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Periodic Polymer-Dispersed Liquid Crystal Structures

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Periodic structures in the form of optical and subwavelength gratings are formed as alternating slabs of polymer and polymer-dispersed liquid crystals in a pentaacrylate system. We analyze the physics of formation as well as the optical properties expected from these structures. Experimental confirmation of these concepts is presented. Possible electro-optical applications in devices are given.

Keywords: holographic gratings; polymer-dispersed liquid crystals

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films have been the subjects of intensive scientific investigation and commercial development.[1] As the name implies, the PDLC is a composite, two-phase material wherein the host phase is a solid polymer and the dispersed phase is liquid crystal (LC). Both polymer and LC are normally transparent in their bulk forms. The dispersed LC is usually in the form of microscopic droplets. They retain anisotropic dielectric and optical properties similar to those found in bulk form. The confined geometry of the droplet results in a director configuration that minimizes elastic free

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energy consistent with anchoring conditions at the LC-polymer interface. In general, this produces an effective refractive index of the droplet, as seen by light incident on the film at some angle, which is different than that of the surrounding polymer.

An important class of PDLC systems proceed to their final state by a process known as polymerization-induced phase separation (PIPS). The system begins as a homogeneous fluid mixture of polymerizable monomer, LC, and other ingredients. As the systems cures, phase-separated LC droplets form in the solid polymer. Two very different types of polymer reaction employed in fabricating PDLCs are free-radical and step-growth polymerization. Free-radical reactions form extremely high molecular weight polymer very early in the reaction, whereas in step-growth reactions the molecular weight grows slowly, achieving high molecular weight only near the end of the reaction. Consequently, the dynamics of phase separation and end-point morphology of the two-phase system are very different for these two reaction mechanisms. One significant difference can be droplet size. Droplets of size ~0.1-10 μm will scatter light significantly if the effective index of the droplet is different than that of the polymer matrix. Such films of typical thickness ~5-20 μm are milky white in appearance and opaque. PDLC films with droplets of size <0.1 μm produce only weak scattering and are optically clear.

A conventional PDLC film formed in a photo-PIPS process consists of a mixture containing a photoinitiator dye that is irradiated uniformly with incoherent light. Droplet nucleation is a stochastic process, and the phase-separated LC is uniformly dispersed throughout the polymer matrix. On the other hand, if the incident light has a spatial pattern, the resulting PDLC may be similarly patterned. A very unique formation of LC droplets is possible if the light is coherent and forms an interference pattern (i.e., a hologram). In a free-radical system with droplets small compared to an optical wavelength, it is possible to form a high quality hologram.[2] Droplet formation is no longer isotropic, and some unique structures can be built. The simplest of these is a structure consisting of periodic planar PDLC layers interspersed by solid polymer layers. The focus of this paper is on these types of structures.

The earliest reported work on the formation of holograms in PDLCs employed a commercial photopolymer manufactured by Norland.[3,4] These systems actually employ a combination of step-growth and free-radical polymerization, and droplet diameters were typically

≥1 μm. Since then several authors have reported on the optical and electro-optical properties of these films.[5-8] In 1993 we described a different system employing a pentaacrylate monomer.[9] We have demonstrated by optical diffraction measurements and scanning electron microscopy that this system allows formation of distinct PDLC layers with droplet diameter <0.1 μm, in some cases as small as 0.02 μm. PDLC layers are often only one droplet thick. Thus, it is now possible to consider holographic PDLC gratings with grating period Λ covering the range from $\Lambda >> \lambda$ to $\Lambda << \lambda$, where λ is an optical wavelength.

In this paper we discuss the formation of periodic PDLC structures in a pentaacrylate system with this range of grating period. We describe the theoretical formation of holographic gratings by anisotropic phase separation and the expected optical and electro-optical behavior of such structures. We then present some experimental data verifying these predictions, and provide some concepts for applying these results to devices.

