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Nematic liquid crystal droplets with an enhanced quasi-linear electro-optical response

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Nematic liquid crystal droplets dispersed in a thermoplastic matrix with a built-in d.c. electric field exhibit a quasi-linear response to an electric field. In this work we show a device characterized by a large light modulation. The device can store fields up to several $V\,\mu m^{-1}$ and operates well from d.c. to several kHz. In addition, we found that the experimental results are in agreement with a simple theoretical model for light scattering by a dispersion of liquid crystal droplets. This device allows us to overcome possible drawbacks, due to a reduced light modulation, in applications where polarity detection is required.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are composite materials containing liquid crystal micro-domains dispersed in a polymer matrix. They can be switched from an opaque to a transparent state by application of a suitable switching field [1, 2]. Recently, PDLCs have attracted considerable interest for their electro-optical response with respect to an external field. The electro-optical response of a PDLC can be either linear or quadratic depending on the mesophase shown by the liquid crystal droplets [3]. A linear response can be much stronger than a quadratic one and is polarity sensitive, i.e. the response is not identical for positive and negative fields. Examples of a linear coupling between liquid crystal dispersions and applied electric fields are: the flexo-electric effect in polymer dispersed cholesteric liquid crystals [4, 5], the deformed helix effect in chiral smectic C phases [6, 7], the electroclinic effect near the phase transition between smectic A and smectic C phases [8, 9], and the responses of ferroelectric and antiferroelectric devices [10, 11]. In contrast, polymer dispersed nematic liquid crystals show a quadratic electro-optical response due to the coupling between the dielectric anisotropy of liquid crystal and the electric field [3].

More recently, a polarity sensitive electro-optical response has been observed in nematic liquid crystal dispersions in a polymer binder [12]. The effect has been attributed to a built-in d.c. electric field obtained by energizing films with an external d.c. field. The addition of a built-in d.c. electric field to the driving field converts the conventional quadratic response of nematic liquid crystal droplets into a linear response. This response is better defined as a quasi-linear effect.

The origin of the internal field is due to a Maxwell–Wagner effect [3, 12], in which ionic impurities (present in the components) are separated at the droplet interface during the charge process. It is expected and experimentally confirmed that ion separation is more effective for softer polymer matrices [12, 13], i.e. for higher charge temperatures and larger liquid crystal contents. Once the ion separation is achieved, the induced polarization field can be stored by cooling the sample. The increase in matrix viscosity traps ion impurities at the droplet interfaces and avoids their reintegration into the matrix, giving rise to a built-in d.c. field, $\mathbf{E}_{dc}$.

In this paper we present our most relevant experimental results concerning the optimization of the quasi-linear electro-optical response in nematic PDLCs charged by means of a d.c. electric field. In addition we will show that they are in agreement with a simple theoretical model.

2. Experimental

Even if we were able to fabricate polymer dispersed nematic liquid crystal films with a large built-in d.c. electric field and with a large frequency range quasi-linear response, the modulation of light from such devices would only be about 10% [12]. Such a low modulation value could represent a drawback in some electro-optical applications. As a consequence, we have tried to enhance the modulation of light by increasing the $\mathbf{E}_{dc}$ values, i.e. by varying liquid crystal weight

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percentage, charge temperature, and charge field strength.

An important limit in the experimental conditions is represented by the induction of memory states [13]. In fact, the combined use of a charge temperature higher than the polymer matrix glass transition temperature and of a high charge field can easily induce the alignment of the polymer chains at a droplet interface, via the alignment of liquid crystal molecules. Polymer chains can be frozen in this aligned state during the cooling process [13]. As a consequence, one can gain a large built-in field, but with a large transparent OFF state due to the alignment of liquid crystal directors induced by the frozen polymer chains. Such a 'mechanical' memory state will mask and reduce the light modulation. In our experiments we have tried to avoid the onset of large 'mechanical' memory states.

