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D. Cupelli[a]; F. P. Nicoletta[b]; G. De Filpo[a]; R. Cassano[a]; F. Puoci[b]; G. Chidichimo[a]
[a] Dipartimento di Chimica, Università della Calabria, 87036 Rende (CS), Italy [b] Dipartimento di Scienze Farmaceutiche, Università della Calabria, 87036 Rende (CS), Italy

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The electro-optical properties of 'charged' PDLCs

D. CUPELLI, F. P. NICOLETTA*†, G. DE FILPO, R. CASSANO, F. PUOCI† and G. CHIDICHIMO
Dipartimento di Chimica, Università della Calabria, 87036 Rende (CS), Italy
†Dipartimento di Scienze Farmaceutiche, Università della Calabria, 87036 Rende (CS), Italy

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The application of high intensity electric fields to polymer dispersed liquid crystal (PDLC) films can induce changes in their electro-optical properties and morphology. In particular, a quasilinear electro-optical response to an external electric field can be achieved if an internal built-in d.c. field is induced. In this work, we show how the liquid crystal/polymer weight ratio influences the electro-optical response of 'charged' PDLCs, i.e. of PDLC films after the application of a high intensity electric field. We observed that a quasilinear electro-optical response can be achieved in a well determined range of composition. Larger liquid crystal concentrations are unable to maintain the built-in field, while PDLCs with lower liquid crystal loadings do not allow the onset of a built-in d.c. field.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are composite materials formed by micron-sized liquid crystal droplets dispersed in a polymer binder [1, 2]. They have attracted the interest of many researchers because of their applications in optoelectronics, smart windows, and display technologies [3]. Specifically, PDLC film transmittance may be easily controlled by the application of a suitable electric field. Recently, there has been some interest in the modification of PDLC electro-optical properties after the cure process. In particular, it is interesting to study the changes induced in PDLCs by the application of high intensity electric fields (charge process) for some minutes. It has been observed that lower reorientation fields and sharper OFF–ON transitions can characterize films after the charge process, as they may induce changes in the morphology, dielectric properties, and surface anchoring energy of PDLCs [4–7]. Such effects are strongly dependent on the temperature at which the charge process is performed. In fact, a high charge temperature greatly affects the matrix viscosity and the anchoring properties of liquid crystal directors at droplet boundaries.

Sometimes, either memory effects (higher values of the zero-field transmittance) or persistence effects (the higher values of zero field transmittance requiring some time to relax to the original OFF-state value) have been observed [6]. In particular, memory states may originate either from a mechanical trapping of the liquid crystal directors in a more aligned state during the cooling process, or from the onset of an internal polarization field at the liquid crystal droplet boundaries. The built-in d.c. electric field arises from ion impurities present in the sample components, which separate out at the droplet interface during the charge process; this phenomenon is also known as the Maxwell–Wagner effect [3]. The ion separation and, consequently, the built-in d.c. electric field may persist during the cooling process as it increases the polymer matrix viscosity, so hindering ion re-mixing. Such an effect is more evident for high charge temperatures. In addition to the onset of a memory state, the induction of an internal polarization field allows the conversion of the conventional quadratic electro-optical response of a polymer dispersed nematic liquid crystal into a quasilinear one [5]. PDLCs with a quasilinear electro-optical response are useful for applications where a polarity detection is required. They can represent a valid and cheaper alternative to dispersions of non-nematic mesogens characterized by a real linear electro-optical response [8–12].

In this paper we present the results of our studies focused on the enhancement of light modulation in the quasilinear electro-optical response of nematic dispersions. The investigation has involved, in particular, changing the weight ratio of components. We have found that the quasilinear electro-optical response can only be achieved in a well defined range of weight ratios, for which the light modulation can be significantly increased.

2. Experimental

Polymethylmethacrylate (PMMA from Aldrich) and a nematic liquid crystal mixture (TN10427 from Rolic)

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*Corresponding author. Email: fiore.nicoletta@unical.it

