Monofunctional Monomer Effects of The Reflection Mode & Transmission Mode of Holographic Polymer Dispersed Liquid Crystals.

Minsang Park, Younghee Cho and Byungkyu Kim

Abstract - Holographic polymer dispersed liquid crystals (HPDLCs) have been fabricated by irradiating an Ar-ion laser (λ =514nm) at various intensity on LC/acrylate monomer mixtures which were sandwitched between two ITO coated glass plates. Monomer systems were composed of dipentaerythritol-hydroxy penta acrylate (DPHPA, f=5)/monofunctional acrylate = 5.5/1 by weight. N-vinyl-pyrrollidone (NVP), butyl-acrylate (BA), and 2-ethylhexyl-acrylate (2-EHA) have been used as monofunctional monomers. The LC used in this system was E7 (BL001, Merck).

Gratings were fabricated by periodic interference of twobeams. Reflection efficiency-irradiation intensity-monomer type relationships were obtained from the UV-visible spectra of the HPDLC films. Peaks were found at a bit smaller wavelength than 514nm, due to the shrinkage of mixture volume upon polymerization. Real time measurements of diffraction efficiency have been obtained according to monomer types and LC contents.

Keywords - holographic grating, HPDLCs, current density-voltage, diffraction efficiency, bandwidth

1. Introduction

Holographic polymer dispersed liquid crystals (HPDLCs) show potential for numerous electro-optic device applications including reflective flat panel displays, graphic art, switchable color filters, and optical interconnection although it was only until the early 1980s that a new class of electro-optical modulators (i.e.,display) could be created with polymer dispersed liquid crystal (PDLC) materials.[1-2]

Several aspects of PDLC film properties make them interesting for display applications ranging from direct driven smart window to active matrix driven information displays. A number of important reviews about PDLC viz., materials, the method of fabrication, properties, application, etc. have become available.[3-7] in lowering applied voltage and high-efficiency emission.

In PDLC systems formed by polymerization, once the LC droplet has phase separated, its growth is governed by the diffusion of LCs from the rapidly growing polymer region into the droplet. The droplet sizes and distributions are influenced by the diffusion rate of growing polymer but an isotropic distribution of LC droplet domains in a polymeric host results. So, several attempts to place LC domains spatially within these hosts have been reported.[8-9] Recently a volume holography technique has been applied to the PDLC.[10-15] This type of PDLC is called holographic PDLC (HPDLC). HPDLCs are used for many applications, and graphic art and security, laser eye protection filters, liquid crystal display system, optical interconnection, and holographic data storage.[16]

HPDLCs are prepared by causing interference between two coherent laser beams in a photosensitive monomer/liquid crystal mixture contained between two substrates coated with a conductive layer, typically of indium-tin oxide (ITO).[17] Intriguing features of this material include its high index modulation, true volume hologram character, unique anisotropic mature, and electro-optical behavior. It is the final morphology that determines the electro-optical properties.

In HPDLCs, phase separation of LCs occurs in anisotropic geometrics. Considerable experimental and theoretical work on anisotropic polymerization indicates that there is diffusion of monomers and other components consumed in the reaction toward the high-intensity region. This gives rise to spatial concentration gradients across a film and through the high intensity region.

The high molecular weight polymer chains and oligomers migrate more slowly than the monomers, which results in the high-intensity regions being polymer rich. Ignoring interactions among various components, the chemical potential of the ith component of a mixture is indicated by Eq. 1.

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$$\mu_i = \mu_i + kT\ l_n(N_i / N_j) \qquad \text{Eq.1}$$

where μ_i is the chemical potential of the pure *i*th component, N_i is the number of molecules of the *i*th component, j is the number of components, k is Boltzmanns constant, and T is absolute temperature. So, for monomer molecules, the chemical potential in the high-intensity region is over that in the low-intensity regions due to the consumption of monomer molecules. In this process, primary importance is the relationship between the rate of polymerization and the rate of LC diffusion. If the rate of polymerization greatly exceeds the diffusion rate, then less anisotropic distribution in the location of LC would be expected. If the rate of polymerization is slow enough, all the LCs can be expected to diffuse into the low-intensity region. But, in this case, phase separation doesn't occur well because LC local volume fraction decreases.[16] This means that anisotropy in the LC domain shape becomes less. We report the effect of the polymerization rate for various systems on the properties of HPDLCs.

Our goal in the present study was to find monofunctional monomers in the performance of HPDLCs. We also report the effects of laser intensity and LC contents on the fabrication and character-ization of holographic Bragg gratings in the HPDLCs.

