Electro-optic Properties of Holographic PDLC with Various PUA Structures

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Abstract

Characteristics of holographic polymer dispersed liquid crystal(HPDLC) were studied according to various matrix materials to improve the electro-optic properties. Various types of polyurethane acrylates (PUAs) have been designed and synthesized. The morphologies of these gratings were measured by atomic force microscopy(AFM) and electro-optic properties were obtained with UV-visible spectroscopy. Real time measurements of grating fabrication have been obtained according to PUA structures. High reflection efficiency was obtained by modifying the molecular structure.

1. Introduction

With regard to portable information display, reflective flat panel technology has been aggressively pursued by many research groups to satisfy many new and emerging portable product categories. A new technologies in these reflective display field is holographic polymer dispersed liquid crystal(HPDLC). Reflective holographic polymer dispersed liquid crystal(HPDLC), which is formed by applying the holography method to the polymer dispersed liquid crystal(PDLC) has been expected as a potential candidate of a high brightness full color reflective display because polarizer and color filter are not necessarily used in HPDLC.

Photopolymer system has been developed for holographic applications, offering significant advantages over the conventional volume phase holographic media. It is possible to form holographic gratings in these materials in a single-step process at relatively high speed, and the selection of different sensitizing dyes allows the use of several different optical wavelengths. A particularly interesting modification is the addition of nematic liquid crystal(LC) materials, which leads to the intriguing possibility of electrooptical properties.

In HPDLC, the dispersion of the LC in the photopolymer matrix is often generated by polymerization induced phase separation (PIPS) where the prepolymer and LC are mixed together and then polymerization is induced photochemically. The domain size in PIPS is relevant to the rates of polymerization and phase separation. In PIPS, phase separation occurs with the progress of polymerization due to the unfavorable increase in Gibbs free energy of mixing(ΔG_{mix}) owing to the decrease in the entropy of mixing(ΔS_{mix}) since progressively smaller number of molecules become involved

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

where T is the absolute temperature.

Phase separation phenomenon is a rate process where such transport property as diffusivity takes an important role in determing the rate of phase separation. Diffusion of low molecular species such as low molecular weight, on the other hand depends on the degree of polymerization.

We extensively studied the effects of prepolymer molecular structure on the properties of HPDLC. Polyurethane acrylates(PUAs) have used as photo-curable materials in our experiment because PUAs have great advantage of easy structure control, i.e., their molecular structures can be easily controlled by varying the molecular parameters of raw material. The functionalty of PPG and hydroxy acrylate in polyurethane acrylate has been systematically varied for HPDLC, and the morphology and reflection efficiency of these HPDLC films have been studied with an emphasis on the role as polymer matrix.

2. Experimental

Urethane oligomers can be prepared from a large, diverse raw materials. PUA is a segmented urethane oligomer tipped with acrylic functionality. Trifunctional polypropylene glycols with different molecular weights (Mn=500, 1000, 2000g/mol) (Korea Polyol) were dried at 80°C, 0.1mmHg for several hours until no bubbling was observed. Extra

pure grade of hexamethylene diisocyanate(HDI) was used without further purifications. Molar excess of diisocyanate was reacted with PPG for over 3 hour at 80°C to obtain NCO-terminated prepolymer. Then, the reaction mixture was cooled down to 40°C and hydroxy ethyl acrylate(HEA) was added to obtain HEA-capped urethane oligomers. Also, highly functionalized PUA was synthesized by capping pentaerythritol triacrylate(PEAT) at NCO-terminated prepolymers which were obtained from bifunctional PPG and HDI. The basic chemistry for preparing Pua is shown in Figure 1.

