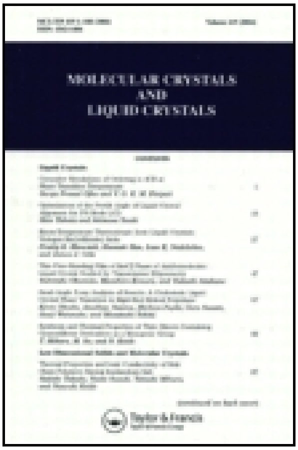

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Fabrication of Reflective Holographic PDLC for Blue

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Reflective holographic polymer dispersed liquid crystals(HPDLCs) have been fabricated with a ternary monomer system composed of dipentaerythritol hydroxy penta acrylate(DPHPA)/trimethylol propane triacylate(TMPTA)/N-vinylpyrrolidone(NVP)=7/2/1 by weight. Gratings were written by irradiating with an Ar-ion laser($\lambda = 488$ nm) at various intensities(20~200 mW/cm^2) on LC/monomers composite films of various composition(25/75, 30/70, 35/65, 38/62, 40/60). Polarized optical micrography(POM) images of gratings and UV-visible spectra were taken and reflection efficiency-irradiation intensity-film composition relationships are subsequently obtained in three dimensional plot which showed that maximum reflection moves from high LC content (38wt%) at low irradiation intensity (20 mW/cm^2) to low LC content (25wt%) at high irradiation intensity (200 mW/cm^2).

Keywords: Holographic polymer dispersed liquid crystal; UV-visible; POM; SEM

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) is a thin composite films composed of micron-sized droplets of nematic liquid crystal(LC) dispersed in a polymer matrix [1-5]. Typically UV-curable acrylates are used to due to their high optical clarity and diverse freedom of property variation[6-10].

Laser grating technique has been applied to fabricate PDLC with controlled architecture of phase separated LC domain[11-15]. This holographic polymer dispersed liquid crystal (HPDLC) is a new technique based on the polymerization induced phase separation (PIPS) and Bragg's law.

Light scattering is virtually minimized in HPDLC since the domain sizes are on the order of nanometers, and hence this device operates based on light reflection or transmittance, and the efficiency is electrically controlled via the refractive index of LC molecules[17,23].

In PIPS method, the rate of polymerization largely governs the phase separation and hence the domain size.

$$R_i = 2\phi I_o [1 - \exp(-2.3\varepsilon [A] b)] \qquad (1)$$

$$R_p = k_p [M] \left(\frac{\phi\varepsilon I_0 [A] b}{k_i} \right)^{1/2} \qquad (2)$$

R_I and R_p are the initiation and polymerization rate, respectively and details of application are available with Decker[16]. In these eqs., ϕ , ε, Io, and b are respectively initiation efficiency, molar absorptivity, incident light intensity, and sample thickness. [M] and [A] are the concentration of monomer and species which undergoes photoexcitation, k_p and k_t are rate constant for propagation and termination reactions, respectively. Irradiation power intensity, concentrations of photoinitiator and monomers contribute to R_p. With a rapid enough rate of polymerization, phase separation can not follow polymerization kinetics since the time scale for polymerization is smaller than that of phase separation due to the slower diffusion of LC molecules in highly viscous media. So, monomers to be used for HPDLC should have higher functionality than those for conventional PDLC.

We optimized holographic PDLC with regard to film composition and irradiation intensity[26-29]. Ternary monomer mixtures with various monomers/LC compositions have been irradiated with Ar-ion(λ =488nm) laser at various intensities. Polarized optical micrography images of the gratings were obtained to visualize the holographic gratings. UV-visible spectra were taken to obtain the architectured reflections from gratings. Three dimensional plots of reflection efficiency-laser intensity-film composition are presented showing contours for maximum reflections.