2. Experimental

2.1 Materials

The selection of materials has a pronounced effect on the morphology and electro-optic properties of HPDLC films. Prepolymer syrups are typically a combination of a fast-curing multi-functional monomer, a reactive diluent, a photoinitiator dye, a coinitiator, and an LC. The photoinitiator requires good absorption at the writing wavelength of the laser and the ability to react with the coinitiator to produce a free radical.

So, in our experiments, we used Rose Bengal (RB, TCI) known as an ideal initiator for holographic recording with an Ar-ion laser as it displays a broad absorption spectrum with a peak molar extension coefficient of ~104 $M^{-1}cm^{-1}$ at about 490nm. To this, a millimolar amount of N-phenyl glycine (NPG, TCI) as a coinitiator was added. The initiation mechanism with RB and NPG by the Ar-ion laser is given in Fig. 1.[18]

RB undergoes an electron transfer reaction in which NPG functions as an electron donor, producing a NPG radical. Free-radical addition polymerization of multi-functional monomers leads to the formation of polymers of high molecular weight in a few seconds. Multifunctional acrylate monomers with functionality (f)4 are effective in this regard. We have used dipentaerythritol hydroxy pentaacrylate (DPHPA, Aldrich, f=5). DPHPA has much higher reactivity as well as high molecular weight.

Monofunctional monomers help to dissolve different compounds in the mixture and form a homogeneous syrup. It is also essential to reduce the viscosity of an LC/monomer mixture. NVP, 2-EHA, and BA have been used as mono-functional monomers.

The choice of the liquid crystal plays a very important role in the electro-optical performance and diffraction efficiency of the HPDLC. We have used E7 (BL001, Merck), an eutectic mixture of four cyanobiphenyl and a cyanoterphenyl mixture with T_{KN}=-10° C, T_{NI}=50.5° C, $\varepsilon_{\parallel}$ =19.0, and $\varepsilon_{\perp}$ = 4.2.

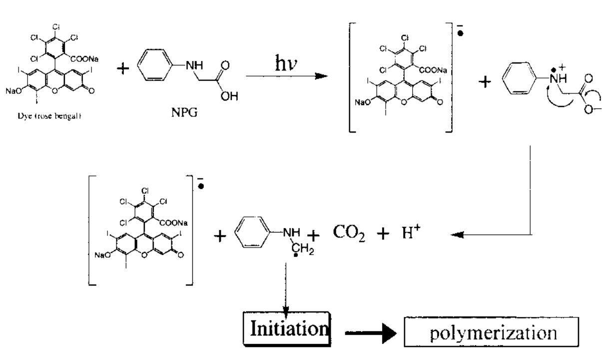


Fig. 1 Mechanism of initiation.

2.2 Experimental Setup

Holograms were formulated with different monomers which were irradiated at various laser intensity and LC contents. Basically, prepolymer composition has been fixed at DPHPA/Monofunctional monomer =5.5:1, RB=0.3wt%, and NPG=1.8wt%.

An Ar-ion laser (=514nm) was used as a light source. Beams pass through a spatial filter, a beam expender, and are splitted into two with identical intensity. These two beams are subsequently passed through a collimator and only the central portion of the beams was reflected from the mirrors and impinged on the cell from the opposite sides(reflection mode) or from the same sides (transmission mode).

The cell was constructed by sandwitching the LC/prepolymer mixture between two indium-tin-oxide (ITO) coated glass plates. This mixture was cured using the Ar-ion laser, and a spatial variation of intensity across the sample is generated.

The interference of the two beams established the periodic interference pattern according to Braggs law which is approximately 514nm. The reflection of a special peak (about 514nm) was analyzed by using the UV-visible spectrometer (Perkin Elmer, Lambda 20), and reflection efficiency is estimated at various intensity.

In the transmission mode, we measured diffraction efficiency and angle selectivity

2.3 Reflection-type HPDLC gratings

The reflection mode can be constructed when the reference and object beams traverse the LC/acrylate mixture from the opposite sides, as in Fig. 2 (a). If both beams are two-plan-wave, the resulting pattern can be visualized by lines. These lines are made by connecting constructive points. Polymer layers are formulated in these lines and LCs diffuse out of these lines according to the equilibrium of chemical potential. Fig. 2 (b) shows the formation of polymer and LC layers. We measured the reflection spectrum with UV-visible spectra.

