

Holographic-Polymer-Dispersed Liquid Crystals Doped with Poly(vinyl carbazole)-Fullerene

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ABSTRACT: The effects of poly(vinyl carbazole) (PVK) doped to a poly(urethane acrylate) matrix in holographic-polymer-dispersed liquid crystals were studied. With the addition and increasing amounts of PVK, the driving voltage and rising time of the films decreased because of the increased effective local electric field across the liquid crystal (LC) droplet. Off-state diffraction efficiency was increased with the addition and increasing amounts of

PVK presumably because of the increased elasticity of the polymer matrix, which augmented the phase separation of the polymer and LC by effectively squeezing the LC molecules out of the polymer matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3108–3113, 2008

Key words: crosslinking; glass transition; modulus; phase separation; polyurethanes

INTRODUCTION

Holographic-polymer-dispersed liquid crystals (HPDLCs) have potential device applications in displays and optical shutters because of their interesting electro-optical properties.^{1–3} Therefore, HPDLC films should have a low driving voltage and a fast response time as well.⁴ The operating voltage of an HPDLC film is controlled by various factors, namely, droplet size and shape, film conductivity and dielectric constant, surface anchoring, and so on.^{5–7}

The distribution of the external electric field to the liquid crystal (LC) and the polymer phase occurs because of the interfacial polarization that exists between the two layers of dielectric materials.⁸

According to the series model, the field distribution is given by

$$\frac{E_{LC}}{E_P} = \frac{\varepsilon_P^*}{\varepsilon_{LC}^*} = \frac{(\omega^2 \varepsilon_P'^2 + \sigma_P^2)^{1/2}}{(\omega^2 \varepsilon_{LC}'^2 + \sigma_{LC}^2)^{1/2}} \quad (1)$$

where E_{LC} and E_P are the fields across the LC droplet and polymer, respectively; ε_{LC}^* and ε_P^* are complex dielectric constants of LC and polymer, respectively. ε_{LC}' , ε_P' , σ_{LC} , and σ_P are the in-phase components of the dielectric constant and conductivities of the LC

and polymer phase, respectively; and ω is the angular frequency. According to the equation, a high σ_P is essential at a low enough ω to augment the effective field across the LC droplet.

When σ_P is too small, a charge builds up at the polymer-LC interfaces and tends to reduce the applied field. On the other hand, when σ_P is too high, a charge will collect at the cell plates and cancel the applied field.⁶ Consequently, an appropriate value of σ_P is desired to augment the effective local field across the LC droplet through the reduction of the depolarization at the polymer-LC interfaces. Hoyle et al.⁹ showed a switching voltage of 6.2 V/ μm in a trithiol pentaerythritol triallyl ether HPDLC film. Sun et al.¹⁰ studied the effect of surfactants on the electro-optical properties of HPDLC and obtained 20 V/ μm at 8 wt % surfactant. Crawford et al.³ used a partially fluorinated polymer matrix to improve the diffraction efficiency and switching voltage in HPDLC. With the addition of 30 wt % 1,1,1,3,3,3-hexafluoroisopropyl acrylate, the switching voltage decreased well to 0.6 V/ μm compared to conventional HPDLC. However, 1,1,1,3,3,3-hexafluoroisopropyl acrylate was shown to have a very low diffraction efficiency of below 10%. In our study, we obtained HPDLC films having a diffraction efficiency of 80% and a switching voltage of about 2 V/ μm at 20 wt % poly(vinyl carbazole) (PVK).

In this study, we added various amounts of a photoconductive dopant, namely, PVK, to a poly(urethane acrylate) (PUA) matrix, together with fullerene (C_{60}) to sensitize it in visible light.^{11,12} The effects of PVK addition and the applicability of the previous equation, which was originally derived for a single droplet for holographic grating, were studied.

