

## Effect of Solubility Parameter Mismatch in Holographic PDLCs

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### Abstract

LC and polymer miscibility in HPDLC has been studied in terms of solubility parameter. It was found that better grating formation and diffraction efficiency were obtained when the difference in solubility parameters between polymer and LC is greater.

### 1. Introduction

Holographic polymer dispersed liquid crystal (HPDLC) has the advantages of modulating refractive index, competitive price, wavelength selectivity and the capability of external modulation in volume hologram applications. Holographic polymer-dispersed liquid crystals (HPDLCs) are a variant of the polymer-dispersed liquid crystals (PDLCs) formed by photo-polymerization induced phase separation (PIPS).<sup>1</sup> Like PDLCs they consist of LC droplets and polymer matrix. However, the position of droplets within the polymer is not random, rather than they are organized in stratified planes. These periodic structures of multilayers have very promising optical properties since a specific component of the incident light is diffracted by the gratings due to the difference in the refractive indices of the polymer and LC. The diffraction efficiency depends on the interface uniformity between LC and polymer layers. Thus, the key parameter to control the diffraction is the clean phase separation between polymer and LC layers.

One of the simplest ideas to represent the solubility parameter in chemistry is that "like dissolves like" Quantitatively, "like" maybe defined in terms of similar chemical groups or similar properties. As you know, the solubility parameter is widely known as the square root of the cohesive energy density as follows:

$$\delta = (\Delta E/V)^{1/2}$$

where  $\Delta E$  is the energy of vaporization and  $V$  is the molar volume of the components.

Solubility parameter should be an important factor to control the performance of HPDLCs. So, the effects

of miscibility in transmission HPDLCs have been studied in two ways. In one way we made prepolymer have similar molecular weight but with different number of urethane groups, and polarities. In other way we prepared prepolymers have differential conformation using assorted isocyanates.

### 2. Experimental

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, 0.1mmHg 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<sub>12</sub>MDI) were used without further purifications. Molar excess of diisocyanate was reacted with PPG for over 1h at 80°C to obtain HDI-terminated prepolymer. Then the reaction mixture was cooled at 40°C and hydroxyl ethyl acrylate(HEA) was added to obtain HEA-capped urethane acrylate oligomers<sup>3-6</sup>.

Basic formation to prepare the PUA is given in Table 1.

The reactive diluents used in this experiment are N-vinyl pyrrolidone(NVP), trimethylol propane triacrylate(TMPTA), and dipentaerythritol pentaacrylate(DPHPA), and the composition of prepolymer/mono functional diluent/multi functional diuent was 4/2/4 by weight.

The LC (E7) was used. And Rose Bengal and N-phenylglycine (NPG) was added as initiator and coinitiator, respectively.

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. Cell was constructed by the resin/LC mixture being sandwiched between two indium-tin-oxide

**Table 1. Solubility parameter and Mc of matrix<sup>7</sup>**

	Diisocyanate	Polyol	Feed ratio	Mc	Solubility parameter
P42H	HDI	PPG 400	3:2	1452.9992	$21.32(\text{Jcm}^{-3})^{1/2}$
P44H			5:4	2531.9984	$21.27(\text{Jcm}^{-3})^{1/2}$
P101H		PPG 1000	2:1	1512.0328	$18.80(\text{Jcm}^{-3})^{1/2}$
P42H <sub>12</sub>	H <sub>12</sub> MDI	PPG 400	3:2	1721.9992	$20.88(\text{Jcm}^{-3})^{1/2}$
P42M	MDI	PPG 400	3:2	1697.9992	$22.51(\text{Jcm}^{-3})^{1/2}$

\* Solubility parameter is calculated to HEA capping.

(ITO) glass plates, with a gap of 10 $\mu\text{m}$ , adjusted by a bead spacer. The prepolymer mixtures have been irradiated with an Ar-ion laser (514nm), at two different intensities (100mW/cm<sup>2</sup> and 400mW/cm<sup>2</sup>), with a exposure time of 600s.

