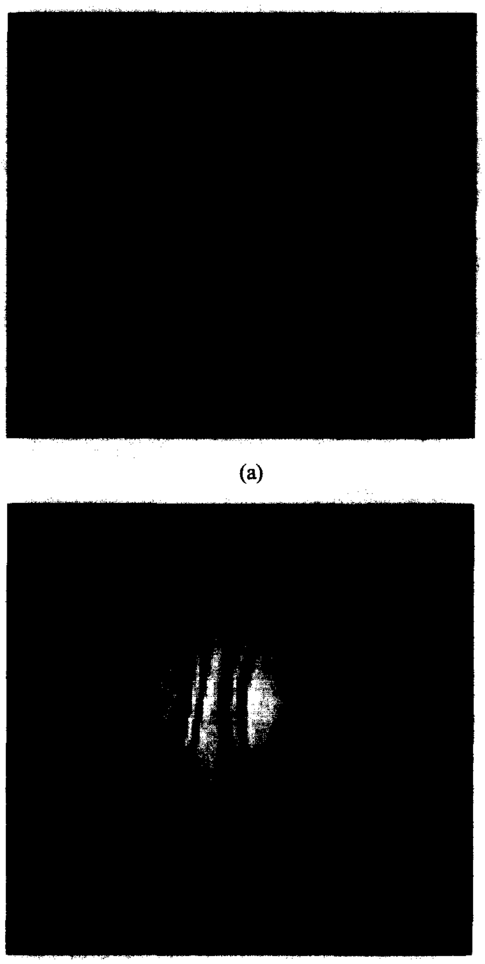


(a)

(b)

Fig. 6 Diffraction efficiency-LC ratio-laser intensity relationships of HPDLC films.

Fig. 7 shows photograph showing the virtual images of a coin recorded in HPDLC films.



(a)

(b)

Fig. 7 Photographs showing the virtual image of a coin recorded in HPDLC films through a digital camera (a) and a CCD camera (b).

4. Conclusion

Holographic grating images were successfully fabricated using the Ar-ion laser and multifunctional monomer mixtures, evidenced by photographs from digital and CCD cameras. Diffraction efficiency measurements indicated that proper LC contents, irradiation power and an appropriate surfactant are essential to make satisfactory gratings.

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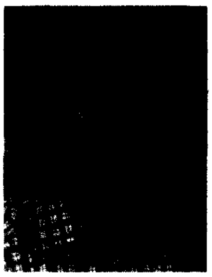

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