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**MORPHOLOGICAL STUDIES OF BRAGG REFLECTION
GRATINGS WRITTEN IN HOLOGRAPHIC POLYMER
DISPERSED LIQUID CRYSTALS BY THIOL-ENE
PHOTOPOLYMERIZATION (PREPRINT)**

Timothy J. Bunning

Hardened Materials Branch

Survivability and Sensor Materials Division

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*//Signature//

TIMOTHY J. BUNNING, Ph.D.
Research Lead
Exploratory Development
Hardened Materials Branch

//Signature//

MARK S. FORTE, Acting Chief
Hardened Materials Branch
Survivability and Sensor Materials Division

//Signature//

TIM J. SCHUMACHER, Chief
Survivability and Sensor Materials Division

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Morphological Studies of Bragg Reflection Gratings Written in Holographic Polymer Dispersed Liquid Crystals by Thiol-ene photopolymerization

Jeremy M. Wofford⁴, L.V. Natarajan², R. L. Sutherland², Vincent Tondiglia², Pamela Lloyd³, Timothy J. Bunning¹
¹AFRL/Wright-Patterson Air Force Base, ² Science Applications International Corporation, 4031 Col. Glenn Highway, Dayton, OH, ³ UES Incorporated, Beavercreek, OH, ⁴ Southwestern Ohio Council for Higher Education: Student Research Program, Wilmington College, OH.

Abstract

Recently, a new photopolymerization system for writing visible light initiated thiol-ene based H-PDLC Bragg reflection gratings was developed. Using this new method, Bragg reflection gratings were written with notch wavelengths out into the NIR. The aim of the present work is to determine the grating parameters like spacing, LC width, polymer width and droplet density from morphological studies and compare with those obtained from optical measurements. The electro-optical performance of the gratings is also interpreted in terms of the morphology. The morphological properties of these gratings were obtained from TEM and cryo-SEM microscopy. The spacing, LC droplet sizes and droplet densities correlate very well with the optical and electro-optical performance of the gratings.

Introduction

Recently, there has been much interest in holographic polymer-dispersed liquid crystals (H-PDLC) formed by non-homogeneous spatial illumination of monomer/LC mixtures.¹⁻³ Constructive interference of laser beams on a pre-polymer syrup containing multi-functional monomers, nematic LC, dye and a co-initiator results in the anisotropic distribution of polymer and LC-rich layers leading to a periodic refractive index modulation which can be electrically modulated. The resulting reflection gratings have potential as electro-optical devices in a variety of display and communication applications⁴. In order to better understand the optical and electro optical properties of H-PDLCs, and compare with the data obtained from optical measurements, morphologies were examined by TEM and Cryo-SEM techniques. Cryo-SEM is needed as previous work indicates classic SEM does not work on thiol-ene gratings. Thus, TEM has been the only morphological method to gather information. Since TEM is labor intensive Cryo-SEM was examined as a complementary technique.

Experimental

The pre-polymer syrup was made up of a visible photoinitiator Rhodamine6G, a co-initiator Benzoyl peroxide, N-vinyl pyrrolidinone a reactive diluent, a nematic LC BLO38, and the commercially available thiol-ene NOA65. Optical characterization of the gratings was done with an Ocean Optics spectrophotometer and a Cary UV-Vis-IR spectrometer. For electrical switching, square waves signal at 1 KHz operating from 0 to 200 V RMS was applied, and changes in DE were noted. Samples for TEM microscopy were embedded in flat molds using Epo-fix resin and cured overnight in a 60° C oven. The blocks were trimmed and ultramicrotomed at room temperature using an RMC Ultramicrotome. Sections of 50-60 nm thickness were cut with a 35° Diatome diamond knife, picked up onto 400 mesh grids and vapor stained with RuO₄. The sections were then imaged using bright field transmission electron microscopy (BFTEM) performed on a FEI CM200FEG TEM.

Cryo SEM studies were made using the Hitachi S5200. The Hitachi S5200 is a high resolution field emission SEM and was operated at 1.5kV and 2kV to image the liquid crystals domains within the gratings. We used a Gatan CT6000 which is a combined CT3500 (cryo transfer holder) and an Alto 2500IL (cryo prep and transfer system for SEMs). Each HPDLC sample was quickly frozen in an LN₂ reservoir within the sample prep chamber. The sample is freeze fractured at -182°C using a cold knife fracturing device within the system. The sample is sublimed to eliminate any frosting that occurred when moving it into the Alto System. The temperature is brought to -90°C and held there for 5 minutes. After coating with Au-Pd, the temperature is lowered back down to -182°C. Once the temperature is reached, the cover shield is placed over the specimen, and the holder is quickly transferred to the microscope. Digital images were taken of the samples at varying magnifications. All measurements, namely, grating spacing, LC-rich width, Polymer-rich width, droplet size and droplet densities were taken from the pictures provided from SEM and TEM. Representation morphology is shown in figures 1 & 2.

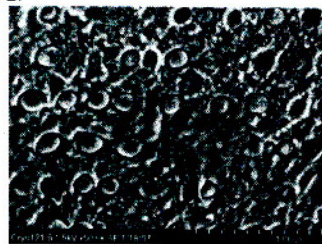


Figure 1: Cryo-SEM picture of 1050 nm grating.