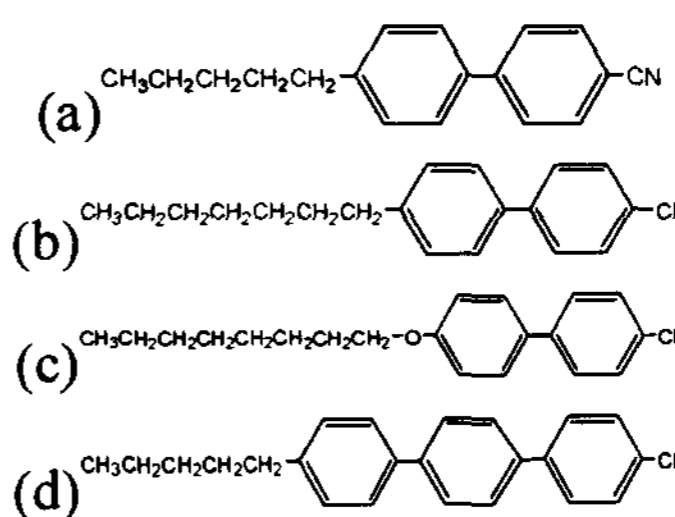
Scanning electron microscopy (SEM) was used to determine the morphology of the grating after the extraction of LC molecules in ethanol.

### 3. Result and Discussion

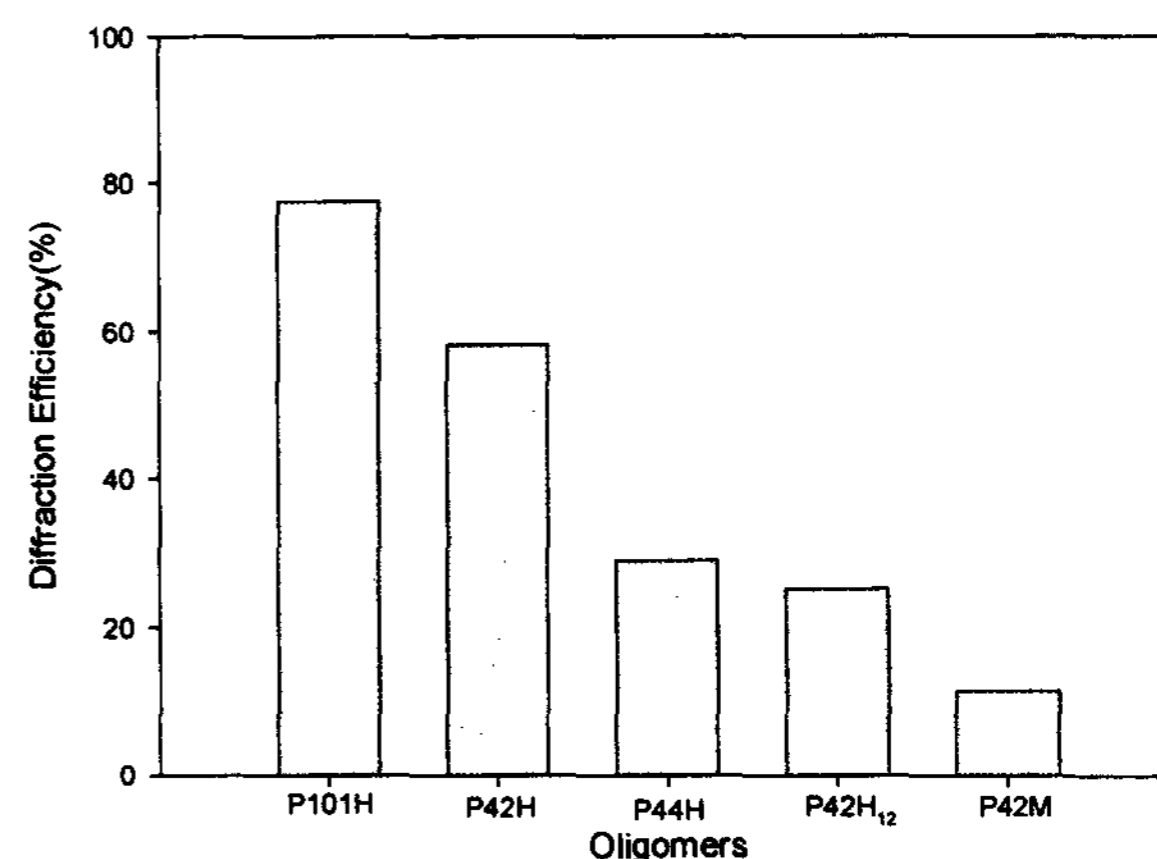
Miscibility of low molecular weight species in polymer depends on several factors including molecular weight of polymer, crosslinking density and structural similarity between the two.

