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Morphology and switching of holographic gratings containing an azo dye

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The effects of an azo dye on the diffraction efficiency, morphology and electro-optic properties of the transmission mode of a holographic polymer dispersed liquid crystal (LC) have been studied. The azo dye induced an induction period which otherwise does not exist, followed by a gradual increase of the diffraction efficiency to a saturation value which increased with increasing azo dye content, as a result of the azo dye reorientating LC molecules within the droplet. The increased diffraction efficiency was caused by the decreased droplet coalescence which was due to the hindered migration of the LC by the dye molecules, and to LC orientation induced by azo dye molecules giving a high refractive index contrast. The droplet size decreased with increasing dye content. The dye also lowered the threshold voltage due to the high dielectric anisotropy caused by the presence of a strong on-axis dipole moment and decreased the response time.

1. Introduction

Holographic polymer dispersed liquid crystals (HPDLCs) are a class of composite materials that are being extensively studied for various electro-optical applications [1–6]. The basic premise of operation is the ability electically to switch the diffraction [7]. HPDLC gratings are formed by the polymerization-induced anisotropic phase separation of liquid crystals from a polymer matrix created through free-radical photopolymerization [8]. Holographic imaging of laser radiation onto a homogeneous mixture of photopolymerizable monomers and liquid crystal results in spatially modulated polymerization kinetics that generates alternating layers of polymer and liquid crystal-rich lamellae [9]. In the hologram writing process, this holographic exposure initiates a counterdiffusion process, i. e. diffusion of liquid crystal to the dark regions and monomer to the light regions of the interference pattern [10]. It should be emphasized that there is a distribution of droplet sizes within typical PDLC films which is related to the kinetics of the phase separation process. The LC-rich regions result in randomly oriented submicrometre droplets where the droplet size depends on a number of factors: monomer functionality, the fraction of LC in the prepolymer syrup, the laser beam intensity, duration of irradiation and the curing temperature. Since the morphology dictates the electro-optic properties, enhanced control of LC domain size and distribution is paramount in optimizing the overall performance of the HPDLC films [9].

There has been considerable interest in the morphology and electro-optic properties of HPDLCs [11–16]. Recently, a major problem with HPDLCs is the need to reduce the threshold voltage [17]. Schulte *et al.* used fluorine-substituted acrylate monomers to prepare HPDLC gratings with visible radiation. The presence of fluorine atoms at the LC/polymer interface presumably enhanced the phase separation and lowered the LC anchoring strength, thus lowering the switching voltage [18]. Natarajan *et al.* added a surfactant-like long chain alkyl fatty acid, and lowered the switching field, which augmented optical quality in both transmission and reflection gratings [19]. More recently, Cupelli *et al.* reported that the addition of conductive polymer molecules induced a large reduction in the reorientation field [20].

In most visibly recorded HPDLCs, a number of additives are typically required [8]. It is well known that dye-doped nematic LCs exhibit enhanced orientational properties up to three orders of magnitude larger than the pure LCs [21]. Azobenzene derivatives have been explored as various kinds of photonic materials because they can change not only their own optical properties

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but also the optical anisotropy of the surrounding LCs by photoirradiation [22]. Azo dye molecules can reorient, depending on the local polarization of light, via photoactivated isomerization; such an angular dependence will tend slowly to align the dye molecules in the minimum energy configuration, which is perpendicular to the local polarization [23, 24]. Addition of a few percent of such a dye into a LC matrix greatly enhances the birefringence, and lowers the threshold voltage of the mixture [25].

To reduce the threshold, we have added to a HPDLC a small amount of azo dye with high dielectric anisotropy induced by the presence of a strong on-axis dipole moment. We measured droplet morphology, real time and saturation diffraction efficiency, and electro-optic properties of the films. From the results, we have interpreted the roles of the dye with regard to the performance of a transmission HPDLC.