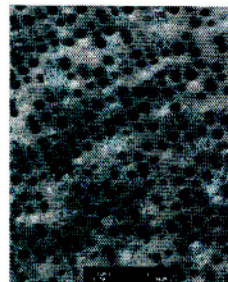


Figure 2: TEM image of 1050 nm grating

Results and Discussion

The d spacing of the gratings is found by taking the position of the notch and dividing by two times the refractive index of the samples. These findings were then compared to the d spacings found from the TEM and Cryo-SEM. The spacing obtained from the optical analysis was found to follow the same trend as that from the TEM and SEM analysis. (Figs.3). The spacings obtained from TEM and cryo-SEM (Two different methods) are in good agreement.

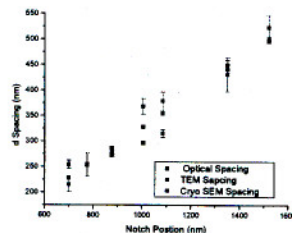


Figure 3: Comparison of spacing obtained from optical and morphology studies

The diffraction efficiency (DE) of the gratings was found to decrease as the notch wavelength increases. DE's varied from 75% for a 700 nm notch and 15% at 1600 nm notch. (Fig. 4) There are several reasons for the DE decrease with spacing. The number of layers in a given thickness decreases as the d spacing increases. The overlap of the laser beams for writing longer wavelength notches also become less efficient as the angle of incidence on the single prism increases. Finally, the birefringence of the LC decreases at longer wavelengths. (Fig. 4)

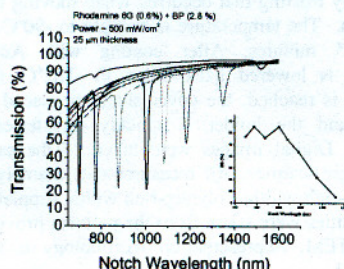


Figure 4: DE decreases with increase of notch wavelength

Polymer and liquid crystal widths were measured and found that as the d spacing increases so does the width of the LC and polymer domains. (Figs. 5 and 6). To better understand the relationship between the polymer and liquid crystal region we look at the ratio of polymer to liquid crystal as the d spacing increases. It was found that the ratio stays relatively constant at all d spacings, showing that there is minimal shrinkage in the gratings.

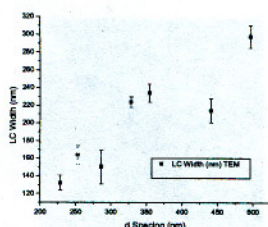


Figure 5: Increase of LC rich region width as notch spacing increases

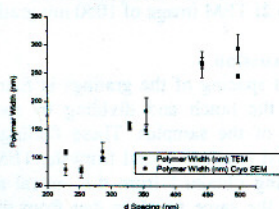


Figure 6: Polymer width variation with notch increase.

The average size of the droplets can be estimated by taking the average radius of the droplets and using $A = \pi r^2$. As the d spacing is increased the size of the droplets was found to increase.

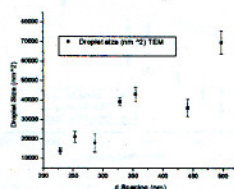


Figure 7: LC droplet size increases with grating spacing

The droplet density was found to decrease in the LC rich region as the d spacing was increased (Fig. 8). This may be due to the increase in the liquid crystal droplet size. It is likely that the diffusion of LC into the dark region is less efficient as d spacing increases. A similar trend was observed in systems that used acrylates as polymer hosts¹.

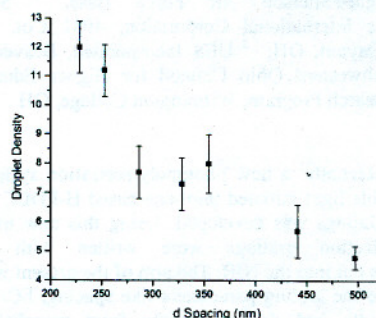


Figure 8: Droplet density decreases with grating spacing

Gratings written on ITO coated glass were used to electrically switch the gratings. The switching voltages for the grating d spacings 241nm, 351 and 424 nm were 10V/μm, 8 V/μm, and 6 V/μm respectively. (Fig. 9). The decrease in the switching voltage is consistent with the increase in the size and density of the liquid crystal droplets.

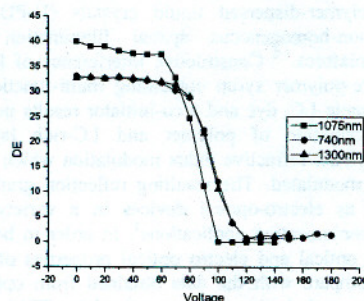


Figure 9: Switching voltage

Summary

Our studies on the morphologies of the reflection gratings demonstrate good agreement with the optically measured d spacing. This is indicative of very minimum shrinkage in the thiol-ene polymers. Second, that the morphology helps to explain the decrease in the DE as the notch wavelength is increased. The third relationship that can be drawn is that the ratio of polymer to liquid crystal stays constant through out the different d spacings. Finally, that the switching voltage is decreased as the notch wavelength is increased.

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