THEORY

Consider a homogeneous mixture of monomer, LC, and other minor ingredients including photoinitiator and co-initiator. Such a mixture is irradiated at t=0 by a spatially sinusoidal intensity pattern as illustrated schematically in Figure 1. Since the rate of polymerization for a free-radical reaction is proportional to the square root of intensity, polymer chains will rapidly form in the regions of high intensity. As monomer is consumed to form the growing chains, a change in the chemical potential results. Monomer diffuses from the dark regions to the light regions. A gradient in the LC chemical potential is in the opposite direction, causing LC to diffuse to the dark regions. This occurs during a diffusion time t_d. Thus, polymer and cross-link density grow quickly in the bright regions, and LC collects in the dark regions.

Eventually the growing polymer network bridges the dark regions, and a gel network is established. This occurs in a time t_g as indicated schematically in Figure 1. The system has now undergone some demixing and is no longer in thermal equilibrium. As in ordinary PDLC materials, the free energy will be minimized by a separation of the two phases. However, the volume fraction of LC is now different in the dark and bright regions.

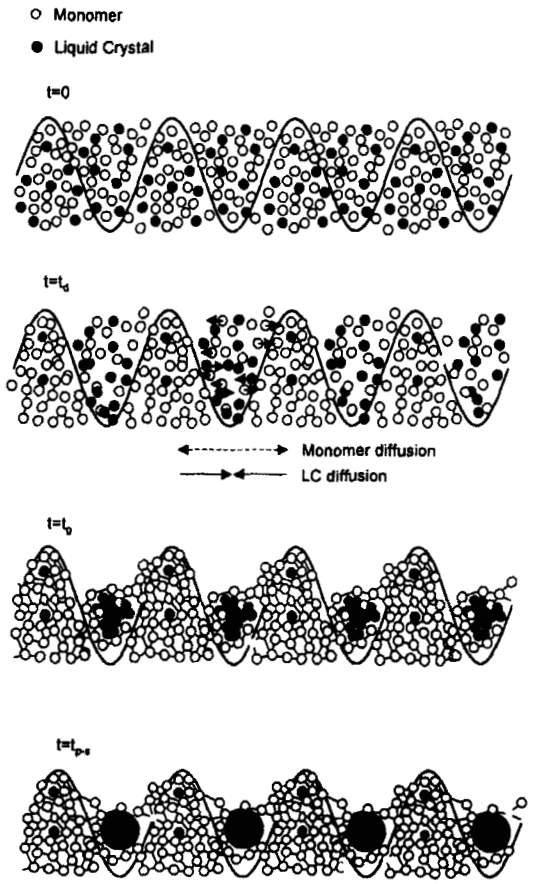

FIGURE 1 Schematic illustration of liquid crystal and monomer diffusion, gelation, and phase separation during holographic recording in a pentaacrylate PDLC system.

Figure 2 shows a typical upper critical solution temperature (UCST) phase diagram for an ideal two-phase system.[1] Above some temperature a homogeneous phase exists. Below this temperature a two-phase system exists, with the concentration of each phase given by the equilibrium tie-lines. In a reaction-induced phase separation, the phase envelope grows upward toward the right as indicated in Fig-

ure 2. When this envelope crosses ambient temperature T_0, the homogeneous phase will separate into two phases. The speed of the reaction determines where under the two-phase envelope the reaction stops. The location defines the tie-line, which in turn dictates the composition of the two phases, either rich or poor in LC. If the volume fraction of LC is low such as in the bright regions, the phase will be polymer-rich and LC-poor, such as point A in Figure 2. In the dark regions where LC concentration has built up due to diffusion, the phase will be LC rich, such as point B in Figure 2.

