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Photoswitching of holographic polymer-dispersed liquid crystals doped with chiral dopant

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Chiral dopants were added to the formulation of holographic polymer-dispersed liquid crystals and the effects studied in terms of grating formation dynamics, morphology, diffraction efficiency, contrast ratio and electro-optical properties of the films. A gradual increase of real-time diffraction efficiency, decrease of droplet size and increase of diffraction efficiency of the composite film were obtained with the addition and increasing content of chiral dopant, due to the increased viscosity of the liquid crystal (LC) doped with the chiral dopant leading to decreased droplet coalescence. The contrast ratio decreased with increasing content of chiral dopant due to the difficult orientation of LC molecules caused by the formation of a helical structure. Addition of a small amount of the chiral dopant increased the driving voltage slightly, whereas the decay time is decreased significantly as a result of the high twisting of the helical structure.

1. Introduction

Holographic polymer-dispersed liquid crystals (HPDLCs) are a class of composite materials that are being extensively studied from both basic and application viewpoints [1–5]. These holographic materials have the combined advantages of photopolymers and the properties of liquid crystals, which provide a switchable behaviour with larger electro-optic effects under low voltage [6].

HPDLC gratings form through holographic illumination of a homogeneous mixture of photopolymerizable monomer and liquid crystal (LC) by photopolymerization-induced anisotropic phase separation. The periodic light intensity gradient resulting from holographic exposure induces mass transport of monomer into the light regions and LC into the dark regions. The morphology of HPDLCs consists of alternating lamellae of predominantly polymer and predominantly LC regions [7]. Some factors known to influence the overall performance of HPDLCs include monomer functionality, the fraction of LC in the prepolymer mixture, the laser beam intensity and duration of irradiation and the curing temperature.

There have been numerous approaches to manipulate and improve the electro-optical performance of HPDLC films [8–15]. Schulte *et al.* [16] used fluorine-substituted acrylate and reported that fluorine atoms at the LC/polymer interface presumably enhanced the phase separation and lower anchoring strength of the LC, thus lowering the switching voltage. Klosterman *et al.* [17] added a non-reactive surfactant-like molecule, and lowered switching field and augmented optical quality in reflection gratings. Cupelli *et al.* [18, 19] reported that the addition of conductive polymer molecules induces a large reduction reorientation fields and relaxation times. Wu *et al.* [20] reported that by adding a dye with high dielectric anisotropy, the threshold voltage of HPDLC can be reduced significantly. Also, photopolymerizable thiolene-based polymers are alternatives that overcome some of the problems associated with acrylate-based HPDLCs and have received recent attention [21]. Dopants to the nematic have been reported to shorten the decay characteristics of PDLC films [22–25]. As far as the present authors are concerned, a cholesteric dopant has not been doped into the HPDLC.

In this paper, we report the addition of a chiral dopant to the LC for the formulation of conventional HPDLC to augment the electro-optic performance of the film. It is also expected that chiral dopants induce high diffraction efficiency of the composite film due to the increased viscosity of LC leading to decreased droplet coalescence. We measured the real-time diffraction efficiency, scanning electron microscopy (SEM) images, diffraction efficiency, switching voltage,

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contrast ratio and response time of the films. Based on the results, we interpreted the roles of chiral dopant regarding the electro-optical properties of transmission HPDLCs.

2. Experimental

2.1. *Materials*

Films were prepared by polymerization-induced phase separation (PIPS) from a homogeneous mixture of multifunctional monomer (oligomers), reactive diluents, additives and LC in the presence of suitable photo-initiator dye and co-initiator.

To synthesize the oligomers, bifunctional polypropylene glycol (PPG) (M_n=400 g mol^{-1}) was reacted with molar excess of hexane diisocyanate (HDI) for over 1 h at 80°C to obtain isocyanate (NCO)-terminated polyurethane prepolymer. Then the reaction mixture was cooled down to 40°C and hydroxyl ethyl acrylate (HEA) was added to obtain HEA-capped urethane acrylate oligomer, which is photosensitive and subject to laser irradiation. The progress of reaction was monitored by measuring the NCO absorption peak at 2270 cm^{-1} using FTIR spectroscopy.

