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Controls of solubility parameter and crosslinking density in polyurethane acrylate based holographic polymer dispersed liquid crystal

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Abstract

The effect of solubility parameter mismatch between liquid crystal (LC) and resin, and crosslinking density of resin phase on morphology and diffraction efficiency of holographic polymer dispersed liquid crystal (HPDLC) have seen systematically studied by varing the chemical structure of polyurethane acrylate resin with regard to the prepolymer molecular weight, type of diisocyanate, and functionality of reactive diluent. It has been found that with dissimilar chemical structure leading to large difference in solubility parameter between LC and resin, and with high crosslinking density under similar solubility parameter difference, fast formation of grating, large droplet size and high diffraction efficiency were generally obtained.

Keywords: Holographic polymer dispersed liquid crystal; Solubility parameter; Diffraction efficiency; Phase separation

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1. Introduction

Holographic polymer-dispersed liquid crystal (HPDLC) is a variant of the polymer-dispersed liquid crystal (PDLC) formed by photo-polymerization induced phase separation (PIPS) [1]. Like PDLC it consists of LC droplets and polymer matrix. However, the position of droplets within the polymer is not random but is organized in stratified planes [2].

Composites are made from a mixture of photosensitive prepolymers and LC molecules which are exposed to two interfering laser beams. Photopolymerization occurs in the bright regions faster than in the dark regions. Therefore, the chemical potential of monomer at bright regions is lower than the dark regions while the chemical potential of LC at dark region is lower than the bright

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regions. To establish equilibrium, LC molecules diffuse into dark regions while the monomers diffuse into bright regions [3].

In HPDLC, there are many factors to affect phase separation. These include solubility parameters, viscosity, reactivity, and curing temperature [1,4]. Effect of chemical structures on the various properties of PDLC has been reported earlier [4–6]. Recently Patnaik and Pachter [7] calculated the solubility parameters of acrylate monomer and polymer, LC, and octanoic acid and showed that prepolymer and LC are miscible before cure but immiscible after cure to form phase separation where octanoic acid is located at polymer–LC interfaces to reduce interfacial tension thus lowering the anchoring strength. To the best knowledge of present authors, earlier works have been confined to the acrylate monomer and polymers and no work has been devoted to polyurethane acrylates which have ample freedom of resin design in PDLC.

In this paper, we consider the effect of solubility parameter difference between LC and polyurethane acrylate resins of various chemical structures as well as crosslinking density of resin phase. So, the chemical structures of resin and consequently the solubility parameter have systematically been varied and the effects were examined in terms of grating morphology and diffraction efficiency of the gratings.

2. Experimental

2.1. Materials and oligomer synthesis

Urethane prepolymers can be prepared from a large, diverse of raw materials. Polypropylene glycols (PPGs) with different number-average molecular weights (400 and 1000) were dried at 80 °C, 0.1 mmHg for several hours until no bubbling was observed. Extra-pure-grade of hexamethylene diisocyanate (HDI), 4,4′-diphenylmethane diisocyanate (MDI), and 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) were used without further purifications. Molar excess of diisocyanate was reacted with PPG for over 1 h at 80 °C to obtain diisocyanate-terminated prepolymer. Then the reaction mixture was cooled at 40 °C and hydroxyl ethyl acrylate (HEA) was added to obtain HEA-capped poly (urethane acrylate) oligomers [8–11]. Basic formation to prepare the poly (urethane acrylate) (PUA) is given in Table 1.

The PUA prepolymers are highly viscous and immiscible with LC that necessitates the use of reactive diluents. The reactive diluents used in this experiment are *N*-vinyl pyrrolidone (NVP), trimethylol propane triacrylate (TMPTA), and dipentaerylthritol penta-acrylate(DPHPA), and the composition of prepolymer/mono functional diluent/multi functional diluent was 4/2/4 by weight.