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TABLE I
Formulation and Diffraction Efficiencies of the Films Prepared Under Various Conditions

Oligomer ^a / NVP	PVK content (wt %)	LC content (wt %)	RB (wt %)	NPG (wt %)	Cell gap (μm)	Diffraction efficiency (%)	Run number
3/1	0	40	0.3	1.8	10	60	1
	5					62	2
	10					67	3
	15					76	4
	20					80	5
	0	45				40	6
	5					46	7
	10					60	8
	15					75	9
	20					67	10

^a HEMA-capped urethane acrylate oligomer with PPG300 is abbreviated as PUA oligomer. The prepolymer mixtures were irradiated with an Ar-ion laser(514 nm) at 150 mW/cm².

EXPERIMENTAL

Materials and oligomer synthesis

The PUA oligomers were synthesized from poly(propylene glycol) (PPG; number-average molecular weight = 300) and a molar excess of hexamethylene diisocyanate to form isocyanate-terminated prepolymers; this was followed by capping with hydroxyethyl methacrylate (HEMA). Detailed synthetic procedures were described in our earlier articles.^{13,14} The composite films were prepared from a homogeneous prepolymer mixture consisting of a PUA oligomer, the nematic LC (E7), and the reactive diluent, namely, *N*-vinylpyrrolidone (NVP). The oligomer was highly viscous and immiscible with LC, which necessitated the use of a reactive diluent, such as NVP, in our experiments. The prepolymer composition was fixed at 3/1 (oligomer/NVP) by weight. Various amounts of PVK were used as photoconductive polymers to enhance the conductivity of the polymer matrix, whereas fullerene (C₆₀) was used as a photosensitizer in visible light.

E7 ($n_o = 1.5216$, $n_e = 1.7462$, $T_{\text{NI}} = 61^\circ\text{C}$) was used as the LC at two loadings, namely, 40 and 45%. n_o , n_e , and T_{NI} are ordinary refractive index, extraordinary refractive index and nematic – isotropic transition temperature of LC, respectively. Rose Bengal (RB) and *N*-phenylglycine (NPG) were used as a photoinitiator and coinitiator, respectively, for holographic recording with an Ar-ion laser. The basic formulations and experimental ranges for the fabrication of the holographic grating are shown in Table I.

Film preparation

All of the PUA films used for dynamic mechanical thermal analysis (DMTA) and UV-visible measurements were cured by UV light (1.5 mW/cm², 365 nm) for 3 min with 0.1 wt % 1-hydroxy cyclohexyl phenyl ketone (HCPK) as an initiator.¹⁵ It is believed that the network structure of the PUA film does not

depend on the light source because it is basically determined by the formulation. On the other hand, UV curing provided a wide film suitable for DMTA measurements, whereas laser curing gave a very narrow area in our experimental setup.

Grating fabrication

The holographic grating was fabricated through the preferential formation of photoproducts in the region of constructive interference arising from the overlap of two laser beams, the object and reference beams.¹⁶

The cell was constructed by the sandwiching of the oligomer mixture between two indium tin oxide coated glass plates with a gap of 10 μm , adjusted by a bead spacer.¹⁷ The Bragg period was calculated according to Bragg's law [$\lambda = 2d(\theta/2)$], where an incident beam of 514 nm was irradiated at 150 mW/cm² for 3 min. λ , d , and θ are incident wavelength, grating period and incident cross angle of beams, respectively. The intersection angle of the two beams outside the cell was fixed at 23°.

Measurements

Visible transmittance and dynamic mechanical properties

The visible spectra of the LC free-PUA films were taken by a visible spectrometer (Optizen 1411 V, Korea), whereas the dynamic mechanical properties of the polymer were measured with a DMTA analyzer (Rheometry Scientific MKIII) with a tensile mode at a heating rate of 4°C/min and at 10 Hz.

