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Polyurethane acrylate-stabilized cholesteric liquid crystal dispersions

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Polymer stabilized cholesteric liquid crystals (PSCLCs) have been fabricated based on various structures of polyurethane acrylate (PUA) as well as conventional acrylate polymer, namely poly(1,6-hexanediol diacrylate). For PUA stabilized films, the transmittance spectra of cured films were essentially identical to those of uncured films, with no ‘dead’ reaction; whereas, using acrylate polymer; reflection greatly decreased upon curing and showed significant ‘dead’ reaction after the cessations of irradiation. The structure of PUA also had significant effects on the electro-optic performance, and these effects are interpreted in terms of elasticity and interfacial interaction between the polymer and LC.

1. Introduction

Liquid crystal dispersion has long been a popular topic for both scientific investigation and potential application in display and information storage [1]. Depending on the dispersion morphology, which is mainly governed by film composition, polymer dispersed liquid crystal (PDLC), polymer network liquid crystal (PNLC), and polymer stabilized liquid crystal (PSLC) can be fabricated [2–4]. At low LC content (60–80%), LC domains are dispersed as separated droplets in polymer matrix to form PDLC morphology. With high LC content (>80%), the LC becomes a continuous phase and three-dimensional polymer networks are dispersed in the LC (PNLC). In PSLC, a small amount (<5%) of monomers or oligomers are added to the LC and polymerized to form a structure similar to an interpenetration polymer network (IPN). In such a morphology, the polymer stabilizes LC molecules against external stimuli such as contact with a pencil, as in a palm top computer.

Most of the LCs used in dispersion are of nematic type for operational simplicity. Cholesteric LC has also been used for dispersion (PSCLC), exhibiting stable bistability of reflection and scattering at field-off [5, 6]. In the absence of an electric field, cholesteric LC forms a planar texture between two ITO coated glass plates. Light is selectively reflected at a specific wavelength determined by the type and combination of nematic LC and dopant. When an electric field is applied to the film, the LC transforms into a focal-conic structure which

scatters light. Upon removal of the field, this texture remains for some time since it is stabilized by the polymer. At a high electric field, the cholesteric structure is untwisted and the cell becomes transparent. The focal conic texture is not stable for long periods of time and this, together with difficulty in fabricating uniformly large areas has been the barrier to overcome for display application of cholesteric LCs [7]. In this regard, the importance of monomer has been pointed out earlier [8, 9].

We consider the molecular design and fabrication of a PSCLC using polyurethane acrylate (PUA) as polymer stabilizer. In comparison with acrylate polymers, PUA has ample degrees of freedom in molecular design. Moreover, volume shrinkage upon chain extension of urethane oligomers is significantly reduced, as compared with the polymerization of acrylate monomer. We report the effects of PUA molecular structure on the electro-optic properties of the PSCLC, and interpret the results in terms of polymer elasticity and interfacial interactions between LC and polymer.

2. Experimental

2.1. Material and oligomer synthesis

Urethane oligomers can be prepared from a large number of diverse raw materials [10, 11]. PUA is a segmented urethane oligomer tipped with an acrylic functionality. Bifunctional polypropylene glycols (PPGs) with different number average molecular masses ($M_n=400, 750, 1000 \text{ g mol}^{-1}$) (Korea Polyol) were dried at 80°C under 0.1 mm Hg for several hours until no bubbling was observed. The chemical reagents of