An eutectic mixture of cyanobiphenyl and cyanoterphenyl 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 4-*n*-pentyl-4′-cyanobiphenyl (K15, commonly known as 5CB), 25% of 4-*n*-heptyl-4′-cyanobiphenyl (K21), 18% of 4-*n*-octoxy-4′-cyanobiphenyl (M24), and 10% of 4-*n*-pentyl-4′-cyano-*p*-terphenyl (T15). The LC content of the composite mixture was 35 wt%. Rose Bengal (RB) was used as photoinitiator for holographic recording. To this millimolar amount of *N*-phenylglycine (NPG) was added as coinitiator.

Table 1
Solubility parameter of polymer matrix

	Diisocyanate	Polyol	Feed ratio	*Mc*	Solubility parameter ($(\mathrm{J\ cm^{-3}})^{1/2}$)
P42H	HDI	PPG 400	3:2	1452	21.32
P44H			5:4	2531	21.27
P101H		PPG 1000	2:1	1512	18.80
P42H_{12}	H_{12}MDI	PPG 400	3:2	1721	20.88
P42M	MDI	PPG 400	3:2	1697	22.51

Solubility parameter is calculated to HEA capping.

2.2. Grating fabrication

Holographic grating was fabricated 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 [12]. Cell was constructed by the LC/resin mixture being sandwiched between two indium–tin-oxide (ITO) glass plates, with a gap of 10 μm, adjusted by a bead spacer. The prepolymer mixtures have been irradiated with an Ar-ion laser (514 nm), at two different intensities (100 and 400 mW/cm^2), with exposure time of 600 s.

2.3. Measurements

Reading of fabricated gratings was accomplished with a 514 nm beam from an Ar-ion laser positioned at the Bragg angle, that is, the same angle as the recording beam. The transmitted beams were detected by a photodiode detector. The efficiency was determined by dividing the output intensity by the input one. On the other hand, to monitor the progress of grating formation real time diffraction was monitored by a detector locatered at first order diffraction angle. Contact angle of LC drop was measured on resin cured by ultra violet (UV) (100 mW/cm^2, 365 nm) for about 3 min with 0.1 wt% 1-hydroxy cyclohexyl phenyl ketone (HCPK) as an initiator. The measured contact angles were compared with solubility parameters differences calculated from the group contribution theory. Scanning electron microscopy (SEM) was used to determine the morphology of the grating after the extraction of LC molecules in ethanol.

3. Results and discussion

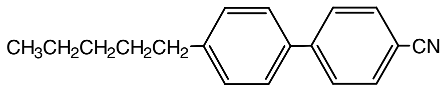
3.1. Solubility parameters

Miscibility of low molecular weight species in polymer depends on several factors including molecular weight of polymer, crosslinking density and structural similarity between the two. Among these, miscibility based on the structural similarity can be estimated by the solubility parameters which can be calculated from the cohesive energy density [7] or group contribution theory [13,14]. Solubility parameter(δ) is defined as the square root of cohesive energy density (Ec)

$$\delta = Ec^{1/2},$$

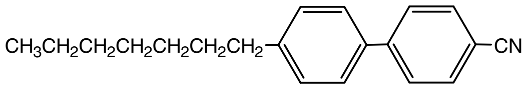
where the Ec can be calculated from the group contribution theory that is Ec of a molecule can be obtained by adding up the Ec of all the groups making up the molecule (see Fig. 1).

Fig. 2 shows the difference in solubility parameters between LC and the resin calculated by the group contribution theory, together with the measured contact angle of LC drop on resin. It is seen that larger difference in solubility parameter gives larger contact angle as expected. Since the grating formation by polymerization and hence diffraction by the gratings are based on the LC–resin phase separation, LC–resin pairs with large solubility parameter difference is expected to give clean grating formation and large diffraction efficiency.



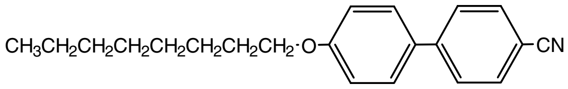
K 15(5CB), 51% (22.40)

(a)



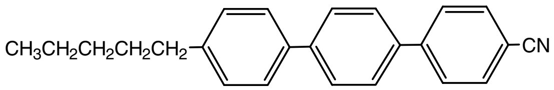
K 21, 25% (21.58)

(b)



M 24, 16% (21.75)

(c)



T 15, 8% (22.85)

(d)

Fig. 1. Chemical structure and solubility parameter ((J cm^{-3})$^{1/2}$) of LC (E7) mixture (average value = 22.19 (J cm^{-3})$^{1/2}$).