PDLCs were prepared by following the procedure outlined elsewhere [12]. Polymethylmethacrylate (Aldrich) and TN 10427 (Rolic), a nematic liquid crystal, were used as film components in different weight ratios (from 1:1 to 1:4). The cell internal gap was about 40 μm. After cell filling, samples were 'charged' by applying different external d.c. electric fields (up to $30\,\mathrm{V\,\mu m^{-1}}$) for different time intervals (up to 3 600 s) at a given temperature, which was varied from 20 to 50°C. The cells were cooled to room temperature (18°C) and the external charge field removed. The internal d.c. electric fields were measured by determining the value of the driving field for which the electro-optical response starts to depart from being linear [14] (see figure 1) .

In this paper we will show our best results, which were obtained with the experimental conditions: $\mathbf{E}_{\mathrm{charge}} \cong 15\,\mathrm{V\,\mu m^{-1}}$, $t_{\mathrm{charge}} \cong 900\,\mathrm{s}$, $\mathbf{T}_{\mathrm{charge}} \cong 45.0 \pm 0.1^{\circ}\mathrm{C}$, PMMA : TN10427 = 2:3 (wt:wt).

3. Results and discussion

Figure 1 shows the electro-optical response to a sinusoidal driving field of a sample prepared with the experimental conditions described. The response is quasilinear up to a value of $\mathbf{E}_{\mathrm{driving}} \cong \mathbf{E}_{\mathrm{dc}} \cong 6\,\mathrm{V\,\mu m^{-1}}$. For $\mathbf{E}_{\mathrm{driving}}$ values larger than $\mathbf{E}_{\mathrm{dc}}$, the response departs from being quasi-linear and a quadratic response is obtained for $\mathbf{E}_{\mathrm{driving}} \cong 2\mathbf{E}_{\mathrm{dc}}$ The quasilinear electro-optical response can be observed up to a driving frequency value of $\sim 10\,\mathrm{kHz}$ (data not shown).

Figure 2 shows the behaviour of the PDLC transmittance to an external d.c. electric field $\mathbf{E}_{\mathrm{ext}}$, which is applied either parallel or antiparallel to the built-in d.c. field. If we apply an $\mathbf{E}_{\mathrm{ext}}$, which is parallel to $\mathbf{E}_{\mathrm{dc}}$, we observe an increase of the transmittance from its OFF state value of about 33% to a saturation value of about 60% for $\mathbf{E}_{\mathrm{ext}} \cong \mathbf{E}_{\mathrm{sat}} \cong 6\,\mathrm{V\,\mu m^{-1}}$. Such a large OFF state