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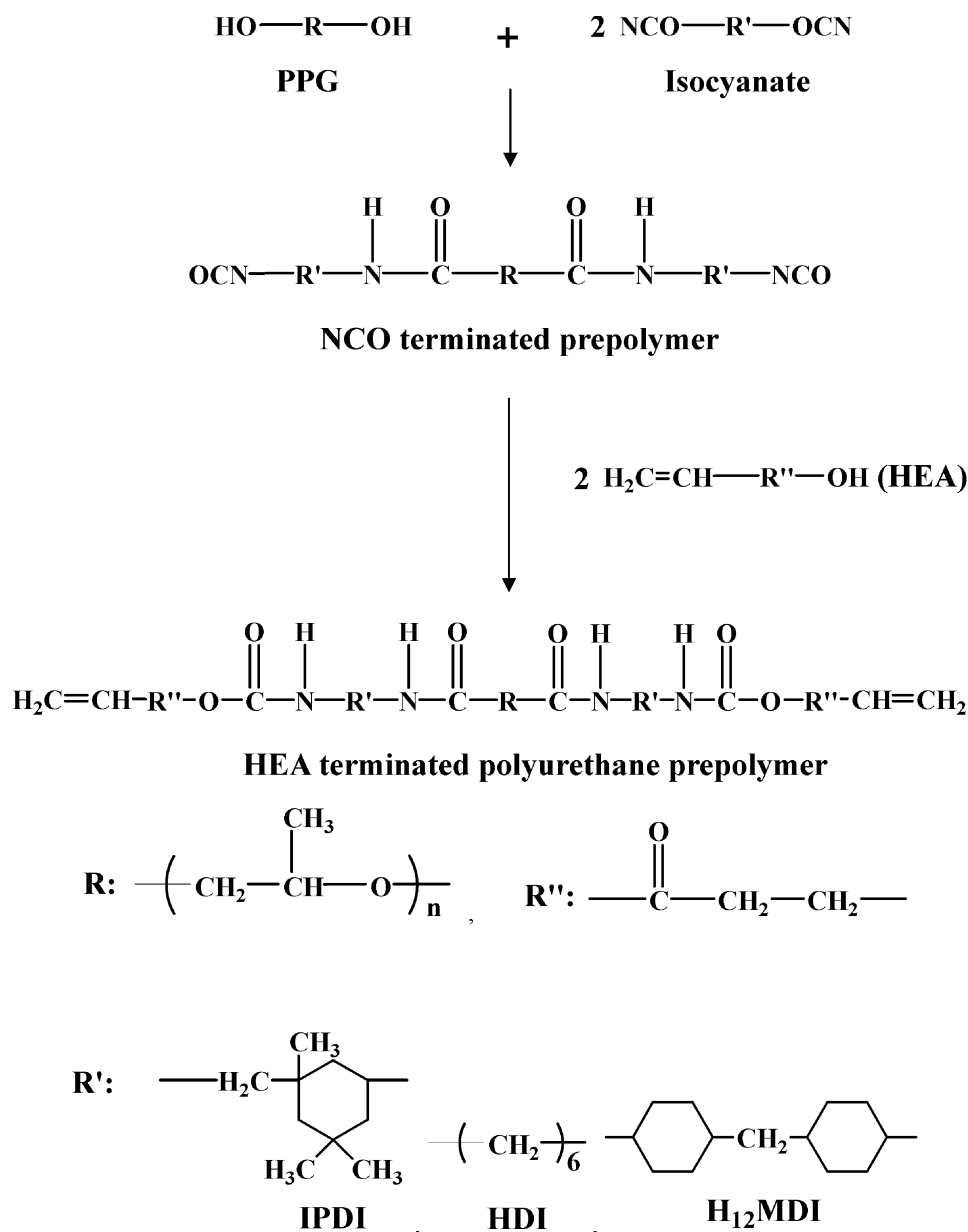
hexamethylene diisocyanate (HDI molecular mass, $M_w=168 \text{ g mol}^{-1}$), 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI , $M_w=262 \text{ g mol}^{-1}$), isophorone diisocyanate (IPDI, $M_w=222.3 \text{ g mol}^{-1}$), hydroxyethyl acrylate (HEA, $M_w=116 \text{ g mol}^{-1}$) and 1,6-hexanediol diacrylate (HDDA, $M_w=226 \text{ g mol}^{-1}$) were used without further purification. A molar excess of diisocyanate was reacted with PPG for 5 h at 80°C to obtain NCO-terminated prepolymer. The reaction mixture was then cooled to 40°C and HEA added to obtain HEA-capped urethane acrylate oligomers. The basic stoichiometry

for preparing PUA is shown in scheme 1; formulations are shown in table 1.

2.2. Cell preparation

Our cholesteric liquid crystal material was prepared from a nematic liquid crystal with positive dielectric anisotropy (Merck MSA-02-3208) and a chiral component (Merck ZLI-811). The central wavelength of reflection (λ) is obtained by

$$\lambda = \bar{n}P \quad (1)$$



Scheme 1. Synthesis of PUA.

Table 1. Formulation for preparation of PSCLCs.