N-vinylpyrrollidinone (NVP) and dipentaerythritol penta-/hexaacrylate (DPHPA) were, respectively, used as mono- and multifunctional monomers. NVP helps to dissolve different compounds in the mixture and reduces the viscosity, whereas DPHPA provides the mixture with high reactivity and a polymer with highly networked structure. The composition of oligomer/monofuctional/multifunctional diluents was fixed at 4/3/3 by weight.

Rose Bengal (RB) was used as photoinitiator for holographic recording with an argon ion laser because it displays a broad absorption in the region from 450 to 560 nm and has a high triplet quantum yield [1]. To this, a millimolar amount of *N*-phenylglycine (NPG) was added as co-initiator [26]. The excited RB undergoes an electron-transfer reaction in which NPG functions as an electron donor, producing an NPG radical. Free radical polymerization is then initiated by the NPG radical [27].

In addition, surfactant (octanoic acid) was added to the mixture to lower the switching field. E7 (BL001, Merck), a eutectic mixture of three cyanobiphenyl and one cyanoterphenyl mixture with high birefringence, adequate T_{NI} and positive dielectric anisotropy ($\Delta\varepsilon$=13.8), was used as the LC. The prepolymer/LC compositions were 65/35 and 55/45, and the compositions are, respectively, abbreviated as LC35 and LC45. Also, chiral dopant (Merck, S-811) was doped into the LC and was kept at 1 wt % such that it does not change the chemical properties of the LC. Formulations for preparation of the transmission mode HPDLCs are given in table 1.

2.2. *Grating fabrication and measurements*

To fabricate holographic gratings, prepolymer mixture was sandwiched between two indium-tin-oxide (ITO)-coated glass plates with a gap of 10 μm, which was adjusted by a bead spacer. The prepolymer mixtures were irradiated with an Ar-ion laser (514 nm) of equal intensity with a total power of 100 mW cm^{-2}, with exposure times of typically 200~300 s. The external incident beam angle between the two lasers outside the cell was set at 13°. The interference of the two beams established the periodic interference pattern according to Bragg's law [$\wedge=\lambda/2\sin\left(\frac{\theta}{2}\right)$, $\wedge$ = grating spacing, λ=wavelength of the writing beam].

The diffraction efficiencies of the holographic gratings 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 incident angle

Table 1. Formulations for preparation of transmission mode holographic gratings.

Composition /wt %									
Oligomer			Diluents		Additives				LC
PPG400	HDI	HEA	DPHPA	NVP	RB	NPG	OA	Chiral dopant	E7
10.7	9.0	6.3	19.5	19.5	0.3	1.8	6	0	35
10.7	9.0	6.3	19.5	19.5	0.3	1.8	6	0.25	35
10.7	9.0	6.3	19.5	19.5	0.3	1.8	6	0.5	35
10.7	9.0	6.3	19.5	19.5	0.3	1.8	6	0.75	35
10.7	9.0	6.3	19.5	19.5	0.3	1.8	6	1	35
9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	0	45
9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	0.25	45
9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	0.5	45
9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	0.75	45
9.1	7.6	5.3	16.5	16.5	0.3	1.8	6	1	45

set at the appropriate Bragg angle, since the material is not sensitive to red light. For electro-optical 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. The grating morphology was visualized by SEM. For this, one side of the ITO glass was removed and sample was soaked in methanol for 24 h before the LC was removed.

3. Results and discussion

3.1. *Real-time grating formation*

The dynamics of the phase separation is a very important process, which is initiated by the change in the chemical potential of the constituents as a result of the polymerization [28]. Figure 1 shows the real-time diffraction efficiency as a function of irradiation time at various chiral dopant contents. For samples containing 35% LC (denoted LC35 in figure 1a), diffraction efficiency increases gradually to a saturation value and a maximum is obtained at a longer irradiation time with increasing chiral dopant content. The gradual increase of diffraction efficiency is due to the slow diffusion of LC, which is caused by its high viscosity. With a slow migration of LC from polymer to LC layer, LC droplets are less vulnerable to coalescence and scatterings to give high saturation efficiency.