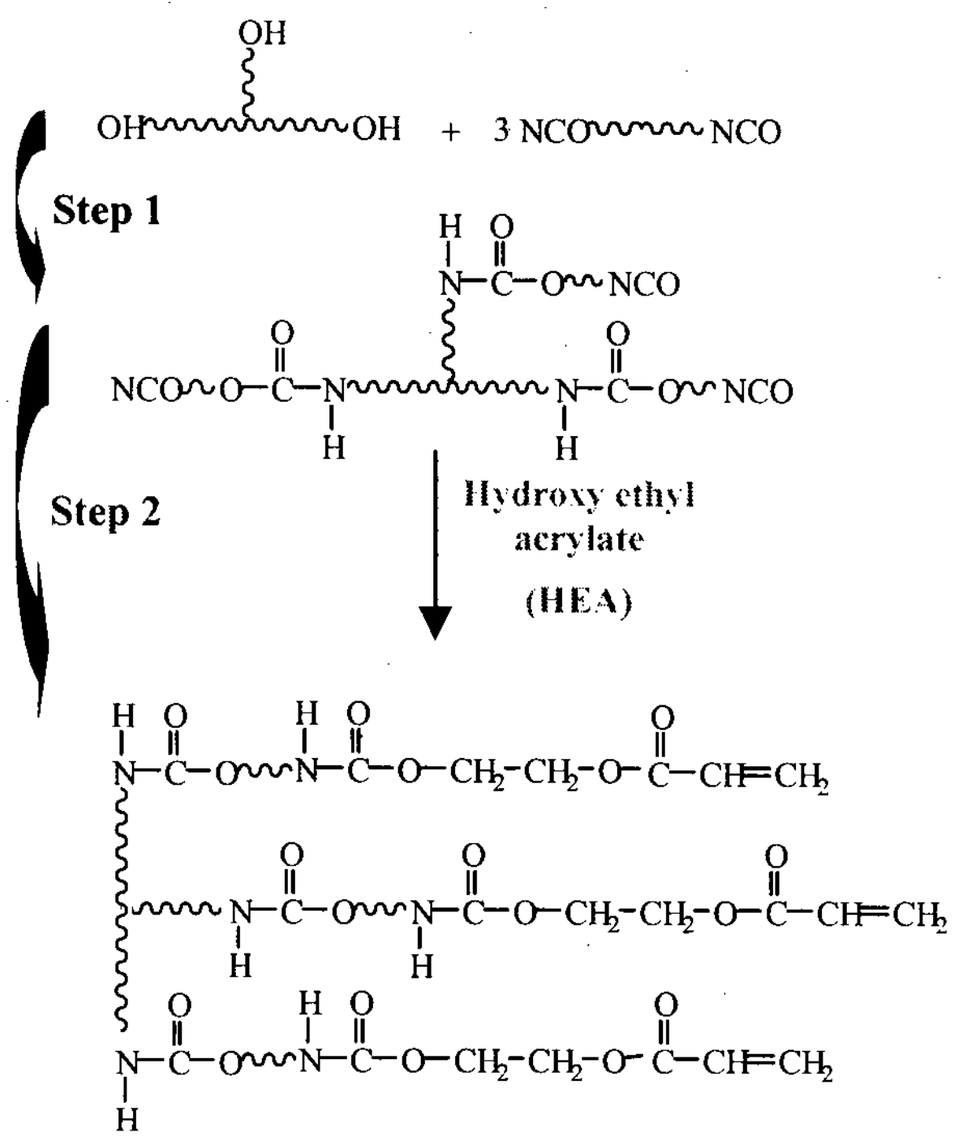

Figure 1. Basic chemistry for preparing PUA.

An eutectic mixture of cyanobiphenyl and cyano terphenyl components with n_o =1.5216, n_e=1.7462, and T_{NI}=61°C(E7) was used as LC. E7 is composed of 47% of K15(4-n-penty-4′-cyanobiphenyl, commonly known as 5CB), 25% of K21(4-n-heptyl-4′-cyanobiphenyl), 18% of M24(4-n-octoxy-4′-cyanobiphenyl), and 10% of T15(4-n-pentyl-4′-cyano-p-terphenyl). The LC content of the composite mixture was 35wt%.

The oligomers are highly viscous and immiscible with LC, which necessitates the use of reactive diluents. The reactive diluents used in our experiments are N-vinyl-pyrrollidone(NVP) and trimethylol propane triacrylate(TMPTA), and the composition of oligomer/monofunctional/multifunctional was 4/2/4 by weight.

A dye, Rose Bengal(RB), was used as photoinitiator for holographic recording with an argon ion laser, because it displays a broad absorption spectrum with a peak molar extension coefficient of about $10^4 M^{-1}cm^{-1}$ at about 560nm. To this millimolar amount of N-phenylglycine(NPG) was added as coinitiator.

Holographic grating was accomplished through the preferential formation of photoproducts in the region of constructive interference arising from the overlap of two laser beams, called object and reference beams. In Figure 2, the holographic recording system is schematically shown. The cell was constructed by sandwitching the monomer/LC between indium-tin-oxide(ITO) coated glss plates, with a gap of 10μm, adjusted by a bead spacer. The prepolymer mixtures with various structures have been irradiated with Ar-ion laser(514nm) at various intensities(50mW/cm^2-200mW/cm^2), with exposure times of typically 50s~200s. Grating formation was monitored in real time using an in-suit HeNe laser probe with incident angle set at the appropriate Bragg angle.

