Optimization of holographic polymer dispersed liquid crystal for ternary monomers

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Abstract: Polarized optical micrography (POM) images of gratings and UV–visible spectra of holographic polymer dispersed liquid crystals (HPDLC) are reported for a ternary monomer system composed of dipentaerythritol hydroxypentaacrylate/trimethylolpropanetriacrylate/N-vinylpyrrolidone (DHPHA/TMPTA/NVP)=7/2/1 by weight. Gratings were written by irradiation with an argon ion laser (λ=488nm) at various intensities (20–200mWcm⁻²) on monomer/liquid crystal (LC) composite films of various compositions (75/25, 70/30, 65/35, 62/38, 60/40). Reflection efficiency–irradiation intensity–film composition relationships are obtained in three dimensional plots which show that maximum reflection moves from high LC content (38%) at low irradiation intensity (20mWcm⁻²) to low LC content (25wt%) at high irradiation intensity (200mWcm⁻²).

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INTRODUCTION

A polymer/liquid crystal composite film, often referred to as polymer dispersed liquid crystal (PDLC), is a thin composite film composed of micrometre-sized droplets of a nematic liquid crystal (LC) dispersed in a polymer matrix, typically made of UV-curable acrylates because of their high optical clarity and other adjustable properties. PDLC has the potential for a variety of electrooptic applications ranging from directly driven windows to active matrix driven information displays. A number of important reviews regarding the methods of preparation, materials, modes of operation, device applications, etc, have become available.

Recently the laser grating technique has been applied to fabricate PDLCs with controlled architectures of phase-separated LC domains. This type of PDLC is called a holographic polymer dispersed liquid crystal (HPDLC) in the literature. This new technique combines polymerization-induced phase separation (PIPS) and Bragg’s law (eqn (1)).

\[ \Lambda = \frac{\lambda}{2 \sin \theta} \] (1)

where \( \lambda \) is the wavelength of light, \( \Lambda \) is the grating spacing, and \( 2\theta \) is the interbeam angle outside the film. The grating spacing, and hence the component of incident light which can be reflected by the grating spacing, can be easily controlled by varying the interbeam angle using the same laser wavelength. This periodic structure of multilayers has very promising optical properties because only a specific component of the incident light is reflected by the LC layers, due to the difference in refractive indices of the polymer and LC.

In HPDLC, light scattering is virtually minimized because the domain sizes are of the order of nanometres, so that this device operates on light reflection or transmittance, and its efficiency is electrically controlled via the refractive index of the LC molecules.

In the PIPS method, the phase separation is driven by the polymerization reaction. The rate of polymerization given below for a photoinitiated radical mechanism largely governs the phase separation and hence the domain size.

\[ R_i = 2\phi I_0 [1 - \exp(-2.3\varepsilon I_0 b)] \] (2)

\[ R_p = k_p [M] \left( \frac{\phi I_0 [1 - \exp(-2.3\varepsilon I_0 b)]}{k_t} \right)^{0.5} \] (3)

where \( R_i \) and \( R_p \) are the initiation and polymerization rates, respectively and details of their application are available from the pioneering works by Decker. In these eqns (2) and (3), \( \phi, \varepsilon, I_0 \) and \( b \) are, respectively, initiation efficiency, molar absorbptivity, incident light intensity, and sample thickness. [M] and [A] are the...
concentrations of monomer and species which undergo photoexcitation, $k_p$ and $k_t$ are the rate constants for propagation and termination reactions, respectively. With a sufficiently rapid rate of polymerization, phase separation cannot follow the polymerization kinetics because the time-scale for polymerization is smaller than that of phase separation due to the slower diffusion of LC molecules in highly viscous media. Therefore, monomers to be used for HPDLC should have higher functionality than those for conventional PDLC.

As a continuation of our efforts in PDLC,26–29 we optimized holographic PDLC with regard to film composition and irradiation intensity. Ternary monomer mixtures with various monomers/LC compositions have been irradiated with an argon ion ($\lambda = 488\text{nm}$) laser at various intensities. Three dimensional plots of reflection efficiency–laser intensity–film composition are presented showing contours for maximum reflections.

EXPERIMENTAL

Materials

A eutectic mixture of four cyanobiphenyl and cyano-terphenyl components with $T_{KN} = -10^\circ\text{C}$, $T_{NI} = 60.5^\circ\text{C}$, $\varepsilon_\parallel = 19.0$, and $\varepsilon_\perp = 4.2$ (E7, Merck) was used as LC. Three types of photopolymerizable monomers (Fig 1) (dipentaerythritol hydroxypentaacrylate (DPHPA, functionality ($f$) = 5), trimethylpropanetriacrylate (TMPTA, $f$ = 3), and N-vinylpyrrollidone (NVP, $f$ = 1) were used in appropriate combinations to prepare the host polymers upon laser irradiation.

