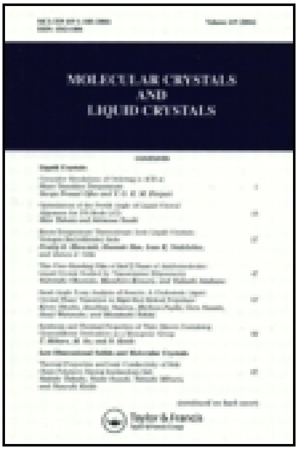

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Morphology of Holographically-Formed Polymer Dispersed Liquid Crystals (H-PDLC)

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Photopolymerization induced phase-separation of liquid crystal /polymer mixtures in holographic gratings show promise as switchable Bragg reflectors for optical communication and reflective display applications. The electro-optic properties of such Holographic Polymer Dispersed Liquid Crystals (H-PDLCs) are strongly dependent on polymer morphology and the degree of separation of the LC/polymer mixture. We report scanning electron microscopy, optical polarizing, and electro-optic studies on H-PDLC materials.

Keywords: polymer dispersed liquid crystal; holography

INTRODUCTION

Although dispersions of liquid crystal were first studied at the turn of the century[1], it is only in the last decade that they have leapt into prominence as materials ripe for application in new and emerging electro-optic technologies. In the mid-1980s it was discovered that one could conventionally disperse submicrometer and micrometer liquid crystal droplets in a rigid polymer binder either by phase separation[2] or emulsification methods[3],[4]. These dispersions became known as polymer-dispersed liquid crystals (PDLCs).

A nematic liquid crystal confined to a micron sized sphere will typically take on a bipolar configuration when homogeneously aligned[5]. A rich variety of other director fields are possible, but the bipolar configuration is most prominent in applications. With no applied field these polar configurations are randomly oriented through the bulk of a PDLC, ensuring a net refractive index mismatch between the droplets and the polymer. As such, the material is strongly light scattering and takes on a translucent white appearance. On application of an applied voltage the bipolar configurations align, and if the ordinary index of refraction of the liquid crystal, n_o, is matched to that of the polymer, the material will appear transparent.

Photocurable polymers, subsequently, have allowed the droplet density to be modulated on the order of the wavelength of visible light by employing holographic techniques. On exposure to an interference pattern, formed typically by two counter-propagating, coherent laser beams, polymerization is initiated in the light fringes. A monomer diffusion gradient is established as the monomer units are depleted in the light fringes, causing migration of the monomers from the dark fringes. Gelation locks the modulation in the polymer density. The result is LC droplet rich areas where the dark fringes were, and LC droplet poor regions where the light fringes were.

Switchable phase gratings formed by these techniques were reported by Sutherland *et al.*[6] in 1993. Setting up an interference pattern within the sample parallel to the substrate, Tanaka *et al.* [7] were able to phase separate the liquid crystal into Bragg planes. In the off state there exists a periodic modulation of the refractive index. The optical interference of the multilayer structure reflects light strongly at the Bragg wavelength, $\lambda = 2nd$ for normal incidence (d is the modulation wavelength), and transmits the rest. The spacing of the Bragg planes is governed by the wavelength of light used in photopolymerization as well as the geometry of the holographic setup. In the on state the index matching condition erases the index gradient and the material becomes transparent at all wavelengths.

Researchers at Xerox PARC[8] have been optimizing these materials for full-color, direct-view, reflective displays, and Foster-Miller Inc. has been developing novel uses of these materials in optical communication devices[9].

MATERIALS

The prepolymer syrup used consists of a nematic liquid crystal, a pentaacrylate monomer, a cross-linking agent, and a visible photoinitiator and coinitiator. The liquid crystal was the eutectic mixture TL205 ($n_o = 1.5$, $n_e = 1.71$) from Merck Ltd. The monomer was SR399* ($n_P = 1.49$) from Sartomer Inc. We obtained the chain-extending monomer N-vinyl pyrrollidone (NVP) from Aldrich Inc. The photoinitiator HNU-470 and coinitiator DIDMA were both made available from Spectra Group.

The materials were initially mixed in two parts: the monomer with the liquid crystal, and the photoinitiator and coinitiator with the NVP. The NVP is an excellent solvent and we could thus ensure that the powdered photoinitiator was thoroughly dissolved before the final mixing. The final mixing was performed under dark room lighting, ensuring no unwanted polymerization due to exposure to ambient room light. The prepolymer syrup was homogenized through repeated heating and mixing.

The mixture was pressed between two 1" x 1", ITO-coated glass plates. Fiber spacers, with nominal thickness 5μm, were used to control the cell gap. The materials were exposed immediately after filling.

