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Transmission Mode of HPDLC Based on Rubbery Polymers

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Abstract

We used three types of reactive diluents with different chemical structures, N-vinyl-pyrrollidone(NVP), ethyl hexyl acrylate(EHA) and hydroxyehtyl methacrylate(HEMA). It was founded that N-vinyl-pyrrollidone(NVP) and ethyl hexyl acrylate(EHA) based PUA with low molecular weight polypropylene glycol(PPG) at low oligomer content give high diffraction efficiency. The morphology of the resultant gratings was analyzed by using scanning electron microscopy(SEM) and Tg of the polymer matrix by dynamic mechanical thermal analysis(DMTA).

1. Introduction

Polymer dispersed liquid crystals(PDLCs) are of technological importance in the development of switchable windows, electro-optic shutters, displays, and most recently switchable gratings[1]. The most versatile method to form PDLC structures is photo-initiated polymerization of an initially homogeneous mixture containing reactive monomers and liquid crystals molecules. Recently, volume holography techniques have been applied to the conventional PDLC and fabricated the controlled architectures of phase separated LC domains[2-4].

Since the polymerization rate is proportional to the square root of laser intensity in radical polymerization[5], polymerization occurs rapidly in bright regions and slowly in dark regions of the interference patterns[6,7]. So, with the progress of polymerization, more monomers are consumed in bright region making a concentration gradient perpendicular to the grating direction. On the other hand, LCs in bright region are separated from the resins(oligomer. monomer, polymer) which undergo polymerization since solubility of LC decreases as oligomers and monomers become polymers giving high concentration of LC in bright region. This results in a counter diffusion of LCs and monomers between bright and dark regions.

This type of molecular diffusion is dominates until the concentration gradient of monomer is significant. As more of monomer is consumed concentration gradient becomes small and the counter diffusions no longer govern the migration of LC molecules. At this stage a second driving force for the migration of LC molecules is built up due to the polymer elasticity called hooping stress[8]. This hooping stress squeezes LC molecules out of the polymer phase and extracted LC forms LC-rich straits in the holograms. This phenomenon is directly related to the polymer elasticity which can be expressed in terms of primary normal stress difference or simply elastic modulus of polymers.

We fabricated the transmission type holographic PDLCs as a function of acrylate type, film and resin compositions, molecular weight of polyol(PPG) and cell thickness. Emphases were made to elucidate the effect of reactive diluent on diffraction efficiency hoping that diffraction can be understood in terms of dynamic mechanical properties of the polymer films.

2. Experimental

Polypropylene glycol(PPG) various molecular weight(Mn=100,200,300,400,500,600, Korea Polyol) was dried at 80℃, 0.1mmHg for several hrs until no bubbling was observed. Chemical reagents of hexamethylene diisocyanate(HDI), hydroxyethyl methacrylate(HEMA) were used without further purification. PPG, HDI and DBTDL(0.03wt% based on base PUs) were mixed and reacted at 80℃ for 3 hrs to obtain NCO terminated prepolymer. The reaction mixtures were then cooled to 45℃ before HEMA was added to obtain HEMA capped urethane acrylate oligomers[9]. The basic formulation in Table 1.

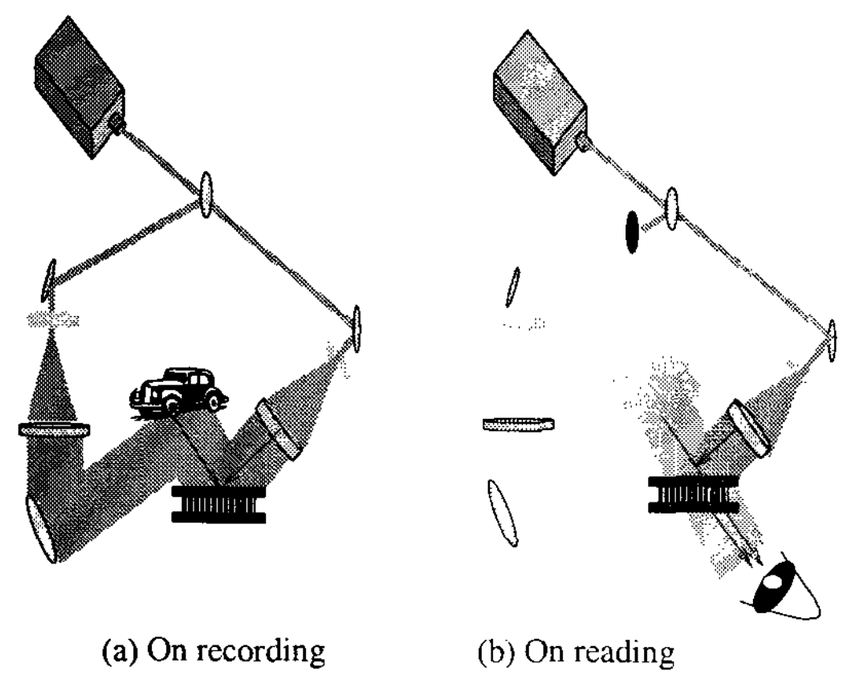
The films used for this study were prepared using a homogeneous prepolymer syrup consisting of a urethane acrylate oligomer, the nematic LC(E7), and the monofunctional monomer, viz. hydroxy ethyl methacrylate (HEMA), ethyl hexyl acrylate(EHA), and N-vinylpylloidone(NVP). The use of mono-

