Electro-optical properties of low viscosity driven holographic polymer dispersed liquid crystals

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Abstract

Relative diffraction efficiency (RDE), operating voltage, and response times are most important performance characteristics of holographic polymer dispersed liquid crystals (HPDLC). Two types of triallyl isocyanurate (TI) having different structures were incorporated into the conventional transmission grating of HPDLC. Premix viscosity decreased by 13–18% with up to 3% TI, beyond which it increased. TI eliminated induction period and augmented initial grating formation rate at all contents. Saturation RDE increased over 200% while threshold voltage and rise time decreased to about half and 2/3, respectively up to 3% TI, beyond which the tendencies were reversed. Among the two TIs, low viscosity monomer (TA) showed high RDE, while high miscibility monomer (TE) low characteristic voltages and short response times. It is concluded that grating formation is largely favored by low viscosity, while interface tensions and electro-optical performances by miscibility at similar viscosities.

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1. Introduction

The dynamic diffraction gratings based on holographic polymer dispersed liquid crystals (HPDLCs) have great potentials in a variety of applications such as flat-panel displays, optical data storage, optical switches for telecommunication, specific lenses, remote sensing, and many other electro-optical devices [1–3]. In most applications, HPDLC films should have high relative diffraction efficiency (RDE), a low threshold and driving voltage, and a fast response time [4–7]. These properties are largely governed by the morphology which mainly depends on the chemical structure of the matrix polymer and polymer-LC interactions in addition to the LC characteristics [8–10].

Effects of diluent functionality and oligomer molecular weight on RDE and shrinkage of PUA based HPDLC have been reported [13,14]. Linear aliphatic diisocyanate which is less miscible with aromatic LC gave clean phase separation and high RDE as compared with aromatic diisocyanate [15]. Silicone monomer increased grating formation rate and decreased the switching voltage due to the increased polymer-LC phase separation which is driven by the increased immiscibility [16]. Great solubility parameter (SP) gap between polymer and LC generally induced fast formation of grating, large droplet size and high RDE.

The thiol-ene polymer synthesized from thiol monomers and ene (vinyl) group monomers recently received attentions due to the stable device performance for up to three years [3,17,18]. As compared with the allyl ether monomer such as trimethylolpropane triacrylate (TMPTA), allyl isocyanurate (called TI) (Scheme 1) is thermally stable and reacts fast. In HPDLC, TI was considered in thiol-ene system. The fast reaction reduces the rate of demixing and droplet size giving rise to increased baseline transmission. On the other hand, poor solubility of LC in TI leads to poor morphological texture and low RDE, which was improved by mixing TI and allyl ether monomer. The morphology of ternary HPDLC formulations showed a well-defined grating structure due to increased LC solubility in the system [11].

TI is a two dimensional ring compound which is expected to reduce the mixture viscosity significantly at low concentrations due to the uncoiling effect of the molecules [19–21]. The uncoiling effect has been noted from the two dimensional graphene [22] and

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hyperbranched polyol (HBP) having globular conformation [23]. When the graphene and HBP were respectively incorporated into PUA, a significant decrease in premix viscosity and increase in grating formation rate and RDE were noted at low contents.

In the present study two types of TI, one carrying three ester groups and the other none, in various amounts were incorporated into the conventional HPDLC formulation. Ester groups are expected to increase viscosity and SP gap with LC due to the polar interactions. Dual effects of viscosity and miscibility from the addition and different types of TI with regard to grating formation kinetics and electro-optical properties are investigated in terms of premix viscosity, real time and saturation RDE, morphology, characteristic voltages and response times.

2. Experimental

2.1. Prepolymer synthesis

To synthesize the PU oligomers, a molar excess of hexane diisocyanate (HDI) was reacted with polypropylene glycol (PPG, \( M_n = 600 \)) to form the HDI terminated polyurethane prepolymer. The prepolymer was then end capped with 2-hydroxyethyl acrylate (HEA), which is photosensitive and subject to laser irradiation. This end capping reaction proceeded until the isocyanate groups had disappeared completely.