Diffraction efficiency and electro-optical property measurements

Reading was accomplished with the 514-nm beam from an Ar-ion laser positioned at the Bragg angle, the same angle as recording beam. The diffraction beam was detected by a photodiode detector. The

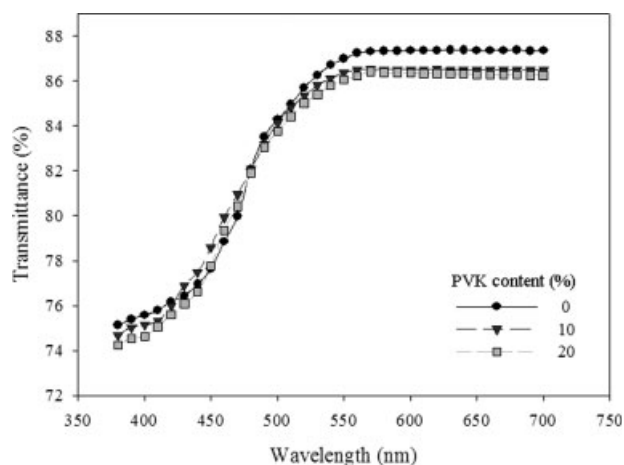


Figure 1 Visible spectra of the LC-free films (oligomer/NVP = 3/1).

diffraction efficiency was determined by division of the diffracted beam intensity of the sample cell by the transmitted beam intensity of a blank cell.

Photoconductivity was calculated by measurement of the photocurrent between the indium tin oxide glasses under an electric field and light.¹⁸ For electro-optic measurement, an electric field was applied across the film from 0 to 40 V at 10 Hz. Response time was monitored with a digital storage oscilloscope (Hitachi VC-6023, Japan).

RESULTS AND DISCUSSION

Visible transmittance and polymer phase elasticity

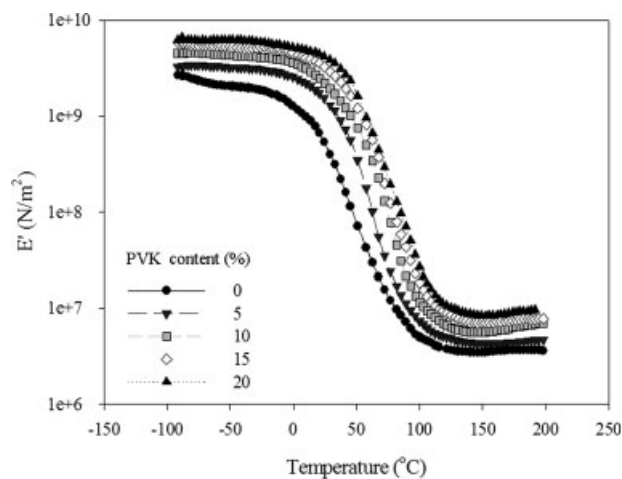
The off-state transmittances of the LC-free film according to PVK content are shown in Figure 1 for the whole visible wavelength. A significant loss in the blue wavelength was related to Rayleigh scattering.¹⁹ The transmittance was not significantly affected by the addition of PVK.²⁰ Transmittance marginally increased up to the green wavelength with the addition of PVK.

Typical dynamic mechanical behavior of the PUA films is shown in Figure 2 for a specific composition of oligomer/NVP of 3/1 with various PVK contents. Regardless of the PVK content, the elastic modulus showed a single point of inflection corresponding to the glass-transition temperature (T_g). This indicated that the PUA and PVK polymers were miscible at the segment level. When two types of polymer are immiscible, generally, two discrete T_g values are obtained. The elastic modulus in the rubbery state and the T_g of the films increased with increasing amount of PVK.²¹ This implied that PVK, having a much higher T_g (200°C), effectively reinforced PUA ($T_g = 62^\circ\text{C}$) and the blends followed simple additive rule, such as Fox's equation.^{22,23} In addition, an increase in elasticity agreed with the increased dis-

tance between crosslinks because of the addition of PVK, which was miscible with PUA. The elastic force of a rubbery material is proportional to the distance between crosslinks. Polymer elasticity is often regarded as a hooping stress that squeezes LC molecules out of the polymer matrix, and hence, it can be regarded as a physical driving force for the migration of LC molecules²⁴ in addition to the concentration gradient for molecular diffusion. The extracted LC molecules form LC layers, which are separated by polymer layers,²⁵ and the incident lights are diffracted at the polymer-LC interfaces because of the difference in refractive indices.²⁶ Therefore, a high diffraction efficiency is expected with a high extent of phase separation. So, the diffraction efficiency was expected to increase with increasing PVK content.

