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Reflective mode of HPDLC with various structures of polyurethane acrylates

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Abstract

Holographic polymer dispersed liquid crystals were prepared from photo-curable polyurethane acrylate of various structures and a nematic liquid crystal mixture upon curing the reactive diluents and hydroxy ethyl acrylate terminated (HEA) polyurethane prepolymers.

The effects of prepolymer molecular structure were studied in terms of reflection efficiency, polymer volume shrinkage and electro-optic properties. Emphases have been made to improve the reflection efficiency and shrinkage of holographic grating during fabrications by modifying soft segment length and hard segment structures of the prepolymer. It was found that polyurethanes with short soft segment and flexible hard segment gave high reflection efficiency and volume shrinkage as well.

Keywords: HPDLC; Polyurethane acrylate; Reflection efficiency

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 [1–3]. A new technology in these reflective display fields is holographic polymer dispersed liquid crystal (HPDLC). Reflective 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 [4].

In HPDLC, the dispersion of the liquid crystal (LC) molecules in the polymer matrix is often generated by polymerization induced phase separation (PIPS) where the prepolymer and LC are mixed together and then polymerization is induced photochemically [5,6]. The dynamics of the phase separation process is a very complex phenomenon which is initiated by the change in the chemical potential of the constituents as a result of the polymerization process [7]. LC droplets are formed and grow at a rate depending on the rate of polymerization and gelation, and also on the change in miscibility of the various components [8,9].

There has been a considerable interest in the morphology and electro-optic properties of HPDLC [10–12]. Recently the effects of prepolymer structure have received considerable attention with regard to HPDLC properties. Maruyama and his co-workers found that the driving voltage was significantly decreased by modeling the acrylic monomer with different alkyl side chain length [13]. The improvement was interpreted in terms of interface modification, i.e. cohesive energy of monomer and surface free energy of cured polymer. Sutherland et.al. reported the effects of varying monomer functionality on HPDLC grating [14]. Recently, a major issue with HPDLC is to minimize the grating shrinkage during the photo-polymerization process. During crosslinking, the polymer volume shrinkage is in the order above 10%, which is fetal to the fabrication of accurate holographic grating. Crawford and his co-workers investigated the degree of shrinkage according to urethane acrylate monomer functionality [15].

This study reports the effects of prepolymer molecular structure on the electro-optic properties of HPDLC. Polyurethane acrylates (PUAs) have been used as photo-curable materials in our experiment because PUAs have great advantage of easy structure control, i.e. their

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molecular structures can be easily controlled by varying the molecular parameters of raw material. The lengths of soft segment and hard segment structure in polyurethane acrylate have been systematically varied and their electro-optic properties have been studied with an emphasis on the role of polymer matrix.

2. Experimental

2.1. Materials and oligomer synthesis

Urethane oligomers can be prepared from a large, diverse of raw materials. PUA is a segmented urethane oligomer tipped with acrylic functionality. Bifunctional polypropylene glycol with different molecular weights ($M_n = 400$, 1000, 2000 g/mol) (Korea Polyol) were dried at 80 °C, 0.1 mm Hg for several hours until no bubbling was observed. Extra pure grade of isophorone diisocyante (IPDI), hexamethylene diisocyanate (HDI), and toluene diisocyanate (TDI) were used without further purifications. Molar excess of diisocyanate was reacted with PPG for over 1 h 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 acrylate oligomers [16,17]. Basic stoichiometry for preparing PUA is shown in Fig. 1. Basic formation to prepare the PUA is given in Table 1.

An eutectic mixture of cyanobiphenyl and cyanoterphenyl components with $n_0 = 1.5216$, $n_e = 1.7462$, 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) [18]. The LC content of the composite mixture was 35 wt%.

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*-vinylpyrrollidone (NVP) and trimethylol propane triacrylate (TMPTA), and the composition of oligomer/monofunctional/multi-functional 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 560 nm [19]. To this millimolar amount of *N*-phenylglycine (NPG) was added as coinitiator.