EXPERIMENTAL

Materials

E7(Merck) (T_{KN}=-10°C, T_{NI}=60.5°C, $\varepsilon_{\parallel}$ =19.0, and $\varepsilon_{\perp}$=4.2) was used as LC. Three types of photopolymerizable monomers, viz., dipentaerythylol penta acrylate(DPHPA, functionality(f)=5), 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.

Multifunctional monomers (DPHPA and TMPTA) have very high reactivity as well as high viscosity due to their high molecular weight and provide the polymers with extensive crosslinkings, whereas monofunctional NVP simply extends the chains at much lower rate. However, the use of monofunctional monomers is often essential to reduce the viscosity of LC/monomer mixture and make the starting mixture homogeneous. Otherwise, polymerization induced phase separation starts with heterogeneous reaction mixture and the morphology of the composite film becomes out of control.

Rose Bengal was used as photo initiator for holographic recording with Ar-ion laser, as it displays a broad absorption spectrum with a peak molar extension coefficient of ~104M-1cm-1 at about 490nm[17]. To this, a millimolar amount of N-phenylgycine(NPG) was added as coinitiator(Fig.2). In this experiment 3× 10^{-6}M of RB and 1.2× 10^{-4}M of NPG were used.

Formulations

Gratings were formulated with different film compositions (monomers/ LC) which were irradiated at various laser intensities. Basic formulations of our ternary(DPHPA/TMPTA/NVP) systems are given in Table 1. Monomer composition was fixed at DPHPA/TMPTA/NVP=7/2/1 by weight and the effects of film composition and irradiation intensity were examined.

Table 1. Formulation to prepare HPDLC from DPHPA, TMTPA and NVP

Monomer			LC: Monomer	Rose Bengal	NVP	Space Thickness (㎛)
DPHPA	TMPTA	NVP	25:75 30:70 35:65 38:62 40:60	0.5wt%	2.5wt%	14.5
7	2	1				

Gratings

An argon-ion laser(λ =488nm) was used as light source. The beam passes through a spatial filter, a beam expander, and is splitted in two beams of identical intensity. These two beams are subsequently passed through a collimator and only the central portions were reflected from the mirrors and impinged normally on the cell from the opposite side. The cell was constructed by sandwiching the monomers/LC between two indium tin-oxide(ITO) coated glass plates, with a gap of 14.5 μm adjusted by bead spacer. Interference of the two beams established the periodic interference pattern according to Bragg's law, which is approximately 488nm in our case. The laser intensity was varied from 20 to 200mW/cm^2, with exposure times of typically 30 to 120s.

Measurements

Gratings were visualized with polarized optical microscopy(POM). The reflection of a specific wavelength by the composite film was analyzed using an UV-visible spectrometer(Perkin Elmer, Lambda 20). Reflection efficiency was estimated from the spectrum data.

RESULTS AND DISCUSSION

Typical images of our gratings shown in Figure 1. The width variation of the grating is very small throughout the film compositions. In general

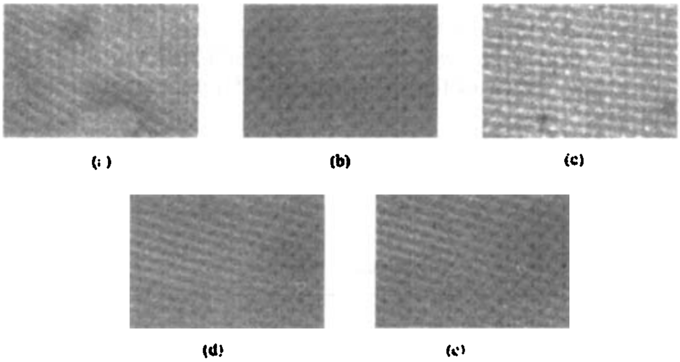
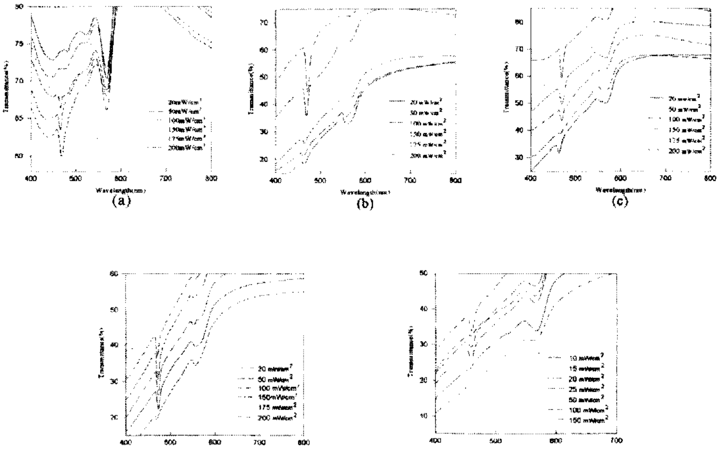