To this PU oligomers, the following diluent monomers and additives were added to form premix. N-vinylpyrrolidone (NVP) was used as monofunctional monomer. A trifunctional allyl ether monomer, viz., TMPTA, and TI, viz., 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (called TA) or tri(2-(acryloyloxy)ethyl) isocyanurate (TE) were used. Chemical structures of the triacylates and their SP and interfacial tension data are shown in Scheme 1. NVP decreases the viscosity, whereas triacylates provide the mixture with high reactivity and highly networked structure of polymers. The composition of the oligomer/monofunctional/multifunctional diluents was fixed to 4/3/3 by weight while the compositions of TMPTA/TI (TA or TE) were varied at 19.5/0, 18.5/1, 17.5/2, 16.5/3, 15.5/4, 9.75/9.75, 0/19.5 by weight, each corresponding to 1%, 2%, 3%, 4%, 6%, 10%, and 20%. They are renamed as TA01, TE02 etc.

2.2. Grating formation

Rose Bengal (RB) and N-phenylglycine (NPG) were used as the photoinitiator and coinitiator, respectively, for a holographic recording with an argon ion laser [24]. A surfactant, i.e. octanoic acid, was used to reduce the switching field by decreasing the interfacial tension between the LC and polymer. E7 (BL001, Merck), which a eutectic mixture of three cyanobiphenyl compounds and one cyanoterphenyl compound with positive dielectric anisotropy (\( \Delta \varepsilon = 13.8, n_o = 1.52, n_e = 1.73 \)), was used as the LC at 35 wt%.

(Table 1)

The holographic grating was fabricated by sandwiching the formulated mixture between two indium-tin-oxide (ITO)-coated glass plates with a gap of 20 \( \mu \)m, which was adjusted with a bead spacer. The sample was irradiated with an Ar-ion laser (514.5 nm) at an intensity of 150 mW/cm\(^2\) for 300 s. The incident beam angle (\( \theta \)) between the two laser beams outside the cell was set to 26°, giving \( \xi \) of 13°. The interference pattern was recorded according to Bragg's law

\[
\Lambda = \lambda / 2 \sin \left( \frac{\xi}{2} \right)
\]

where \( \Lambda \) = grating spacing, \( \lambda \) = wavelength of the writing beam. The grating morphology was observed by scanning electron microscopy (SEM). For this, one side of the ITO glass was removed and the sample was soaked in methanol for 24 h before removing the LC.

2.3. Measurements

Fourier transform infrared (FTIR) spectroscopy was used to follow the HEA capping reaction of the isocyanate terminated prepolymer, where the characteristic absorption peak of the isocyanate group was monitored. The RDE was determined with a photodiode using an Ar-ion laser. The RDE is defined as the diffracted intensity divided by the sum of the diffracted and transmitted intensities [25]. The electro-optical properties of the film were examined using a He–Ne laser (633 nm) because the material is insensitive to red light. A square wave voltage operating from 0 to 80 V was applied across the film to drive the shutter. The relaxation times of the cells were monitored using a digital storage oscilloscope. The premix viscosity was measured at room temperature using a vibration type viscometer (Vibro viscometer, SV-10, A&D, Japan).

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 shows the FTIR spectra of the PU prepolymer before and after HEA capping. The absorption peak at approximately 2270 cm\(^{-1}\), which was assigned to the stretching vibration of the NCO group, disappeared completely, and the vinyl group peak at approximately 750 cm\(^{-1}\) newly appeared after capping the PU prepolymer with HEA.

