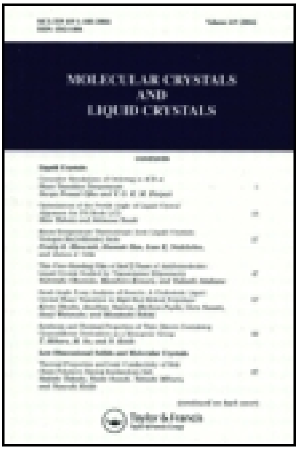

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Two Wave Mixing in Holographic Polymer Dispersed Liquid Crystal (H-PDLC) Formation

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The intensity of transmitted laser beams is monitored during the holographic formation of polymer dispersed liquid crystal gratings. Significant attenuation of the total transmitted intensity is experienced after brief illumination. In most cases the attenuation increases for several seconds before reaching a steady-state value. Analysis of the individual beam intensities reveals energy exchange between the beams in a nonlinear two-wave mixing process. This information is analyzed to help gain insight into the complex dynamics of H-PDLC formation.

Keywords: holographic polymer dispersed liquid crystal; two-wave mixing

INTRODUCTION

Liquid crystal and polymer composites have been a highly active area of both applied and fundamental research for almost two decades [1]. Holographically-formed polymer dispersed liquid crystals (H-PDLCs) are one such composite material class which show great promise for numerous applications including reflective displays [2, 3], fiber-optic switches [4] and diffractive optical elements [5], to name a few. They are formed by the photopolymerization of a homogeneous mixture of a reactive monomer and low molecular weight liquid crystal in a holographic intensity grating (see Fig. 1). The monomers polymerize most rapidly in the bright intensity fringes. A monomer concentration gradient is established and monomers diffuse from the dark fringes into the bright fringes [6, 7]. Excluded volume effects, as well as the increasing chemical potential of the liquid crystal in the bright fringes result in a counter-diffusion process of the liquid crystal into the regions of low light intensity. As the local LC concentration increases it becomes energetically favorable for a two-phase system to exist in the dark fringes, and the liquid crystal phase separates into discrete droplets. The polymer gels, locking in the morphology. The final material consists of planes of low molecular weight liquid crystal droplets embedded in rigid polymer binder.

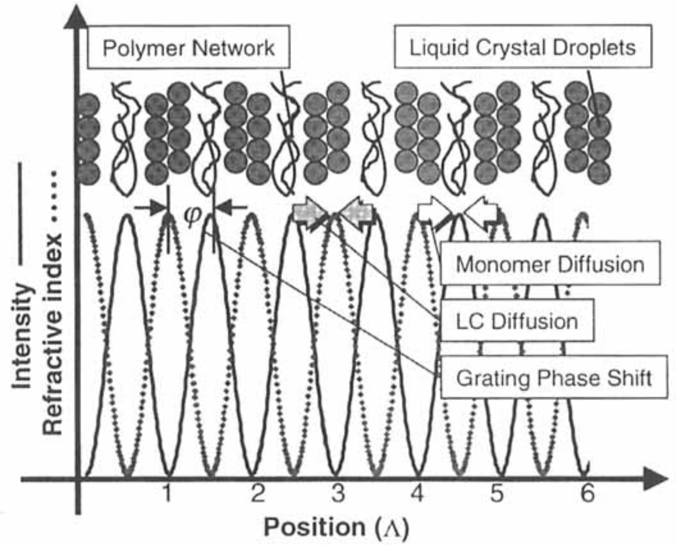

FIGURE 1. H-PDLC formation. Exposure of the homogeneous prepolymer to an interference pattern results in anisotropic photopolymerization. Monomers diffuse into the bright fringes where polymerization rates are highest. Liquid crystal diffuses into the dark fringes, where nematic droplets phase separate out.