Diffraction efficiency

Diffraction efficiencies of the HPDLC films are given in Table I, which shows a maximum (80%) with 20% PVK at 40% LC (run 5). The diffraction efficiency monotonically increased with increasing PVK content at 40% LC. The tendency agreed with the increasing elasticity of the polymer matrix (Fig. 2). This supported the theory that the polymer elasticity squeezed LC molecules out of the polymer matrix to form LC layers, which were separated by the



PVK content (%)	T_g (°C)	E' (10^6 N/m ² , 423K)
0	62	3.5
5	67	4.3
10	73	5.6
15	77	7.0
20	81	8.7

Figure 2 Storage modulus of the LC-free films with various PVK contents (irradiated at 1.5 mW/cm² and 365 nm with 0.1 wt % HCPK for 3 min).

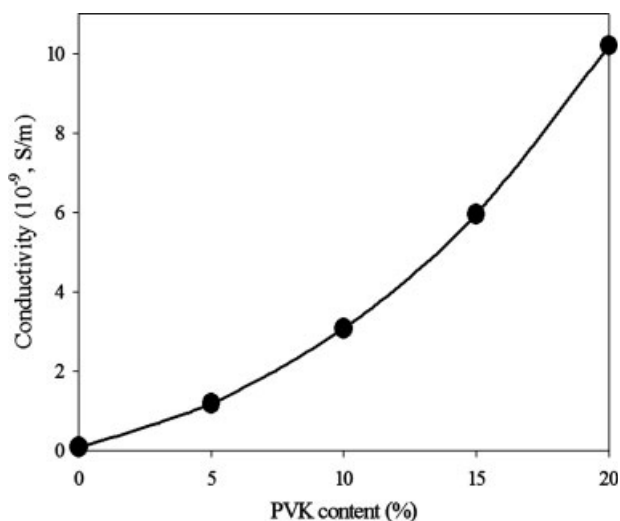


Figure 3 Photoconductivity of the LC-free films with various PVK contents (irradiated at 1.5 mW/cm² and 365 nm with 0.1 wt % HCPK for 3 min).

polymer layers in an alternating fashion.²⁷ With increased polymer elasticity, a great phase separation, a great mismatch in the refractive indices at the interfaces, and enhanced diffractions were expected.

The diffraction efficiencies of films with 40% LC (runs 6–10) were higher than those of films with 45% LC (runs 1–5) and showed a maximum at 15% PVK. It seemed that the LC molecules at higher LC and PVK concentration were more vulnerable to coalescence, which led to large droplets with small droplet densities. Large domains caused scatterings and decreased the diffraction efficiency.

Electro-optical characterizations

The local electric field across the LC droplet (E_{LC}) is different from the applied voltage (E), and it is approximated the following equation:²⁸

$$E_{LC} = E \frac{3\varepsilon_p^*}{(2\varepsilon_p^* + \varepsilon_{LC}^*)} \quad (2)$$

where the magnitude of the complex dielectric constant (ε^*) is given by

$$\varepsilon^* = \sqrt{\varepsilon'^2 + \varepsilon''^2} \quad (3)$$

where ε' is the storage dielectric constant.