3.2. Premix viscosity

Fig. 2 shows that the premix viscosity decreased significantly with the addition of TI at low concentrations and increased at high concentrations showing a minimum at 3%. At this composition, viscosity is decreased by about 18% (TA03) and 13% (TE03) compared with TI-free premix. Among the two TIs, TE carrying three ester groups shows larger viscosities than TA at all compositions due to the polar interactions of three ester groups.
More pronounced effects were observed when HBP and graphene were added to the premix, where the viscosity was decreased by about 25% (graphene) [22] and 60% (HBP) [23] and at 0.03% addition. Addition of fillers to the organic polymers normally augments the mixture viscosity according to the Einstein equation [24]. The contradiction should come from the globular or planar structure of the additives, which disturbs the chain entanglements of polymers [19,20]. Chain entanglements are essential for the viscosity build-up in polymers [25]. At a high content, the fillers are vulnerable to aggregation and agglomeration to form a three dimensional networks, which increases viscosity. The high premix viscosity should retard the diffusion of LC and monomers, grating formation kinetics and LC-polymer phase separation.

3.3. Real time and saturation diffraction efficiencies

Fig. 3 and Table 2 show the RDE of the films incorporating various amounts of TI into the polymer during recording, and Fig. 4 the saturation RDE. RDE of TI-free premix (T100) increases sigmoidally with cure time to a saturation value of approximately 28% in about 125 s. The sigmoidal shape is due to the exponential type refractive-index modulation as

$$\Delta n(t) = \Delta n_{sat}(1 - e^{-\frac{t}{\tau}})$$

where the DE at the Bragg angle is given by
\[ D = \frac{\Delta n \pi d}{1 - \sin^2 \theta/2} \]  

which nicely follows such sigmoidal shape \[26\]. The sigmoidal behavior indicates the existence of an induction period (IP) for the cure reaction. With the addition of TI, RDE increases asymptotically signaling the disappearance of IP. This is due to the high reactivity of allyl isocyanurate (TI) over allyl ether (TMPTA) owing to the high double bond electron density \[11\]. The initial rate of grating formation and time to saturation increase simultaneously up to 3% TI. This produces a monotonic increase in the saturation RDE. Beyond the content, the rate of grating formation and saturation RDE decrease significantly with increasing TI content below those of TI-free premix at high contents.

It is important to note that the grating formation kinetics and saturation RDE follow TI dependent viscosity, i.e., low premix viscosity gives fast grating formation kinetics and high saturation RDE. Among the two TIs, low viscosity TA shows high RDE and RDE formation rate than the high viscosity TE at the same compositions. The fast grating formation to high saturation RDE seems primary due to the fast curing rate of TI, followed by fast diffusion of diluents monomers and LC molecules through the less viscous premix, giving rise to high extent of phase separation and droplet growth. However, at high TI contents over 3%, diffusion becomes sluggish and the overall process is governed viscosity.

3.4. Solubility parameters and anchoring energy

The anchoring energy of LC on a polymer surface can be defined as the interfacial tension between the two surfaces \( \gamma_{12} \) \[10,27\] which is given in terms of SP \( \delta \) as

\[ \gamma_{12} = 0.75 \left( \delta_2^{3/2} - \delta_1^{3/2} \right)^2 \]  

The SP gap becomes an important parameter in determining the anchoring energy, operating voltage, and response times in addition to the grating morphology. Presently, SPs for TMPTA and TI segments were estimated based on the group contribution theory \[28\], and are shown in Scheme 1 along with interfacial tensions calculated using the above equation. It is seen that the SP gap and anchoring energy increase as

\[ \text{TMPTA} < \text{TE} < \text{TA} \]  

along which an increase of phase separation, decrease of operating voltage and response times are expected.

3.5. Morphology

The morphology is a key issue in optimizing the overall performance of HPDLC films in a number of contributions \[29–31\]. Fig. 5 shows the SEM morphologies of gratings. The dark regions, which
are separated by the bright polymer walls, are the original location of LC.