For homogeneous parallel anchoring of the liquid crystal to the polymer wall, a nematic liquid crystal will typically exist in a bipolar configuration. In the absence of a biasing field, the symmetry axes of these droplets will be randomly aligned from droplet to droplet. Along the optical axis there is typically a refractive index mismatch between the liquid crystal droplets, and the polymer. Light incident along this axis will experience a periodic refractive index modulation between the polymer and liquid crystal droplet planes, and the material will behave as a grating coherently scattering the light. When a voltage is applied across the material the dielectric anisotropy of the bipolar droplets will cause the bipolar directors to preferentially align with the field. Incident light will now propagate purely as an ordinary ray through the droplet. By design, we choose materials such that the ordinary index of the liquid crystal, n_o, is approximately equal to the polymer index, n_p. The refractive index modulation between the polymer and liquid crystal droplets planes is erased, and the materials become optically transparent.

Achieving switchable holographic gratings with high efficiency and good contrast is a function of the birefringence of the liquid crystal, the degree to which the materials can be phase separated during the formation of the grating, and the integrity and stability of the final binding polymer morphology, among other things. Unfortunately, the high degree of complexity of their formation and the sensitivity of the materials to light, mean that these systems are extremely difficult to probe. Experiments in which the diffracted intensity of a HeNe probe beam was monitored during the holographic exposure allowed measurement of the speed of grating formation [8] and revealed the dominance of thermal grating effects at early exposure times [9]. Despite these efforts most models of H-PDLC formation are highly speculative, with little empirical fact to back them up.

Systems in which a refractive index grating is formed in response to an interference pattern is a familiar scenario to researchers in the field of nonlinear optics. Electro-optic crystals, such as LiNbO3, exhibit photorefractivity via the Pockels' effect [10]. Illumination of such a medium with a spatially varying radiation field results in the formation of a space-charge field, which in turn induces a change in the local refractive index of the crystal. This property has made such crystals popular materials for probing nonlinear optical phenomena, such as optical phase conjugation and wave mixing.

For many nonlinear optical media the local index of refraction can often be written as

$$n = n_0 + n_2 I, \tag{1}$$

where n_0, n_2 are constants and I is the intensity. The constant n_2 is known as the Kerr coefficient. Electro-optic crystals are not the only systems that exhibit this phenomenon. Photorefractive polymers are an active field of research [11]. Liquid suspensions of dielectric spheres have also been studied as artificial Kerr media [12]. Colloidal suspensions of dielectric spheres are trapped in an optical interference pattern by radiation pressure. This leads to a refractive index grating as a result of the index mismatch between the spheres and the liquid. These systems have been used as a medium with which to study nonlinear optical phenomena [13], and more recently the nonlinear optical properties have been used to probe some of the fundamental material properties of the composite [14].

The high degree of anisotropy associated with many of the physical parameters of liquid crystals, and the relative ease with which an LC's properties can be locally perturbed by an optical field result in many liquid crystalline materials having highly nonlinear optical properties [15]. Liquid crystal dispersions, such as PDLCs, have also been investigated as nonlinear optical media [16]. The material is usually made photorefractive by the introduction a hole transport agent.

H-PDLCs can in some senses be considered a Kerr medium, in that exposure of the prepolymer to a radiation interference pattern induces a refractive index grating, satisfying Eq. 1. Note that for H-PDLCs the Kerr coefficient, n_2, is negative as the regions of highest index are the fringes in which the LC droplets form – i.e. the dark fringes. A major difference between an H-PDLC and the photorefractive media mentioned above is that the index grating does not relax back to a homogeneous optical state in an H-PDLC. The index grating is locked into the material by photopolymerization of the prepolymer.

In this paper we report on the results of experiments in which we monitored the transmitted intensity of the curing beams during H-PDLC formation. Several interesting features were observed, including the transfer of power from one beam into the other in a nonlinear two wave mixing process. This information offers further insight into the highly complex dynamics of H-PDLC formation. Further understanding could allow this technique to be used as a process control in H-PDLC element fabrication.

EXPERIMENTAL DETAILS

Our experimental setup is shown in the schematic in Fig. 2. We used a mode-stabilized Ar+ laser operating on the 514nm line. The beam was linearly polarized using a polarizing beamsplitter. The expanded beam was apodized using an adjustable iris yielding an exposure area of approximately 3mm^2. This beam was split using a 50/50 quartz beamsplitter.