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were dissolved in a common solvent (dichloromethane) in different weight ratios (from 4:1 to 1:4). After solvent evaporation, a small amount of the mixture was sandwiched between two conductive substrates with an internal gap of 40 µm, heated to about 120°C, and then cooled to room temperature in order to induce phase separation. The electro-optical properties were investigated at room temperature (18°C) with the optical line described previously [13]. The light intensity transmitted with no sample in place was assumed to be the full scale intensity. Samples were charged by applying a d.c. field of strength $\mathbf{E}_{\mathrm{charge}}$ ($0 \leqslant \mathbf{E}_{\mathrm{charge}} \leqslant 50\,\mathrm{V\,\mu m^{-1}}$) at a controlled temperature T_{charge} ($18^\circ\mathrm{C} \leqslant T_{\mathrm{charge}} \leqslant 60^\circ\mathrm{C}$, $\Delta T_{\mathrm{charge}} = \pm 1^\circ\mathrm{C}$) for different charge times t_{charge} ($5\,\mathrm{min} \leqslant t_{\mathrm{charge}} \leqslant 60\,\mathrm{min}$). The field was removed only after the films were cooled to room temperature. The strengths of the built-in d.c. electric fields were measured with the experimental set-up described elseswhere [13] i.e. by determining the value of the driving field for which the PDLC electro-optical response departs from being quasilinear (see later). Particular care was taken in order to avoid the induction of mechanical memory states. As described in the introduction, the onset of a mechanical memory state determines a more transparent OFF-state due to the trapping of the liquid crystal directors along a direction almost parallel to the applied charge field (i.e. perpendicular to the glass supports). Consequently, even if one is able to build-in a large strength polarization field, the memory state will reduce the light modulation of the device. We have avoided the combined use of charge temperatures greater than the polymer matrix glass transition temperatures and of large strength charge fields, which can easily induce a detrimental mechanical memory state.

3. Results and discussion

The conventional electro-optical transmittance, of a nematic PDLC is quadratic as is proportional to the square of the driving field, $\mathbf{E}_{\mathrm{driving}}$, due to the coupling between the liquid crystal anisotropy and the electric field [3], as shown in figure 1 (*b*). If a d.c. electric field $\mathbf{E}_{\mathrm{d.c.}}$ is built-in in a PDLC, the effective field will be $\mathbf{E}_{\mathrm{driving}}+\mathbf{E}_{\mathrm{d.c.}}$, figure 1 (*a*); the electro-optical transmittance will be shifted upwards, figure 1 (*c*), and will give a quasilinear response for $\mathbf{E}_{\mathrm{driving}} < |\min(\mathbf{E}_{\mathrm{d.c.}}, \mathbf{E}_{\mathrm{sat}} - \mathbf{E}_{\mathrm{d.c.}})|$. Min ($\mathbf{E}_{\mathrm{dc}}$, $\mathbf{E}_{\mathrm{sat}}-\mathbf{E}_{\mathrm{dc}}$) is the function which gives the minimum value between $\mathbf{E}_{\mathrm{d.c.}}$ and $\mathbf{E}_{\mathrm{sat}}-\mathbf{E}_{\mathrm{d.c.}}$; $\mathbf{E}_{\mathrm{sat}}$ is the saturation electric field, i.e. the field which ensures the maximum value of transmittance. If the $\mathbf{E}_{\mathrm{driving}}$ strength varies sinusoidally at a frequency ν ($\nu < 1\,\mathrm{kHz}$, generally), the transmittance will behave as shown in figures 1 (*c*) and 1 (*d*) for the cases with $\mathbf{E}_{\mathrm{d.c.}} > \mathbf{E}_{\mathrm{driving}}$ and $\mathbf{E}_{\mathrm{d.c.}} = \mathbf{E}_{\mathrm{driving}}$, respectively.