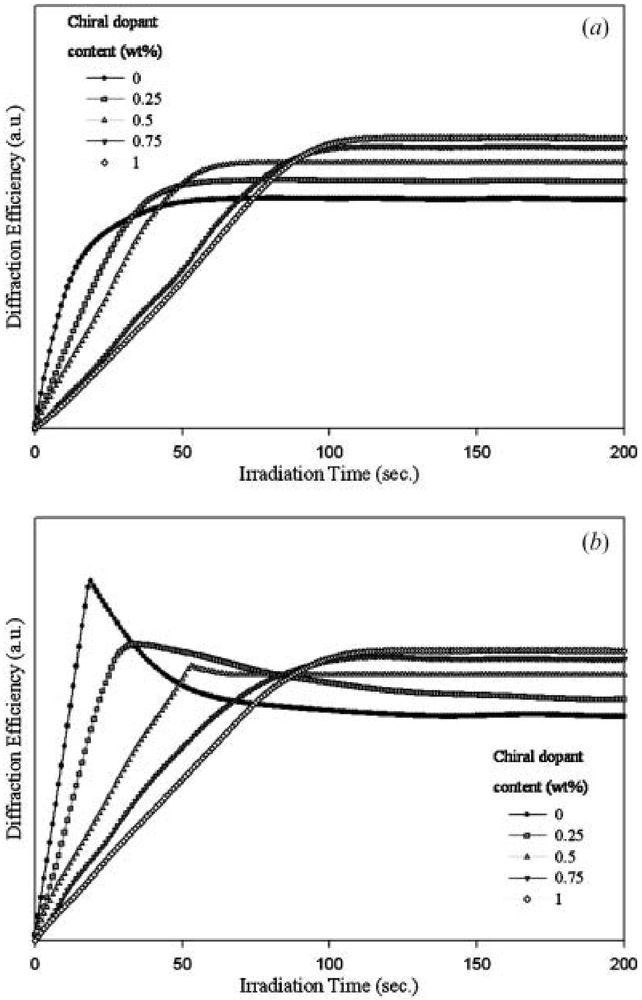


Figure 1. Real-time diffraction efficiency as a function of irradiation time at various chiral dopant content in the developing HPDLC gratings LC35 (a) and LC45 (b) (irradiated at 633 nm).

For samples containing 45% LC (LC45 in figure 1b), the chiral dopant-free sample exhibits an early maximum, followed by an asymptotic decrease to a stable value. The overshoot is indicative of serious droplet coalescence caused by the fast migration of LC out of the polymer layer, and small medium viscosity due to the plasticizing effect of LC. However, as chiral dopant content increases, the overshoot disappears and diffraction efficiency increases gradually to the saturation value for LC35.