The dielectric loss (ε'') and the electric conductivity (σ) are related by the following equation:

$$\varepsilon'' = \sigma/\omega \quad (4)$$

Then, when eqs. (3) and (4) are substituted into eq. (2), this gives

$$E_{LC} = E \frac{3\sqrt{\varepsilon_p'^2 + \frac{\sigma_p^2}{\omega^2}}}{\left(2\sqrt{\varepsilon_p'^2 + \frac{\sigma_p^2}{\omega^2}} + \sqrt{\varepsilon_{LC}'^2 + \frac{\sigma_{LC}^2}{\omega^2}}\right)} \quad (5)$$

σ of the polymer matrix depended on the formulation, but on average, the measured value was about 3.3×10^{-9} S/m and that of LC was 10^{-8} S/m according to the literature.²⁹ Also, the dielectric constant of the polymer matrix was about $3\varepsilon_0$ (Dielectric constant in vacuum) ($\varepsilon_0 = 8.85 \times 10^{-12}$), that of LC was $9.8\varepsilon_0$, and the frequency (f ; $\omega = 2\pi f$) was 10 Hz.^{6,30} Therefore, $\varepsilon' < \sigma/\omega$, and conductivity effects dominated the dielectric terms in HPDLC; the field across the LC droplets could be approximated by^{8,31}

$$E_{LC} = E \frac{3\sigma_p}{(2\sigma_p + \sigma_{LC})} \quad (6)$$

Figure 3 shows the photoconductivity of LC-free PUA films as a function of PVK content. The conductivity of PVK without light was about 10^{-10} S/m,³² whereas that of virgin PUA was 3.3×10^{-9} S/m. The photoconductivity of the LC-free films increased about 10 times as the PVK content increased from 0 to 20 wt %, which implied that the local electric field across the LC droplet significantly increased.

Figure 4 shows the applied voltage dependence of the diffraction efficiency of the HPDLC films. When a voltage was applied across the film, the diffraction efficiency decreased because of the orientation of LC molecules along the electric field direction.⁹

The driving voltage decreased with increasing PVK content. This was an indication that the local electric field imposed on the LC droplets increased because of the increased conductivity of the polymer phase,³³ as noted in eq. (6).

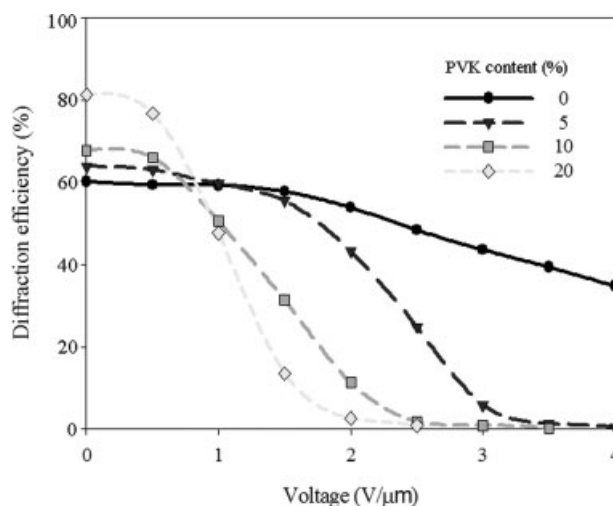


Figure 4 Diffraction efficiency versus applied voltage (LC = 40%, 150 mW/cm²).

Figures 5 and 6 show typical rise time (τ_R) and decay time (τ_D) values of the HPDLC films as a function of PVK content and applied voltage, respectively. The film with no PVK was not driven with the highest voltage applied. τ_R , which is related to the applied field, rapidly decreased with increasing PVK content and applied voltage,³⁴ whereas τ_D increased with increasing PVK content probably because of the great distortion of LC molecules by the increased local field across the LC droplet. The response time ($\tau_R + \tau_D$) was less than 5 ms. The increase with PVK content led to an increase in effective local field. However, τ_D was much larger than τ_R , especially at high PVK contents and applied voltages, which implied that the relaxation occurred in two steps, as suggested by Jain and Rout³⁵ for conventional polymer dispersed liquid crystal (PDLC) morphology. That is, under low applied voltage, the LC distortion inside the droplet took place without the rotation of bipolar axes. Upon field removal, LC quickly went back to the initial state. However, because the bipolar axes were rotated at the high field, the LC molecule slowly relaxed to the initial state upon field removal.