2. Experimental

2.1. *Materials*

Material selection plays a very important role in the fabrication of a HPDLC and strongly affects its performance. To form a HPDLC device, a homogeneous mixture of a multi-functional monomer/(oligomer), reactive diluent, photoinitiator dye, coinitiator, additives and LC is prepared. Polyurethane acrylate (PUA) is a segmented urethane oligomer capped with acrylic functionality, which offers excellent toughness, chemical resistance and adhesion to difficult substrates, more than any other class of radiation curable oligomer. Bifunctional polypropylene glycol (PPG) (M_n=200, 400 g mol^{-1}) was reacted with a molar excess of hexane diisocyanate (HDI) for over 1 h at 80°C to obtain an isocyanate(NCO)-terminated polyurethane prepolymer. The reaction mixture was then cooled to 40°C and hydroxylethyl acrylate (HEA) was added to obtain a HEA-capped urethane acrylate oligomer [26, 27]. These oligomers are highly viscous and immiscible with LC. Monofunctional monomer helps to dissolve various compounds in the mixture, forming a homogeneous mixture; it also reduces the viscosity of the mixture. *N*-vinylpyrrolidinone (NVP) has in the post been used as the monofunctional monomer. The multifunctional monomer dipentaerythritol penta-/hexa-acrylate (DPHPA) has a much higher reactivity and gives a polymer with extensive crosslinking. The composition of oligomer/monofuctional/multifunctional diluents was 4/3/3 by weight. Small amounts of Rose Bengal (RB) and *N*-phenylglycine (NPG) were added to sensitize the monomers for a visible cure.

In addition, a monofunctional fluorinated monomer (2,2,2-trifluoroethyl acrylate) was added to the homogenous mixture to reduce the interfacial tension between resin and LC and to improve the optical properties. A surfactant (octanoic acid) was also added to the mixture to lower the switching field. 4′-(2-Hydroxyethyl)ethylamino-4-nitroazobenzene (Disperse red 1) was used as the azo dye. Usually, dye molecules contain several phenyl rings and conjugated linking groups, so that their melting points are high and give high viscosity; 0.5 and 1 wt% azo dye were added to the monomer mixtures in our experiments. As liquid crystal we used E7 (BL001, Merck) a eutectic mixture of four cyanobiphenyls and a cyanoterphenyl; the LC content was 45 wt%. The basic formulation to prepare the holographic gratings is given in table 1.

Table 1. Formulations (compositions in wt%) in the preparation of transmission mode HPDLCs. Prepolymer mixtures were irradiated with an argon ion laser at 90 mW cm^{-2}; cell gap was adjusted to 10 µm by bead spacers.

		Oligomer		Diluents		Additives					
		HDI	HEA	DPHPA	NVP	Rose Bengal	NPG	TFEA	OA	DR1	LC (E7)
PPG200	5.7	9.6	6.7	16.5	16.5	0.3	1.8	6	6	0	45
PPG200	5.7	9.6	6.7	16.5	16.5	0.3	1.8	6	6	0.5	45
PPG200	5.7	9.6	6.7	16.5	16.5	0.3	1.8	6	6	1	45
PPG400[a]	9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	6	0	45
PPG400	9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	6	0.5	45
PPG400	9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	6	1	45

[a] PPG400 designates PPG of molecular mass 400.

2.2. *Grating fabrication and measurements*

Cells were constructed by sandwiching the prepolymer 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 were irradiated osing an Ar-ion laser (514 nm) at 90 mW cm^{-2}, with exposure times of typically 300–600 s. Holographic gratings were obtained by combining an object beam and a reference beam in a recording medium. The angles of incidence of the two beams outside the material were each 13°; an interference pattern formed according to the Bragg law ($\Lambda = \lambda/2 \sin \theta$). Figure 1 shows the experimental set-up used to fabricate a transmission HPDLC.

The diffraction efficiencies were measured with a photodiode using an Ar-ion laser. Grating formation was monitored in real time using a He-Ne laser probe (633 nm) with the angle of incidence set at the appropriate Bragg angle, since the material is in sensitive to red light. For electro-optic measurements, a square wave voltage operating from 0 to 80 V was applied across the HPDLC sample. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope. Grating morphology was identified by scanning electron microscopy (SEM); samples were prepared by freezing and fracturing the HPDLC cells in liquid nitrogen, and extracting the LC molecules with methanol for 24 h.

3. Results and discussion

3.1. *Grating formation dynamics*

Figure 2 shows the real time diffraction efficiency of our system. A sample without dye shows a very short induction period of about 100 µs and reaches a maximum in about 50 s, followed by an asymptotic decrease to a stable value in about 120 s. However, when dye is present the induction period becomes long and diffraction efficiency increases gradually to an asymptotic value higher than that seen without dye, because the azo dye reorientation process occurs over a much longer period of time. This implies that the dye absorbs polarized light, which leads to low power exposure, and slows the rate of polymerization and phase separation. Due to the slow rate of phase separation, LC droplets are less vulnerable to droplet coalescence keeping them small and uniform. As noted, high dye content gives a slow increase in diffraction efficiency as a result of the azo dye reorientating LC molecules within the droplet.