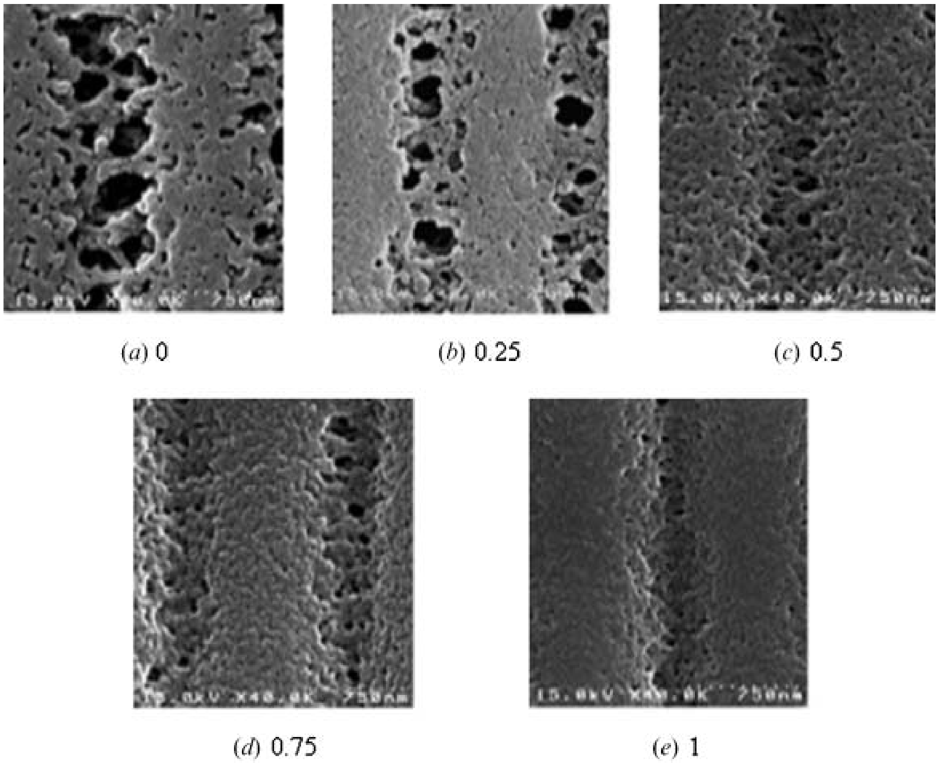
3.2. *SEM morphology*

Figure 2 shows SEM images of the transmission gratings as a function of chiral dopant content. Small black voids are the original location of the LC droplets in layers separated by dense polymer regions. In all cases, the grating spacing is about 1000 nm, which is slightly different from the theoretical value of 1267 nm according to Bragg's law due to shrinkage upon polymerization. It can be clearly seen that the average size of LC domains formed with chiral dopant is smaller than that observed without chiral dopant. It is also noted that the LC domain size decreases with increasing chiral dopant content in the transmission grating. Small droplet size seems to be due to the slow migration of LC toward the LC layers, allowing less time for droplet coalescence leading to the high diffraction efficiency, as noted from the real-time measurement of diffraction efficiency. Small droplets inherently improve optical quality of HPDLCs, and need much larger voltages to switch [7].

3.3. *Diffraction efficiency*

Figure 3 shows the diffraction efficiency as a function of chiral dopant content of the holographic gratings. The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam (I_d) to the intensity of the incident beam (I_i) according to

$$\eta(\%) = \frac{I_d}{I_i} \times 100.$$


(*a*) 0 (*b*) 0.25 (*c*) 0.5

(*d*) 0.75 (*e*) 1

Figure 2. SEM images of the transmission grating as a function of chiral dopant content (LC35).

As expected from the real-time measurements, higher diffraction efficiency is obtained with LC35. This seems reasonable since high LC content (LC45) causes rapid migration of LC molecules into the LC-rich phase due to the small viscosity, which leads to extensive coalescence to form large LC droplets. This lowers droplet density and enlarges domain size leading to high scattering loss. Also, regardless of LC content, the diffraction efficiency monotonically increases with increasing chiral dopant content, which can be attributed to the slow LC diffusion and phase separation, leading to less droplet coalescence and uniform distribution. It has been observed through SEM morphology that domain size decreases with the addition of chiral dopant.

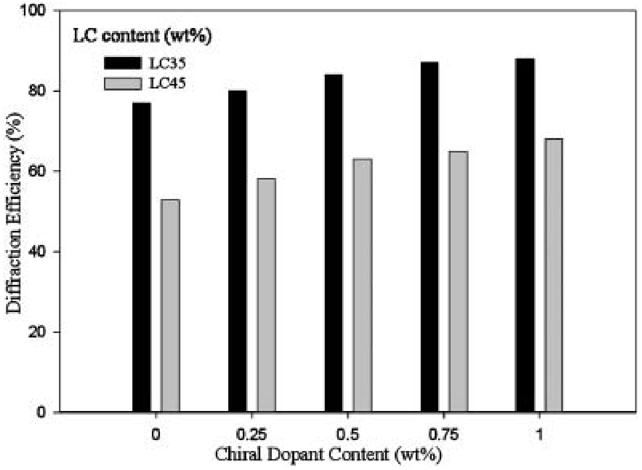


Figure 3. Diffraction efficiency as a function chiral dopant content of the holographic gratings.

