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Comprehensive Examination of the Morphology of Holographic Polymer Dispersed Liquid Crystal Reflection Gratings Written in Thiol-ene Polymer Hosts

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Holographic polymer-dispersed liquid crystals (H-PDLC) are formed by the non-homogeneous spatial illumination of monomer/LC mixtures. The anisotropic distribution of polymer and LC-rich lamellae give rise to a periodic refractive index modulation, which can be electrically modulated. Thiol-ene polymers are well known for their role in the preparation of UV curable coatings and adhesives. These polymers are formed by the combination of step growth and free radical reactions between multifunctional aliphatic thiols and vinyl monomers. The initial steps involve free radical initiation processes, followed by a step growth propagation mechanism. The MW of the polymer increases slowly, as the number of monomers increases above a critical concentration, a liquid-liquid phase separation occurs. Because both phases are liquid and the viscosity is low, the discontinuous phase typically is spherical due to surface tension effects. As the reaction progresses, at some point the polymer/monomer phase vitrifies and traps the oval domains (Figure 1 (a) and (b)). The optical properties of these two phase composites can then be electrically modulated.

We routinely use SEM (Hitachi S5200) and TEM (Philips CM 200 LaB_6) techniques to investigate the internal morphology of these grating systems. One problem that is encountered is the physical collapse of the grating structure in the SEM due to the removal of the LC domains during sample preparation. While we do get a sense of the overall morphology of the grating, the grating spacing is somewhat smaller than those measured through optical techniques. TEM methods, while providing somewhat better agreement with optical methods, is time consuming. In order to fully characterize the H-PDLC morphology we have investigated a suite of techniques to capture the morphology of these complex composites. Low voltage TEM, (Figure 1(c)) obtained using the Delong LVEM 5 was also investigated. Due to sample thickness limitations for LVTEM, ultramicrotomy was accomplished using a DiATOME oscillating diamond knife. Low voltage STEM (Figure 1(d)) (Hitachi S5200) was also used to help minimize the shrinkage due to electron beam interactions. However, we experienced the same problems as before. We have also utilized STEM tomography (Figure 1(e)) (FEI Tecnai G^2 S-Twin). The tomographic analysis provides some information as to the bulk morphology and shows promise and will be investigated further. The most promising technique so far is using cryo-SEM (Figure 1(f)). In room temperature SEM, the LC must be extracted with methanol prior to imaging. This creates voids in the grating, which leads to the aforementioned shrinkage. In cryo-SEM (Hitachi S5200 with a Gatan cryo-stage) we are cooling the sample to -190^{o}C, which locks the LC within the grating. This technique shows no shrinkage, is relatively quick and has allowed us for the first time to image the as formed LC droplets within the grating. Cryo-FIB is another technique that will provide us with a better understanding of the bulk morphology. Three dimensional reconstruction of the bulk grating can be accomplished utilizing the

serial sectioning capabilities of a dual beam FIB. This paper will compare and contrast all of these methods.

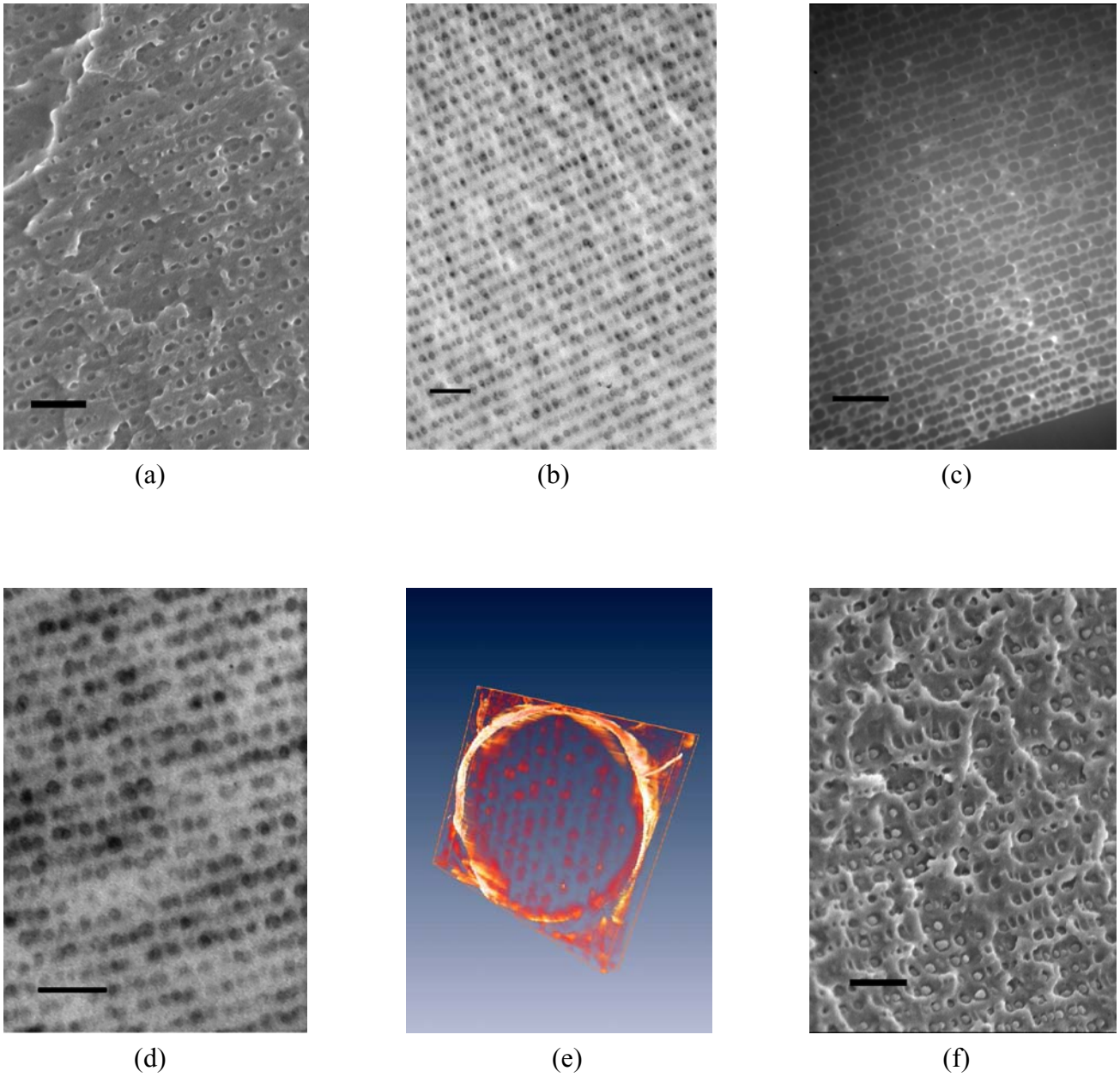

Figure 1: (a) SEM scale bar is 500 nm, (b) BFTEM scale bar is 500 nm, (c) LVTEM scale bar is 500 nm; (d) LVSTEM scale bar is 500 nm, (e) Tomographic STEM, (f) Cryo-SEM scale bar is 500 nm

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