The 0<sup>th</sup> order diffraction efficiencies of the gratings fabricated with DPHPA as a reactive diluent are shown in Figure 2. The effect of structural dissimilarity between LC and resins were studied with three different types of diisocyanates to prepare PUA while keeping the crosslinking density, i.e., the molecular weight between crosslinks const. As expected diffraction efficiency increases as the solubility parameter difference increases, i.e., P42M (0.32)<P42H<sub>12</sub> (1.31)<P42H (10) (Number in ( ) designates solubility parameter difference). This implies that solubility parameter, 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 being incorporated between crosslinks were different as 1000(P101H) and 400(P42H). P42H has two urethane groups between crosslinks while P101H has one, resulting in high solubility parameter and small

solubility parameter difference with LC for P42H. It is seen that the diffraction efficiencies of P101H and P42H are about 80 and 60%, respectively. The LC molecules left in resin phase, enriched as the two solubility parameters approach, makes the refractive index mismatch small.



**Figure 1. Structure of (LC) E7; (a)K15, (b)K21,(c) M24, (d) T 15 and average of solubility parameter is  $22.19(\text{Jcm}^{-3})^{1/2}$ .**



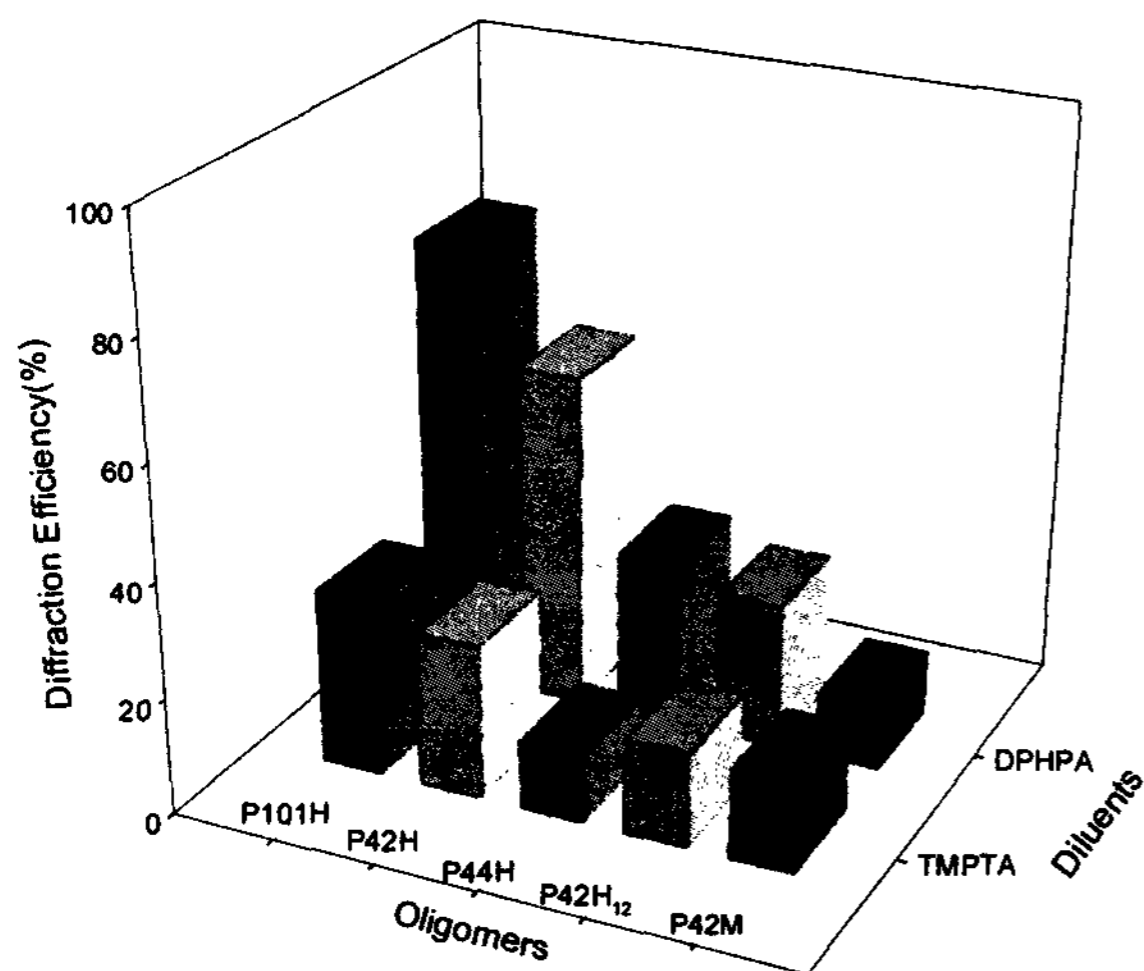
**Figure 2. Diffraction efficiency of HPDLC films using DPHPA; the laser intensity is 100mW/cm<sup>2</sup>, 35wt% LC.**