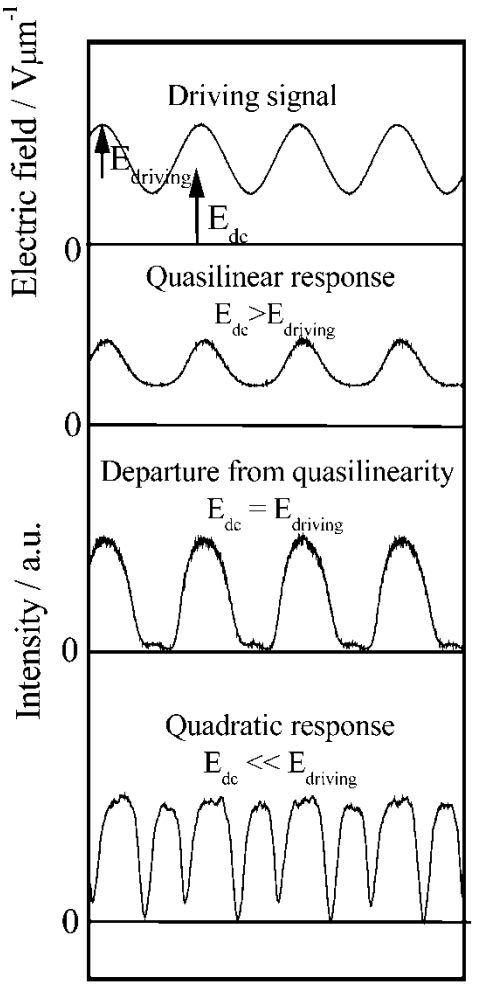

Figure 1. Response of a PDLC film with a built-in d.c. field, $\mathbf{E}_{\mathrm{dc}} \cong 6\,\mathrm{V\,\mu m^{-1}}$, for different driving electric field strengths. The driving frequency is 40 Hz. The electro-optical response is quasi-linear if $\mathbf{E}_{\mathrm{driving}} < \mathbf{E}_{\mathrm{dc}}$. The displayed quasi-linear and quadratic responses are obtained for $\mathbf{E}_{\mathrm{driving}} = 2$ and $12\,\mathrm{V\,\mu m^{-1}}$, respectively. The departure from quasi-linearity is gained for $\mathbf{E}_{\mathrm{driving}} = \mathbf{E}_{\mathrm{dc}} = 6\,\mathrm{V\,\mu m^{-1}}$.

transmittance value can be attributed both to a memory state induced by a mechanical action of aligned polymer chains and to a reorientation of liquid crystal directors due to $\mathbf{E}_{\mathrm{dc}}$. We will show later that this latter effect is the major cause for the OFF state transmittance. The application of an external d.c. field parallel to a $\mathbf{E}_{\mathrm{dc}}$ will increase the effective field strength acting on liquid crystal droplets, $\mathbf{E}_{\mathrm{eff}} = \mathbf{E}_{\mathrm{dc}} + \mathbf{E}_{\mathrm{ext}}$. Consequently, the effective field will increase the transmittance as it determines both a better alignment of liquid crystal directors parallel to the external field in larger droplets and the reorientation of liquid crystal directors in smaller droplets.

By contrast, if $\mathbf{E}_{\mathrm{ext}}$ is applied antiparallel to $\mathbf{E}_{\mathrm{dc}}$ we

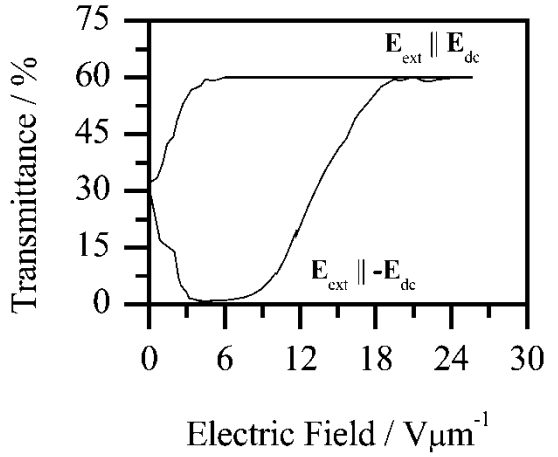

Figure 2. Dependence of the transmittance as a function of the external d.c. electric field strength and direction: (*a*) $\mathbf{E}_{ext}$ parallel to $\mathbf{E}_{dc}$, (*b*) $\mathbf{E}_{ext}$ antiparallel to $\mathbf{E}_{dc}$. The built-in d.c. field strength is $6\,\mathrm{V}\,\mu\mathrm{m}^{-1}$.

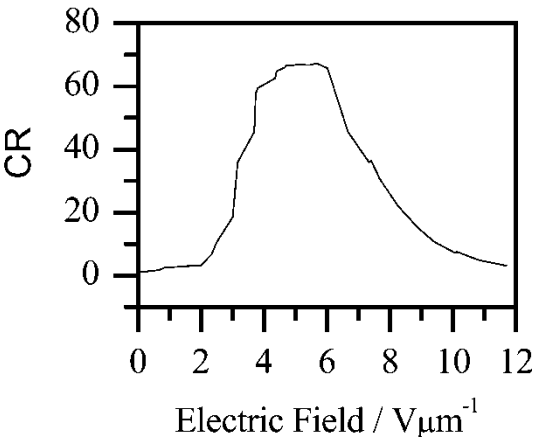

Figure 3. Contrast ratio, *CR*, in a PDLC film with a built-in d.c. electric field of $6\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ as a function of the external d.c. electric field strength.

