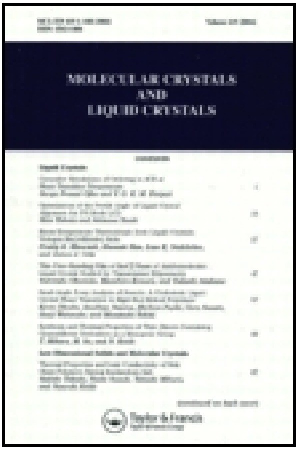

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Optimization of Holographic PDLC for Green

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Optimization of Holographic PDLC for Green

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Reflective holographic polymer dispersed liquid crystals(HPDLC) have been fabricated by irradiating Ar-ion laser(λ=514 nm) of various intensities on LC/monomer mixtures sandwiched between two ITO coated glass plates. Gratings were written for various monomer compositions and laser intensities. UV-visible spectra have been analyzed. Eventually, reflective efficiency-irradiation intensity-monomer composition relationships have been obtained.

Keywords: Holographic polymer dispersed liquid crystal; UV-visible

INTRODUCTION

Much attention has been focused on polymer dispersed liquid crystal(PDLC) as novel materials for various flat display devices. PDLCs are composed of micron-sized droplets of liquid crystal(LC) embedded in a polymer matrix[1-3]. Several aspects of PDLC films make them interesting for display applications[4,5]. PDLCs are able to modulate light under external electric field without the use of polarizers. PDLCs modulate light by controlling scattering effect at the interfaces between polymer and LC droplets.

PDLCs are made with several methods of preparation-solvent induced phase separation(SIPS), thermally induced phase separation(TIPS), and polymerization induced phase separation(PIPS)[6-9]. PIPS with ultra-violet irradiation is preferred over the SIPS and TIPS due to its simplicity and easiness of preparation.

In recent years, holographic technique is introduced for the preparation of PDLC[10-16]. Volume holographic polymer dispersed liquid crystals (HPDLC) have been investigated for numerous applications including optical data storage, diffractive optics, and various optical interfaces and interconnects. HPDLCs 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 viable approach to form volume gratings[17~20]. Especially, reflection grating can be used for reflective liquid crystal displays which are expected to be used in portable information devices because of their low power consumption[21,22].

Reflective HPDLC has been proposed for use in reflective color display devices[14]. HPDLC display devices that reflect three primary colors i.e., red(633nm), green(514nm), and blue(488nm) can be fabricated using three different wavelengths of Ar-ion and He-Ne lasers. A full color display can be constructed by stacking these three HPDLC devices, each reflecting one of the primary colors.

The fabrication process is the same as the recording process for a volume hologram, as shown in Figure 1. The mixtures of liquid crystal and photo-curable monomer are irradiated with two laser beams, which

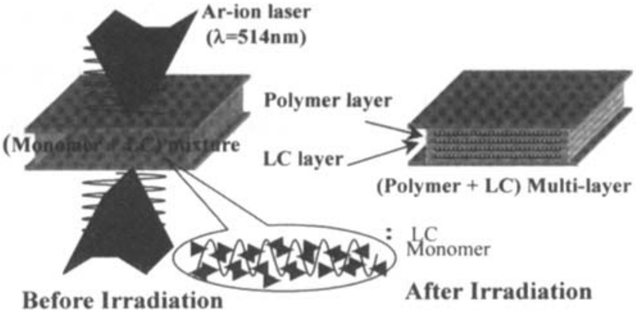

FIGURE 1 Fabrication method for holographic PDLC.

are in-line but with opposite directions. These two beams produce interference fringes, whose period depends on the cross angle of the two beams. The interference fringe peaks of the two laser beams form polymer-rich layers. This periodic modulation of polymer and LC layers generate reflection at a specific wavelength because the refractive index of LC(n_{LC}) is different from that of the polymer(n_p). And hence the reflection intensity is electrically controlled.

We optimized the reflection of holographic PDLC as a function of monomer composition and irradiation intensity. Binary monomer mixtures with different compositions have been irradiated with Ar-ion(514nm) laser at various intensities. UV-visible spectra were taken to obtain the architectured reflections from gratings. Three dimensional plots of reflection efficiency-laser intensity-monomer composition are presented showing contours for maximum reflections.