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 pronouncing effect of crosslink is to physically squeeze the LC molecules out of the resin phase. The squeezing power is often estimated by the ideal rubber theory given by

$$G_N^\circ = \frac{\rho RT}{Mc}$$

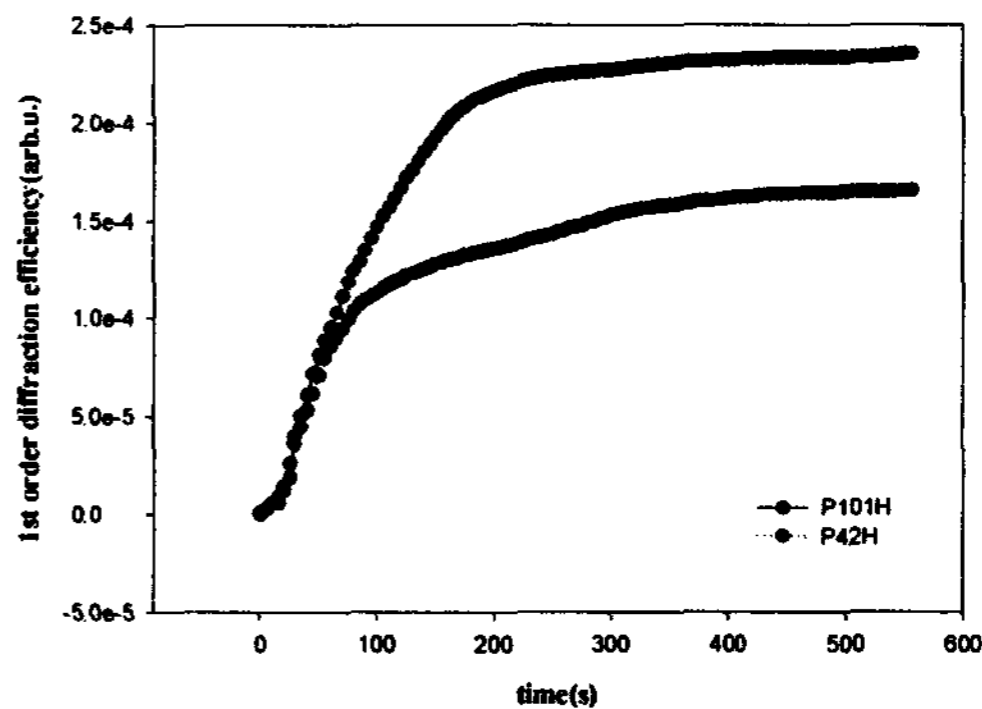
where  $G_N^\circ$ , R, and T are rubbery modulus, density, universal gas constant, and absolute temperature, respectively.