Polyacrylate		LC	Initiator		
HDDA		Cholesteric LC	Darocur		
Polyol	PU acrylate Diisocyanate	End-capping acrylate	LC	Initiator	$M_n^a/\text{g mol}^{-1}$
PPG 400	HDI	HEA	Cholesteric LC	Darocure	968
PPG 750					1318
PPG 1000					1568
PPG 400	IPDI H ₁₂ MDI				1076.6 1156

^a M_n =Prepolymer molecular mass (molecular mass between crosslinks).

where \bar{n} is the average refractive index of the LC and P is the chiral pitch given by

$$\bar{n} = \frac{n_e + n_o}{2} \quad (2)$$

where n_e and n_o are the extraordinary and ordinary refractive indices of the LC.

$$P = \frac{1}{C \times HTP} \quad (3)$$

where C and HTP are the weight fraction and helical twisting power of the dopant. With C (0.258) and HTP ($11 \mu\text{m}^{-1}$), P and λ were calculated as $0.35 \mu\text{m}$ and $0.55 \mu\text{m}$, respectively. A low concentration (4%) of a reactive monomer or oligomer was added to the liquid crystal with a substantial amount of photoinitiator (Ciba-Geigy Darocur 1173). The cell was constructed by sandwiching the monomer(oligomer)/LC mixture between two ITO coated glass plates, with a gap of $4.2 \mu\text{m}$, adjusted by a bead spacer. The mixture was mechanically mixed thoroughly before filling into the cell by capillary action, and cured by a UV source at 1.8 mW cm^{-2} for 10 min.

2.3. Measurement

Spectral data were obtained with a UV-visible spectrophotometer (Mecasys Optizen 1411v) in transmission mode at ambient temperature. The baseline was drawn with ITO glass substrates. Contact angles (Atago contact angle meter) were determined by dropping cholesteric LC on a film surface at room temperature. For electro-optical measurements, the PSCLC films sandwiched between two ITO-coated plates were placed normal to the direction of collimated beam of an Ar-ion laser ($\lambda=514 \text{ nm}$). Transmitted light intensity was measured with a photodiode. The elastic properties of polymers were measured with a dynamic mechanical

thermal analyser (Rheometric Scientific, DMTA MK-IV) operated at 10 Hz, 4°C min^{-1} and 0.03% strain over the temperature range -50 – 100°C .

3. Results and discussion

3.1. Effects of curing

Transmittance spectra of the films before and after curing are shown in figure 1. Before curing, the transmittance spectra of the films are essentially identical regardless of the type of polymer stabilizer. That is, all of the films selectively reflect light at a narrow range of wavelength corresponding to $\bar{n}p$. Upon curing, however, reflection by HDDA polymer [hereafter called PA (polyacrylate)] stabilized film is significantly lower and broadened, with a large blue shift; whereas the reflections of PUA-based films are almost the same as those of uncured films except for a small blue shift of the reflection peak. Broadening is mainly due to the PA concentration gradient along the light path [12]. The intensity of light is a maximum near the surface and is attenuated along the light path due to absorption by the medium. Thus the rate of UV cure (R_p) is high near the surface according to [13]:

$$R_p = k_p[M] \left(\frac{\phi \varepsilon I_0 [A] b}{k_t} \right)^{\frac{1}{2}} \quad (4)$$

where ϕ , ε , I_0 , and b are, respectively, initiation efficiency, molar absorptivity, light intensity, and sample thickness. $[M]$ and $[A]$ are the concentrations of monomer (oligomer) and photoinitiator, respectively, and k_p and k_t are the respective rate constants for the propagation and termination reactions. With high light intensity near the surface, monomers are consumed quickly causing a concentration gradient along the thickness direction, which drives counter diffusion of the monomer and LC. As the reaction progresses,