observe a decrease in the transmittance from its OFF state value to a minimum of about 1% for $\mathbf{E}_{ext} = \mathbf{E}_{dc} \cong 6\,\mathrm{V}\,\mu\mathrm{m}^{-1}$. The decrease in transmittance is due to the reduction of the effective field acting on liquid crystal directors, $\mathbf{E}_{eff} = \mathbf{E}_{dc} - \mathbf{E}_{ext}$ The minimum value in transmittance is reached when the external field strength completely 'erases' the $\mathbf{E}_{dc}$ value, i.e. $\mathbf{E}_{eff} = 0$. This minimum value confirms that the memory state induced during the cooling process slightly affects the OFF state transmittance. In other words, these new PDLCs can modulate more than 90% of the light transmitted in the OFF state. If $\mathbf{E}_{ext}$ is increased further the transmittance starts to increase as $\mathbf{E}_{eff}$ strength grows and reaches the saturation value for $\mathbf{E}_{eff} = \mathbf{E}_{sat}$.

Figure 2 shows that a PDLC with a built-in d.c. field can be turned into either a more transparent state or a more opaque one by application of d.c. fields of opposing directions.

The achieved contrast ratio *CR*, i.e. the ratio between the transmittance gained with an external field, $+\mathbf{E}_{ext}$ (parallel to $\mathbf{E}_{dc}$, upper curve in figure 2), and the transmittance obtained with an external field of opposite direction, $-\mathbf{E}_{ext}$ (antiparallel to $\mathbf{E}_{dc}$, lower curve in figure 2), is shown as a function of $\mathbf{E}_{ext}$ strength in figure 3. The electric field dependent contrast ratio shows large values in the range $4\,\mathrm{V}\,\mu\mathrm{m}^{-1} < \mathbf{E}_{ext} < 6\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, where it is possible to 'switch off' the ON state transmittance by a simple change of field direction.

In order to establish a theoretical understanding of our data, we calculated the light scattered by a dispersion of liquid crystal droplets in a polymer matrix as a function of an external field, $\mathbf{E}_{ext} = \mathbf{E}_{dc} + \mathbf{E}_{driving} \sin \omega t$. By adapting the model of Li *et al.* [15] for the optical transmittance of a PDLC in a magnetic field, we assumed that the light transmittance, *T*, obeys the following exponential behavior:

$$T = \exp(-\beta\sigma d) \tag{1}$$

where β is the liquid crystal droplet number density, σ is the scattering cross-section, and d is the sample thickness. The scattering cross section can be expressed as a function of a reduced field h:

$$h = \mathbf{E}_{ext} r \left(\frac{\Delta\varepsilon}{k}\right)^{1/2} \tag{2}$$

where k is the elastic constant of the liquid crystal in the one-constant approximation, $\Delta\varepsilon$ is the liquid crystal dielectric anisotropy, and r is the droplet radius. In the anomalous diffraction approximation [16], which holds in the limit $\frac{2\pi r}{\lambda} \gg 1$ (λ is the wavelength of the impinging light), σ can be written as:

$$\sigma(h, r) = \pi r^2 \int_0^{\pi/2} \left[1 - \frac{2\sin v}{v} + 2\frac{(1-\cos v)}{v^2}\right] \sin\theta \, \mathrm{d}\theta \tag{3}$$

with

$$v(h, r, \theta) = \frac{4\pi}{\lambda} r \frac{n_e - n_o}{n_{matrix}} \left[1 - \frac{h^2 + \cos 2\theta}{(h^4 + 2h^2 \cos 2\theta + 1)^{1/2}}\right] \tag{4}$$

where n_e and n_o are, respectively, the extraordinary and ordinary refractive indices of liquid crystal droplets, n_{matrix} is the polymer matrix refractive index, and θ is the angle between the applied external field and liquid crystal directors. The calculations were carried out by assuming a random distribution of directors in the OFF state, by using the known liquid crystal refractive indices ($n_e = 1.7366$, $n_o = 1.5101$), and by estimating that