2.2. Grating fabrication

Holographic grating was fabricated through the preferential formation of photoproducts in the region of

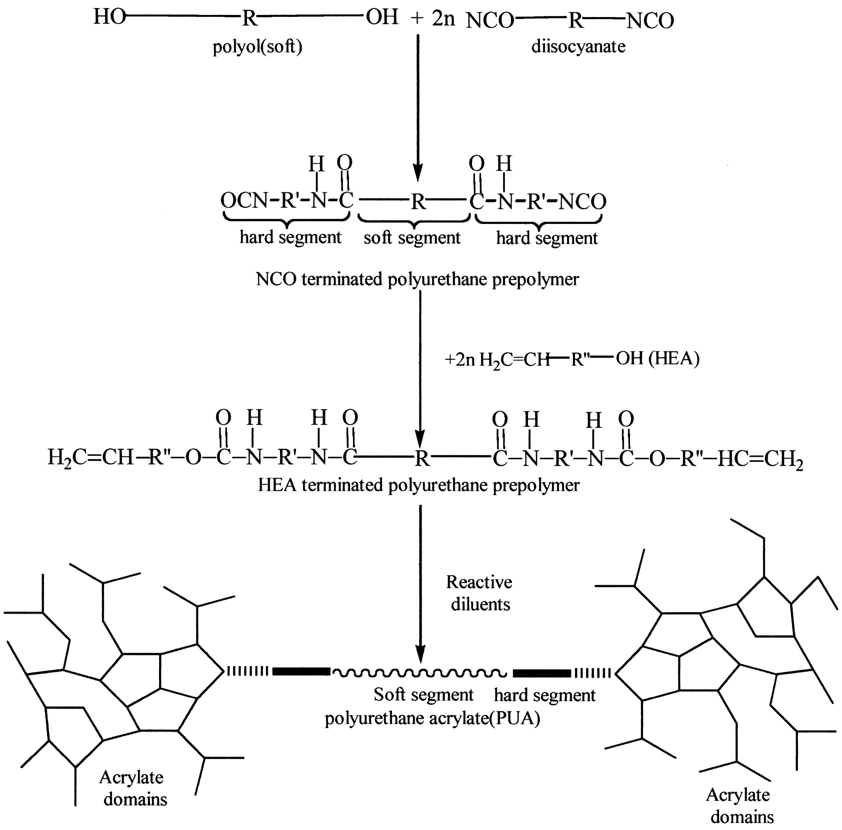


Fig. 1. Basic chemistry for preparing PUA.

Table 1
Formulation to prepare polymer networks of HPDLC

No.	Polyurethane acylate oligomer			Mono-functional diluent	Multi-functional diluent	Photo-initiater
	Polyol	Diisocyanate	End-capping acylate			
P4H	PPG400	HDI	HEA	NVP	TMPTA	NPG and Rose Bengal
P4I		IPDI				
P4T		TDI				
P10H	PPG1000	HDI				
P10I		IDPI				
P10T		TDI				
P20H	PPG2000	HDI				
P20I		IPDI				
P20T		TDI				

constructive interference arising from the overlap of two laser beams, called object and reference beams [20]. In Fig. 2, the holographic recording system is schematically shown. The cell was constructed by sandwiching the monomer/LC mixture between the two indium-tin-oxide (ITO) coated glass plates, with a gap of 10 μm, adjusted by a bead spacer. The prepolymer mixtures with various structures have been irradiated with Ar-ion laser (514 nm) at various intensities (50–250 mW/cm^2), with exposure times of typically 30–180 s.

2.3. Measurements

The reflection of a specific wave length and the degree of grating shrinkage of the composite film was analyzed using an UV–visible spectrometer (Perkin Elmer, Lambda 20). Reflection efficiency was estimated upon dividing the peak depth by base line height [21]. The shrinkage of the film upon polymerization was obtained by comparing the measured grating spacing with the Bragg grating spacing given by Eq. (1).

