# Switchable Holographic Polymer Dispersed Liquid Crystals for Full Color-Reflective Display

Younghee Cho, Byungkyu Kim and Jaechang Kim

**Abstract** - Reflective holographic polymer dispersed liquid crystal(HPDLC) device has a multilayer structure consisting of alternate layers of polymer and liquid crystal droplets. Periodic modulation of a refractive index reflects light of a specific wavelength in accordance with Braggs law. Samples cured isotropically were illuminated with an Argon-ion laser at 514nm. We optimized the reflection efficiency of HPDLC as a function of monomer functionality, LC composition and irradiation intensity. The properties of the HPDLC films were observed by UV-visible spectroscopy. We found that the maximum reflection efficiency depends on the monomer functionality, LC composition, and laser intensity. We expect these films could be used in full-color reflective display by stacking them to obtain a mixture of colors.

## 1. Introduction

Much attention has been focused on polymer dispersed liquid crystals (PDLCs) as novel materials for various flat display devices. PDLCs composed of micron-sized droplets of liquid crystals (LCs) are embedded in a polymer matrix[1-7].

In recent years, holography techniques have been introduced for the preparation of PDLCs[8-15]. Volume holographic polymer dispersed liquid crystals (HPDLCs) have been investigated for numerous applications, including optical data storage, diffraction optics, and various optical interfaces and interconnects. HPDLCs possess advantages over conventional surface relief gratings in combining high diffraction efficiency with narrow band wavelength and angle selectivity. The formation of both transmission and reflection gratings in photopolymers cured using a fringe pattern (a periodic intensity profile) has been demonstrated to be a visible approach to form volume gratings. Especially reflection gratings can be used for reflective liquid crystal displays which are expected to be used in portable information devices because of their low power consumption. Thus, we have developed a new optical device that can electrically control reflection intensity at specific wavelengths without using a polarizer, a color filter or a dichroic mirror.

The conventional PDLC makes use of light scatterings in the absence of an external field and light transmittance in the presence of the external field. Therefore, it is imperative that the droplet size be the order of micrometers with certain size distribution so that the broad spectrum of visible-range lights can scatter and the interfaces under power off to make the film white [16-19]. But an HPDLC device has a multi layer structure consisting of alternate layers of plymers and luquid crystal droplets. The periodic modulation of a refractive index usually reflects the light of a specific wavelength (for example, grating spacing of 488nm reflects blue) in accordance with Bragg's law (Eq. 1) given below.

$$d=\frac{\lambda}{2\sin\theta} \tag{1}$$

where $\lambda$ is the wavelength of the light, d is grating spacing, and $2\theta$ is the interbeam angle outside the film.

Optical alignments to control the grating spacing using the same wavelength laser are available[20]. The interference fringe of laser irradiation onto and LC/monomer mixture sets up a periodic intensity profile, which in turn causes a periodic spatial modulation of polymerization kinetics[11]. LC molecules are phase separated with the progress of polymerization reaction, and diffused out of the polymer lamellae to form LC domains, which ideally are also macroscopically lamellae. Consequently, periodic lamellae of LC domains separated by polymer walls are fabricated. A full color display can ideally be constructed by stacking three different elements, each reflecting one primary color, respectively[20]. Upon applying the electric field, the refractive index of LCs matches that of polymers, and all components of the incident light pass through the film and the film becomes transparent.

We attempted to maximize the reflection efficiency of the holographic PDLC device. Different monomer functionality and film compositions have been irradiated with an Ar-ion( $\lambda$ =514nm) laser at various intensity.

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UV-visible spectra were taken to obtain the architecture reflections from gratings.

## 2. Experimental

### 2.1 Materials

E7 (BL001, Merck) used as a liquid crystal of a nematic type is composed of mixtures of four cyanobiphenyl and cyanoterphenyl compounds with $T_{KI}$=-10℃, $T_{NI}$=60.5℃, $\varepsilon_{\parallel}$=19.0, and $\varepsilon_{\perp}$=4.2.

Four types of photopolymerizable monomers viz., dipentaerythritol hydroxy penta acrylate (DPHPA, functionality(f)=5, trimethylolpropanetriacrylate (TMPTA, f=3), tripropanglycol diacrylate (TPGDA, f=2), and N-vinylpyrrollidone (NVP, f=1) have, in appropriate combinations, been used to prepare the host polymers upon laser irradiation. DPHPA has much higher reactivity as well as high viscosity due to its high molecular weight and provides the polymers with extensive crosslinkings, whereas low multifunctional monomers (TMPTA, TPGDA) and a monofunctional monomer (NVP) simply reduce the viscosity of the LC/monomer mixture and form a homogeneous syrup.