3.4. *Electro-optical properties*

The switching field is a function of many physical parameters, including droplet size, conductivities of the LC and polymer, elastic constant (especially of bending), droplet anisotropy and dielectric anisotropy [29]. Figure 4 shows the diffraction efficiency of the film as a function of applied voltage at various chiral dopant contents. Upon applying a voltage the diffraction efficiency decreases, implying that LC molecules are oriented along the electric field direction and light is transmitted. Regardless of LC content, the switching voltage is approximately constant when the content of chiral dopant is below 0.5 wt %. However, as chiral dopant content is increased above 0.5 wt %, the switching voltage increases rapidly from $5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ to $7\,\mathrm{V}\,\mu\mathrm{m}^{-1}$. This is due to the decreased LC droplet size because the anchoring effect of the polymer matrix on the LC molecules increases as the size decreases [30].

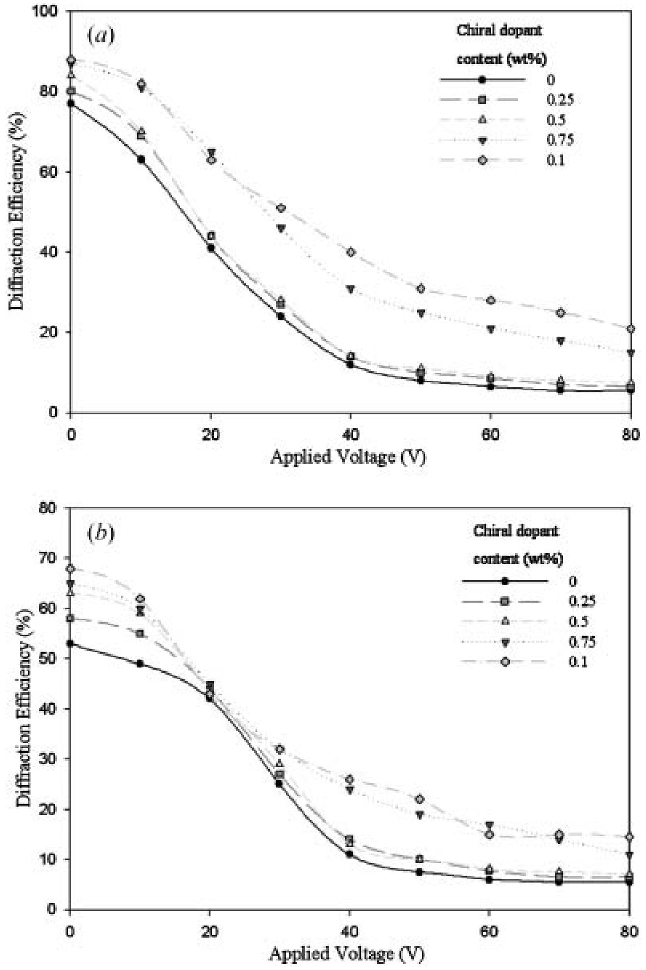


Figure 4. Diffraction efficiency of the film as a function of applied voltage at various chiral dopant content of HPDLC films LC35 (a) and LC45 (b).

Furthermore, as the chiral dopant content is increased, the twist elastic energy of bipolar droplets is increased, and it needs a larger electric field to reorient LC droplets.

Figure 5 shows the contrast ratio of the film as a function of chiral dopant content. The contrast ratio is defined as the ratio of the diffraction efficiency at zero field (DE_{off}) to the diffraction efficiency at high fields (DE_{on}) according to [1]

$$\text{contrast ratio} = DE_{off}/DE_{on}.$$

It can be seen that higher contrast ratio is obtained with LC35 than with LC45. It seems that the diffraction efficiency at zero field in LC35 is higher than that of LC45 due to the less LC droplet coalescence. Also, the contrast ratio is decreased with increasing chiral dopant content due to the difficulty of LC orientation caused by helical structure.