The driving voltage was measured using the optical system shown in Fig. 3. The light emitted from a white-light source (a halogen lamp) was collimated and applied normal to the cell surface. Light transmitted from the center of the cell was focused on the tip of an optical fiber, which guided the light to an optical spectrum analyzer (MCPD-3000, Otsuka Electronics). An electric field formed by an arbitrary waveform generator (WFG500, FLC Electronics) and 50 Hz square-wave electric field was used [22].

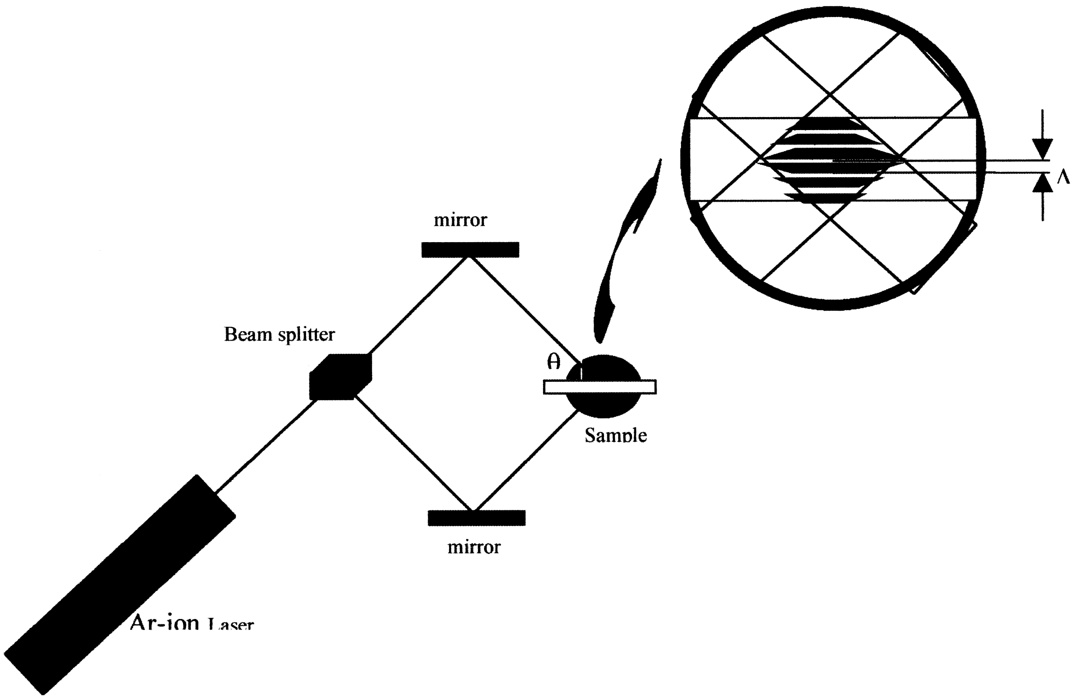


Fig. 2. Fabrication method for reflection mode HPDLC film.