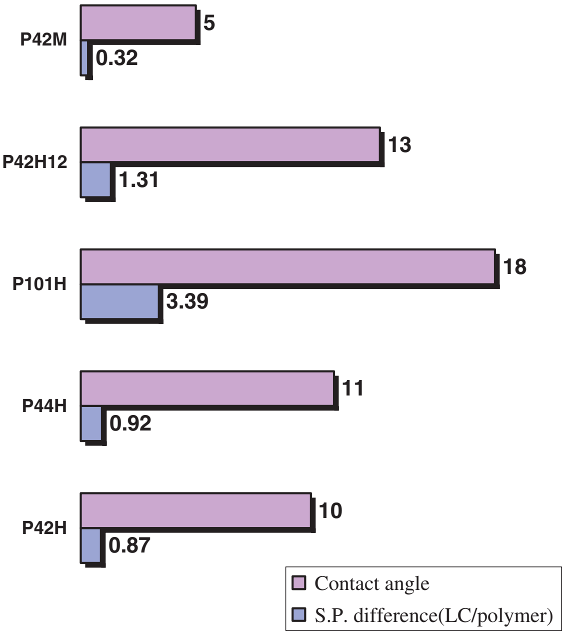


Fig. 2. Contact angle and solubility parameter differences between LC and prepolymer.

3.2. Diffraction efficiency

The zeroth order diffraction efficiencies of the gratings, that is the diffraction by the fabricated gratings with DPHPA as a reactive diluent are shown in Fig. 3.

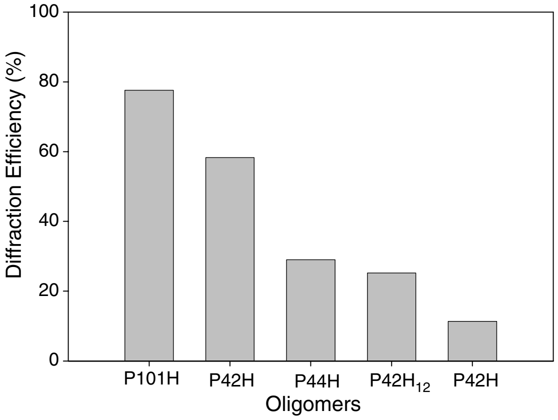


Fig. 3. Diffraction efficiency of HPDLC films from DPHPA (100 mW/cm^2, 35 wt% LC).

3.3. Effect of structural dissimilarity

The effect of structural similarities between LC and resin were studied with three different types of diisocyanates to prepare PUA while keeping the crosslinking density, i.e., the molecular weight between crosslinks constant. As expected diffraction efficiency increases as the solubility parameter difference increases, i.e., P42M (0.32) < P42H$_{12}$ (1.31) < P42H (10) (Number in ( ) designates solubility parameter difference). This implies that solubility parameter which is a simple structure dependent property can be used to design the resin formulation for high diffraction gratings.

A second type of design to demonstrate the structural effect is seen with P101H and P42H. In this molecular design, type of diisocyanate (HDI), and molecular weights between crosslinks were approximately fixed, and only the molecular weight of polyol was different as 1000 (P101H) and 400 (P42H). P42H has two urethane groups between crosslinks while P101H has one, resulting respectively in high and small solubility parameter differences with LC. It is seen that the diffraction efficiencies of P101H and P42H are about 80% and 60%, respectively. The amount of LC molecules left in resin phase is increased as the two solubility parameters approach making the refractive index mismatch small.