CONCLUSIONS

An additive amount of PVK was doped to a conventional HPDLC, which was based on PUA, and the effects were studied in terms of the diffraction efficiency and electro-optical properties of the films.

The photoconductivity of the LC-free films increased about 10 times as PVK content increased from 0 to 20 wt %.

With the addition and increasing amounts of PVK, the off-state diffraction efficiency increased due to the increased mismatch of refractive indices and the phase separation between the polymer and LC,

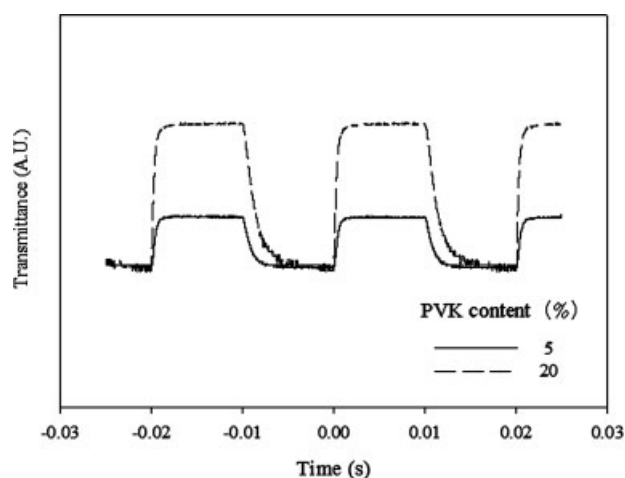


Figure 5 Response time versus PVK content for the HPDLC films (LC = 40%, 20 V).

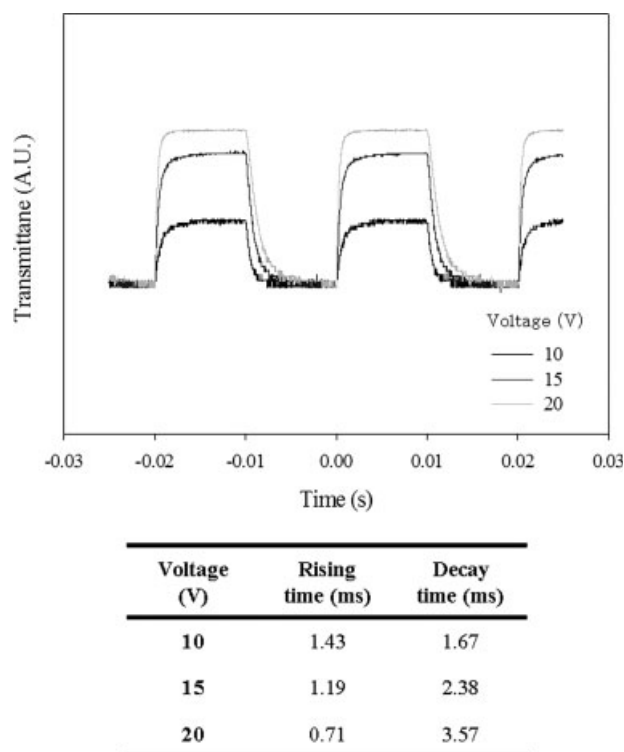


Figure 6 Response time versus applied voltage for the HPDLC films (LC = 40%, PVK = 20%).

which was driven by the high polymer elasticity. The elasticity of PUA increased with the addition of PVK because of the increased distance between cross-links coupled with the reinforcing effect of PVK.

Conductive PVK doped to the polymer matrix augmented the effective local electric field across the LC droplet and reduced the driving voltage and τ_R , which implied that the theoretical field distribution for a single droplet was qualitatively applicable for HPDLC. On the other hand, the increase in τ_D with PVK addition was interpreted in terms of the great distortion of LC molecules by the increased local field across the LC droplet.

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