EXPERIMENTAL

Materials

The LC used in our experiments was E7(BL001, Merck), a eutectic mixture of four cyanobiphenyl and cyanoterphenyl mixture with T_{KN}=-10°C, T_{NI}=60.5°C, n_o=1.5216, and n_e=1.7462. Two types of photopolymerizable monomers viz. dipentaerythrol hydroxy penta acrylate(DPHPA, Aldrich,functionality(f)=5), and N-vinylpyrrolidinone (NVP, Aldrich, f=1) have in various combinations been used to prepare the host polymers upon laser irradiation. Multifunctional monomer viz. DPHPA has much higher reactivity as well as high viscosity due to their high molecular weight, and provide the polymers with extensive crosslinkings. On the other hand monofunctional monomer viz. NVP simply extends the chains at much lower rate. However, the use of monofunctional monomers is oftentimes essential to reduce the viscosity of LC/monomer mixture and make the starting mixture homogeneous. Otherwise, PIPS starts with heterogeneous reaction mixture and the morphology of the composite film becomes out of control.

Rose bengal(RB, TCI) is known as an ideal initiator for holographic recording with Ar-ion laser as it displays a broad absorption spectrum with a peak molar extension coefficient of ~$10^4 M^{-1} cm^{-1}$ at about 490nm[23]. To this, a millimolar amount of N-phenylgycine(NPG, TCI) as coinitiator was added. In this experiment 3×10^{-6}M of RB and 1.2×10^{-4}M of NPG were used. Chemical structures of monomers are given in Figure 2.

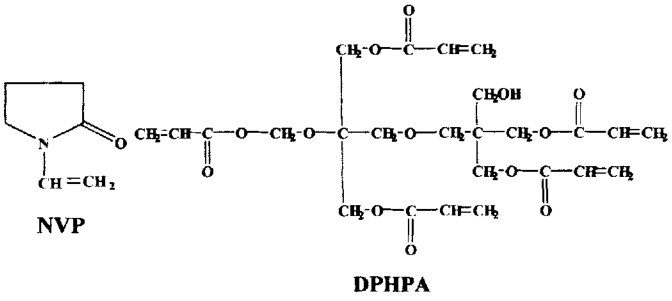

FIGURE 2 Chemical structures of photopolymerizable monomer.

Cell Preparation and Characterizations

Holograms were formulated with different monomer compositions which were irradiated by laser beam of various intensities[24,25]. Basically, binary(DPHPA/NVP) systems at a fixed film composition (LC/monomer=35/65 by weight) were considered and their formulations are given in Table 1. The effects of monomer ratio(DPHPA/NVP=4 ~ 7) as a function of irradiation intensity(20 ~ 200mW/cm^2) were studied. Ar-ion laser(λ =514nm) was used as light source. Beam passes through a spatial filter, beam expander, and is splitted into two with identical intensity. These two beams are subsequently passed through collimator and only the central portion of beam was reflected from the mirrors and impinged normally on the cell from the opposite sides. Cell was constructed by sandwiching the LC/monomer mixture between two indium tin-

TABLE 1 Formulation to Prepare HPDLC from DPHPA and NVP

Monomer Ratio (DPHPA:NVP)	LC:Monomer	Rose Bengal (wt%)	NPG (wt%)	Intensity (mW/cm^2)
4 : 1	35 : 65	0.3	1.8	20~200
4.5 : 1				
5 : 1				
5.5 : 1				
6 : 1				
6.5 : 1				
7 : 1				

oxide(ITO) coated glass plates, with a gap of 14.5μm adjusted by bead spacer[26]. Interference of two beams established the periodic interference pattern according to Bragg's law which is approximately 510nm for our case. The laser intensity was varied 20~200mW/cm^2 with exposure time of typically 30~120s. All the holographic gratings were recorded at room temperature.

The reflection of specific wavelength by composite film was analyzed using an UV-visible spectrometer(Perkin Elmer, Lambda 20). Relative reflection efficiency was estimated from the peak intensity of the spectra.

RESULTS AND DISCUSSION

The UV-visible spectra and reflection efficiency of the composite films having various monomer ratios which were irradiated at various laser powers are shown in Figure 3 and Figure 4. Two peaks are found at about 510 and 580nm, each corresponding to the reflection by holographic grating and absorption by dye Rose Bengal. The Bragg spacing is a bit smaller than the incident laser wave length(514nm), due presumably to the shrinkage of mixture volume upon polymerization. As mentioned above, 510nm peak will be approximated as reflection by gratings since scatterings are small with nanometer sized domains. It is noted that the 510nm peak becomes much sharper and it more intensive as the monomer ratio increases. The intensification of 510nm peak with increasing functionality seems related to the low irradiation laser power to be discussed later.

With the increase in laser intensity, the intensity of 510nm peak becomes much stronger as compared with 580nm peak. This is particularly true with lower monomer ratio. The peak intensity of higher monomer ratio is greater than the lower one at lower irradiation power, and it also generally increases with the increase in irradiation power. However, the effect of increasing irradiation power on peak intensity is more pronounced with lower monomer ratio.