3.4. Effect of crosslinks

When the solubility parameter difference is similar, crosslinking density seems to mainly control the grating formation and diffraction efficiency. Solubility parameters of P42H and P44H are essentially identical (21.32 and 21.27). However, diffraction efficiency of P42H (~60%) is over about two times of P44H (~30%), which should come from high crosslink density of P42H. As the crosslinking density increases solubility of low molecular species such as LC in polymer decreases. However, more pronounced effect of crosslink is to physically squeeze the LC droplets out of the resin phase. The squeezing power can be estimated by the elasticity of resin [15]

$$G_N^0 = \frac{\rho RT}{Mc},$$

where G_N^0, ρ, R and T are rubbery modulus, density, universal gas constant and absolute temperature. Molecular weight between crosslinks (Mc) calculated based on the formulation (Table 1) is 1452 for P42H, and 2531 for P44H. So, P42H is more elastic and better grating formulation by effective squeezing of LC domains is expected.

3.5. Effect of reactive diluent

Diffraction efficiencies obtained with TMPTA as reactive diluent are shown in Fig. 4. It is seen that effect of structural dissimilarity and crosslink density show identical tendency with DPHPA. However, the diffraction efficiencies with TMPTA based resins are lower than these of DPHPA, which most likely is due to the lower crosslinking density of trifunctional acrylate (TMPTA) as compared with pentafunctional acrylate(DPHPA). With higher crosslinking density of resin phase, solubility of LC in resin phase should decreases. Moreover, high elasticity of resin should give more pronounced effect on clean grating formation by effective squeezing the LC droplets out of the resin phase [4,16,17].

3.6. Real time diffraction efficiency

Typical real time diffraction efficiencies, that is the diffraction by the in situ forming gratings have been monitored as a function of cure time (Fig. 5). This is done by measuring the first order diffraction at an off-angle from the Bragg's law. It is noted that the diffraction efficiency is much smaller as compared with the zeroth order diffraction. P42H gives slower increase in diffraction efficiency with lower saturation value as compared with P101H. The slower formation of grating and lower saturation value for P42H are an indication of slower diffusion of LC and monomer and high chemical affinity between the two. This results are also consistent with the solubility parameter difference discussed above.

With different type of diisocyanates, $P42H_{12}$ gives much faster and higher first order diffraction as compared with P42M, while P42H lies between

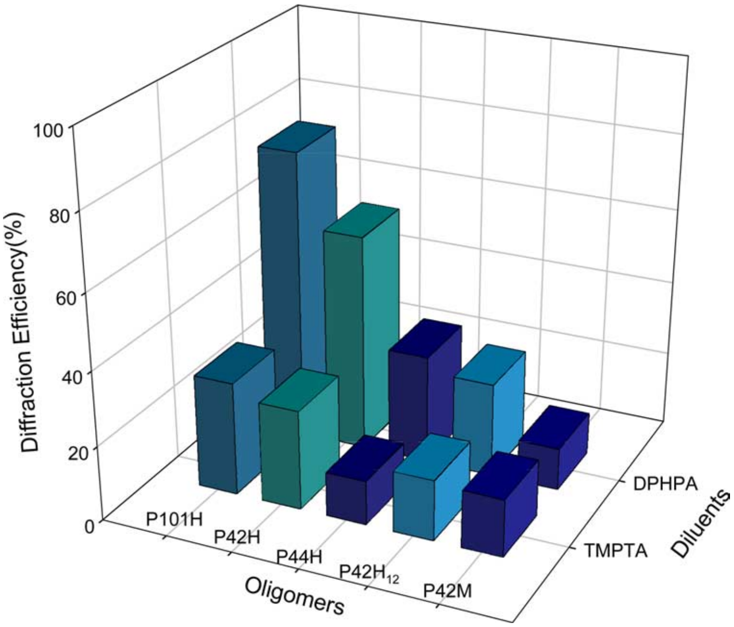


Fig. 4. Diffraction efficiencies of HPDLC films for variant types of oligomers and diluents (100 mW/cm^2 laser intensity, 10 μm cell gap, 35 wt% LC).