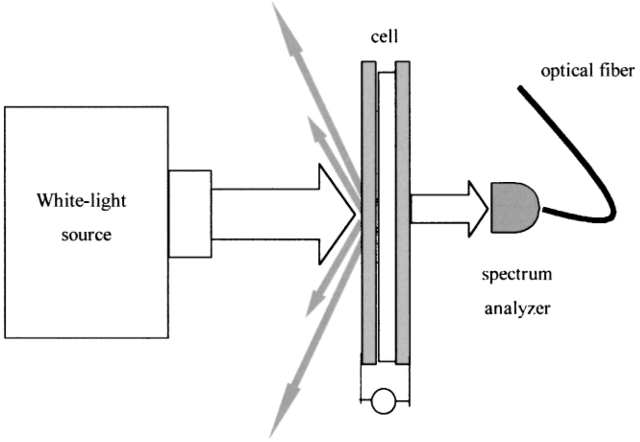


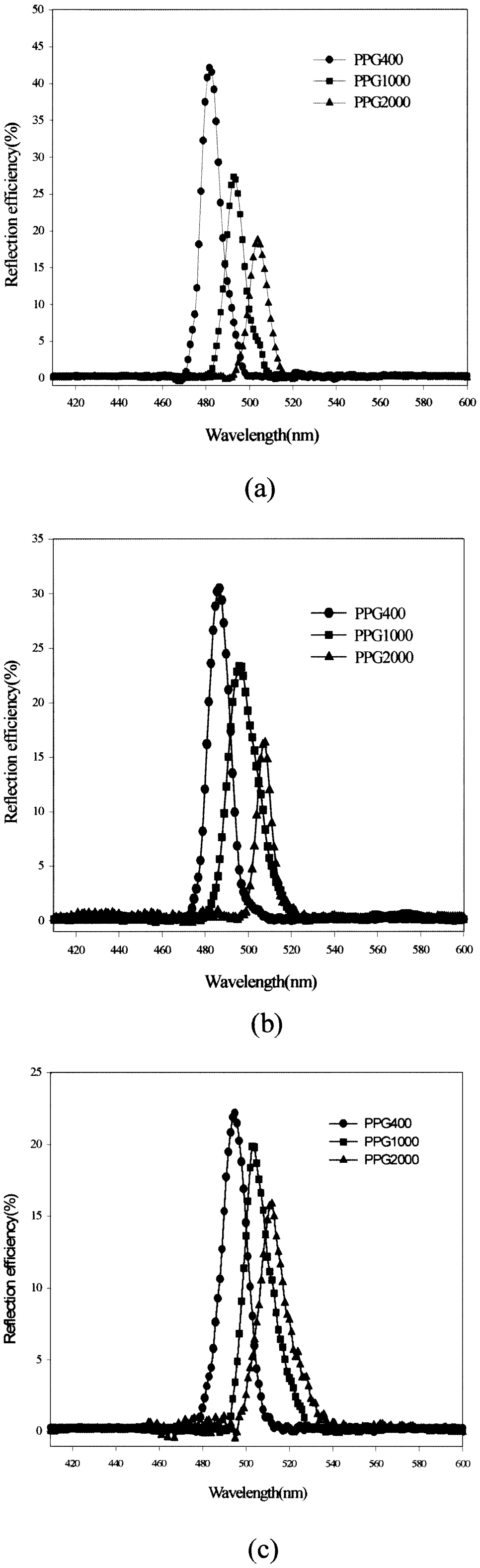
Fig. 3. Experimental setup for measurement of electro-optic property.

3. Results and discussion

3.1. *Effect of PPG molecular weight and diisocyanate structure on reflection efficiency*

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 [23]. Fig. 4 shows the reflection efficiency vs. wavelength relationships of the composite films prepared from three different PPG molecular weights ($M_n = 400$, 1000, and 2000) and hard segment types. It is clearly seen that the reflection efficiency decreases with increasing M_n of PPG. Since 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), M_n of PPG corresponds to the molecular weight between crosslinks (M_c) bridging the acrylate domains (Fig. 1). Therefore, small M_n of PPG gives high crosslinking density, small LC droplets and high droplet density [24].

The urethane linkages are formed by the reaction between the hydroxyl group of PPG and one of the two isocyanate groups of the diisocyanate. These urethane linkages and the remaining fragments of isocyanate compound (parts not joining the urethane linkage) form the hard segments, whereas the long chain polyols become soft segments. Three types of diisocyanate, viz. flexible aliphatic diisocyanate (HDI), rigid and bulky cycloaliphatic diisocyanate (IPDI), and rigid and cohesive aromatic diisocyanate (TDI) have been incorporated in PU. Reflection efficiency increases along TDI < IPDI < HDI, an order exactly the same with increasing immiscibility with LC, and chain flexibility of PU. LC molecules which are mixtures of aromatic isocyanates give best miscibility with aromatic diisocyanate (TDI) and the lowest with aliphatic diisocyanate (HDI). Better miscibility between matrix and LC should give smaller extent of phase separation, leading to relatively blur interfacings and gratings.