functional monomer is essential to reduce the viscosity of LC/oligomer mixture to ensure the starting mixture is homogeneous. Rose Bengal(0.03wt%) was used as photoinitiator for holographic recording with Ar-ion laser, where NPG(0.18wt%) was added as coinitiator.

Table 1. Formulation to prepare HPDLCs

Oligomer/ diluent	LC Content (wt%)	Rose Bengal (wt%)	NPG (wt%)
3:1	25	0.03	0.18
	30		
5:1	35		
	40		
7:1	45		

The holographic recording system we used is schematically shown in Figure 1. An Ar-ion laser(λ =514nm) was used as light source. Beams pass through a spatial filter, a beam expander, and are splitted into two of identical intensity.



(a) On recording (b) On reading

Figure 1 Experimental setup for transmission mode HPDLCs.

Dynamic mechanical properties of PUA films were measured using a Dynamic Mechanical Thermal Analyzer(Rheometry Scientific DMTA MKⅢ) with a tensile mode at a heating rate of 4℃/min and 10Hz. SEM(scanning electron microscopy) morphology of the gratings were obtained upon extracting the LC molecules in methanol.

3. Results and discussion

Typical dynamic mechanical behavior of the polyurethane acrylate(PUA) films is shown in Figure 2. We had controlled Tg by altering the kinds of mono-function monomer. The glass transition temperatures of each sample were measured to be 55℃(NVP system), 47℃(HEMA system), 21℃(EHA system). This leads to an order of room temperature modulus of EHA< HEMA< NVP. The lowest Tg of EHA based PUA comes from the large pendant group of PUA which separates the main chains away from each other. On the other hand, a five-numbered cyclic group attached to the vinyl carbon of NVP augments the rigidity of NVP main chain. Also, these results show that polymer matrix of EHA system is being used at its rubbery state at room temperature. With low Tg system, the anchoring energy at the interface of the LC and the polymer matrix could be lower and give smaller driving voltage.

The diffraction efficiencies of the HPDLC films are given in Figure 3. Three types of monofunctional acrylates, viz. hydroxy ethyl methacrylate (HEMA), ethyl hexyl acrylate (EHA), and N-vinylpylloidone(NVP) are being used with HEMA capped polyurethane prepolymer to give oligomer/ NVP, oligomer/HEMA and oligomer/EHA systems. The diffraction efficiencies of HPDLC films of NVP system are greater than those of HEMA and EHA systems. Also, with decreasing soft segment length of the oligomer, diffraction efficiency is significantly increased. Diffraction in HPDLC is based on the difference in refractive indices between resin and LC domains, i.e., the perfectness of phase separation governs the diffraction efficiency. On the other hand, LC-resin phase separation depends on the rate of cure and rate of diffusion. As soft segment length of the oligomer decreases, elasticity could increases due to the increased elasticity of polymer domains via hooping stress. The increased elasticity should squeeze the LC molecules out of the polymer domains. However, although HEMA system has great modulus than EHA at room temterature, the diffraction efficiencies of EHA system are greater than those of HEMA system. This is because the pendant methyl group could provide the molecules

with steric hindrance resulting in phase separation as well.