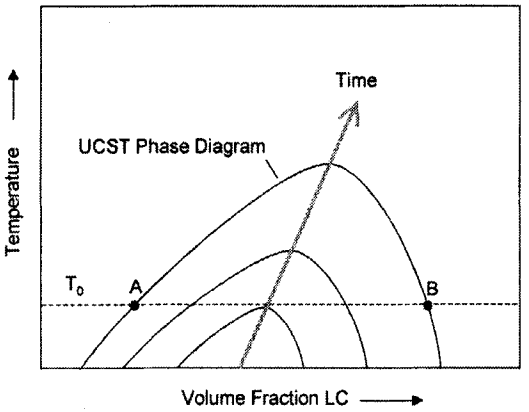

FIGURE 2 Schematic phase diagram for a reaction-induced phase separation.

The period of phase separation is marked as the time $t_{p\text{-}s}$ in Figure 1. The LC has now coalesced to microscopic droplets in the dark regions. A small amount of LC remains trapped in solution in the polymer-rich bright regions. Because of the rapid growth of polymer in the free-radical reaction and the exclusion of phase-separated LC by the dense cross-linked network in the pentaacrylate, the size of LC droplets is restricted to the order of $\Lambda/2$.

The directors in the phase-separated LC droplet assume some configuration imparting to the droplet an effective refractive index that is different from that of the surrounding polymer.[1] Thus, a periodic index modulation is established in the film. The optical properties of such a film will depend on the relative size of the period to the optical wavelength and the physical thickness L of the film.

Raman-Nath Gratings

A parameter Q may be defined as

$$Q = 2\pi \frac{\lambda L}{n\Lambda^2}, \tag{1}$$

where n is the average refractive index of the film.[10] For a sufficiently large period Λ or thin grating L, we arrive at the condition $Q<<1$. This is known as the Raman-Nath diffraction regime. Generally, $\Lambda>>\lambda$ for such a grating. In this regime, the effect of the periodic index modulation on an incident light wave is to essentially impart a periodic modulation on the phase of the wave front. When this periodic phase modulated light diffracts to the far field, it produces an amplitude-modulated wave with maxima at equally spaced points along a line perpendicular to the direction of wave propagation. A beam of light, e.g., from a laser, would thus diffract into a series of spots about the zero-order with angular separation $\theta\approx\lambda/\Lambda$. For example, with n=1.5, λ=0.633 μm, L=10 μm, and Λ=10 μm, we find Q=0.27. The angular separation of consecutive orders would be ~63 mrad.

As in an ordinary PDLC, the effective refractive index of the LC droplets can be modified by the application of an electric field. At some voltage, the LC index may match that of the polymer. The diffraction grating will then disappear, and only the zero-order beam will be transmitted.

Bragg Gratings

If conditions are such that $Q>>1$, then we are in the Bragg diffraction regime. Here there is no significant diffraction unless light is incident in a specific direction known as the Bragg angle, measured with respect to the film normal. At the Bragg angle, there is only one diffracted order, and it is possible for the diffraction efficiency in this order to approach 100%. For example, assuming the same parameters as above but with Λ=0.8 μm, we find Q=41. If Λ is reduced to 0.2 μm, then Q=663.

Two basically different types of Bragg diffraction grating can be formed. In a transmission grating the PDLC layers are perpendicular to the film plane, while in a reflection grating these layers run parallel to the plane. The diffraction efficiency for these types of grating has a different functional dependence on the index modulation.

Consider first an ideal planar transmission grating. The diffraction efficiency can be written as[10]

$$\eta = \sin^2 v \,, \tag{2}$$

where $v \propto n_1 L$, and n_1 is the index modulation amplitude due to the phase-separated LC. Notice that the diffraction efficiency will increase with the product $n_1 L$, reaching a theoretical maximum of 100% at $v=\pi/2$. If $n_1 L$ is increased further, η will decrease. This is known as the region of over-modulation for a transmission grating.

When an electric field is applied to a PDLC transmission grating, n_1 will decrease. The grating is effectively switched off when the LC index matches that of the polymer. The decrease in diffraction efficiency would generally be monotonic unless the grating is originally in an over-modulated condition. In this case the diffraction efficiency would actually increase at first as a voltage is applied, then decrease to zero when the LC and polymer indices are matched.