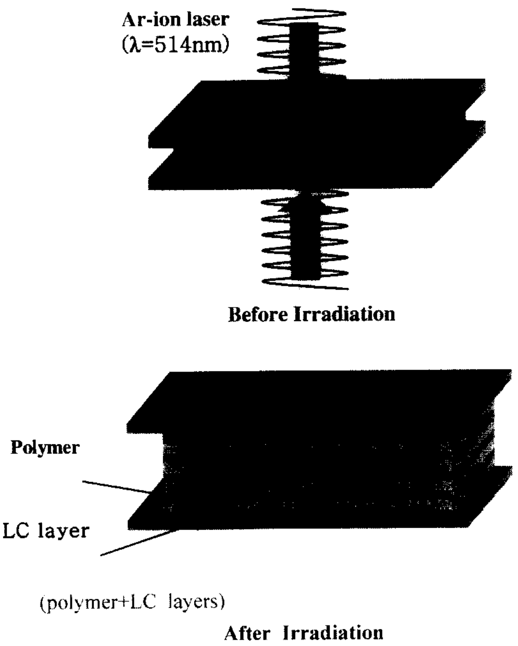


Fig. 2 Fabrication method for reflection-type HPDLC

2.4 Transmission-type HPDLC Gratings

Unlike the reflection mode, two beams, the reference beam and the object beam, should traverse the film from the same sides to fabricate the transmission mode. Fig. 3 shows the optical setup to measure the transmittance of the transmission mode HPDLC device. Samples were characterized for diffraction efficiency and angle selectivity using the Ar-ion laser (514nm) and the He-Ne laser (633nm).

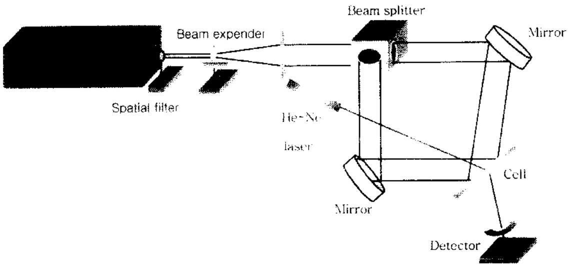
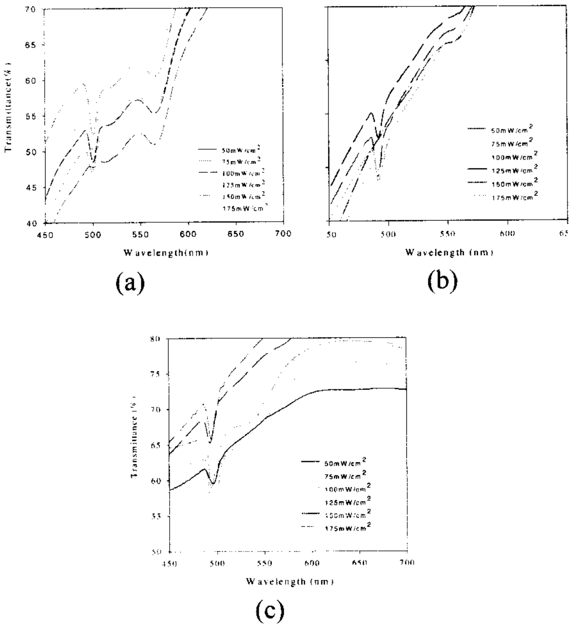


Fig. 3 Holographic recording and real time reading time optical experimental setup.

3. Results and Discussion

3.1 Measurement of UV-visible Spectra

Fig. 4 and Fig. 5 show the UV-visible spectra and reflection efficiency of the composite films having various monomer types which were irradiated at various laser intensity (50mW/cm^2~175mW/cm^2). In Fig. 3, (a), (b), and (c) are respective UV spectra for NVP, 2-EHA, and BA systems.



(a) (b)

(c)

Fig. 4 Irradiation intensity dependant UV-vis. spectra of HPDLC films for
(a) NVP (b) 2-EHA, and (c) BA (LC contents 35wt%).

With NVP, the maximum reflection efficiency is obtained at 75mW/cm^2, a relatively low irradiation power while compared with the almost monotonic increase of reflection efficiency with irradiation power for 2-EHA and BA. This implies that diffusing LC viscous media induced by fast reaction due to high irradiation power would be slow.

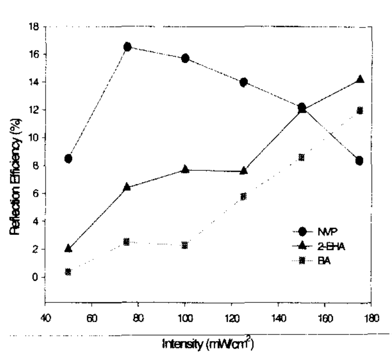


Fig. 5 Reflection efficiency vs. laser intensity of HPDLC films prepared with various monofunctional types.