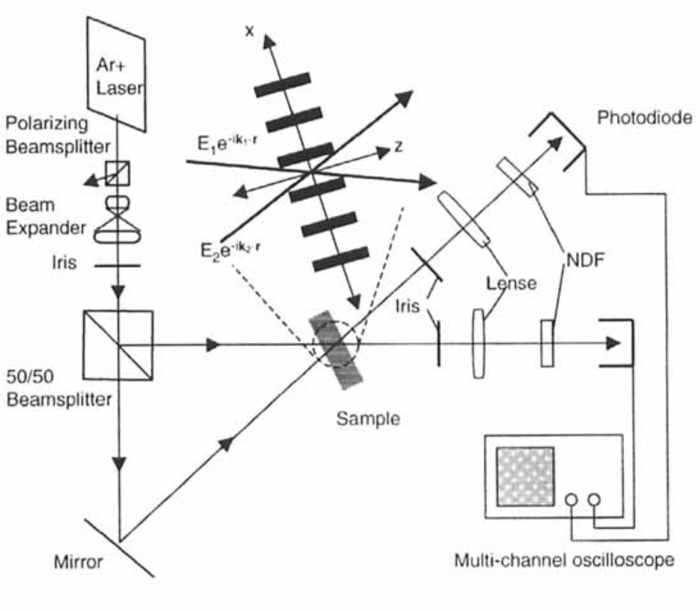

FIGURE 2. Schematic showing experimental setup for H-PDLC formation. The intensity of the transmitted beams is monitored during cure. The oscilloscope trace is downloaded to a PC. The grating axes are shown in the expanded view.

The beams were incident on the same side of the sample, forming an interference pattern across the plane of the sample. This results in the formation of a transmission-type H-PDLC grating. The transmitted beams were each focused onto silicon photodiodes (Melles Griot 13 DSI 007), which in turn were connected to channels one and two of an oscilloscope. Neutral density filters were placed in front of the diodes to ensure a linear response. The incident beam intensity was measured and the detector/oscilloscope setup calibrated using a Vector S310 (Scientech) optical power meter. The incident beams were measured to have power 10.6 mW and 6.5 mW respectively.

The prepolymer materials consisted of a monomer blend formed from commercially available urethane acrylate resins that have been optimized for practical display applications [17]. The blend consisted of monomers with functionality 6 and 3. These are the number of reaction sites available on each monomer and the high functionality will result in a highly cross-linked network. We also used the nematic liquid crystal BL038 (n_o=1.5270 and n_e=1.7990) from EM Industries. The monomers were sensitized to the laser wavelength by the addition of the photoinitiator Rose Bengal and the coinitiator n-Phenylglycine. Both were obtained from Sigma-Aldrich Inc. We also added the monofunctional monomer 1-vinyl-2-pyrrolidone, also from Sigma-Aldrich. This material was well mixed to ensure adequate homogeneity.

Sample cells were prepared by drop-filling the prepolymer between two 1"×1" pieces of glass. The cell gap was controlled using 20μm fiber spacers. The cells were placed in an optical mount and exposed immediately. The sample cells were deliberately aligned asymmetrically in the beams to ensure that any specular reflections off the surfaces were not in the direction of either of the incident or transmitted beams. The angle between the beams was ~20°. Exposure times were typically for ~30 seconds. The final mixing of the prepolymer, plus the exposure, were performed under darkroom lighting conditions to avoid any polymerization due to exposure to ambient room light.

Following initial exposure, the diffraction efficiency of each grating was then measured by blocking one of the curing beams and measuring the diffracted beam intensity.

RESULTS AND ANALYSIS

The total transmitted intensity is measured as the sum of the intensity detected in the diodes. Fig. 3 shows the total intensity transmitted through a curing H-PDLC cell. After a brief delay (~1 second) the initial intensity is seen to fall steadily from ~16.5 mW to a steady final value of ~11 mW, reached at after approximately 10 seconds.