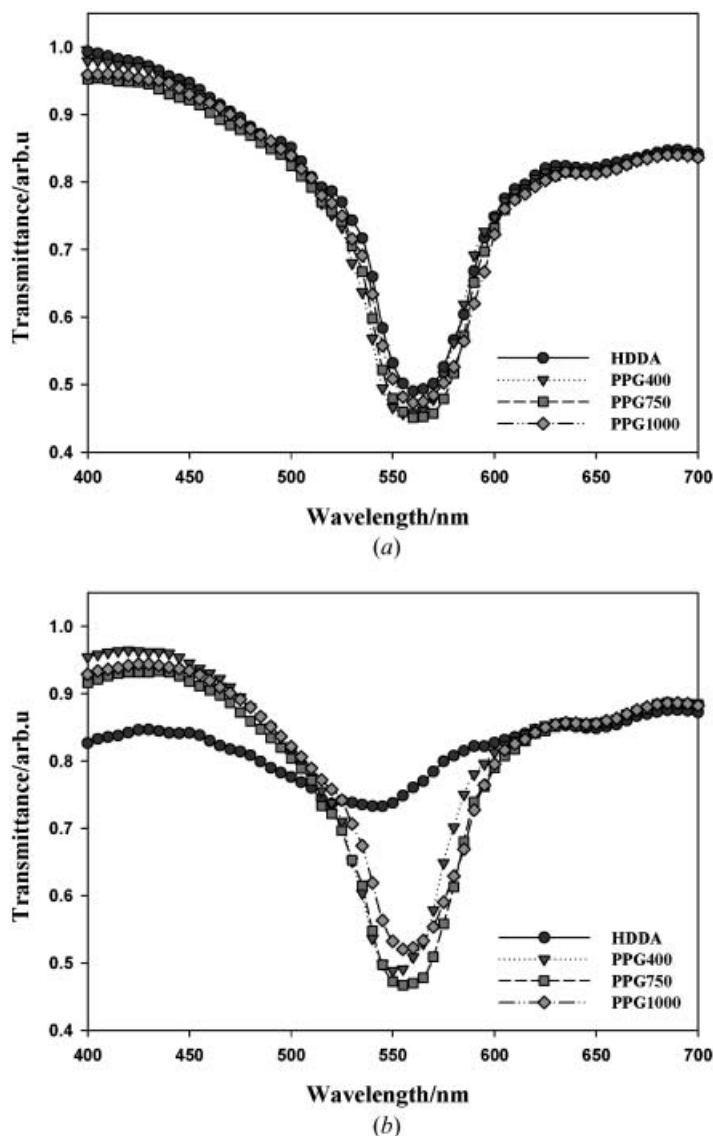


Figure 1. UV-visible spectra vs. PPG molecular mass of PUA (a) before and (b) after curing.

concentration gradients of polymer and LC are established along the film thickness. On the other hand, the volume of monomer is decreased by polymerization [14], especially with the high functionality monomers, forming glassy networks after polymerization such as HDDA. So, with more polymer near the surface, LC molecules are more likely to be strained and shrunken, giving rise to conformational distortion. When the distortion is along the axis direction, a blue shift of the reflection wavelength is expected. However with the three-dimensional distortion which is more likely to occur, random distortion of LC molecule is more probable, giving rise to focal-conic texture which leads to scattering such as that shown in figure 1(b) for PA.

It seems that planar texture is not distorted with the curing of PUA, since the molecular mass of the prepolymer before curing is already large enough and it is already in its rubbery state with limited networks. Therefore, chain conformations of cholesteric LC molecules are constrained little by the polymers; unlike with PA, which is in its glassy state has a high crosslink density. However, a weak distortion by PUA is noted in the small blue shift and marginally broadened spectrum. Also, no effect of PUA molecular mass is noted.

The effect of isocyanate type on the transmittance spectrum of the cell before and after curing is shown in figure 2. Again, no significant difference is noted either by the curing or by the type of diisocyanate. The latter implies that the conformation change of cholesteric LC