For an ideal planar reflection grating, the diffraction efficiency of the reflected order can be expressed by[10]

$$\eta = \left[1 + \frac{\left(1 - \xi^2 / v^2\right)}{\sinh^2 \sqrt{v^2 - \xi^2}} \right]^{-1} . \tag{3}$$

The transmittance T of the zero-order is then $T=1-\eta$. The transmission spectrum thus has a notch with minimum transmittance at the Bragg wavelength $\lambda_B = 2n\Lambda$. Note that for $\lambda_B = 0.5$ μm, we must have $\Lambda = 0.17$ μm for $n=1.5$. Thus, LC droplets are smaller than ~0.08 μm. The detuning parameter $\xi \propto (\lambda - \lambda_B)$ determines the fall-off of η (or rise in T) as the wavelength departs from the Bragg condition, and is hence related to the width of the transmission notch. We note from the functional dependence of Equation (3) that there will never be an over-modulation regime for reflection gratings. When a voltage is applied, the index modulation would decrease and the transmission notch would reduce to a flat spectrum, i.e., the reflection grating would become transparent at all wavelengths.

We see that in a Bragg grating $\Lambda \sim \lambda$. For a transmission grating, we normally have $\Lambda > \lambda$, while with a reflection grating $\Lambda < \lambda$. However, the two parameters are always of the same order of magnitude.

Subwavelength Gratings

Now consider a structure similar to a transmission grating, but with period $\Lambda << \lambda$. This is referred to as a subwavelength grating. This can be described as alternating thin slabs of PDLC and polymer with

thickness d_{PDLC} and d_{pol}, respectively, and refractive index n_{PDLC} and n_{pol}, respectively. The volume fractions of the two slabs are $f_{PDLC}=d_{PDLC}/(d_{PDLC}+d_{pol})$ and $f_{pol}=d_{pol}/(d_{PDLC}+d_{pol})$.

When $d_{PDLC}+d_{pol}<<\lambda$, the subwavelength grating exhibits a property known as form birefringence.[11] It acts effectively as a negative uniaxial crystal with an optic axis perpendicular to the PDLC slabs. The birefringence of such a medium is given by

$$\Delta n = n_e - n_o = -\frac{f_{PDLC} f_{pol}\left(n_{PDLC}^2 - n_{pol}^2\right)}{2\bar{n}\left(f_{PDLC} n_{PDLC}^2 + f_{pol} n_{pol}^2\right)}, \tag{4}$$

where $\bar{n}=(n_e+n_o)/2$, and n_e and n_o are the extraordinary and ordinary refractive indices. These are not to be confused with the indices of the bulk LC, which has a *positive* birefringence.

Light incident on a subwavelength grating will not be diffracted, but its polarization may be affected by the form birefringence. Hence, the subwavelength grating is useful as an artificial birefringent material, and may be employed as an optical retarder. Note that the net birefringence depends on the difference of the refractive indices of the polymer and PDLC slabs.

Generally, $n_{PDLC}>n_{pol}$. Therefore, Δn is negative. When a field is applied, n_{PDCL} would be reduced toward the polymer value n_{pol}. Hence the birefringence would be reduced and can become zero when the LC droplet index matches that of the polymer. The PDLC subwavelength grating would thus function as an electro-optic retarder.

EXPERIMENTAL

The recipe used in these investigations has been reported earlier,[9] and consists of pentaacrylate monomer, nematic LC, photoinitiator dye, co-initiator, and chain extender monomer. The LC concentration is typically in the range of 30-40 wt-%. The photoinitiator used is rose bengal. We recorded gratings in the standard way using either the 514.5-nm line of an Ar ion laser or at 532 nm from a diode-pumped, frequency-doubled Nd:YVO_4 laser. Samples were nominally 8-10 μm thick and sandwiched between transparent electrodes consisting of indium-tin-oxide (ITO) coated glass substrates.