(a)

(b)

(c)

Fig. 4. Effect of PPG molecular weight on reflection efficiency of HPDLC films at 250 mW/cm^2; (a) HDI, (b) IPDI, (c) TDI.

Better reflection of HDI may also come from its flexibility. One PPG molecule, two diisocyanate molecules, and hydroxyl ethyl segment of HEA become the bridges between polyacrylate domains which are highly crosslinked

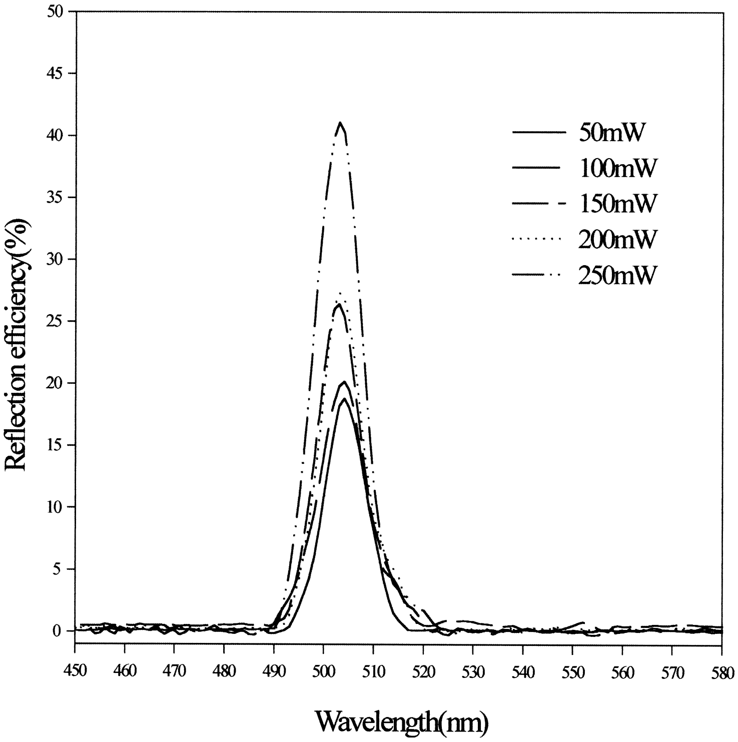


Fig. 5. Irradiation intensity dependent reflection efficiency of HPDLC films prepared form PPG400 and HDI.

and provide sort of hooping stress to squeeze the LC molecules out of the polyurethane domains which are relatively less dense. Polyurethanes of flexible segments resist less toward compression stress exerted by the surrounding polyacrylate networks and smaller LC domains could result.

Also, viscosity of polymer network which increases with increasing chain rigidity (HDI < IPDI < TDI) also plays an important role in determining the droplet size and density. This is because the coalescence of LC droplets during polymerization becomes more difficult in more viscous medium, resulting in LC domains which are too small for effective phase separation and gratings.

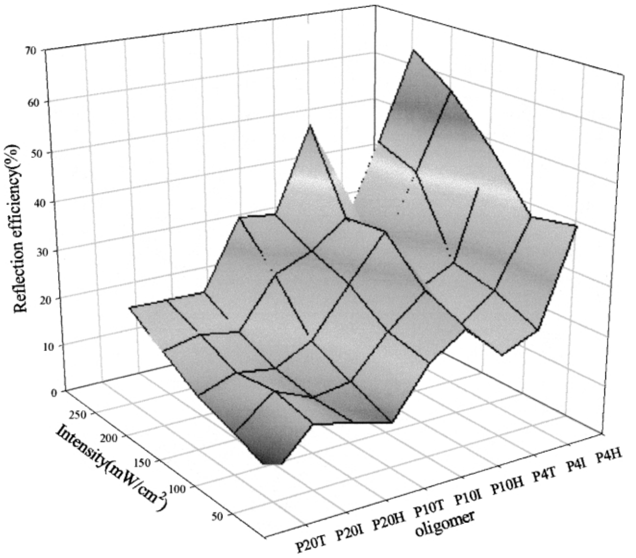


Fig. 6. Reflection efficiency–irradiation intensity–oligomer structure relationships of HPDLC films.