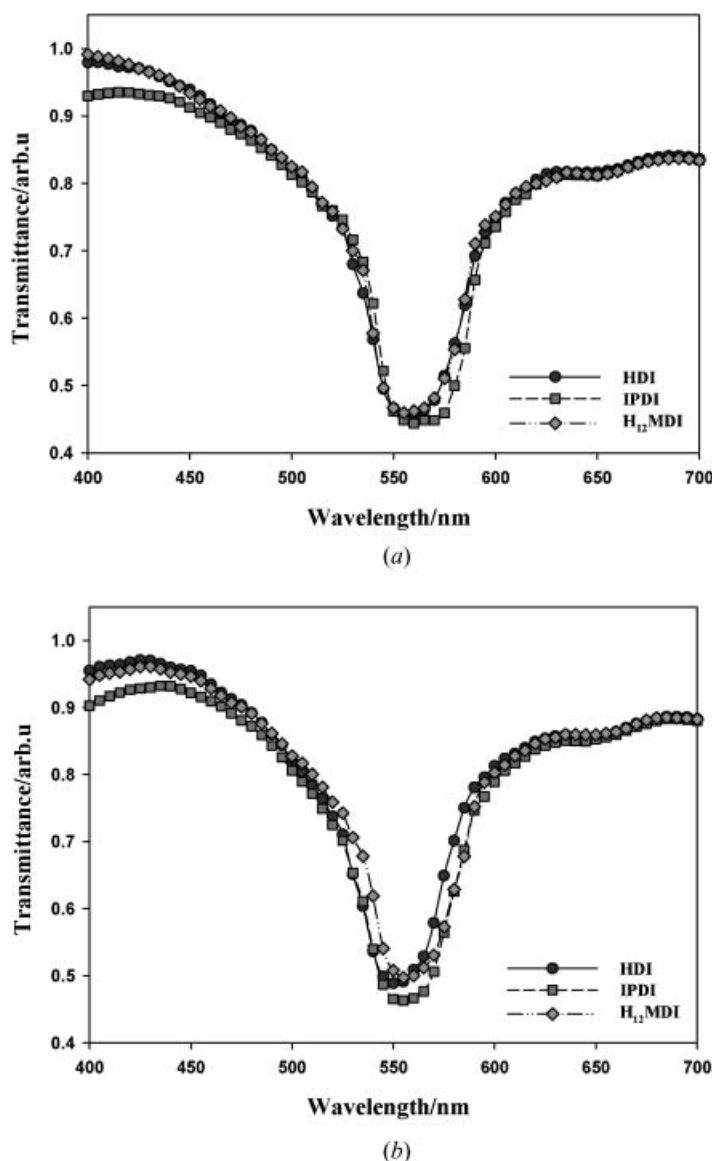


Figure 2. UV-visible spectra vs. isocyanate type of PUA (a) before and (b) after curing.

molecules is not influenced by the local chain rigidity of PUA.

3.2. Film stability

The stability of the film was studied by measuring the transmittance spectra up to seven days after curing (figure 3). The reflection peak of a PA-based film continuously decreases even after the cessation of irradiation, and in about two days the reflection peak completely disappears. This is probably due to the 'dead' reaction of acrylate monomers reported elsewhere [15]. On the other hand, only a small blue shift is obtained with a PUA-stabilized film, while keeping the

intensity identical to the original. This would be a great advantage in using PUA as stabilizer to enhance the stability PSCLC.

In an attempt to understand the origin of the blue shift (i.e. the decrease of cholesteric pitch), the shift of reflection wavelength during 11 days from the cessation of curing was measured for various PUA structures. A lower molecular mass of PPG, corresponding to high crosslink density, gave a greater shift, see figure 4(a). The shift also increased along the series HDI < H₁₂MDI < IPDI, see figure 4(b). In PSCLC, LC molecules are stabilized by the network structures of the polymers, providing the LC with elastic force. So, the extent of pitch reduction should depend on the polymer

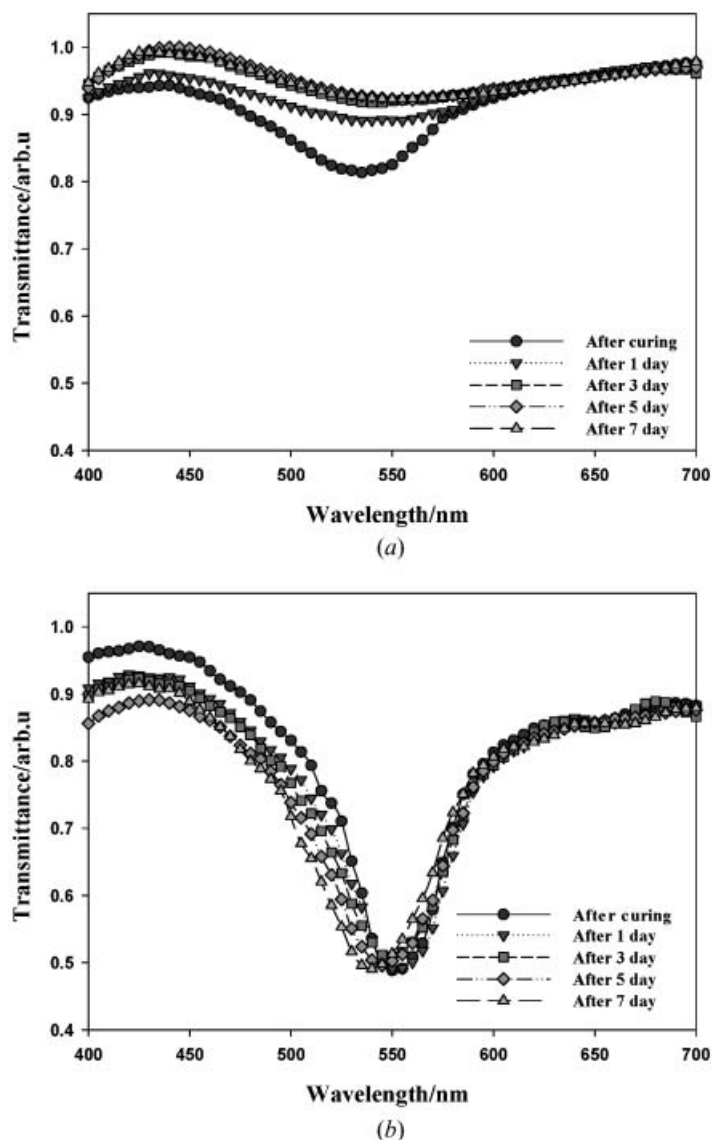


Figure 3. UV-visible spectra vs. time of (a) PA and (b) PUA.

elasticity. In this regard, the elastic modulus of PUA was measured for different isocyanates (figure 5). The elastic modulus of PUA at room temperature increases along the series HDI<H₁₂MDI<IPDI, an order in agreement with the increasing shift of the central wavelength of reflection.