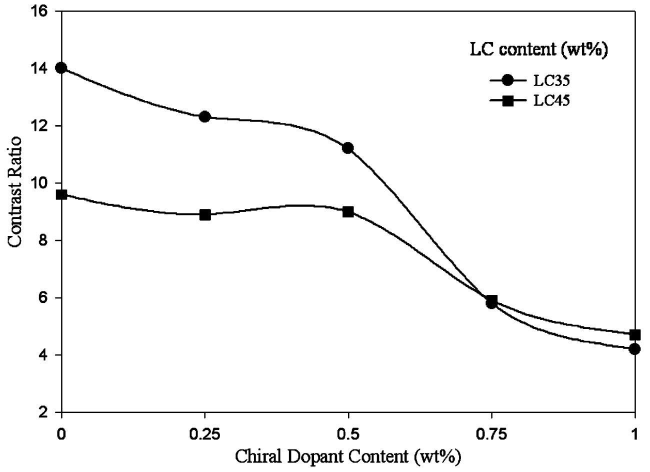


Figure 5. Contrast ratio of the film as a function of chiral dopant content.

Figure 6 shows a typical wave form of the response time of HPDLC film as a function of time and the detailed data are given in table 2. The hologram is initially diffracted until the applied field realigns the LC in the droplet, thus changing the index modulation of the periodic phase grating and clearing film. Upon removal of the voltages, due to the inherent properties of LC (droplet size, viscosity, elastic force) and film geometry, LC molecules relax to their initial equilibrium distribution [29]. Rise time, defined as the time required for the transmittance to rise from 10 to 90% in the wave form, is less than 1 ms and it increases slightly with increasing chiral dopant content due to the longer time to overcome the helically twisting power of chiral dopant. Decay time, defined as the opposite to the rise time, is approximately one order of magnitude larger

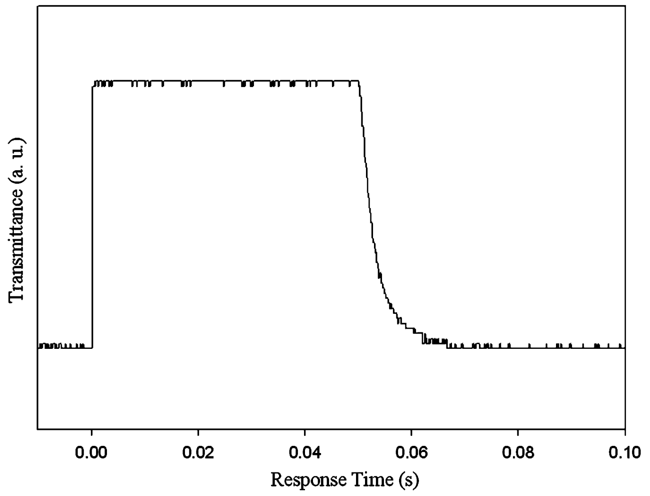


Figure 6. Typical wave form of the response time of HPDLC film as function of time (50 V, 0.5 wt % chiral dopant, LC35).

Table 2. Response time of the film as a function of chiral dopant content (50 V).

Response time /ms	LC content /wt %	Chiral dopant content /wt % 0	0.25	0.5	0.75	1
Rise time	35	0.20	0.30	0.35	0.40	0.40
	45	0.30	0.40	0.40	0.45	0.50
Decay time	35	13.75	9.45	7.95	7.10	6.45
	45	19.05	13.85	11.90	10.05	9.25

than the rise time. It was also found that decay time significantly decreases with increasing content of chiral dopant due to the increased elastic energy from helical structure. For LC35 it decreases from 13.75 to 6.45 ms as the chiral dopant content increases from 0 to 1 wt %.

4. Conclusions

Chiral dopant has been doped into the formulation of a conventional holographic polymer-dispersed liquid crystal based on polyurethane acrylate, and the effects have been studied in terms of grating morphology, diffraction efficiency and electro-optical properties of the films.

Droplet size decreased with the addition and increasing content of chiral dopant due to the decreased droplet coalescence, which on the other hand is caused by the increased viscosity of LC.

The decreased droplet size gave increased diffraction efficiency by minimizing scattering. On the other hand, chiral dopant gave a decrease in contrast ratio due to the difficult orientation of LC molecules by the formation of helical structure.

Also, the drive voltage is kept almost constant, whereas the decay time is decreased significantly as a result of high twisting due to the formation of helical structure with the addition of chiral dopant. The experimental results showed a minimum switching voltage of 5 V μm^{-1}, a rise time of 0.35 ms and a decay time of 7.95 ms and a contrast ratio over 10 with 0.5 wt % chiral dopant.

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