Certainly, reflection efficiency strongly depends on the structure of prepolymer (PU) both on the M_n of PPG and diisocyanate structure. However, the effect of diisocyanate structure becomes more significant at low M_n of PPG. At low M_n of PPG, the composition of soft segment becomes small and effect of hard segments seems pronounced.

3.2. Effect of irradiation intensity on reflection efficiency

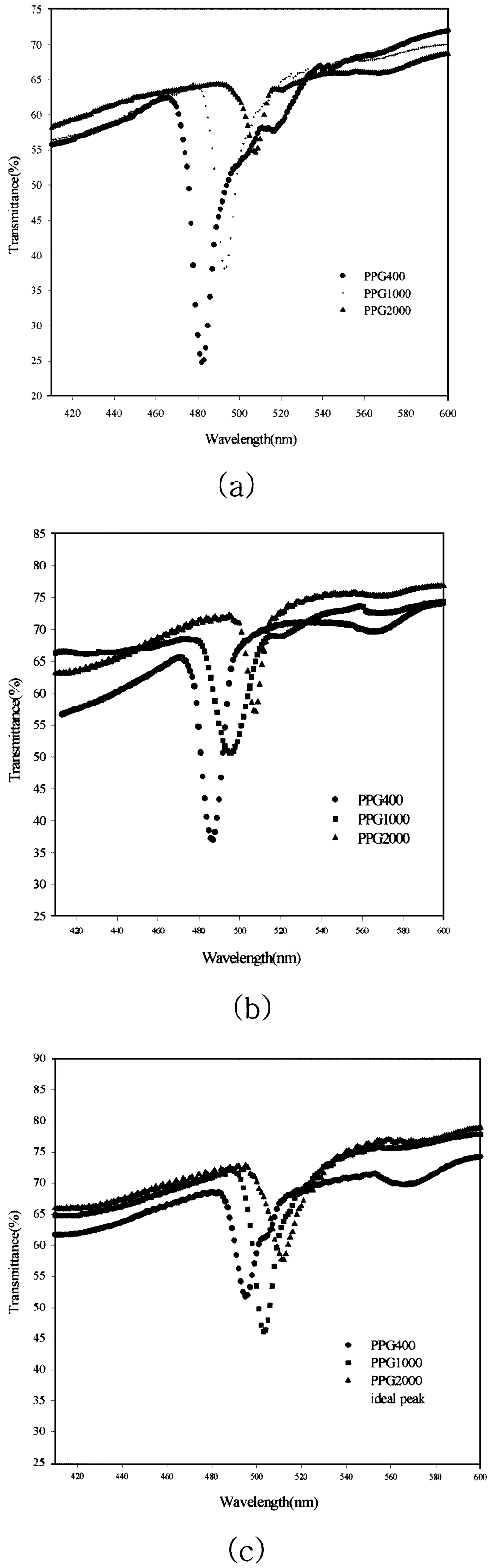
The rate of polymerization in radical polymerization is proportional to the concentration of monomer (average functionality of reactive diluents and acrylate functionality of PUA), and square root of the irradiation intensity [25]. Fig. 5 shows that the reflection efficiency monotonically increases with increasing irradiation intensity within the experimental range. This implies that phase separations immediately follow the polymerization.

A tri-dimensional representation of the reflection efficiency–irradiation intensity–oligomer structure relationship is shown in Fig. 6. The maximum reflection efficiency (>60%) is obtained with the lowest M_n of PPG (400) and flexible aliphatic hard segment (HDI) at the highest irradiation intensity (250 mW/cm^2).