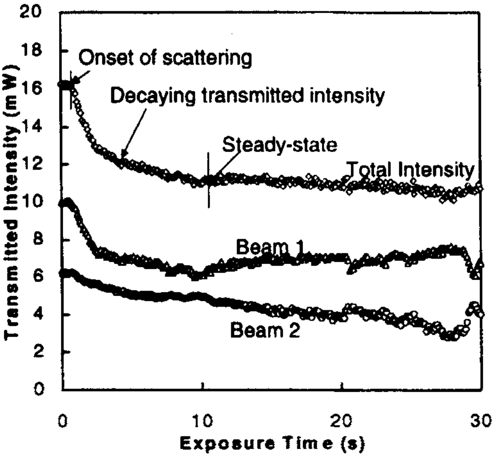

FIGURE 3. Total and individual transmitted beam intensity for 30 second H-PDLC cure.

We attribute the loss in transmitted intensity to radiation absorption and incoherent scattering as in a regular PDLC, which is characterized by a simple exponential law

$$I(L,t) = I_0 \exp(-\alpha(t)L), \tag{2}$$

where I_0 is the total incident intensity on the H-PDLC, L is the pathlength of the beam through the film, and $\alpha(t)$ is the dynamic attenuation coefficient [18]. During H-PDLC formation, the attenuation coefficient can be written as

$$\alpha = \alpha_{ABS} + \alpha_{SCAT}, \tag{3}$$

in which two contributions to attenuation are considered. Laser light is absorbed by the photoinitiator, Rose Bengal, in the formation of free radicals for photopolymerization. The contribution by absorption to the total

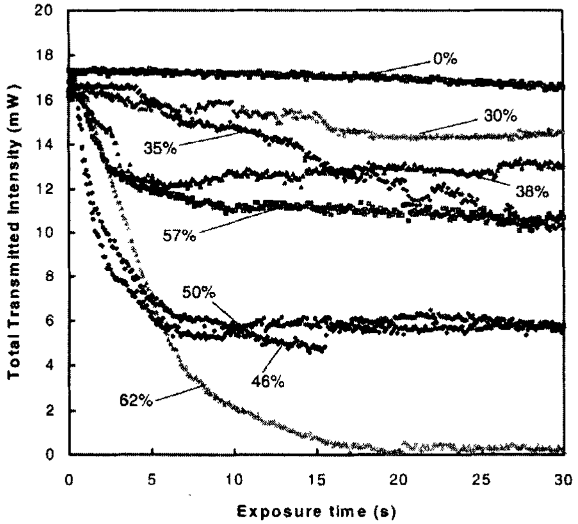

FIGURE 4. Total transmitted intensity shown for 30s exposure at different liquid crystal loadings (indicated as wt.%). The inset shows the final attenuation coefficient of the H-PDLC as a function of LC mass fraction. The line is plotted as an aid.

attenuation coefficient is written α_{ABS}. The other contribution to attenuation of the transmitted beams is the incoherent scattering from individual nematic droplets. Scattering from H-PDLC droplets (10-200nm in size) typically falls in the Rayleigh-Gans scattering regime [18], which is characterized by the condition $2kR|n_{LC}/n_p - 1| << 1$. Here k is the wavenumber of the incident radiation ($k=2\pi/\lambda$), R the droplet radius, and n_{LC} and n_p the average refractive indexes of the liquid crystal and polymer, respectively. In this case, this contribution to the attenuation is given by

$$\alpha_{SCAT} = \rho_0(\sigma_t / v), \tag{4}$$

where ρ_0 is the volume fraction occupied by the droplets, v is the average droplet volume ($v = (4\pi/3)\langle R^3\rangle$), and σ_t the total droplet scattering cross section, which for bipolar droplets has been shown to obey

$$\sigma_t \propto k^4\langle R^6\rangle. \tag{5}$$

Materials prepared with regular amounts of the initiator and coinitiator, but with no liquid crystal, show negligible attenuation indicating that $\alpha_{ABS} << \alpha_{SCAT}$. This is evident in Fig. 4, which show the total transmitted intensity at several different initial liquid crystal loadings.