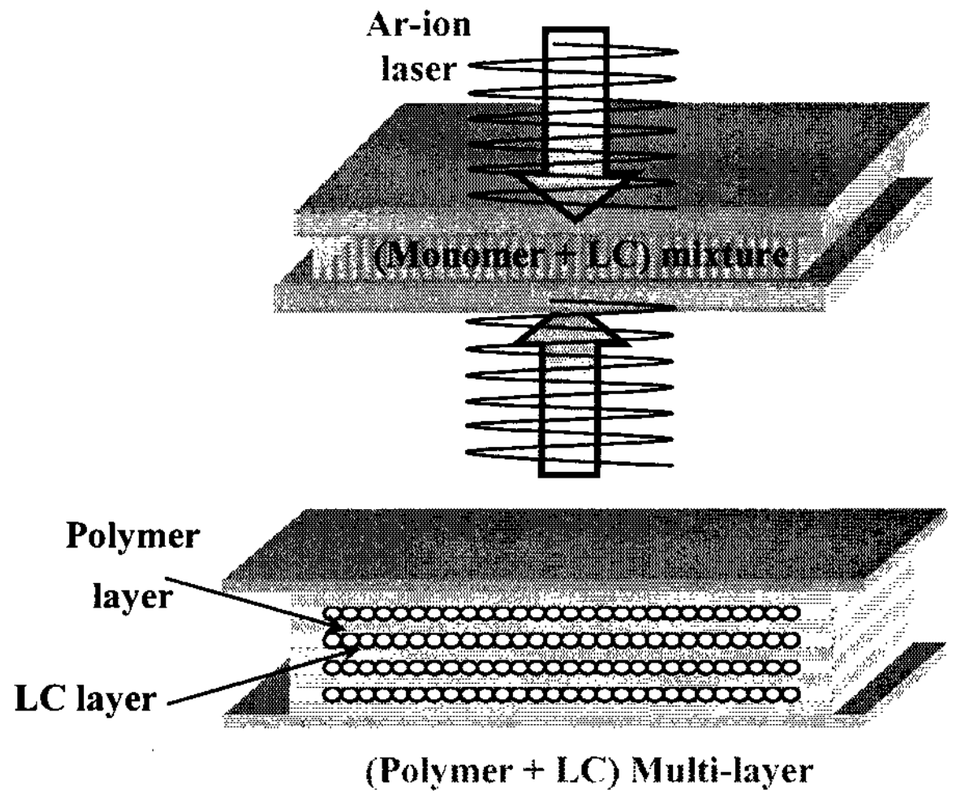

Figure 2. Fabrication method for reflection mode HPDLC film.

3. Results and Discussion

Mechanism and Rate of Grating Formation

The laser beam was reflected according to the Bragg angle and reflected beam intensities were measured with the use of a power meter. The reflection efficiency (RE) as a function of time is given in Figure 3, showing three main regions: (1) a short induction period; (2) a period of polymerization indicated by rapidly increasing reflection efficiency; and (3) a plateau where reflection efficiency doesn't increase anymore. The time of rapid rise in RE is involved with the growth and final development. The early portion of the curve in Figure 3 may be indicative of the nucleation time for phase separation of the LC droplet.