In the absence of TI, the LC layers are shallow and broad, suggesting that phase separation is insufficient. With the addition of TI up to 3% (TA01-TA03, TE01-TE03), LC layers become deep and narrow, indicative of increased phase separation. Also, the interface curvature representing the debris of LC droplet becomes large which is a direct indication of large domain size [30–32]. Great phase separation is driven by the large SP gap and becomes rapid owing to low viscosity. However, as TI content increases further, LC layer becomes shallow (TA06, TE06) and eventually grating formation is incomplete (TA10, TE10, TA20, TE20), implying that large viscosity slows phase separation and practically controls the grating formation process. Among the two TIs, TA show a bit clear polymer-LC phase separation due to its low viscosity.

3.6. Electro-optic properties

Electro-optic performance of HPDLC depends on a number of factors including domain size, anchoring energy, glass transition temperature \( (T_g) \) of polymer in addition to the LC characteristics. Generally, small domain size, high anchoring energy, and high \( T_g \) gives high operating voltage and rise time [13–16].

Fig. 6 shows the RDE of the film as a function of applied voltage. The TI-free film (TI00) gives the off-state RDE of approximately 28%. Upon applying electric field, RDE decreases in an inverse sigmoidal manner to approximately 14% at 50 V with threshold \( (V_{th}) \) and operating \( (V_{op}) \) voltages of 16 and 44 V, respectively. With the addition of TI, off-state RDE increases to a maximum while \( V_{th} \) and \( V_{op} \) decreased to minima at 3% TI (TA03, TE03). Beyond the content, RDE decreased while \( V_{th} \) and \( V_{op} \) increased below and above the TI-free values at 20% TI (TA20, TE20) (Table 2).

![Fig. 5. SEM images of the gratings for TI-free film (a) and films with various contents of TA (b) and TE (c).](image-url)
Presently, $V_{th}$ and $V_{op}$ largely vary with the viscosity dependent domain size. Contradiction to this is found between TA and TE, where high viscosity TE having small domain size shows low $V_{th}$ and $V_{op}$ than low viscosity TA at the same TI content. The results are rather agreed with the anchoring energy. That is, small anchoring energy of TE needs low characteristic voltages when the viscosities are similar.

Fig. 7 shows the wave forms and responses times of the films. Rise time ($s_R$) is the time required for transmittance increase from 10% to 90% upon applying electric field. $s_R$ decreases with TI up to 3%, beyond which it increases. Namely, $s_R$ varies with viscosity or viscosity dependent domain size. This implies that orientation of LC molecules along electric field needs to overcome the viscoelastic force of surroundings.

Decay time ($s_D$) is the opposite to $s_R$ measured upon turning electric field off. So, $s_D$ corresponds to relaxation or randomization of the oriented LC molecules and becomes fast as the viscoelastic force of polymer increases. Consequently, variation of $s_D$ with TI content is exactly the opposite to $s_R$. Contrast to the viscoelastic and domain size effects is found between TA and TE, where high viscosity TE shows short $s_R$ and $s_D$. In this regard, small anchoring energy of TE is seemingly responsible for the small energy to overcome for orientation and for relaxation like the voltage characteristics.

4. Conclusions

Premix viscosity decreased with TI up to 3% due to the uncoiling of aromatic molecules, beyond which it increased due to the agglomerations of TI molecules.

With the addition of TI, induction period disappeared and initial grating formation rate increased due to the high reactivity of TI, which is based on the high electron density of the isocyanurate double bonds.

Saturation RDE, phase separation and domain size increased while threshold and operating voltages, response times decreased up to 3% TI, beyond which the tendency was reversed showing respective maxima and minima at 3%. Among the two TIs, TA showed high RDE due to the low viscosity while TE showed small characteristic voltages and response times due to the low anchoring energy.

It is concluded that premix viscosity mainly controls the rate process, viz., grating formation kinetics, followed by morphology and diffractions while anchoring energy governs the interface interactions and electro-optical performance of the PDLC films.
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