On the other hand, the increase in elasticity with decreasing PPG molecular mass, i.e. decreasing molecular mass between crosslinks (M_c), is predicted by the ideal rubber theory [16] as:

$$G_N^0 = \frac{\rho RT}{M_c} \quad (5)$$

where G_N^0 , ρ , R , and T are the rubbery modulus, density, universal gas constant and absolute temperature,

respectively. Since the glass transition temperature (T_g) of these PUAs is below room temperature (point of inflection in figure 5), the above ideal rubbery theory should apply. Clearly, a lower molecular mass PPG gives a higher G_N^0 , which presumably leads to a larger shift of wavelength.

3.3. Voltage-transmittance characteristics

The voltage-transmittance relationship of the films prepared using various types of PUA were measured using Ar-ion laser light incident and collected normal to the film surface (figure 6). A continuous sine wave of 60 Hz was used and the amplitude was varied slowly to drive the films. Measurements were started from the

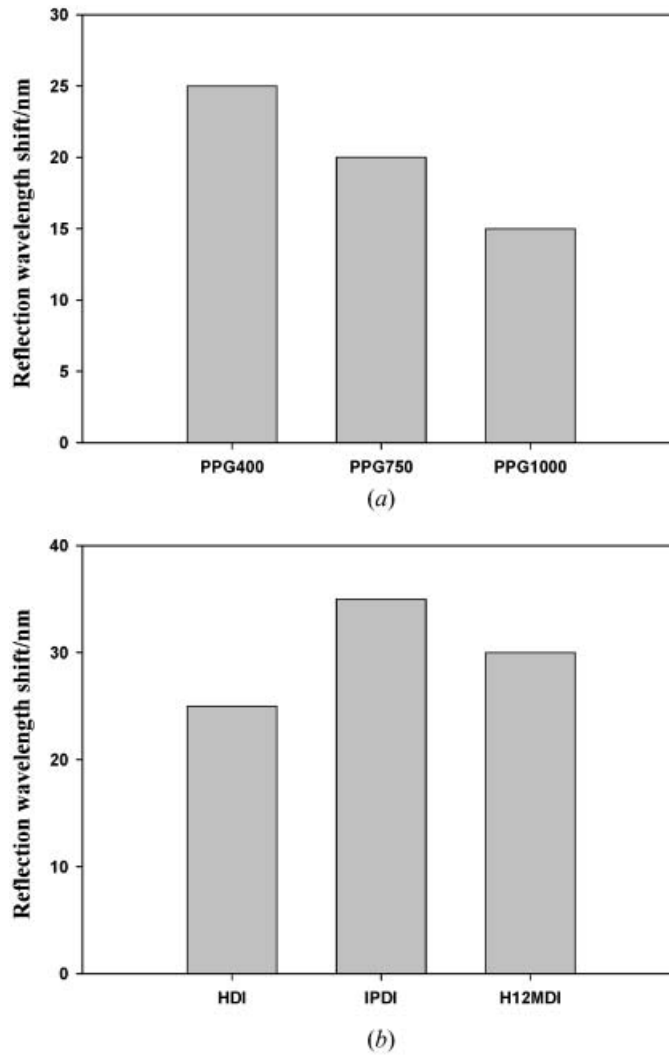


Figure 4. Reflection wavelength shift vs. molecular weight of (a) PPG and (b) type of isocyanate of PUA based cells (measured after 11 days from the cessation of curing).

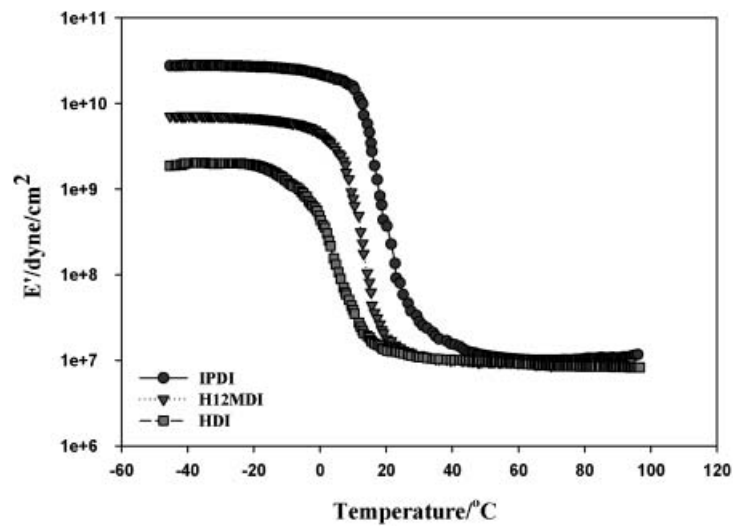


Figure 5. Storage modulus of PUA vs. temperature for different types of isocyanate.