Diffraction efficiencies obtained with TMPTA as reactive diluents are shown in Figure 3. 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 molecules in resin phase

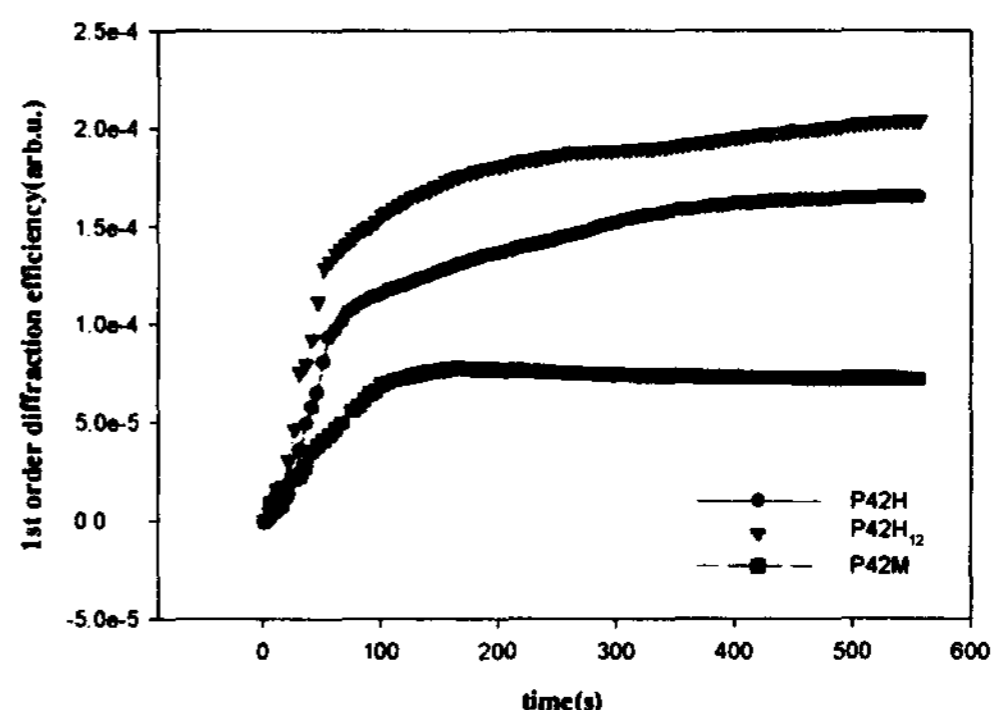


**Figure 3. Diffraction efficiency of HPDLC films for different diluents, DPHPA and TMPTA; 100mW/cm<sup>2</sup> laser intensity, 10µm cell gap, 35wt% LC.**

should be decreased. In fact, high elasticity of likely crosslinked resins should give more pronounced effect on clean grating formation by squeezing the LC molecular out of the resin phase.



(a)



(b)

**Figure 4. Real time of first-order diffraction efficiency; (a) P101H vs. P42H, (b) differential diisocyanates; using DPHPA, 100mW/cm<sup>2</sup> intensity, 10µm cell gap, 35wt% LC.**

Typical real time diffraction efficiency is monitored from the first order diffraction and shown in Figure 4. P42H gives slower increase in diffraction efficiency with lower saturation value as compared with P101H. This implies that the built-up gratings are less perfect and diffusion of LC molecules through the resin phase is slow with P42H, which presumably is related to the chemical affinity between LC and resin.

With different type of diisocyanates, P42H<sub>12</sub> is less miscible with LC than P42H. The rate of phase separation is increased with decreasing miscibility, i.e. P42M < P42H < P42H<sub>12</sub> (to 90 second). But higher viscosity of P42H<sub>12</sub> is referred to its structural composition so it is resulted in smaller 0<sup>th</sup> order diffraction efficiency than P42H.

#### 4. Conclusion

General requirements for HPDLC transmission gratings are diffraction efficiency, high angular selectivity (narrow bandwidth), low driving voltages, and fast switching times<sup>8</sup>.

To obtain higher diffraction efficiency, it is important to clean grating. Clean grating can be gained easily when the prepolymer and LC are immiscible each other. And the prepolymer is more immiscible with LC, it has faster rate of phase separation.

#### 5. Reference

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