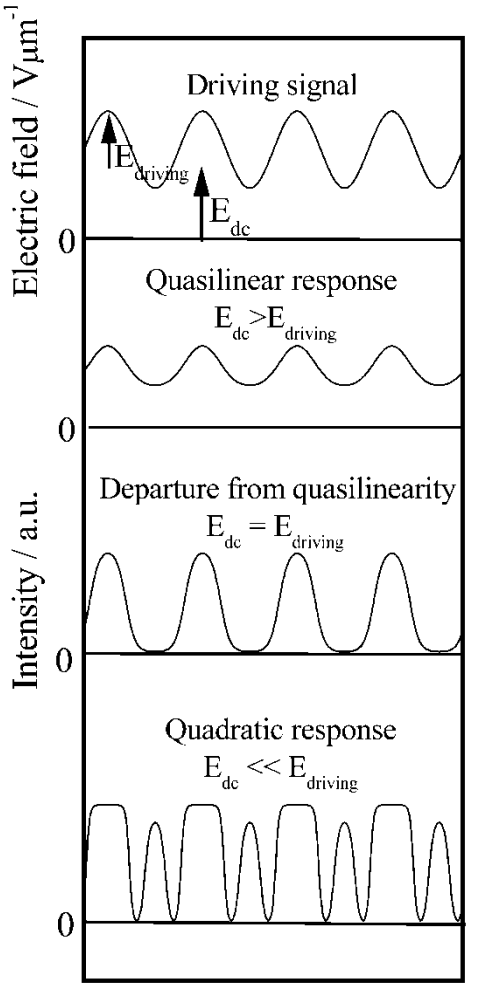

Figure 4. Theoretical curves of the response of a PDLC film with a built-in d.c. field, $\mathbf{E}_{dc} = 6\,V\,\mu m^{-1}$, for different driving electric field strengths (cf. figure 1).

the liquid crystal in the polymer matrix is about 20 wt % ($n_{matrix} = 1.506$).

The results of these calculations are shown in figure 4, which shows the electro-optical response to an external field, $\mathbf{E}_{ext} = \mathbf{E}_{dc} + \mathbf{E}_{driving} \sin \omega t$, for different values of $\mathbf{E}_{driving}$ at a fixed built-in d.c. field ($\mathbf{E}_{dc} = 6\,V\,\mu m^{-1}$). The theoretical response is quasi-linear up to a value of $\mathbf{E}_{driving} = \mathbf{E}_{dc}$. The response departs from being quasi-linear for $\mathbf{E}_{driving}$ values larger than $6\,V\,\mu m^{-1}$, and can be considered quadratic for $\mathbf{E}_{driving}$ strengths larger than $2\mathbf{E}_{dc}$. The results show an excellent agreement with the experimental data, see Figure 1. In figure 4 we assumed a Gaussian distribution of liquid crystal droplets with a mean value of 1.00 μm and a standard deviation of 0.13 μm. In fact, calculations with a monodisperse size of 1.00 μm gave a very sharp OFF-ON transition.

4. Conclusions

We have been able to prepare nematic PDLCs with an enhanced quasi-linear electro-optical response by applying 'charge' electric fields for some minutes and carefully choosing the component weight percentages and charge temperature. The light modulation has been increased up to more than 90%, thus overcoming possible drawbacks concerning some applications. Lower costs and more facile preparation (with respect to other liquid crystal devices with a linear electro-optical response) characterize films with a quasi-linear response. They are self-adhesive to glass supports and no polarizer is required. In addition, they are switched on with lower electric fields (a few $V\,\mu m^{-1}$ rather than tens of $V\,\mu m^{-1}$) and offer a wider working range (from d.c. to some kHz rather than from d.c. to some Hz).

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