In HPDLC the peak intensity should depend on the perfectness of holographic gratings. Obviously, more perfect gratings give higher peak intensity. Then, this indicates that the proper LC-polymer phase separation governs the perfectness of grating. Phase separation in polymerization system is regarded as a liquid-liquid demixing process where spinodal decomposition prevails. Elementary Flory-Huggins theory is often used to obtain the interaction energy which is progressively increased with the progress of polymerization reaction.

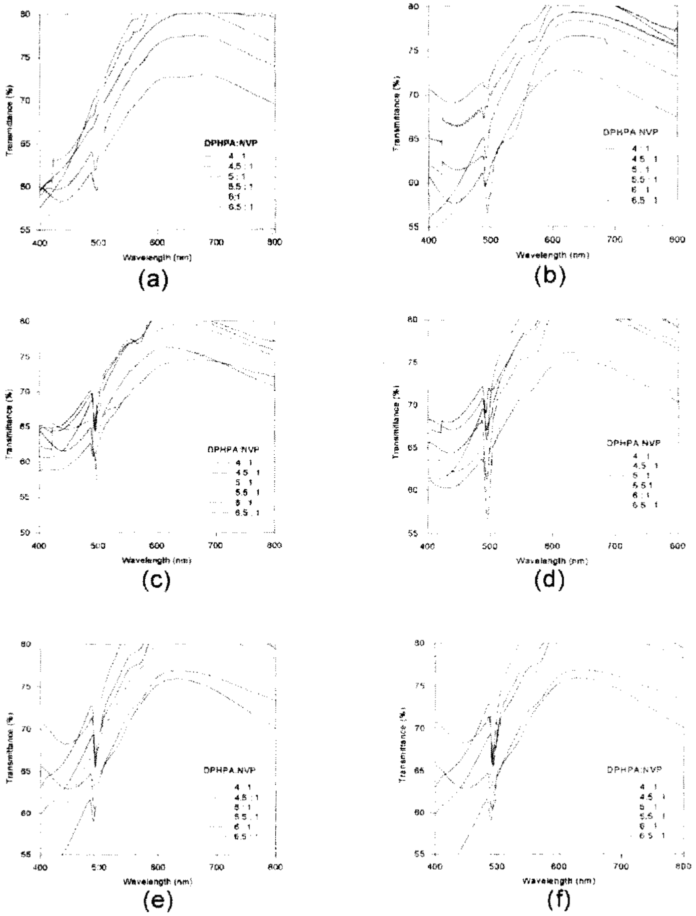

FIGURE 3. Monomer ratio dependent UV-visible spectra of HPDLC films irradiated at : (a) 20mW/cm^2, (b) 50mW/cm^2, (c) 100mW/cm^2, (d) 150mW/cm^2, (e) 175mW/cm^2, and (f) 200mW/cm^2.

Following Tanaka et al.[14], small sized and high density LC droplets give higher reflection efficiency. Our results indicate that there may exist an optimum extent of LC-polymer phase separation according to the reaction kinetics of photoinitiated radical polymerization.