The initiator and co-initiator chosen in this work for holographic recording with the Ar-ion laser were Rose Bengal (RB, TCI) and N-phenylglycine (NPG, TCI), respectively. RB is excited by the light source and then NPG is activated by RB, and a radical for photopolymerization is generated.

### 2.2 Formulations

Holograms were formulated with various laser intensity and film composition (LC/monomer mixture composition) at different monomer functionality (DPHPA/TMPTA, TPGDA, NVP). For green gratings, the formulation of various laser intensity and different monomer functionality at a fixed LC content (35wt%) is given in Table 1. And for red gratings, the formulation of various film composition and different monomer functionality at fixed laser intensity (300mW/cm$^2$) is given in Table 2. The effects of monomer functionality, laser intensity, and film composition were studied with regard to reflection efficiency.

**Table 1** Formulation to prepare HPDLCs for green gratings

| Monomer Ratio | LC Contents (wt%) | RB (wt%) | NPG (wt%) | Laser Intensity (mW/cm$^2$) | Spacer ($\mu$m) |
|---|---|---|---|---|---|
| DPHPA:TMPTA<br>DPHPA:TPGDA<br>DPHPA:NVP<br>=8:1 | 35 | 0.3 | 1.8 | 50<br>100<br>150<br>175<br>200 | 20 |

**Table 2** Formulation to Prepare HPDLC for Red Gratings

| Monomer Ratio | LC Contents (wt%) | RB (wt%) | NPG (wt%) | Laser Intensity (mW/cm$^2$) | Spacer ($\mu$m) |
|---|---|---|---|---|---|
| DPHPA:TMPTA<br>DPHPA:TPGDA<br>DPHPA:NVP<br>=8:1 | 25<br>30<br>35<br>40<br>45 | 0.3 | 1.8 | 300 | 20 |

### 2.3 Gratings

The holographic recording system is schematically shown in Fig. 1. An Ar-ion laser(=514nm) was used as a light source. Beams pass through a spatial filter, a beam expander, and are splitted into two with equal intensity. These two beams are subsequently passed through a collimator and only the central portions of the beams was reflected from the mirrors and impinged normally on the cell from the opposite sides. These two beams produce interference fringes, whose period depends on the cross angle($2\theta$) of the two beams (Fig. 2).

In our case, for green gratings, $\theta$ was fixed at 90° and for red gratings, $\theta$ was calculated using Bragg's law and Snell's law. This periodic modulation of polymers and LC layers generates reflection at a specific wavelength because the refractive index of LCs is different from that of the polymer. And hence the reflection intensity is electrically controlled.

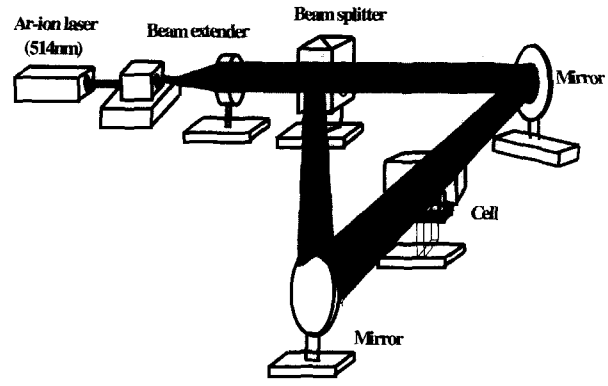


**Fig. 1** Experimental setup for a holographic PDLC film.

The cell was constructed by sandwiching the LC/monomer mixture between two indium tin-oxide (ITO) coated glass plates, with a gap of 20$\mu$m adjusted by a bead spacer[21]. The interference of the

two beams established the periodic interference pattern according to Bragg's law which is approximately 514nm for the green mode and 633nm for the red mode. Laser intensity varied 50~350mW/cm$^2$ with exposure time of typically 30~120s.

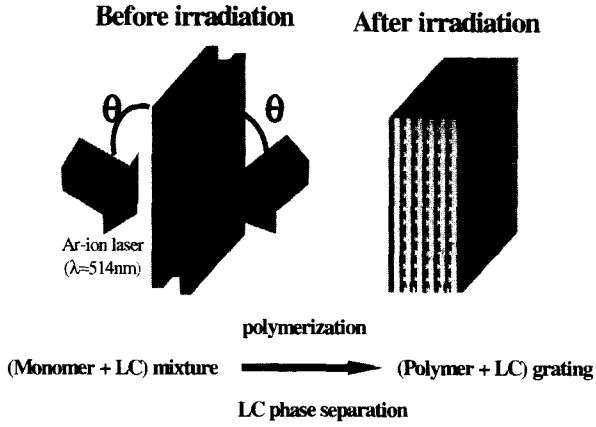


**Fig. 2** Fabrication method for a holographic PDLC film.

### 2.4 Measurement

The reflection of a specific wavelength by an HPDLC film was analyzed using a UV-visible spectrometer (Perkin Elmer, Lambda 20). Reflection efficiency was estimated from the spectrum data.