FIGURE 1. POM micrographs of HPDLC versus film composition (monomer/LC): (a) 75/25; (b) 70/30: (c) 65/35: (d) 62/38: (e) 60/40 (I_0=100mWcm^{-2}).

spatial variation of the grating width is often observed due to the inhomogeneity of the laser spot. This can be minimized by using a more square beam profile, which is obtained by expanding and collimating the Gaussian beams and passing only the central portion through an aperture in contact with the front plate of sample[19]. This procedure was taken into account in our experiments. With the increase of LC content in the film, the thickness of LC lamella (bright area) increases while keeping the Bragg spacing constant.

Figure 2 shows the UV-visible spectra of the films. Two peaks are found at about 480 and 580nm, which correspond to the reflection by holographic grating and absorption by dye Rose Bengal, respectively. The Bragg spacing is slightly smaller than the incident laser wavelength (488nm), presumably because of the shrinkage of the mixture upon polymerization. As mentioned above, the 480nm peak will be approximated as reflection by gratings since scattering is small with nanometer sized domains. At low LC content (monomer/LC=75/25), the reflection intensity is maximum for high irradiation power, and at high LC content (60/40), the peak intensity is maximum for low irradiation power, and at intermediate composition(62/38), the maximum reflection is obtained for intermediate irradiation power.



(a) (b) (c)

(d) (e)

FIGURE 2. Irradiation intensity dependent of UV-visible spectra HPDLC films (monomer:LC) (a) 75/25 (b) 70/30 (c) 65/35 (d) 62/38 (e) 60/40.

The peak intensity should depend on the perfectness of holographic gratings. Obviously, more perfect gratings give higher peak intensity. Following Tanaka et al[14], small and high density LC droplets give higher reflection efficiency. Our results indicate that there may exist an optimum extent of polymer-LC phase separation. According to the reaction kinetics of photoinitiated radical polymerization described earlier, it has been noted that Rp as well as Ri increases with irradiation intensity(I_0), although the effect of I_0 on R_i is more pronounced. R_p also increases linearly with monomer concentration, which corresponds to the monomer content of the composite film. So, high monomer content directly gives high reaction rate and hence augments crosslinking density of host polymers.

The polymerization rate is the fastest when the films of highest monomer content are irradiated at the highest laser intensity and conversely, it is the lowest when the films of lowest monomer content are irradiated at the lowest laser intensity. When the polymerization rate is too fast, rate of phase separation can not follow the rate of network formation and LC domains are entrapped within the polymer nets leading to imperfect gratings. Also, coalescence of LC domains into larger ones becomes less plausible with highly viscous host polymer matrix, and this also retards phase separation. On the other hand, when the polymerization rate is too slow, phase separation can not take place thermodynamically. Therefore, there exists an optimum monomer content for the desired maximum reflection depending on the irradiation intensity.

The reflection efficiency-irradiation power relationship is shown in Figure 3. One observes a monotonic increase, followed by an asymptotic increase and finally a maximum when the LC content increases from 25 wt% to 40wt%.