3.2. *Morphology*

As the Bragg period in an HPDLC is of the order of nanometers, electron microscopy techniques (SEM) are available, allowing direct determination of the morphology [28, 29]. Figure 3 shows SEM images of a transmission grating as a function of dye content. The performance of the holographic gratings in terms of diffraction efficiency, switching voltage, speeds, and background scatter is inherently related to the solid state morphology of the grating structures [30]. Morphological factors including droplet size, shape and density, Bragg period, and interfacial roughness all contribute to the electro-optic properties of a HPDLC. The average size of LC domains (dark region) found with dye, figures 3 (*b*) and 3 (*c*), is smaller than that found without dye, figure 3 (*a*). It is also noted that the

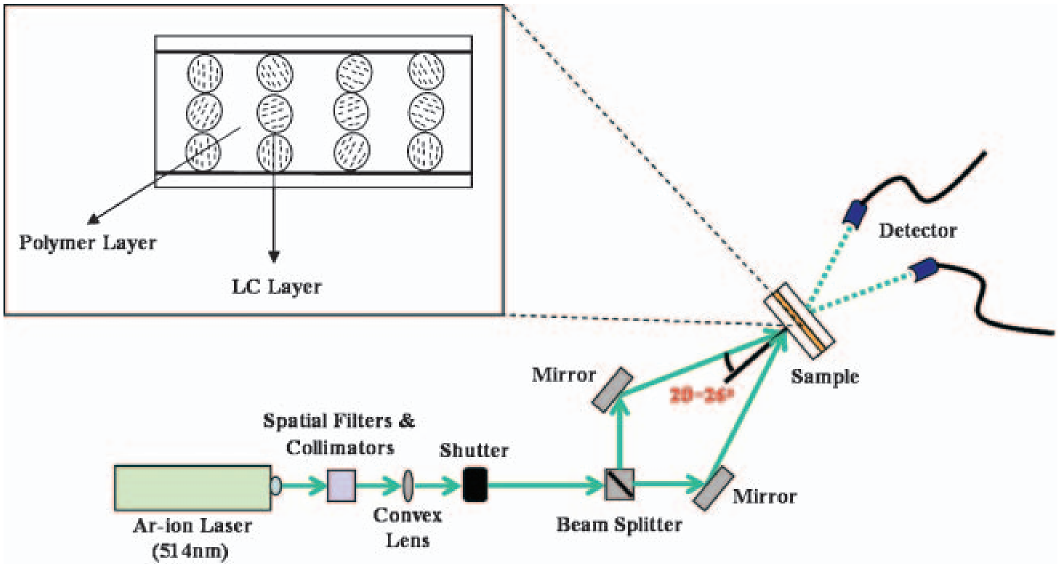


Figure 1. Experimental set-up for measuring the electro-optical properties of the transmission gratings.

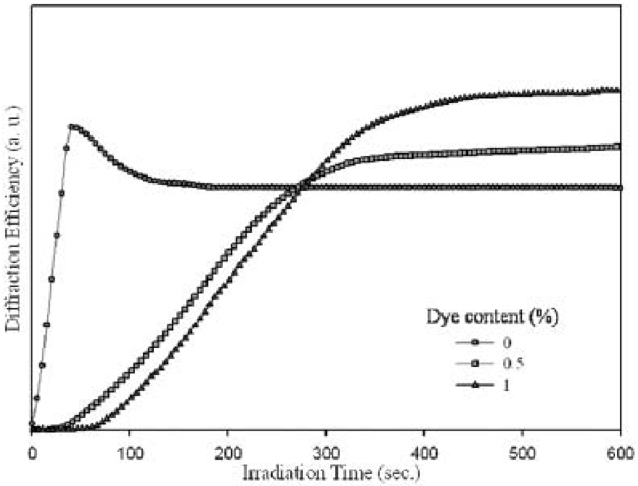


Figure 2. Diffraction efficiency as a function of irradiation time at 633 nm in a HPDLC film prepared with and without azo dye (PPG400).