## 3. Results & Discussion

### 3.1 Effects of laser intensity an monomer functionality (for green gratings)

Fig. 3 shows the UV-visible spectra of the films to confirm the reflection by holographic gratings. Strong absorption peaks at about 490nm confirm the formation of green gratings, i.e., lights of 490nm wavelength are reflected and the other components of the light pass the HPDLC films. However, the grating spacing of the film (490nm) is slightly smaller than the Bragg spacing (514nm), due presumably to the shrinkage of mixture volume upon the polymerization of monomers. The broad absorption peaks at about 560nm are the peaks by Rose Bengal. In Fig. 3 (a) and 3 (b), namely, at low average monomer functionality (DPHPA/NVP, TPGDA=8/1), the reflection peak at 490nm generally increased with the increase in laser intensity. At high monomer average functionality (DPHPA/TMPTA =8/1) (Fig. 3 (c)), maximum reflection is shown at 175mW/cm$^2$.

Generally, neat reflection efficiency is obtained when the LC droplet size is small and droplet density is high[22]. Therefore, in our study, laser intensity should be high enough for phase separation leading to high droplet density in low average monomer functionality. However, in Fig. 3 (c), there exists proper irradiation intensity for polymer-LC phase separation, because when the polymerization rate is too fast, phase separation cannot take place in a laboratory time scale.

The reflection efficiency-functionality of the monomer mixture-laser intensity relationship is plotted in a three dimensional form in Fig. 4. This plot shows that maximum reflection efficiency depends on monomer functionality and laser intensity. The reflection efficiency of higher average monomer functionality was smaller than that of lower one at all laser intensity. Namely, reflection efficiency monotonically decreased with increasing monomer functionality (NVP<TPGDA<TMPTA). It seems that when the polymerization rate is too fast with high functionality monomers, the rate of phase separation cannot follow the rate of network formation and LC domains remain with a highly viscous host polymer matrix, and this also retards phase separation leading to small LC droplet density. The polymerization rate should neither be too high nor too low to augment reflection efficiency. Only at a controllable polymerization rate, the rate of phase separation is comparable with the rate of polymerization and the domain size is appropriately small and its density is high enough to reflect the maximum.

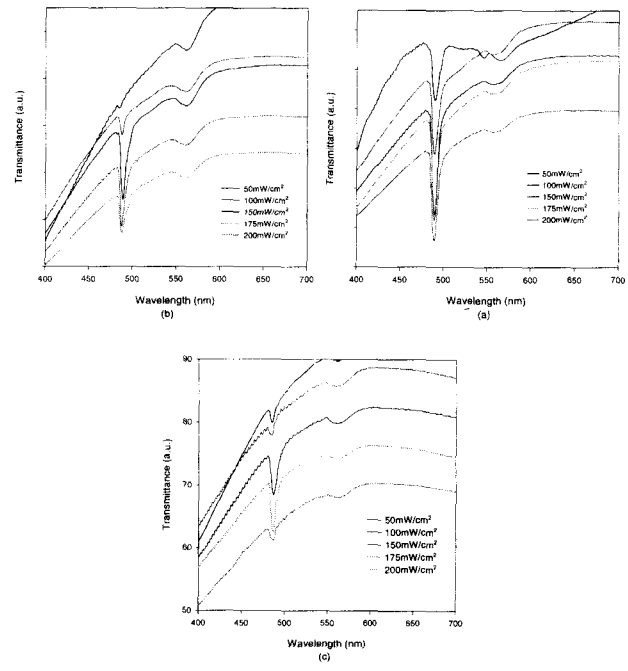


**Fig. 3** UV-visible spectra vs. irradiation power intensity: (a) DPHPA:NVP=8:1, (b) DPHPA:TPGDA=8:1, (c) DPHPA:TMPTA=8:1 (LC content=35wt%).