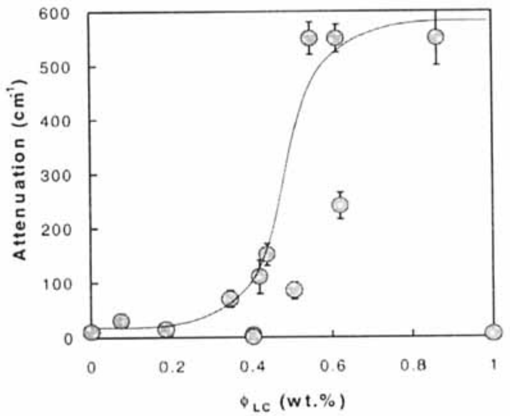

FIGURE 5. Attenuation (α) as a function of liquid crystal mass fraction (ϕ_{LC}). There is a marked increase in attenuation at $\phi_{LC} \sim 0.4$. The line is fit to guide the eye.

Also shown in Fig. 3 are the individual beam intensities, which are also observed to decay from their *t=0* values, but not in the same monotonic fashion as the summed intensity. After ~10 seconds the intensity of beam 1 clearly increases, while the intensity of beam 2 dips.

This "mirror" nature of the intensity change in beams 1 and 2 is strikingly evident when one examines the fraction of total detected intensity in each beam (see Fig. 6). This behavior is characteristic of two wave mixing, where energy is coupled anisotropically via the grating from one beam and into the other. Energy is preferentially transferred first from beam 1 into beam 2. After about 15 seconds the direction of transfer is reversed and beam 2 gains energy at the expense of beam 1.

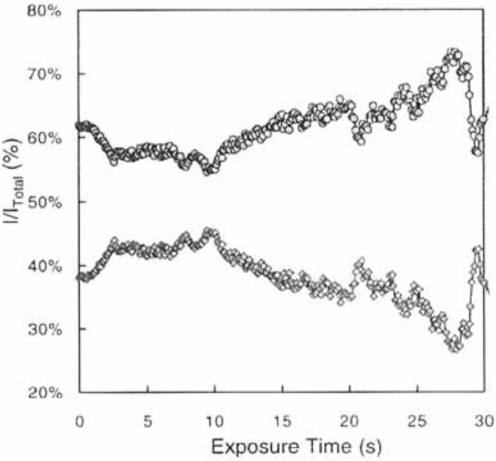

FIGURE 6. Fraction of total intensity in each beam during cure. Energy is first coupled from beam 1 into beam 2. After 15 seconds beam 1 gains at the expense of beam 2.

Nonlinear two wave mixing is characteristic of a photorefractive system in which a phase mismatch, φ, exists between the intensity grating and the resulting index grating [10]. For these systems, the nonlinear gain, g, defined as the ratio of the exiting probe beam to the incident probe beam, can be written

$$g = \frac{I_2(L)}{I_2(0)} = \frac{1+m}{1+me^{-\gamma L}} e^{-\alpha L}. \tag{6}$$

Here, $m \equiv I_1(0)/I_2(0)$, the ratio of incident pump to probe beam, α is the attenuation coefficient defined in Eq. 2, and γ is the real part of the beam coupling constant, which, for a sinusoidal index grating, is equal to

$$\gamma = \frac{2\pi n_1}{\lambda \cos\theta} \sin\varphi. \tag{7}$$

In Eq. 7, θ is the half the angle between the pump and probe beams, λ the laser wavelength, n_1 the index modulation of the sinusoidal grating, and φ the phase shift between the gratings. It is obvious that maximal energy exchange will occur for 90° phase-shifted gratings.