Diffraction efficiency of transmission gratings was measured by directing the polarized output of a HeNe laser at 632.8 nm at the Bragg angle on a sample and measuring the power in the incident and first-

order diffracted beams, taking into account Fresnel reflection losses. Reflection gratings were characterized using an Ocean Optics fiber-coupled grating spectrometer. White light is collected from a fiber, collimated, and directed normally onto the sample. Transmitted light is collected by another optical fiber and directed to the grating spectrometer. A spectrum of the light with no sample in place is collected and used to obtain a baseline. Subwavelength gratings were placed between crossed polarizers and used in the same Ocean Optics spectrometer setup. For these experiments, the optic axis (grating vector) was placed at 45° with respect to the two polarizer axes.

Electro-optical measurements were performed in the same setups described above. A square-wave bipolar voltage was applied to the sample electrodes. Typical frequency of the waveform was 0.5-2.0 kHz. When voltage values are given, note that for a square-wave, root-mean-square voltage is the same as voltage amplitude or one-half of peak-to-peak voltage.

RESULTS AND DISCUSSION

Raman-Nath Gratings

Raman-Nath gratings are easily made in this system, as has also been demonstrated in Norland systems.[3] We have fabricated gratings in samples as thin as 5 μm with a 1-μm period. For 632.8 nm light, this gives Q~10. Between ideal Raman-Nath and Bragg regimes, multiple orders can be observed and are erased by the application of a suitable voltage. Since these types of gratings have been extensively reported in the literature,[3,4,7,8] we did not pursue these further.

Bragg Transmission Gratings

These gratings were recorded with a period Λ~0.8 μm in samples that are ~9 μm thick. Voltage-dependent diffraction efficiency of two different samples is shown in Figure 3. These two samples demonstrate the difference between the normal and over-modulated regimes. In the normal case, sample A, the diffraction efficiency drops monotonically with voltage, while the over-modulated grating, sample B, shows an initial rise in diffraction efficiency, hitting a maximum before declining. Both gratings can be switched effectively off at suitable voltage.

The transmission gratings are highly angle selective, showing very small diffraction efficiency a few degrees off the Bragg angle. The side-lobes in the angular sensitivity data are generally small. Large side-lobes are indicative of over-modulation, which is what we observed in the case of sample B.

Diffraction efficiency is typically in the range of 50-70%. We have, however, achieved η~90% in samples as thin as 5 μm.

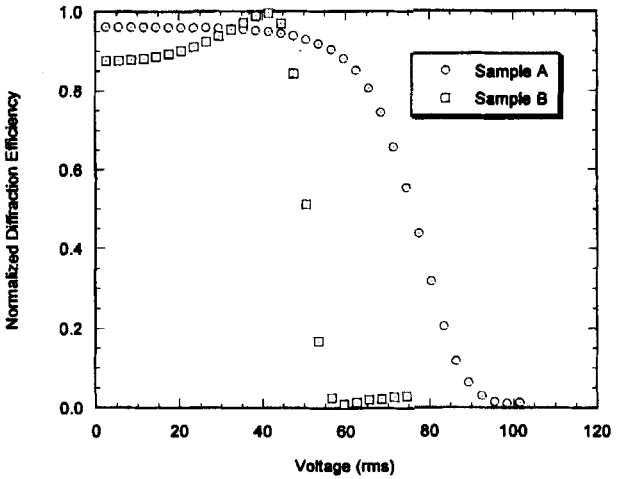

FIGURE 3 Normalized diffraction efficiency as a function of voltage in PDLC Bragg transmission gratings.

The switchable Bragg transmission grating is useful for dynamic beam steering and can be used as an optical switch. One example would be to switch the output of an optical fiber between two separate channels in a telecommunications system.

Bragg Reflection Gratings

The transmission spectrum of a PDLC reflection grating is shown in Figure 4. A bright green reflection could be seen from this sample in white light, indicating that the transmission loss is due to Bragg diffraction. The spectral notch is at 540 nm, indicating that the grating period Λ~0.18 μm. This is confirmed in scanning electron microscopy study of samples. The sample in Figure 4 achieved a diffraction effi-

ciency ~50%. With an applied field of 23 V/μm, the grating is effectively switched off.