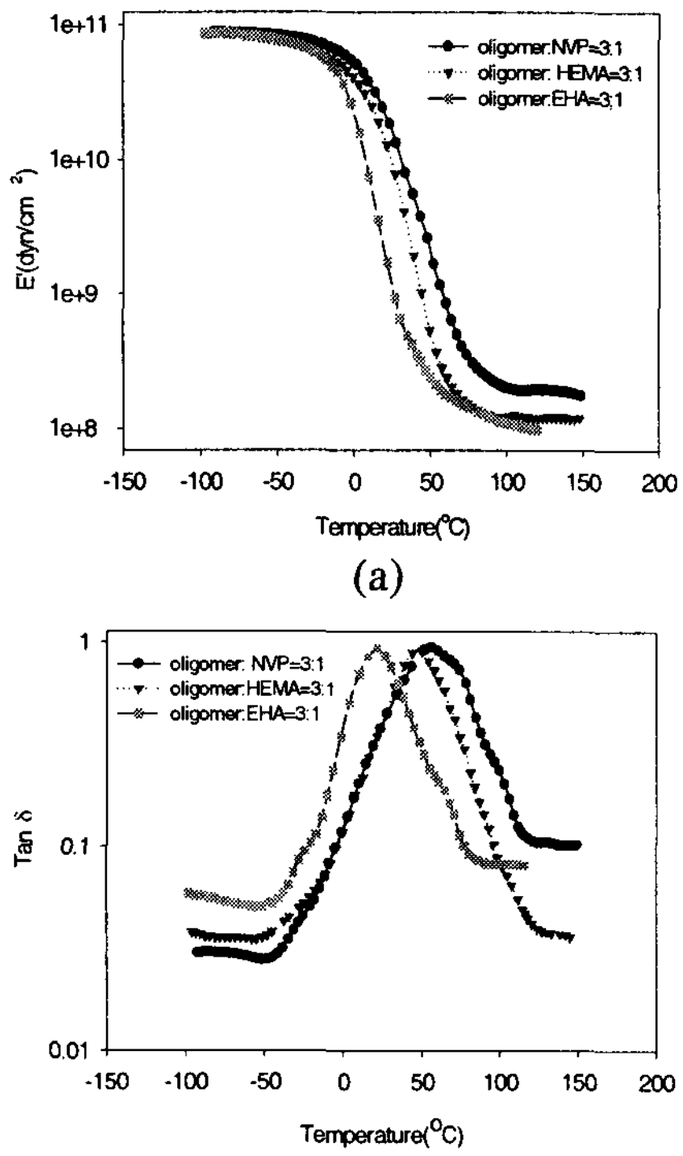
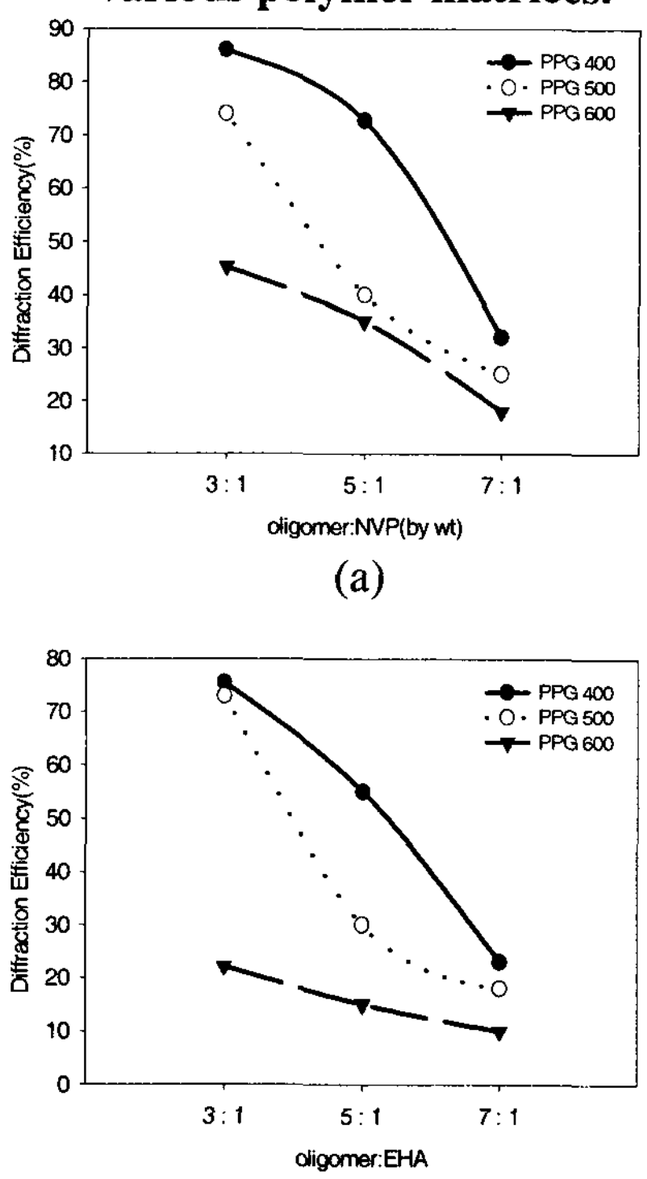


Figure 2 Storage modulus and tanδ of various polymer matrices.