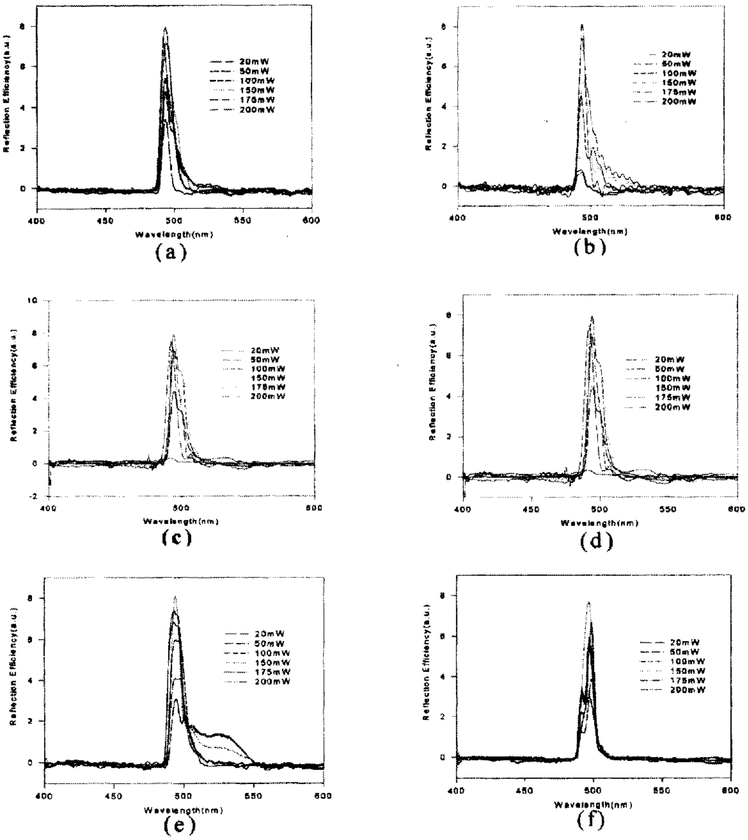

FIGURE 4 Monomer composition dependent reflection efficiency of HPDLC films irradiated at ; (a) 4:1, (b) 4.5:1, (c) 5:1, (d) 5.5:1, (e) 6:1, and (f) 6.5:1 (DPHPA:NVP, LC content 35wt%).

The polymerization rate is by far the fastest when the highest monomer ratio is irradiated at the highest laser intensity, and it is by far the lowest when the lowest monomer ratio is irradiated at the lowest laser intensity. Phase separation does not follow the rate of network formation and LC domains remain too small leading to imperfect gratings. Alternatively, coalescence of LC domains into larger ones become less plausible with highly viscous host polymer matrix, and this also retards proper phase separations. On the other hand, when the polymerization rate is too slow, phase separation can not take place in laboratory time scale due to the insignificant increase in heat of mixing. Therefore, there should exist an optimum monomer ratio for the desired maximum reflection depending on the irradiation intensity.

Reflection efficiency-irradiation power relationships are collected in Figure 5 which shows monotonic increase of reflection efficiency with irradiation power for low monomer ratio(DPHPA/NVP≤ 5), and maximum for high monomer ratio (DPHPA/NVP≥ 5.5). The power intensity of maximum reflection efficiency becomes lower as the monomer ratio increases.

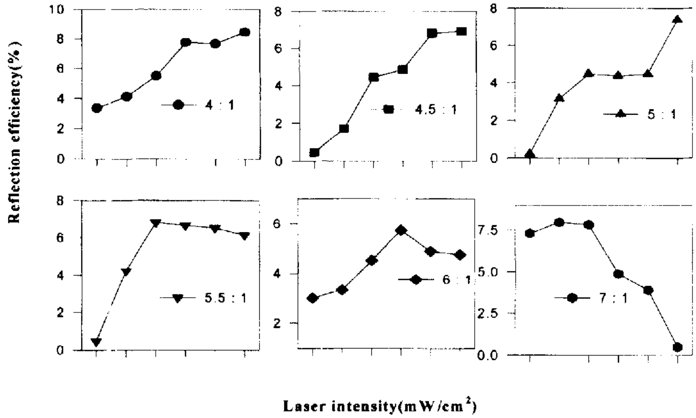

FIGURE 5. Reflection efficiency vs. laser intensity of HPDLC films prepared with various monomer ratios(DPHPA/NVP).

Same data were reported for reflection efficiency-monomer ratio in Figure 6 which shows monotonic increase at low, asymptotic increase at medium, and monotonic decrease at high laser power as well. This may imply that reflection efficiency is more sensitive to the monomer ratio as compared with irradiation power.

Reflection efficiency-monomer ratio-irradiation intensity relationships are plotted in Figure 7. From this plot, it is visualized that contour for maximum reflection generally follows the diagonal connecting the two points (highest monomer ratio and lowest irradiation power) and (lowest monomer ratio and highest irradiation power). This implies that the rate of phase separation is comparable with the rate of polymerization and

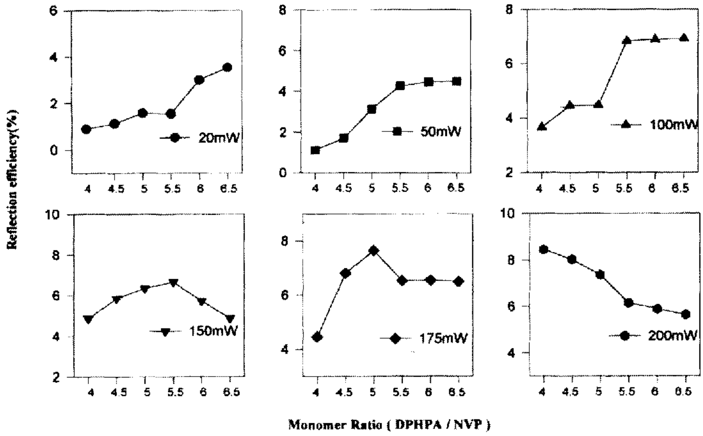

FIGURE 6. Reflection efficiency vs. monomer ratio of HPDLC films prepared with various laser intensities.