Reflection gratings can be routinely recorded with diffraction efficiency ~30-60%. We have achieved η~80% in some samples. We have also successfully recorded reflection gratings with Bragg wavelengths across the visible spectrum into the near infrared.

Switchable Bragg reflection filters are of interest for reflective displays. They may also find use in dynamic color filters for projection displays or sensor protection.

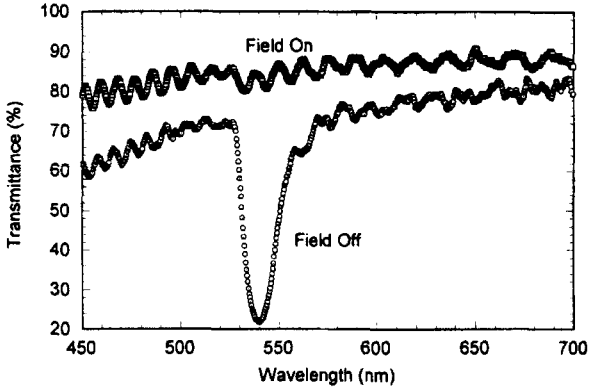

FIGURE 4 Transmission spectrum of a Bragg reflection grating formed in a pentaacrylate PDLC system.

Subwavelength Gratings

When polarized light traverses an optical retarder set at 45°, the plane of polarization for some wavelengths will be rotated by 90°. Those wavelengths will be passed by the second polarizer. Other wavelengths achieve less rotation and are hence blocked. An electro-optical retarder will experience a change in retardance with voltage, and hence a different set of wavelengths will experience 90° rotation and be passed by the polarizer. Hence the electro-optic retarder set between two polarizers functions as a tunable filter.

We placed a PDLC transmission grating between crossed polarizers and observed the spectral transmission. The results are shown in Figure 5. Note that the wavelengths of maximum transmission shift toward the blue with applied voltage. Thus, the PDLC is exhibiting electro-optically controlled birefringence.

The limiting speed of the tunable filter is given by the relaxation time when the voltage is turned off. This is ~250 μs, which is at least an order of magnitude faster than bulk nematic LC devices. We have observed relaxation times in some holographic PDLC devices that are at least a factor of 5 shorter.[2]

Subwavelength PDLC gratings may find several applications. Two possible areas are tunable filters for spectrometers and polarization switching.

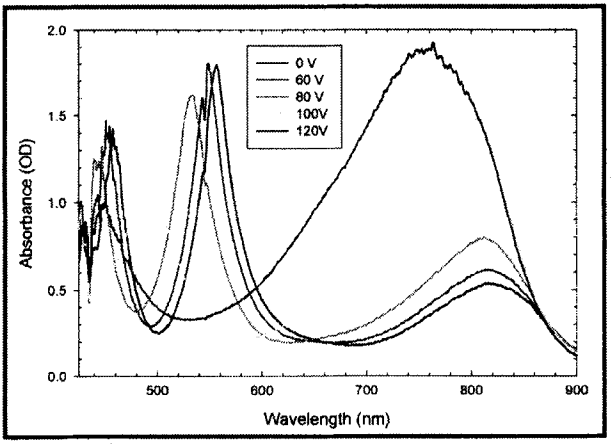

FIGURE 5 Spectrum of a pentaacrylate PDLC transmission grating situated between crossed polarizers. The grating vector (optic axis) is at 45° with respect to the polarizer axes.

CONCLUSIONS

We have shown that periodic structures may be formed in PDLC systems by free-radical photopolymerization combined with holographic recording. Submicron phase-separated LC droplets make possible gratings with period ranging from large to small compared to an optical wavelength. We have thus demonstrated that a range of devices from Raman-Nath gratings to artificial birefringent media can be synthesized holographically. The optical properties of each of these may be controlled electronically through the dielectric anisotropy of the LC droplets. Several potential device applications are possible.

Acknowledgments

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