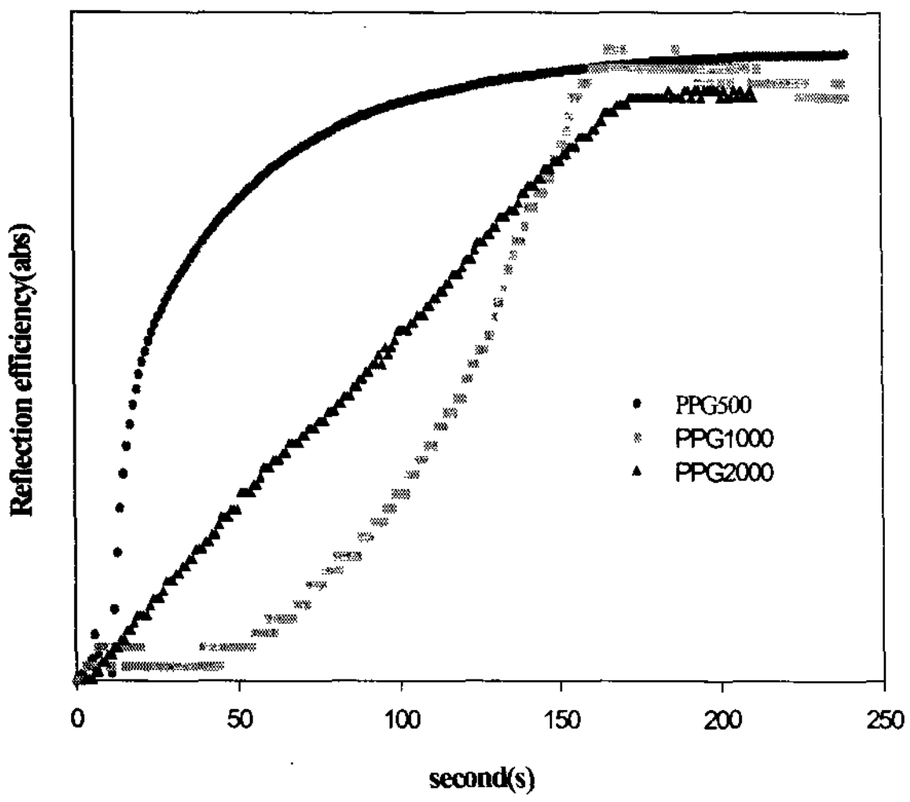

Figure 3. Reflection efficiency as a function of time at 633nm in a HPDLC sample.

It is seem that second period varies according to the molecular weight of PUA. The saturation time of these systems is decreasing along PPG2000>PPG1000>PPG500. This is due to different polymerization rate according to PUA molecular weights. As molecular weight of PUA decreases, the ratio of terminated acrylate group increases, which makes the rate of polymerization fast. It is clear that the rate of polymerization become fast with increasing the number of functional group in PUA

Effect of Prepolymer Structure on Reflection Efficiencty

In reflective HPDLC, reflection efficiency should depend on LC droplet size and density. Small droplet size and high droplet density generally increase the reflection efficiency. Figure 4 shows the reflection efficiency of the composite films prepared from three different molecular weight of PPG, i.e., Mn=500, 1000, and 2000.

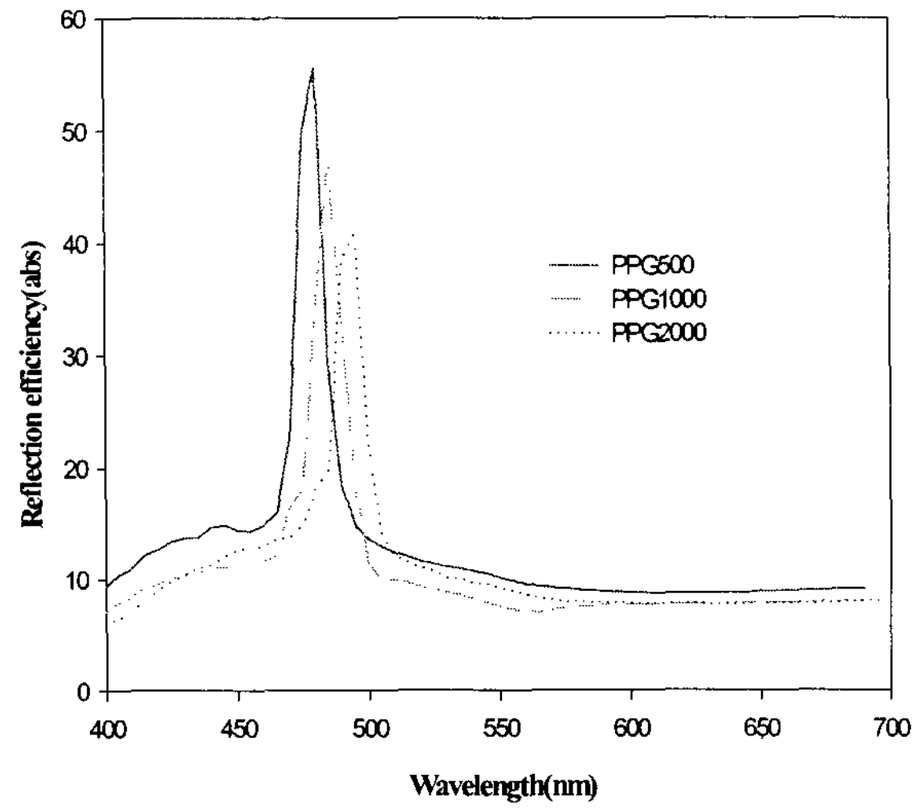

Figure 4. Effect of PPG molecular weight on reflection efficiency of HPDLC films at 250mW/cm^2.

It is clearly seen that the reflection efficiency decreases with increasing Mn of PPG. The NCO terminated polyurethane(PU) prepolymers were reacted with the hydroxyl group of HEA and irradiated by Ar-ion laser to build up acrylate blocks on the vinyl groups of HEA to form polyurethane acrylate(PUA), Mn of PPG is proportional to the molecular weight between crosslinks(Mc) bridging the acrylate domains(Figure 1). Therefore, as Mn of PPG decreases crosslinking density increases. This morphology control seems to give small LC droplets and high droplet density.