HOLOGRAM RECORDING

The LC-polymer syrup was cured by exposure to two coherent, counter-propagating laser beams. The 514nm line from a Coherent Innova 90 Ar+ laser was employed. An etalon ensured single mode operation. The beam was expanded to approximately 1.5" diameter and then attenuated using an adjustable iris to about 0.75" diameter yielding reasonable intensity uniformity across its width. A laser-quality, quartz, 50/50 beam-splitter was used to split the beam into two equal-intensity, coherent beams. These were redirected back onto each other by two high-quality mirrors. The mirrors were easily adjustable allowing for multiple interference geometries to be readily used. A custom-made mounting stage was carefully placed at the confluence of the beams. Care was taken to ensure no more than a few centimeters difference in path length from the beam splitter to the stage for each beam, far less than the coherence length of the laser. Our optical setup was firmly mounted atop an 8' x 5' x 18" vibration isolation table. Exposure was typically for a 30-second time period. Laser intensity was approximately 200mW.

ELECTRO-OPTIC PROPERTIES

Reflectance spectra of the H-PDLCs were measured using a SpectraScan 705 spectroradiometer from Photo Research Inc. The samples were illuminated with a broadband white light source (20W Quartz Tungsten Halogen lamp from Oriel Corp.), which was collimated to provide parallel light rays. The specular nature of Bragg reflection dictated that extreme care had to be taken when aligning the sample to ensure that the H-PDLC peak was directed onto the spectroradiometer aperture. We had deliberately placed the sample mount slightly asymmetrically in the laser beams to make certain the specular reflection from the glass plates would not contaminate our measurements. The reflection from an regular mirror was also measured. This provided a benchmark against which all H-PDLC measurements could be normalized.

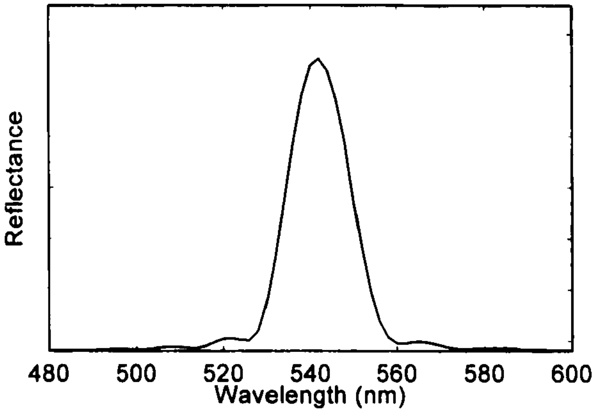

FIGURE 1 Typical reflectance peak of an H-PDLC.

Figure 1 shows one such spectrum. The ~15nm FWHM is typical of H-PDLCs. This sample has a peak reflectance of 25%, suggesting that index of refraction modulation amplitude is far smaller than that theoretically possible*.

SEM STUDIES

The morphology of the H-PDLC polymer networks was investigated by scanning electron microscopy (SEM) using a JEOL 840 field-emission SEM.

SEM Preparation

Selected samples were freeze fractured following immersion in liquid nitrogen. The sample fragments were placed in cyclohexane for several hours, extracting the liquid crystal from the polymer binder. During this process the peak reflection wavelength blue-shifted dramatically, corresponding to a

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* Modelled with Berreman 4x4 matrix method as a dielectric stack with a sinusoidally modulated index of refraction, using:

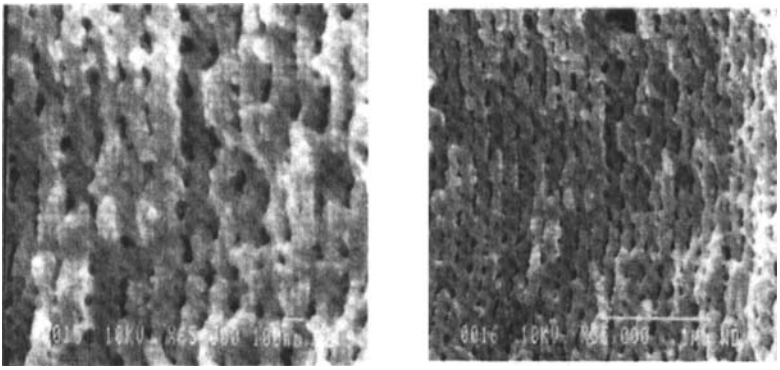
$\Delta n_{\text{theory}} = \langle n_{LC} \rangle - n_P \sim 0.08$, where $\langle n_{LC} \rangle = (2n_o + n_e)/3$

shortening of the optical thickness of the LC-rich layers. We attribute this to a combination of shrinkage and a decrease in the average refractive index following LC extraction.