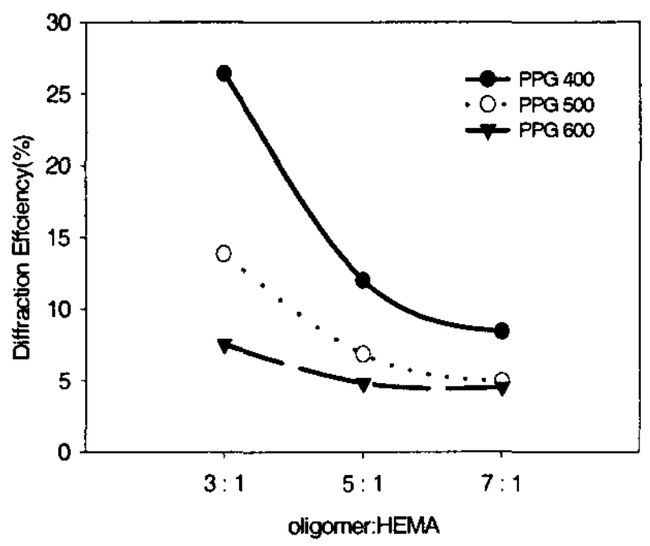
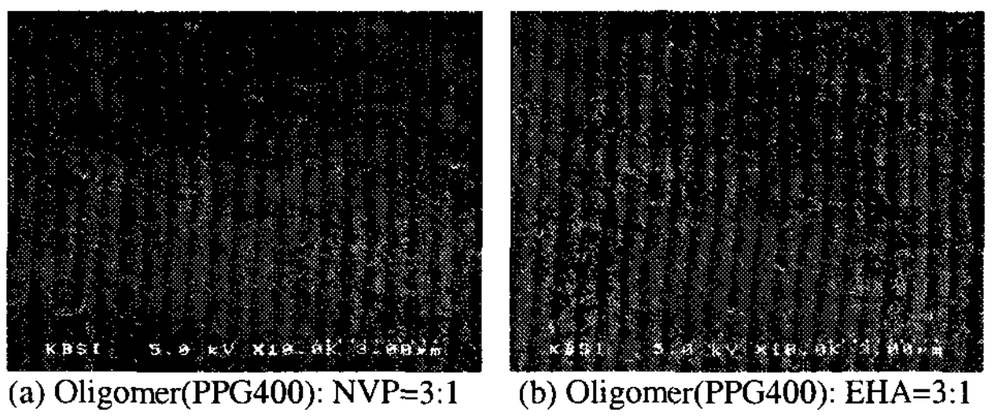


Figure 3 Diffraction efficiencies of the various resin compositions (35wt% LC, 90mW/cm^2).

Typical SEM morphology of the holographic gratings fabricates at 514nm, 90mW/cm^2 for 150s exposure time is shown in Figure 4. Channels of EHA based films are a bit distorted along the grating irection as compared with NVP based one. This is probably due to the flexible nature of EHA based PUA.



(a) Oligomer(PPG400): NVP=3:1 (b) Oligomer(PPG400): EHA=3:1

Figure 4 SEM morphologies of Bragg gratings at incident angle 45° (35wt% LC , 90mW/cm^2,)

4. Conclusion

Transmission modes of holographic polymer dispersed liquid crystal(HPDLCs) have been designed and fabricated based on the molecular structure of polymers, film and resin compositions. NVP and EHA gave much higher diffraction efficiency as compared with HEMA based PUA It is interpreted in terms of low reactivity of HEMA which leads to slow rates of reaction and diffusion and grating formation.

ffraction efficiency generally decreased with increasing PPG molecular weight and oligomer contents of film. This is due to the slow rate of cure by the decreased number of reactive sites, high viscosity,

and low PUA elasticity to squeeze the LC molecules out of polymer-rich phase.

5. Acknowledgements

The research has been supported by the Korea Ministry of Science and Technology(MOST) and Ministry of Information and Communication(MIC) via IMT2000.

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