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

A dye, Rose Bengal (RB), was used as photoinitiator for holographic recording with an argon ion laser, because it displays a broad absorption spectrum with a peak molar extension coefficient of about $10^4\text{M}^{-1}\text{cm}^{-1}$ at about $490\text{nm}$.17 To this, a millimolar amount of N-phenylglycine (NPG) was added as coinitiator. In this experiment $3 \times 10^{-6}\text{M}$ of RB and $1.2 \times 10^{-4}\text{M}$ of NPG were used.

Formulation

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. The monomer composition was fixed at DPHPA/TMPTA/NVP = 7:2:1 by weight, and the effects of film composition and irradiation intensity were examined.

Gratings

The holographic recording system used is schematically shown in Fig 2. An argon ion laser ($\lambda = 488\text{nm}$) was used as light source. The beam passes through a spatial filter, a beam expander, and is split in two beams of identical intensity. These two beams are subsequently passed through a collimator and only the central portions are reflected from the mirrors to impinge 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 μm adjusted by a bead spacer. Interference of the two beams establishes the periodic interference pattern according to the Bragg law; this is approximately 488 nm in our case. The laser intensity was varied from 20 to 200 mW/cm$^2$, with typical exposure times of 30–120 s.

Figure 2. Experimental set-up for holographic PDLC.

Figure 3. POM micrographs of HPDLC versus film composition (monomers/LC): (a) 75/25; (b) 70/30; (c) 65/35; (d) 62/38 and (e) 60/40 ($I_0=100\text{ mW cm}^{-2}$).

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Measurements
The morphology of the composite film was studied by polarized optical microscopy (POM). The reflection of a specific wavelength by the composite film was analysed using a UV–visible spectrometer (Perkin Elmer, Lambda 20). The reflection efficiency was estimated from the spectral data.

RESULTS AND DISCUSSION
Polarized optical microscopy (POM) images of our gratings for various film compositions are shown in Fig 3. The width variation of the grating is very small throughout the film compositions. In general, spatial variation of the grating width is observed due to 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 the sample. This procedure was used in our experiments. With the increase of LC content in the film, the thickness of the LC lamella (dark area) increases while the Bragg spacing remains constant.

UV–visible spectra of the films are shown in Fig 4. Two peaks are observed at about 480 and 580 nm, which correspond to the reflection by the holographic grating and absorption by the dye Rose Bengal, respectively. The Bragg spacing is slightly smaller than the incident laser wavelength (488 nm), presumably

![Graphs and images]

Figure 4. Irradiation intensity dependence of UV–visible spectra of HPDLC films (monomers/LC): (a) 75/25; (b) 70/30; (c) 65/35; (d) 62/38 and (e) 60/40.
because of the shrinkage of the mixture upon polymerization. As mentioned above, the 480 nm peak will be approximated as reflection by the gratings because the scattering is small, with nanometre 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; at intermediate composition (62/38), the maximum reflection is obtained for intermediate irradiation power.

In HPDLC, the peak intensity should depend on the perfectionness of holographic gratings. Obviously, more perfect gratings give higher peak intensity. Then, what is governing the perfection of the gratings? The answer should be the proper LC–polymer phase separation, where nanometre sized LC domains imbedded in polymer layers are separated by almost LC-free polymer layers. Phase separation in the polymerizing 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 increases with the progress of the polymerization reaction.

Following Tanaka et al.,22 small LC droplets of high density give higher reflection efficiency. Our results indicate that an optimum polymer–LC phase separation may exist. According to the reaction kinetics of photoinitiated radical polymerization described earlier, it has been noted that both R_p and R_i increase 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. Therefore, high monomer content directly gives a high reaction rate and hence augments the crosslinking density of host polymers.

The polymerization rate is highest when the films of highest monomer content are irradiated at the highest laser intensity; conversely, it is lowest when the films of lowest monomer content are irradiated at the lowest laser intensity. When the polymerization rate is too fast, the rate of phase separation cannot 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 a highly viscous host polymer matrix, and this also retards phase separation. However, when the polymerization rate is too low, phase separation cannot 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 Fig 5 for various LCs. One observes a monotonic increase, then an asymptotic increase, and finally a maximum when the LC content increases from 25 to 40 wt%. It seems that some monomers necessitate more powerful irradiation.

The same data were replotted for reflection efficiency–film composition in Fig 6. Regardless of the irradiation power, the reflection efficiency shows a maximum for a given LC content, its value increasing as the irradiation power increased. However, the LC content of maximum reflection decreased with increasing irradiation power.

A three-dimensional representation of the reflection efficiency–irradiation intensity–film composition relationships is shown in Fig 7. This plot shows that the maximum reflection depends on film composition and laser intensity, and the optimum set of conditions is much narrower than with binary monomers. The maximum reflection moves from high LC content (38 wt%) at low irradiation intensity (20 mW cm^{-2}) to low LC content (25 wt%) at higher irradiation intensity (200 mW cm^{-2}).

CONCLUSIONS

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

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REFERENCES

Figure 6. Reflection efficiency versus LC content of HPDLC films irradiated at various laser intensities.

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