Besides, the decreased mutual solubilities of PUA and LC with decreasing Mn of PPG should also contribute to the increased reflection efficiency via the decreased miscibility between polymer matrix and LC molecules. Solubility parameter(δ) is one method of determining the miscibility of polymer and low molecular weight species, and quantifies the relative strength of the interactions between polymer and low molecular weight species viz. LC. Solubility parameter can be related to the cohesive energy(E_{coh}) density by

$$\delta = \left(\frac{E_{coh}}{V} \right)^{1/2}$$

For PUA, cohesive energy density increases with increasing Mn of PPG leading to a large deviation of δ

from that of LC molecules. The increased hydrophobicity of PUA with increasing PPG content should give decreased interactions with LC molecules which are highly polar, and consequently large droplet size and small droplet density are expected

RGB Stacking

Figure 5 shows that peak of RGB reflection from a stack of HPDLC films. A white light source was impinged on the stack of three films with electric field off, and the corresponding absorption peaks composed of 470nm, 490nm, and 610nm, each representing blue, green, and red gratings are recorded. Upon applying the electric field, the refractive index of LC matches with that of polymer, and all components of the incident light pass through the film and the film becomes transparent.

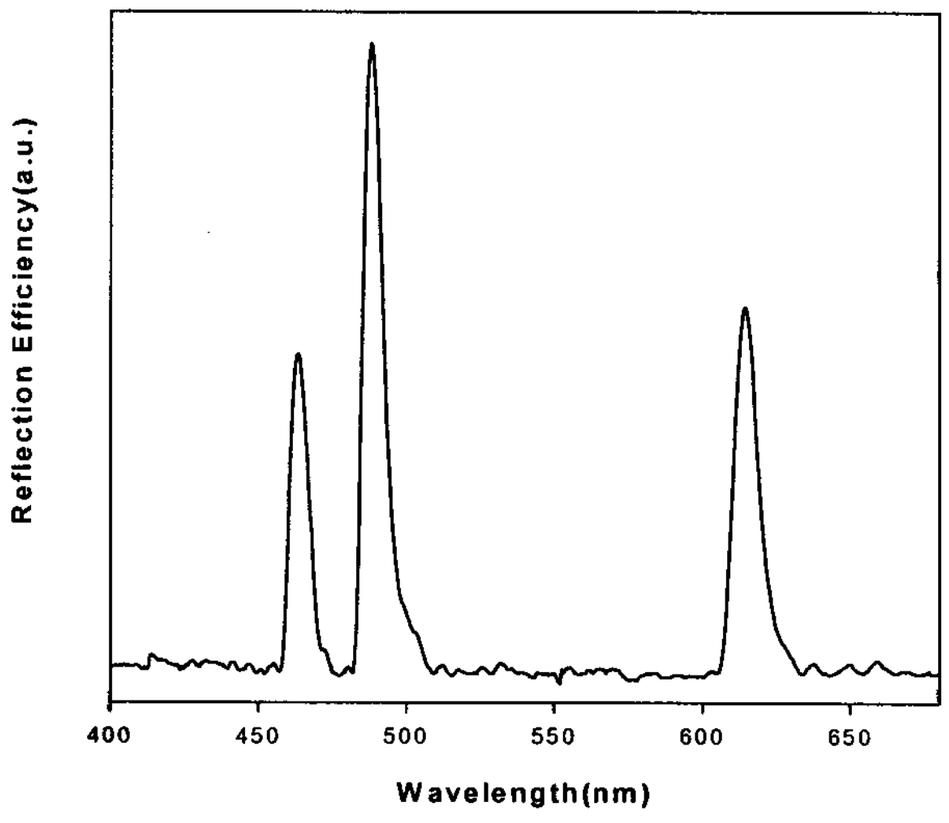

Figure 5. The UV-visible spectra of the stacked RGB holographic films.

4. Conclusion

Investigation of the effects of varying prepolymer molecular structure has been conducted in holographic PDLC gratings. As the molecular weight of PPG (soft segment length of PU) increases reflection efficiency decreases. This was possibly interpreted in terms of decreased crosslinking density of matrix polymers and decreased miscibility between polymer and LC.

Among tree types of Mn of PPG and functionality of PUA, the highest reflection efficiency was obtained at Mn=500 and f=3. This result indicates that a decrease in the prepolymer functionality leads to decreased LC phase separation as indicated by the lower diffusion through polymer matrix. Besides, very high functionality of prepolymer also leads to the same result. This can be understood in terms of unvalance of the polymerization rate and LC diffusion rate.

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