LC domain size decreases with increasing dye content in the transmission grating. Small droplet size gives a short switching time, since the relaxation time scales as the square of the droplet size, and reduces the amount of random optical scattering producing a high optical quality in the grating [31].

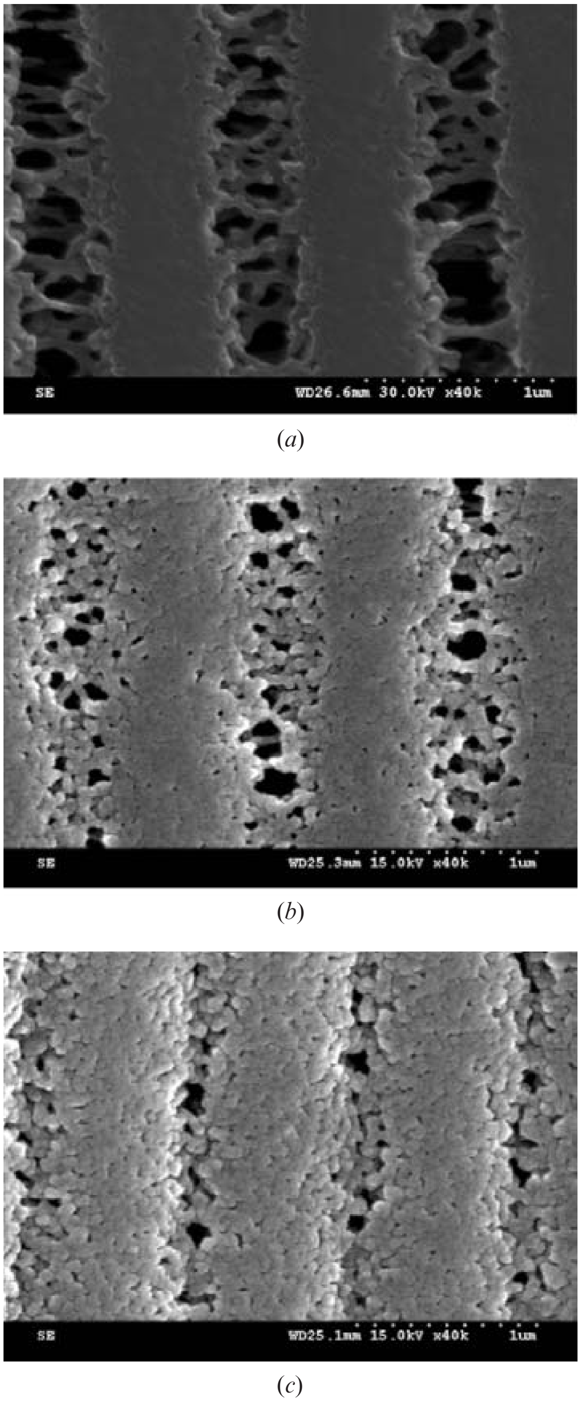
3.3. *Diffraction efficiency*

Figure 4 shows the diffraction efficiency/PPG molecular mass/dye content relationship. The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam (η_d) to the intensity of the incident beam (η_i) according to

$$\eta(\%) = \frac{\eta_d}{\eta_i} \times 100.$$

The effect of PPG molecular weight seems two-fold. Without dye, a higher diffraction efficiency is obtained with high PPG molecular weight (PPG400), but the tendency is reversed with the addition and increasing amounts of dye. This seems reasonable since low PPG molecular mass quickly induces a highly networked resin phase and causes rapid migration of LC molecules into the LC-rich phase, which leads to extensive coalescence to form large LC droplets. This lowers droplet density and increases domain size leading to high scattering loss. By contrast, when the dye is present, the rate of polymerization becomes slower. In such a case, a low PPG molecular mass which gives high crosslinking density would help the migration of LC molecules, which otherwise is too slow.

The diffraction efficiency increases monotonically with increasing content of dye, which can be attributed to the slow rate of polymerization and phase separation, leading to less droplet coalescence and a uniform distribution of droplet size. It has been observed through SEM morphology that the size of the LC domains decreases with the addition of dye. Also, the



(*a*)

(*b*)

(*c*)

Figure 3. SEM micrographs for a transmission HPDLC prepared (*a*) without and with (*b*) 0.5%, (*c*) 1% azo dye (PPG400).

