

Polymer/LC Composite for Holographic Grating

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Introduction

Holographic polymer dispersed liquid crystals (HPDLC) are prepared by causing interference between two coherent laser beams in a photopolymerizable monomers/liquid crystal (LC) mixture contained between two substrates coated with a conductive layer typically of indium-tin oxide (ITO)[1]. HPDLC has such advantages as high diffraction efficiency, high color purity, fast response and easy fabrication. So, HPDLC devices have a number of potential applications in optical communications, flat panel displays, information storage and integrated optics[2].

We report the effects of various additives and prepolymer molecular structures on the droplet morphology and electrooptic properties of holographic polymer dispersed liquid crystal and describe the structure, operation, fabrication method, and the electrooptical characteristics of the HPDLC device based on the various structures of polyurethane acrylate (PUA).

Experimental

To form a HPDLC device, a homogeneous mixture of monomer (oligomers), reactive diluents, LC, and additives are prepared. Polyurethane acrylate is a segmented urethane oligomer tipped with acrylic functionality and it offers excellent toughness and chemical resistance than any other class of radiation curable oligomers. N-vinyl-pyrrolidinone (NVP) and dipentaerythritol penta-hexa-acrylate (DPHPA) were respectively used as mono- and multi-functional monomers[3]. Rose Bengal (RB) was used as photoinitiator for holographic recording with an argon ion laser because it displays a broad absorption in the region of 450 to 560nm and has a high triplet quantum yield. To this, millimolar amount of N-phenylglycine (NPG) was added as coinitiator.

The choice of the liquid crystal plays a very important role in the electro-optical performance and diffraction efficiency of the HPDLC. We have used E7 (BL001, Merck). Also, various additives (fullerene, pentaerythritol tetrakis(3-mercaptopropionate)(PETMP), octanoic acid) were used.

The cell was constructed by sandwiching the LC/prepolymer mixture between the two indium-tin-oxide (ITO) coated glass plates, with a gap of 4.2 ~ 20 μ m adjusted by a bead spacer. The prepolymer mixtures have been irradiated with two Ar-ion laser (514nm) of equal intensity with a total power of 100mW, and exposure time of typically 180-600s. The incident angles of the two beams outside the cell was respectively 13°. Interference pattern was made according to the Bragg's law ($\Lambda = \lambda / 2 \sin \theta$).

Results and discussion

Effect of fullerene. Fullerene-free sample showed no induction period, but an early overshoot and asymptotic decrease to a saturation value of diffraction efficiency. This series of event are indicative of fast reaction, fast phase separation, fast grating formation and subsequent droplet coalescence to sizes large enough for random scatterings. Fullerene induced an induction period due to its preferential absorption of green light, followed by a gradual increase of diffraction efficiency to a saturation being increased with fullerene content. The increased saturation efficiency is based on the decreased droplet size and increased droplet density being visualized by SEM.

In the presence of fullerene, decreased droplet size with increased droplet density augmented off state diffraction, while increased local electric field overcome the threshold and reduced operating and saturation voltages. Both decay time and rise time decreased with fullerene due respectively to the increased local electric field and decreased droplet size which are regarded as the dual effects of fullerene.

Effect of pentaerythritol tetrakis. With the addition and increasing amount of thiol, gel content increased while the crosslink density of polymer decreased. This implies that thiol-seeded radical consumes additional monomers in addition to its role as chain transfer

agent. This, together with significantly decreased induction period gave early and high degree of monomer conversion into polymer of rather low molecular weight, allowing the mobility of mixture.

However, with an excessive amount of thiol (> 1%, presently), reaction notably chain transfer reaction dominates phase separation and much of the LC is entrapped within the polymer phase. This gives a decreased mismatch of refractive index and narrow LC channel as noted from the SEM morphology. The optimum content of thiol seems about 1% for film containing 35% LC. An optimum amount of LC seems to exist from the viscosity and kinetic points of view. With insufficient LC, mixture viscosity becomes too high and mobility too low resulting in slow reaction, poor phase separation and low diffraction efficiency. In contrast, reaction is too slow with too much LC due to the low monomer concentration, which again leads to poor phase separation as noted from the SEM morphology. This seems especially true with more thiol where networks are loosely structured.

Effect of octanoic acid. Addition of a surfactant viz. octanoic acid to the holographic polymer dispersed liquid crystal (HPDLC) gave significant effect on the switching performance by modifying interfaces and droplet morphology. OA seems to envelope LC droplet, as predicted by the positive value of spreading coefficient, thus reducing the interfacial tension (anchoring energy), droplet coalescence and size, switching voltage and response time.

Small droplet with high droplet density augmented the off state diffraction by minimizing random scatterings, and lowered the on state diffraction due to the increased orientation of directors owing to the low anchoring energy. Reduced anchoring energy seems to overcome the large elastic energy of small droplet to lower the on state diffraction and switching voltage.

The spreading coefficient predicted the encapsulation of LC droplet by OA and the miscibility decrease between LC and polymer with increasing PPG molecular weight, and proved useful to evaluate surfactant performance. On the other hand, a dimensionless group introduced by the dimensional analysis possibly explained the droplet coalescence behavior with the variations of LC and OA contents.

Conclusions

A number of new ideas have been implemented to control the droplet morphology and electrooptic properties of holographic polymer dispersed liquid crystal. Doping of conductive fullerene particles to the conventional HPDLC induced dual effects of reducing both droplet coalescence and operating voltage. Fullerene induced an induction period which otherwise does not exist, followed by a gradual increase of diffraction efficiency to a saturation value being increased with increasing fullerene content. The increased diffraction efficiency was caused by the decreased droplet coalescence which was due to the hindered migration of LC by the fullerene particles. On the other hand, doped fullerene particles augmented the conductivity of polymer phase and hence the local electrical field imposed on LC droplet, which overcome the threshold for driving and reduced operating voltage and response times.

Transmission grating of HPDLC prepared in the presence of chain transfer agent gave higher gel content with lower crosslink density, less dark reactions and less grating shrinkage with much smooth LC-polymer interfaces, smaller induction period and fast saturation of diffraction efficiency showing a maximum of 95% with 1% CTA. An optimum LC content of 35% has also been verified based on morphology and reaction kinetics.

Addition of octanoic acid to the formulation of HPDLC gave a decrease in droplet size and monotonic increase of the off state diffraction throughout the OA content. However, decrease of the on state diffraction with increasing applied voltage showed a minimum at 6% OA, where a minimum switching voltage (5V/m) and maximum contrast ratio (10) were obtained. Rise time and decay time decreased with increasing OA content. On the other hand, the interposition of OA between polymer and LC droplet was theoretically predicted by the spreading coefficient.

References

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