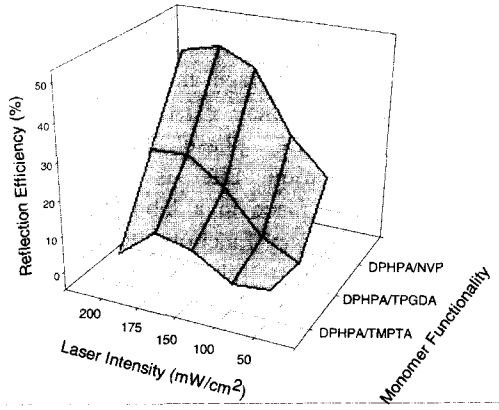


**Fig. 4** Reflection efficiency-monomer functionality-laser intensity (LC contents=35wt%).

### 3.1 Effects of LC contents (for red gratings)

Fig. 5 shows the UV-visible spectra (a) and reflection efficiency (b) of the composite films having various LC contents which were irradiated at 300mW/cm$^2$. The peak is found at about 610nm, corresponding to the reflection by holographic red gratings. As mentioned above, the red grating spacing (610nm) is slightly smaller than the Bragg spacing (633nm), presumably because of the shrinkage of the mixture upon polymerization. At the LC content of 35wt%, peak intensity was the maximum with the given monomer ratio (DPHPA/ NVP = 8/1). This means that the LC content of 35wt% has proper LC-polymer phase separation where the domain size is presumably small and its density is high enough to reflect the maximum.

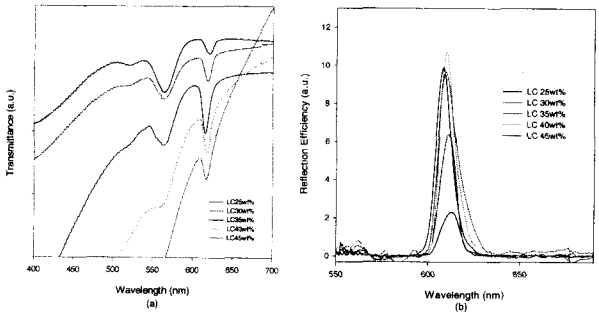


**Fig. 5** UV-visible spectra vs. LC contents (a), and reflection efficiency vs. LC contents (b) of DPHPA:NVP=8:1 composite films.

Fig. 6 shows the UV-visible spectra of different monomer functionality PDLC films with 35wt% of LC contents irradiated at 300mW/cm$^2$ laser power. Like the green grating system, the extent of peak intensity is in the increasing order of TMPTA<TPGDA<NVP. This is again due probably to the difficult phase separation at too fast a polymerization rate.

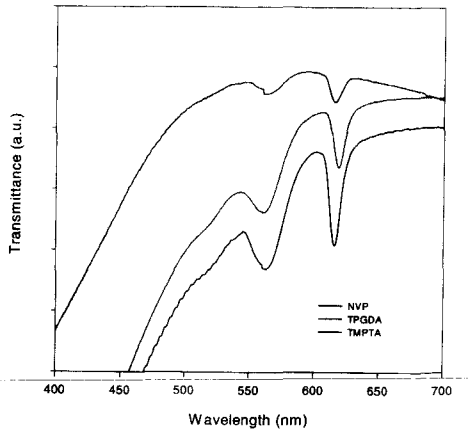


**Fig. 6** UV-visible spectra vs. monomer functionality (LC contents=35wt%, laser intensity: 300mW/cm$^2$).

Fig. 7 shows that an RGB reflection from a stack of HPDLC films (a) and the resulting UV-visible spectral response (b). A white light source was impinged on the stack of three films with an electric field off, and the corresponding absorption peaks, composed of 470nm, 490nm, and 610nm, each representing blue, green, and red gratings, are recorded (Fig. 7 b).

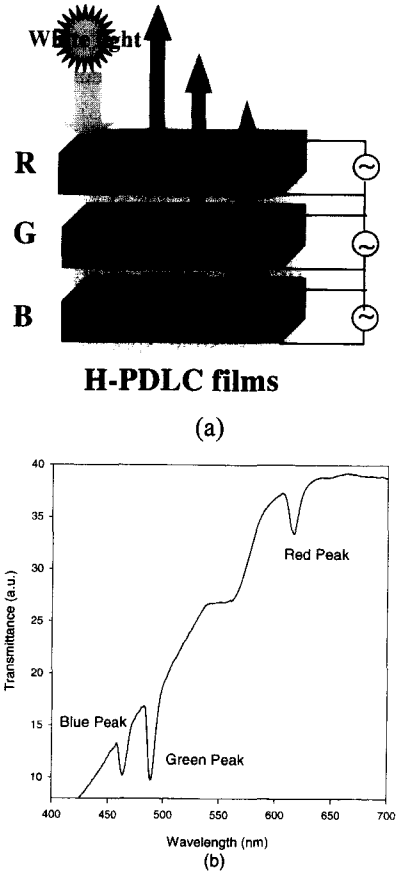


**Fig. 7** Stacking of RGB holographic PDLC films (a) and the UV-visible spectra of the stacked films (b).

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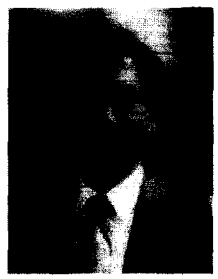

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