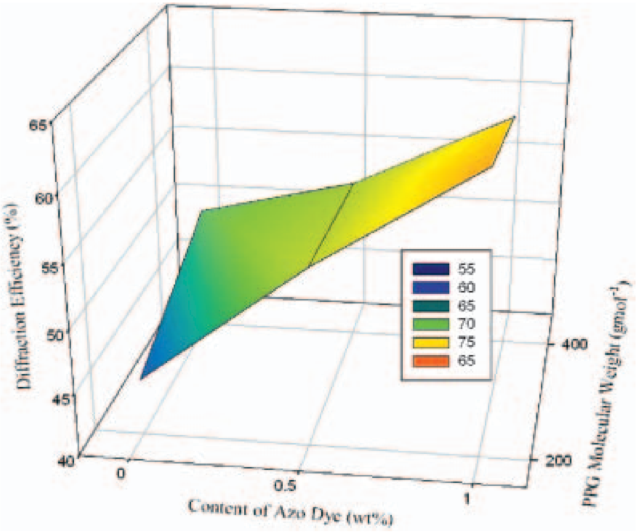


Figure 4. Diffraction efficiency/molecular weight of PPG/content of azo dye relationships of HPDLC films.

photoinduced alignment of the azo dye molecules strongly reorients LC molecules perpendicular to the grating. The refractive index contrast of the grating is further enhanced when the azo dye and LC molecules are oriented perpendicular to the grating, resulting in a higher diffraction efficiency.

3.4. *Electro-optic properties*

The electro-optic characteristics of a HPDLC are highly sensitive to the material, and changes in the materials system can be used to achieve a wide range of performance and optimization. Figure 5 shows the applied voltage dependence of the diffraction efficiency. In the off state, the diffraction efficiency is higher in samples with azo dye than without, due to the decreased droplet size and higher LC ordering. When a voltage is applied, diffraction efficiency decreases, implying that LC molecules are oriented along the electric field direction. It is seen that the HPDLC samples prepared with dye have lower switching voltages than those without dye. This implies that the azo dye enhances the optical torque acting on the LC molecules due to the high dielectric anisotropy, which is due to the presence of a strong on-axis dipole moment. Regardless of the content of azo dye, the switching voltage has significantly decreased to $3\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, with a contrast ratio greater than ten.

Operationally, the response time is defined as the time taken to switch from 90 to 10% of the maximum switching difference under an electric field. The temporal response of a HPDLC film is shown in figure 6 for 1 wt% dye. The hologram is initially diffracted until the applied field rotates the droplets, thus changing the index modulation of the periodic phase grating. As the voltage increases further, the degree of droplet rotation increases to a constant value. On removal of the voltage, due primarily to the elastic forces, the LC molecules relax to their initial configuration.

Figure 7 shows the rise and decay times of the film as a function of applied voltage. The rise time is expected to be field-dependent and rapidly decreases with increasing voltage. It is seen that the rise time slightly decreases with increasing dye content due to the decreased droplet size and LC orientation induced by azo dye molecules. On the other hand, the decay time shows the opposite tendency, that is it increases with increasing voltage. A slow decay of an internal electric

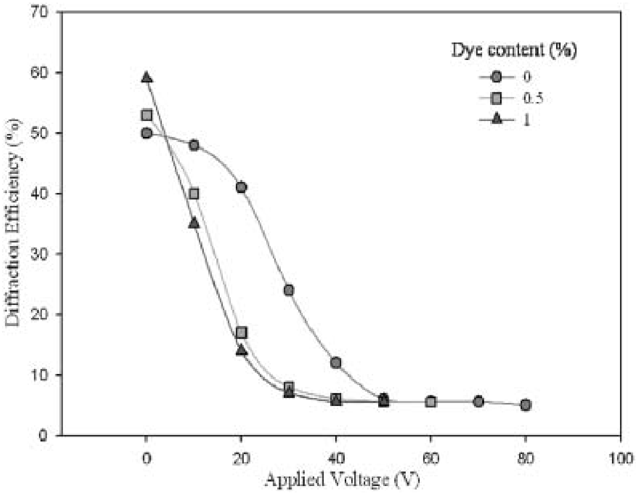


Figure 5. Diffraction efficiency as a function of applied voltage of HPDLC films (PPG400).