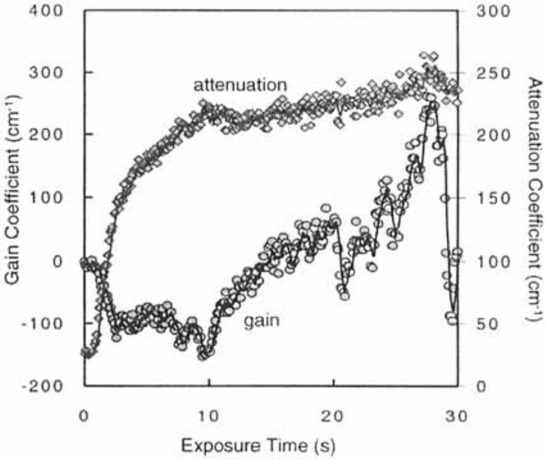

FIGURE 7. Plot showing dynamic gain and attenuation coefficients for 30 second H-PDLC cure.

Eq. 3 plus knowledge of the total transmitted beam intensity allows us to extract the attenuation coefficient (α) as a function of cure time. This is shown in Fig. 6. Attenuation for this sample peaks at ~250 cm^{-1}. Knowledge of the attenuation coefficient, and rewriting Eq. 6 as

$$\gamma = \frac{1}{L}\ln\left(\frac{mg}{(1+m)e^{-\alpha L}-g}\right) \qquad (8)$$

allows us to determine the coupling constant, γ, where we take beam 1 as the probe beam and beam 2 as the pump. The dynamic gain coefficient is also shown in Fig. 6 for this sample. This coefficient is seen to have negative values for $t<15$ seconds, corresponding to the probe beam being coupled into the pump beam. Maximum gain is seen in the final few seconds of the exposure, reaching a value of ~250 cm^{-1}.

DISCUSSION

The observation of nonlinear two wave mixing suggests that H-PDLC formation is a more complex process than the simple diffusion-counter diffusion models imply. The development of low-index polymer planes in the bright fringes, and high-index liquid crystal droplet planes in the dark fringes result in a π phase-shift between the static intensity and index gratings. According to Eq. 7, $\gamma = 0$ in this scenario, and no mixing occurs.

There are two dynamic parameters in Eq. 7 that contribute to the non-zero γ. These are the refractive index modulation, n_1, and the phase shift φ. The development of the refractive index modulation can be inferred from the attenuation coefficient. Both the coherent and incoherent contributions to the scattering are due to the formation of liquid crystal droplets in the dark fringes. From this we can infer that the growth of the attenuation coefficient corresponds identically to the growth of the grating index modulation, assuming that all the scattering centers form in planes. This information suggests that the index grating is formed in the first ~10 seconds of the exposure (see Fig. 6).

The gain coefficient, γ, continues to change dramatically at times long after this. In fact, samples left exposed to the beams continued dynamic energy exchange for up to 45 minutes after the initial illumination. This indicates that the mechanism responsible for the phase shift operates on time scales much longer than that of grating formation.

The optical performance of acrylate-based H-PDLC gratings is known to change marginally over time periods of several hours due to shrinkage of the polymer network [19]. Measurement of the peak shift in H-PDLC reflection gratings suggest that shrinkage may result in as much as 5% volume change in these materials [20]. Shrinkage of the polymer network to a "zero-point" located off-center in the region of exposure could serve to drag the index grating through the intensity grating, leading to the phase shift necessary to explain two wave mixing. Experiments are planned to probe this effect.

CONCLUSIONS

We have monitored the transmitted intensity of coherent, monochromatic beams during formation of H-PDLC transmission gratings. After a short period (< ~1 second) the total transmitted intensity is observed to decay. The degree to which this occurs is strongly dependant on the initial mass fraction of LC in the prepolymer. We attribute this to the formation of discrete scattering centers in the film, namely liquid crystal droplets.

Analysis of the single beam intensity reveals energy transfer between the beams in a two wave mixing process. This is evidence of a phase shift between the intensity grating writing the H-PDLC, and the resulting refractive index grating. The coupling shows no preferred direction and the direction of energy transfer is seen to shift from beam to beam. Coupling is observed for time periods far longer than the time period over which the gratings are formed. We suspect that mechanical shifts in the polymer matrix due to shrinkage are responsible for introducing the phase shift. Subsequent experiments are planned to probe this phenomenon.

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