On removal from cyclohexane the samples were oven baked at 50°C for several more hours. Finally the remaining polymer films were sputter coated with ~250Å AuPd before being mounted on the SEM chuck with Cu tape. When mounting, care was taken to ensure that the sample could be viewed edge on, so that the Bragg planes could be studied.

SEM Results and Discussion

SEM micrographs are shown in figure 2. Clearly evident are the alternating polymer-rich-polymer-poor planes composing the Bragg grating. The polymer density modulation wavelength of ~170 ± 10nm suggests that, for normal incidence, the Bragg condition is satisfied for $\lambda \sim 530 \pm 30$nm (for $n = 1.55$). This result is in good agreement with our spectroradiometer measurements.



(a) (b)

FIGURE 2 SEM Micrographs of H-PDLC's, (a) at 65kX and (b) at 35kX.

The cross-sectional view of the H-PDLC suggests that the liquid crystal is confined to droplets. The droplets do not display the spherical symmetry typical of regular PDLCs, instead being extended in the plane. This anisotropy could have significant impact on the nematic configurations within the droplets, which in turn could affect the electro-optic performance of these materials. Deciphering the droplet configuration is extremely challenging. Figure 3 shows a schematic illustration of an H-PDLC. For simplicity we can assume an elongated, ellipsoid-like droplet structure. In Figure 3 (a) the droplet director is along the long axis of the ellipsoid, and (b) is along the short axis. Based on elastic free energy arguments, (a) is certainly more energetically favorable than (b). Assuming a structure as in (a), one might expect a strong polarization dependence upon reflection if the droplets are aligned in one direction. Close examination of the SEM micrographs and preliminary polarization studies indicate that this is not necessarily the case. Our point here is that we do not know what the configuration is but it is clearly more sophisticated than conventional PDLC's. It is highly unlikely that a single optics or magnetic resonance technique can determine such a structure. Magnetic resonance techniques are going to be heavily diffusion averaged in cavities ~100nm in size.

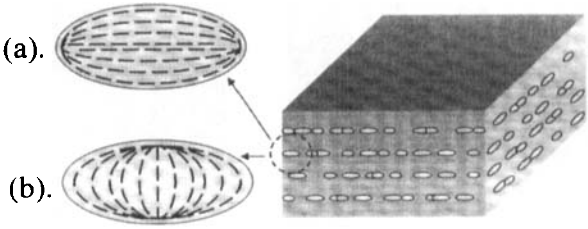


FIGURE 3 Illustration of possible director configurations within ellipsoid cavities. (a) shows a more energetically favorable configuration than (b).

A further departure from traditional PDLC characteristics are the size of the droplets. H-PDLC droplets have diameters on order of ~100nm, an order of magnitude smaller than the 1-3μm typical of PDLCs. This has direct consequences for the electric fields required to switch such materials which scales as the inverse of the droplet diameter. Hence voltages one or more orders of magnitude greater than those required for PDLC's are needed to switch H-PDLC's. Initial studies indeed show this to be the case.

Arial density studies of such micrographs reveal that only ~10-15% of the material consists of LC droplets. Some of this can be attributed to shrinkage of the polymer on LC extraction, however having an LC loading of ~40% suggests that the degree of separation of the polymer and LC is far from ideal. An obvious consequence of this is a reduced refractive index modulation amplitude (Δn) than that posssible, reducing the reflection efficiency of the stack. Clearly, achieving a greater degree of separation is equivalent to fully optimizing the constituent material properties of H-PDLC's.

CONCLUSIONS

We have fabricated and analyzed holographic volume gratings in polymer dispersed liquid crystalline materials. Our materials exhibit a strong reflection at the Bragg wavelength. Scanning electron microscope studies reveal a dramatic modulation of the polymer density through the depth of the grating.

Many characteristics of these materials warrant further study, especially if they hope to realize their potential for application in direct-view reflective displays and as switchable optical elements in the myriad of technologies now employing electro-optics.

Firstly, a more thorough understanding of polymerization induced phase separation (PIPS) is required, especially for photo-PIPS employing spatially inhomogeneous exposures, in order to maximize the degree of separation and control polymer morphology.

Determination of director fields for nematic LC's confined to asymmetric submicrometer cavities should be investigated if one hopes to accurately model the electro-optic characteristics of these materials. This problem is extremely difficult in such small cavities, and it is our feeling that it will require a battery of both experimental and theoretical techniques to draw any conclusions regarding these director configurations.

Acknowledgments

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