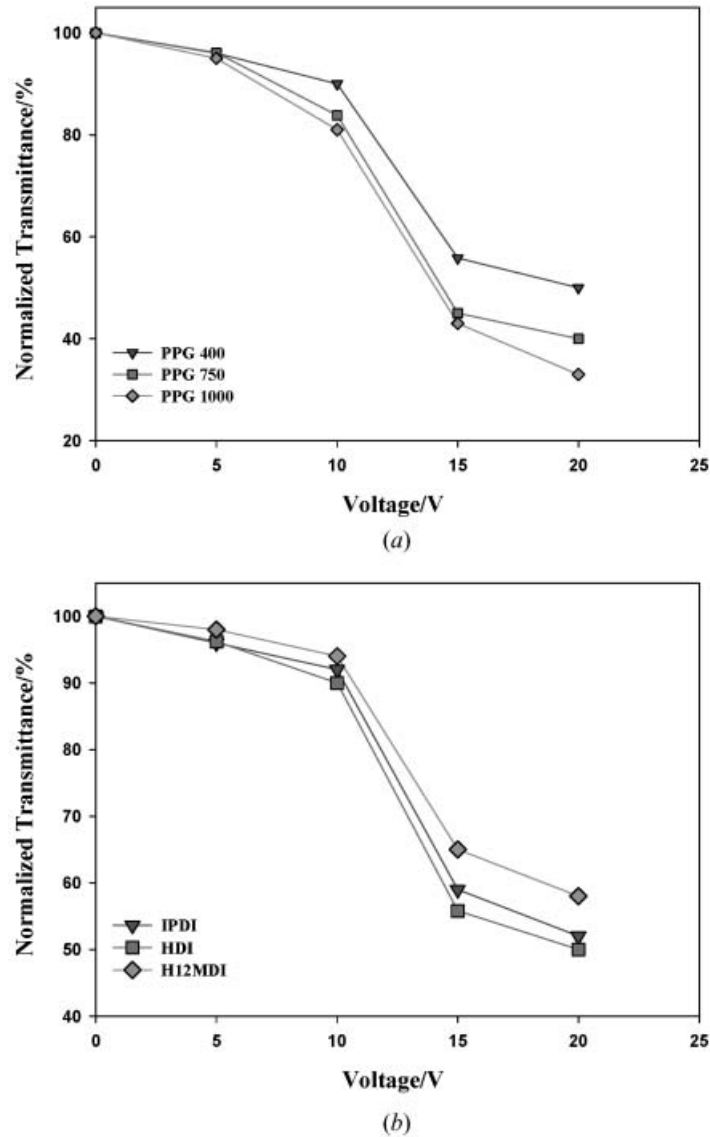


Figure 6. Transmittance vs. applied voltage for PUA based cell for various (a) PPG molecular weights and (b) types of isocyanate.

planar texture where the transmittance is high since the wavelength of Ar-ion laser light (514 nm) is far from the planar reflection peak. In this state, approximately half of the light is scattered and the other half transmitted [7]. As the voltage is increased, transmittance decreases due to the transformation into focal conic texture where scatterings becomes dominant. It is seen that the threshold voltage increases with decreasing PPG molecular mass, figure 6 (a), in order of increasing polymer elasticity. In this regard, de Gennes [17] suggested the following field strength for the cholesteric–nematic phase transition (E_{CN}):

$$E_{CN} = \left(\frac{\pi^2}{P_0} \right) \left(\frac{K_{22}}{\epsilon_0 \Delta \epsilon} \right)^{\frac{1}{2}} \quad (6)$$

where P_0 , K_{22} , $\Delta \epsilon$, and ϵ_0 are, respectively, the helical pitch in the absence of an electric field, twist elastic constant, dielectric anisotropy and dielectric constant in vacuum. Then the threshold voltage (V_{th}) is given by [18]:

$$V_{th} = E_{CN} d \quad (7)$$

where d is the cell gap.