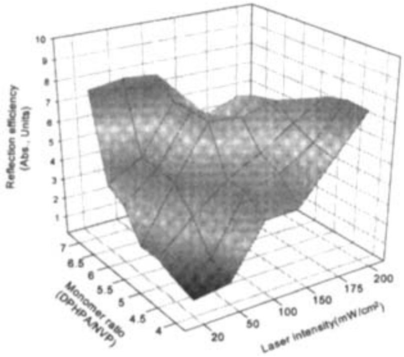

FIGURE 7. Reflection efficiency-monomer ratio-laser Intensity relationships of HPDLC films.

hence the domain size is appropriately small and its density is high enough to reflect maximum. At the other two extremes, i.e., when both the monomer ratio and irradiation intensity are too high or too low, phase separation is too small due to the extremely fast and slow polymerization rates and appropriate phase separations do not occur.

Acknowledgment

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References

[1] J.L. Fergason, *U.S. Patent* 4, 435, 047 (1984).

[2] S. Zumer and J.W. Doane, *Phys. Rev. A*, 3373 (1986).

[3] G.P. Montgomery, *Proc. SPIE*, **242(9)**, 1080 (1989).

[4] P. Drzaic, *Mol. Cryst. Liq. Cryst.*, **154**, 289 (1989).

[5] J.L. West, *Mol. Cryst. Liq. Cryst.*, **157**, 427 (1988).

[6] B.K. Kim and Y.S. Ok, *J. Polym. Sci., Polym. Phys.*, **32**, 561 (1994).

[7] B.K. Kim and S.H. Kim, *J. Polym. Sci., Polym. Phys.*, **36**, 55 (1998).

[8] B.K. Kim, Y.S. Ok, and C.H. Choi, *J. Polym. Sci., Polym. Phys.*, **33**, 707 (1995).

[9] B.K. Kim, S.H. Kim, and C.H. Choi, *Mol. Cryst. Liq. Cryst.*, **261**, 605 (1995).

[10] R.L. Sutherland, L.V. Natarajan, and V.P. Tondiglia, *Chem. Mater.*, **5**, 1533 (1993).

[11] R.L. Sutherland, L.V. Natarajan, and V.P. Tondiglia, *Proc. SPIE*, **2404**, 132 (1995).

[12] T.J. Bunning, L.V. Natarajan. V.P. Tondiglia, an R.L. Sutherland, Polymer, **37(14)**, 3147 (1996).

[13] R.L. Sutherland, L.V. Natarajan, V.P. Tondiglia, and R.L. Crane, *U.S. Patent* 5698343 (1997).

[14] K. Tanaka, K. Kato, M. Date, and S. Sakai, *SID 95 DIGEST*, 267 (1995).

[15] M. Date, N Naito, K. Tanaka, K. Kato, and S. Sakai, *ASIA DISPLAY'95*, 603 (1995).

[16] K. Tanaka, K. Kato, S. Tsuru, S. Sakai, U.S. Patent 5, 751, 452 (1998).

[17] H. Murai. T. Gotoh, M. Suzuki, E. hasegawa, and K. Zizoguchi, *SPIE*, **1665**, 230 (1992).

[18] J. Zhang, C.R. Carlen, S. Palmer, and M.B. Sponsler, *J. Am. Chem. Soc.*, **116**, 7055 (1994).

[19] Y.G. Fuh, M.S. Tsai, L.J. Huang, and T.C. Liu, *Appl. Phys. Lett.*, **74**(18), 2572 (1999).

[20] D. Duca, A V. Sukhov, and C. Umeton, *Liquid Crystal*, **26**(6), 931 (1999).

[21] R.T. Ingwall and H.L. Fielding, *Opt. Eng.*, **24**, 808 (1994).

[22] A.M. Weber, W.K. Smothers, T.J. Trout, and D.J. Mickishi, *Proc. SPIE*, **1212**, 30 (1990).

[23] T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, G. Dougherty, and R.L. Sutherland, *J. Polym. Sci. Polym. Phys.*, **35**, 2825 (1997).

[24] . B.K. Kim, Y.C. Jeon, and J.C. Kim, *Mol. Cryst. Liq. Cryst.*, **326**, 319 (1999).

[25] Y.H. Cho, B.K. Kim, J.C. Kim, and K.S. Park, *Polym. Int'l*, **48**, 1085 (1999).

[26] B.K. Kim, E.Y. Hong, and Y.S. Ok, *Korea Polym. J.*, **5**(2), 77 (1997).