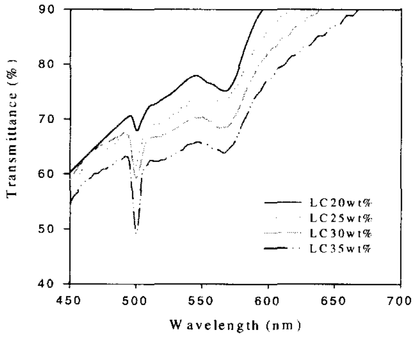


Fig. 6 LC contents dependent UV-vis. spectra of HPDLC for 2-EHA system.

Fig. 6 shows reflection efficiency as a function of LC contents for 2-EHA system at 175mW/cm^2. The peak intensity of higher LC contents is greater than that of lower ones indicating that intensity-LC contents relationship plays an important role in obtaining good Braggs grating.

3.2 Diffraction Efficiency (DE)

The laser beam is diffracted away from the zero order and first order. The diffracted beams are measured with the use of a power meter.

The diffraction efficiency as a function of time is given in Fig. 7, showing three main regions: (1) a short induction period; (2) a period of polymerization indicated by rapidly increasing diffraction efficiency; (3) a plateau where diffraction efficiency doesn't increase anymore.

The time of rapid rise in DE is involved with the growth and final development. We can see that DE goes high as the second period becomes short. The saturation time of these systems is decreasing as ordered by NVP>2-EHA>BA. This indicates that the rate of polymerization should go faster to obtain the higher efficiency for these conditions.

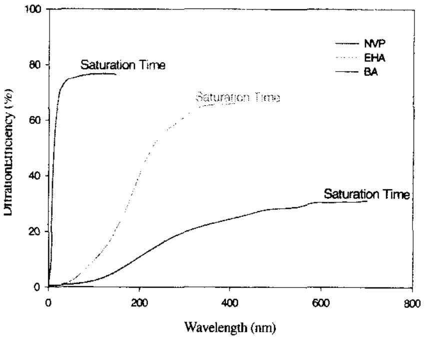


Fig. 7 Real time diffraction efficiency as a function of exposure time with the 633 He-Ne laser. Recording wavelength was 514nm (LC 35wt%, 40mW/cm^2).

3.3 Angle Selectivity

From the coupled wave theory[19], diffraction efficiency (DE) is given by Eq. 2.

$$\eta = \sin^2(\nu^2 + \varepsilon^2)^{1/2} / (1 + \zeta^2/\nu^2) \qquad \text{Eq. 2}$$

where $\nu = \pi n_1 L / \lambda \cos\theta$ and $\zeta = \pi n L \Delta\theta$. L is the physical thickness of grating, n is an average refractive index, n1 is the amplitude of the index modulation, 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. If the grating is read out of the Bragg condition, i.e., $\Delta\theta = 0$, then $\zeta = 0$ and Eq. 2 simplifies to $\eta = \sin^2\nu$.

In order to determine angle selectivity, we monitored the diffracted power as a function of the read out angle. A typical experimental angular DE response is presented in Fig. 8, which also shows the theoretically predicted response, calculated according to Eq. 2

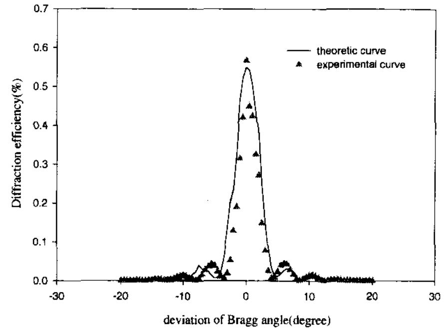


Fig. 8 Angular selectivity plots for HPDLC grating written at 514nm.

As shown in Fig. 8, an excellent fit to the theoretical curve is obtained, with the parameters used for the calculations as indicated. The holographic gratings of Fig. 9 are of the thickness volume type with an angular bandwidth of about 5. There is little difference of bandwidth from three other systems.

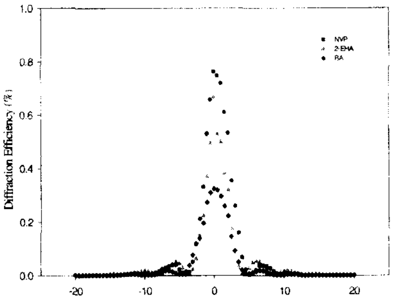


Fig. 9 Experimental curve for various monofunctional monomer systems.

4. CONCLUSION

In this work, we have presented the effects of monofunctional monomers. We find that monofunctional monomers play an important role in the electro-optic properties of HPDLC films. It is possible to improve Bragg gratings by controlling the rate of polymerization.

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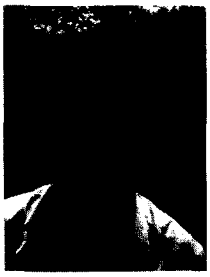

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