In a PSCLC, texture transformation is constrained by the surrounding polymer networks. So, the polymer networks should act as an elastic field, having the same effect as an increase in the elastic constant [19]. The effect should be more pronounced with a more elastic polymer, which is in agreement with the effect of PPG molecular mass.

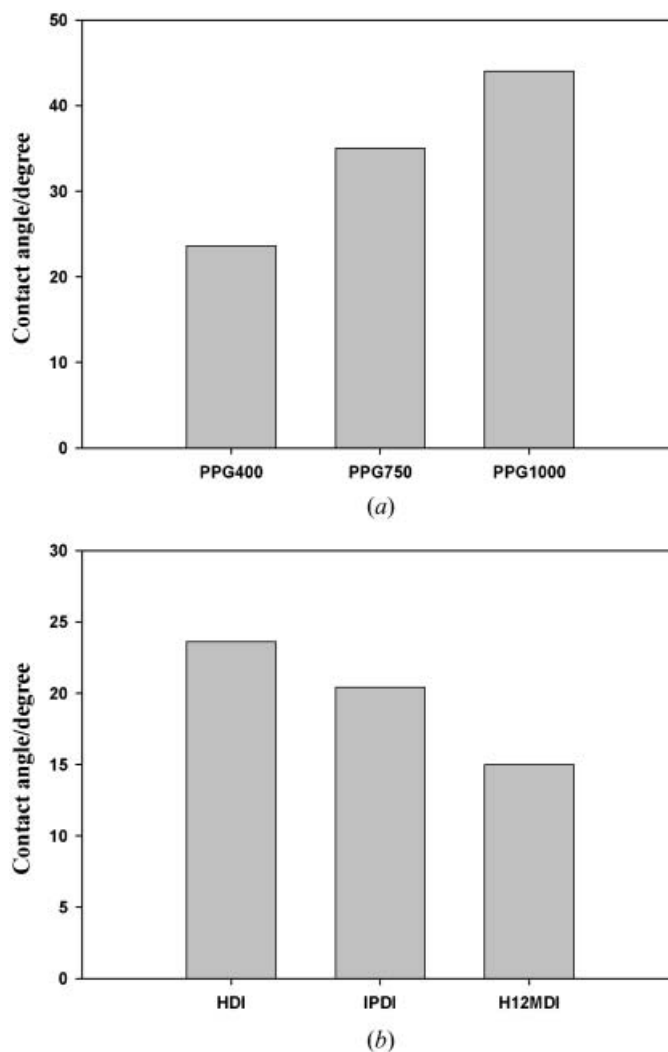


Figure 7. Contact angle vs. (a) PPG molecular weight and (b) type of isocyanate of PUAs.

Regarding the effect of isocyanate structure, aliphatic HDI, having by far the lowest elasticity gives the lowest restriction and hence threshold voltage. However, the elasticity effect alone does not explain the higher threshold voltage of H₁₂MDI over IPDI, which is probably due to a similar elastic effect of the two. In this regard, interfacial interaction between the LC and polymer has been further considered. As a simple measure of interfacial interaction, the contact angle of the PUA film with a LC drop was measured (figure 7); this showed that contact angle decreases along the series HDI>IPDI>H₁₂MDI, an order consistent with the increasing threshold voltage. High and low contact angles with H₁₂MDI and HDI based PUA, respectively, indicate low and high chemical affinity with the LC, which is due to their structural similarity and dissimilarity. It is also noted that a high molecular mass PPG gives a high contact angle, indicative of lower

interaction with the LC due to the lower numbers of polar urethane groups (–CONH–) incorporated. This should give less anchoring energy to overcome the texture transformations. The effect of PPG molecular mass is in agreement with the interfacial consideration as well as with polymer elasticity.

4. Conclusions

The electro-optic properties and stability of a polymer stabilized cholesteric liquid crystal (PSCLC) have been studied, with reference to the various structures of the polymer stabilizer.

Acrylic polymer (PA) stabilized film showed a dramatic decrease in reflection at the central wavelength and a large blue shift upon curing, and significant ‘dead’ reaction after the cessation of irradiation. In contrast, polyurethane acrylate (PUA) stabilized films showed essentially

identical transmittance spectra upon curing, and long time stability after the cessation of irradiation. Such advantages of using PUA should be of great importance for the potential display applications of PSCLCs.

Threshold voltage increased with decreasing molecular mass of PPG due to the increased elasticity of the polymer. When the elasticity was similar, a second parameter, the interfacial interaction, had to be considered for the texture transformation. That is, an increase in interfacial tension ($\text{HDI} < \text{IPDI} < \text{H}_{12}\text{MDI}$) gives an increase in threshold voltage when the elasticities are similar.

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