3.3. Polymer shrinkage

Reflection gratings are governed by the Bragg's law

$$\Lambda = \frac{\lambda}{2}\sin\theta \tag{1}$$



(a)

(b)

(c)

Fig. 7. UV–visible spectra vs. PPG molecular weight at 250 mW/cm^2 (ideal peak position corresponds to the Bragg grating, 514 nm); (a) HDI, (b) IPDI, (c) TDI.

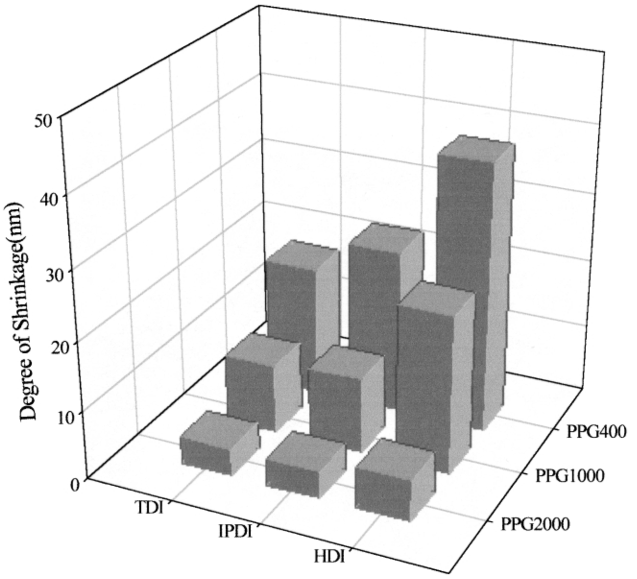


Fig. 8. Degree of shrinkage–PPG molecular weight–diisocyanate structure relationship of HPDLC films at 250 mW/cm^2.

where λ is the wavelength of incident light, θ is the interbeam angle outside the film, and Λ is the grating spacing. In our experiments, wavelength of incident laser light was 514 nm and interbeam angle was set at 90°. Therefore, theoretical grating spacing, viz. 2Λ (Bragg grating) should be 514 nm. However, the obtained grating spacing was smaller than the Bragg grating due to the mixture volume shrinkage upon polymerization.

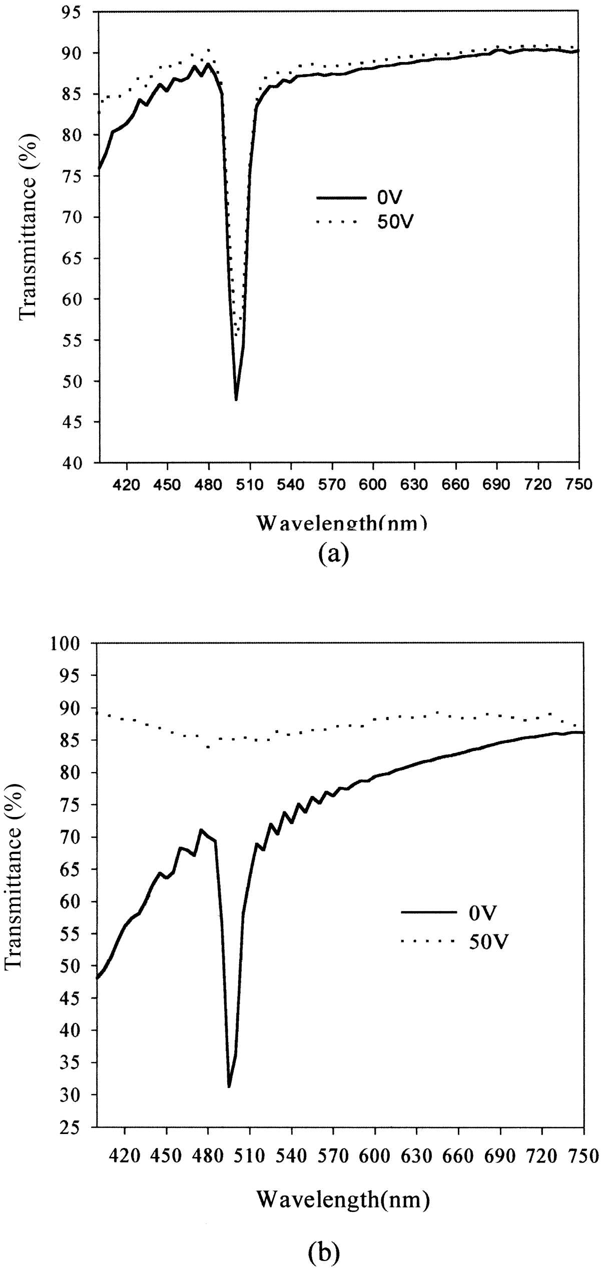
Fig. 7 shows the UV–visible spectra of HPDLC reflection gratings obtained from three different PPG and diisocyanates. It is noted that prepolymer with the lowest M_n of PPG, i.e. smallest M_c gives the greatest shift in wavelength. The greatest shift, viz. shrinkage should come from its largest crosslinking density leading to the greatest elasticity of polymer networks according to the ideal rubber theory