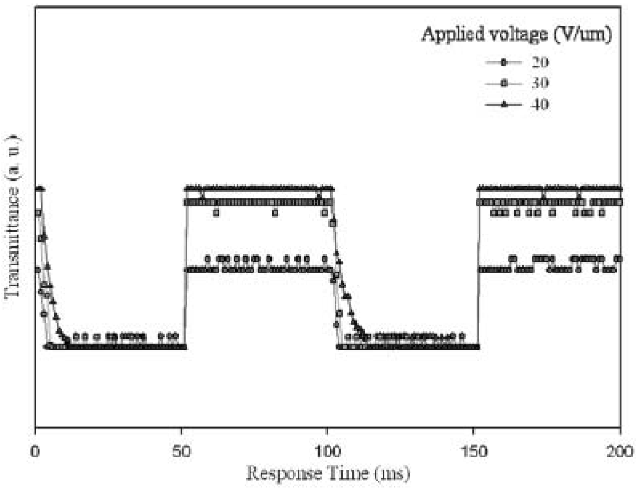


Figure 6. Optical response as a function of applied voltage for the HPDLC films (PPG400, 1% azo dye).

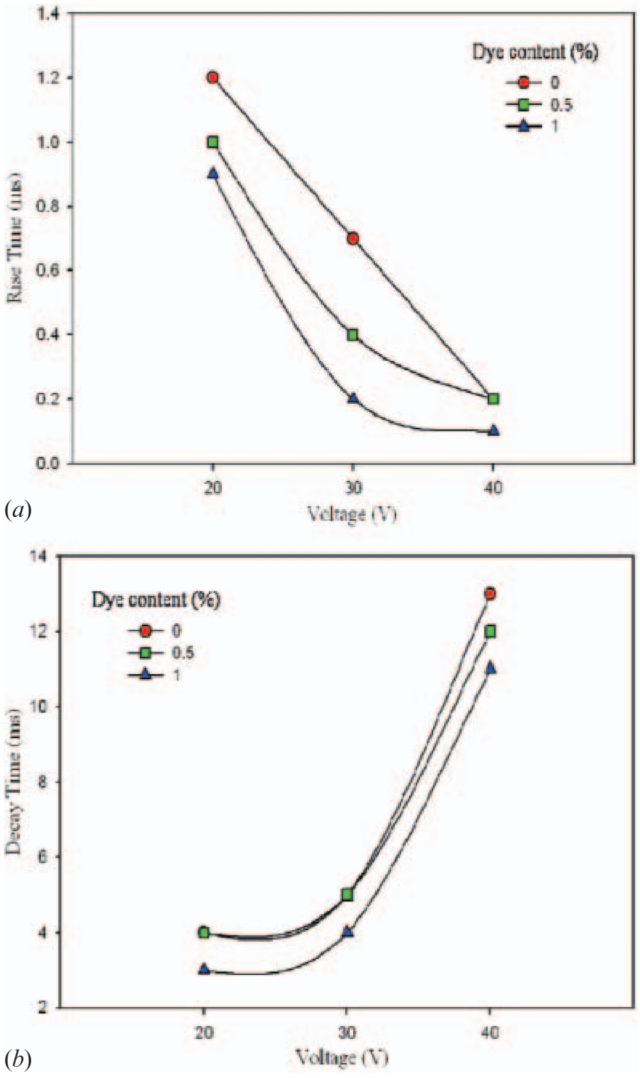


Figure 7. (*a*) Rise time and (*b*) decay time of HPDLC films as a function of applied voltage and azo dye content (PPG400).

field caused by the migration of ions in the film could explain the increase of decay time with increasing field [32]. We found that the decay time decreases with increasing content of azo dye due mainly to the small droplet size and LC orientation induced by azo dye molecules.

4. Conclusions

The effects of an azo dye on a holographic polymer dispersed liquid crystal have been studied in terms of grating morphology, diffraction efficiency and electro-optic properties. The addition of azo dye was likely to favour a lowering of the switching field. This implies that the dye assists LC orientation due to its high dielectric anisotropy. As the content of dye molecules increases, the LC droplets became small due to the slow rate of polymerization. In addition, azo dye molecules strongly reorient LC molecules perpendicular to the grating, giving rise to enhanced diffraction efficiency and short response times. The experimental results for 1% dye content showed a rise time of 0.1 ms, a decay time of 11 ms and a contrast ratio greater than ten.

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