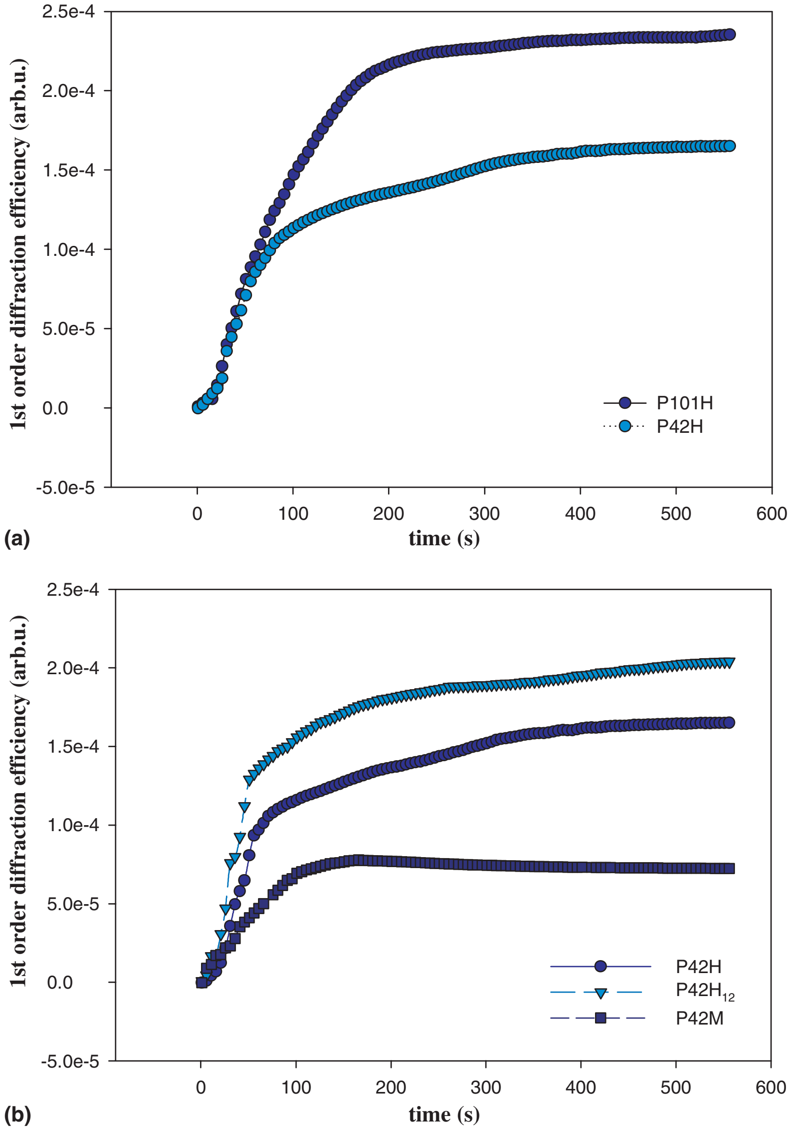


Fig. 5. Real time diffraction efficiency of DPHPA based HPDLC as a function of PPG molecular weight (a) and isocyanate type (b) (100 mW/cm^2, 35wt% LC).

the two. Great miscibility of aromatic diisocyanate (P42M) with LC, and relatively small elasticity of aliphatic diisocyanate (P42H) should, respectively, be responsible for the reactively low value.

3.7. Morphology

The SEM morphologies of the films are given in Fig. 6. Clean layered gratings are generally obtained. High diffraction efficiency and large droplet size obtained with aliphatic HDI based resins (P101H, P42H), as compared with cycloaliphatic (H_{12}MDI) and aromatic diisocyanate (MDI) based ones is caused by the structural dissimilarity of HDI with aromatic LC droplets. In addition lower viscosity of HDI based resin, observed experimentally should give fast diffusion of monomers and LC, allowing time for the droplet to