$$G^\circ_N = \frac{\rho RT}{M_c} \tag{2}$$

where G°_N, R, and T are rubbery modulus, density, universal gas constant, and absolute temperature. The glass transition temperature of the PU from PPG and three types of diisocyanate should be below 0 °C, and hence the PUs are in their rubbery state at room temperature and the above relationship should work basically.

It is also seen that the peak shift is in an increasing ordered of TDI < IPDI < HDI. Since volume shrinkage occurs by close packing during polymerization, the chain flexibility is also an important factor for shrinkage. As mentioned above, TDI is rigid and has bulky aromatic ring which effectively resists to compression and gives small shrinkage. On the other hand, flexible HDI segments can be easily deformed.

Fig. 8 shows that shrinkage increases with decreasing M_n



(a)

(b)

Fig. 9. Voltage (50 V) response of HPDLC films from (a) PPG400, (b) PPG2000 and HDI.

of PPG (2000 < 1000 < 400) and increasing hard segment flexibility (TDI < IPDI < HDI). Effect of soft segment length is more pronounced with flexible diisocyanate (HDI), whereas effect of hard segment type is more pronounced with short soft segment. So, the lowest shrinkage is obtained with PU from PPG2000 and TDI.

3.4. Electric characteristics

Fig. 9 shows the applied voltage dependence of the transmittance when a square wave voltage of 50 Hz was applied to an HPDLC film. When a 50 V-field is applied, absorption peak for PPG of high M_n completely disappeared implying that LC molecules are oriented along the electric field direction. However, the peak for low molecular weight PPG is virtually unchanged. This implies that the applied voltage is above and below the threshold voltage of high and low M_n PPGs. Larger threshold voltage for low M_n of PPG comes from the small droplet size resulting in great interfacial area between polymer and LC and high anchoring energy to overcome.

4. Conclusions

Reflection efficiency and volume shrinkage of HPDLC have been studied in terms of prepolymer molecular structure and irradiation intensity. With low molecular weight of PU bridging the crosslinked acylate domains, high reflection efficiency and high volume shrinkage were obtained. This can possibly be interpreted in terms of increased crosslinking density and elasticity of polymer networks.

Among tree types of diisocyanates being used as hard segments of PU, HDI gave the highest and TDI gave the lowest reflection efficiency. Chain flexibility, low viscosity and high immiscibility of HDI with the aromatic LC molecules should give clean phase separation from physical and chemical points of view. When the above two molecular parameters are considered together, effect of diisocyanate structure was more pronounced when the soft segment length was short. This could be so since with short soft segment, composition of soft segment becomes small, and the hard segments should govern the properties of the composite films.

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