The same data were replotted for reflection efficiency-film composition in Figure 4. Regardless of the irradiation power, reflection efficiency shows a maximum for a given LC content with its value decreasing as the irradiation power increase.

A tri-dimensional representation of the reflection efficiency-irradiation power intensity-film composition relationships is shown in Figure 5. This plot shows that maximum reflection depends on the film composition and laser intensity, and optimum set of conditions is much narrower than with the binary monomers[17]. The maximum reflection moves from high LC content(38wt%) at low irradiation intensity (20mW/cm^2) to low LC content(25wt%) at high irradiation intensity (200mW/cm^2).

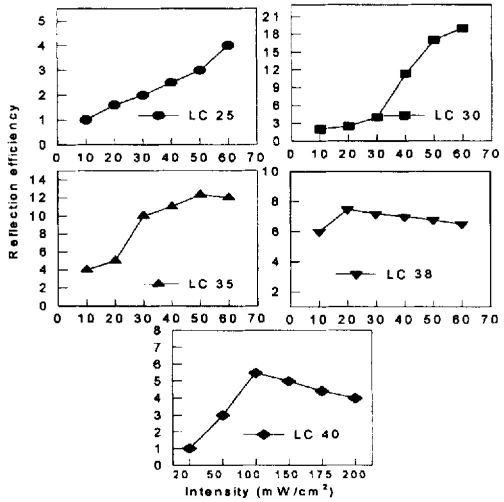


FIGURE 3. Reflection efficiency versus laser intensity of HPDLC films for various LC contents

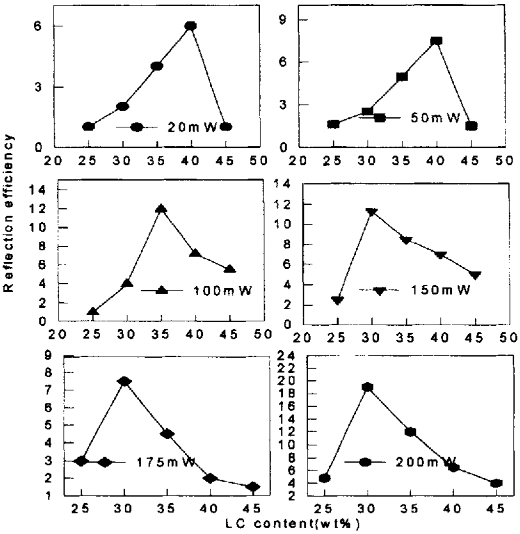


FIGURE 4. Reflection efficiency versus LC content of HPDLC films irradiation at various intensities.

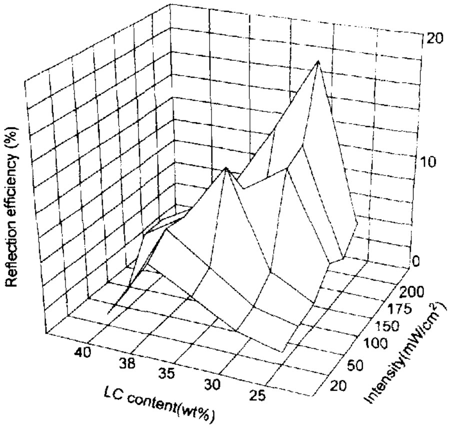


FIGURE 5. Reflection efficiency-LC content-laser intensity relationships of HPDLC films (NVP/TMPTA/DPHPA=1/2/7).

CONCLUSION

Reflection efficiency of holographic polymer dispersed liquid crystal has been studied as a function of film composition and irradiation intensity. Regardless of the irradiation power, reflection efficiency showed a maximum with regard to the LC contents and the maximum value generally increased with increasing irradiation power. In contrast, higher irradiation power gave maximum efficiency at lower LC content, implying that optimum power should depend on the amount of monomers to be cured.

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