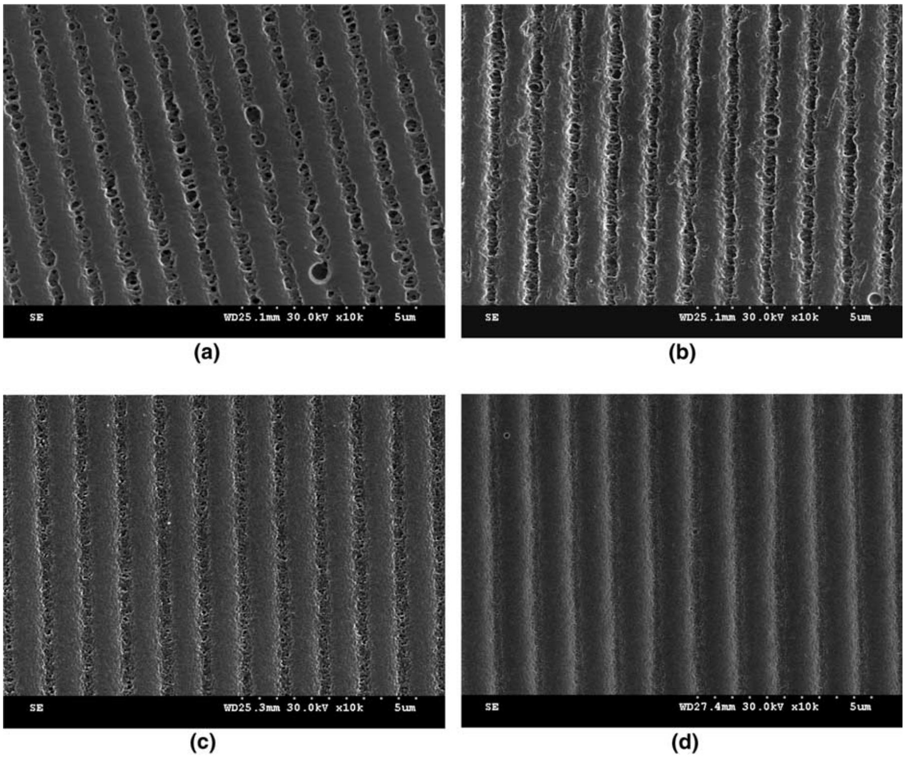


Fig. 6. SEM morphology of DPHPA based HPDLC films for 100 mW/cm^2 laser intensity, 10 μm cell gap, 35 wt% LC: P101H, 10,000× (a), P42H, 10,000× (b), P42H$_{12}$, 10,000× (c), P42M, 10,000× (d).

grow. Extremely fine LC droplets with MDI based resin are indicative of slow diffusion of LC droplets due to the great interactions between LC and resin.

4. Conclusion

The difference in solubility parameter between LC and resin has been a good parameter to design the morphology and diffraction efficiency of HPDLC by varying the interfacial adhesion or anchoring strength of LC molecule on resin surface.

Regarding the effect of diisocyanate structure, aliphatic diisocyanate (P42H) having the greatest difference in solubility parameter with LC gave the highest, and aromatic one (P42M) having the smallest solubility parameter difference with LC gave the lowest diffraction efficiency.

Regarding the effect of molecular weight of PPG, PPG1000 (P101H) having less urethane group in prepolymer structure leading to a larger difference in solubility parameter gave a greater diffraction efficiency as compared with PPG400 (P42H) having less urethane groups and similar solubility parameter with LC.

When the solubility parameters of LC and resins are similar crosslinking density of resins, designed either by the prepoymer molecular weight or by the functionality of multifunctional acrylates has been another useful parameter to control the morphology and diffraction performance of the HPDLC. That is, high crosslinking density (P42H and DPHPA series) gave much higher diffraction efficiency as compared with low one (P44H and TMPTA series) due in part to the decreased solubility of LC in resin, but mainly to the large elasticity of highly crosslinked resin.

Measured real time diffraction efficiency and morphology generally supported the above findings. That is, fast increase in diffraction efficiency and large saturation value were obtained with large difference in solubility parameter which gave large droplet size and high diffraction efficiency.

Large difference in solubility parameter between LC and resin gave large contact angle of LC drop on resin surface. So, measurement of contact angle could be an easy and direct way to estimate the interface interactions in HPDLC.

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