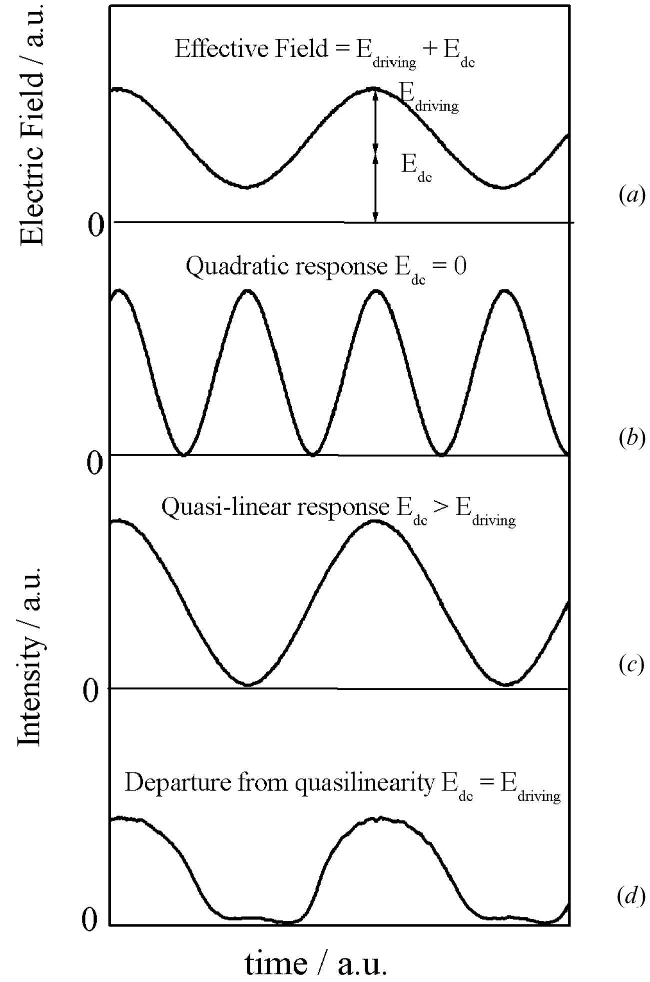

Figure 1. The effective field acting on samples is $\mathbf{E}_{\mathrm{driving}}+\mathbf{E}_{\mathrm{d.c.}}$ (*a*). Electric field dependent transmittance in the absence (*b*) and in the presence (*c*) of a built in d.c. electric field and (*d*) when $\mathbf{E}_{\mathrm{driving}}=\mathbf{E}_{\mathrm{d.c.}}$. The driving field varies as $\mathbf{E}_{\mathrm{driving}} \sin(2\pi\nu t+\phi)$.

We prepared for this investigation several samples with different liquid crystal percentages. In particular, the liquid crystal loading was varied from 20 to 80 wt %, as these represent the boundary contents for the onset of liquid crystal phase separation in droplets and for obtaining stand-alone films.

Two different behaviours were observed when such films were charged. If the TN10427 percentage was either lower than 60 wt % or larger than 70 wt % we were unable to build-in any d.c. field. Samples with a TN10427 loading lower than 60 wt % either underwent shorting during the charge process or were just characterized by persistence effects rather than memory states, i.e. the field eventually induced decreased to zero within a few hours. Neither long term stable electric fields nor persistence fields were observed in the case of TN10427>70 wt%. Both behaviours (TN10427<60 wt% and TN10427>70 wt%) may be accounted for by taking into account the inappropriate value of the polymer matrix viscosity. In fact, in previous work we observed that persistence effects rather than memory states were induced when the polymer matrix viscosity was in sufficiently high to store the ion separation for a long time [6]. At the same time, a very large matrix viscosity does not allow ion separation and, consequently, the onset of built-in d.c. field, even if one uses a charge field strength up to $50\,\mathrm{V\,\mu m^{-1}}$ and high charge temperatures. Such PDLCs often underwent shorting because of the high intensity of the charge fields. In contrast, when the liquid crystal content was varied in the range 60–70 wt% we were able to induce very large $\mathbf{E}_{\mathrm{d.c.}}$ values in the samples.

Figure 2 shows the typical experimental electro-optical responses of 'charged' PDLCs (for TN10427 wt%=60, 65 and 70%) to an effective electric field, the strength of which is given by the sum of the driving field, $\mathbf{E}_{\mathrm{driving}}$, and the built-in d.c. field, $\mathbf{E}_{\mathrm{d.c.}}$figure 2 (*a*). Obviously the electro-optical response is quadratic as a function of $\mathbf{E}_{\mathrm{driving}}$ (data not shown) if no $\mathbf{E}_{\mathrm{d.c.}}$ is built into the films in agreement with figure 1 (*b*). If the built-in d.c. field strength is larger than the driving field, the electro-optical response is quasilinear as shown in figures 2 (*b*). When the driving field intensity is increased to a value as large as $\mathbf{E}_{\mathrm{d.c.}}$ the electro-optical response departs from being quasilinear figure 2 (*c*). If $\mathbf{E}_{\mathrm{driving}}$ is further increased, the small peaks grow and the electro-optical response is almost quadratic when $\mathbf{E}_{\mathrm{driving}} >> \mathbf{E}_{\mathrm{d.c.}}$.

The induced $\mathbf{E}_{\mathrm{d.c.}}$ field shows a maximum value of $7\,\mathrm{V\,\mu m^{-1}}$ for a TN10427 content of 65 wt%, because for this composition the polymer matrix viscosity has the best value for the onset and storage of high intensity fields. As a consequence this PDLC sample shows the largest range of quasilinearity.

It is expected that the frequency range of a quasilinear response induced in charged PDLCs would be the same as the working range of conventional PDLCs (from d.c. to some kHz). Figure 3 shows the frequency-dependent quasilinear response of PDLC films when the same driving field is applied ($\mathbf{E}_{\mathrm{driving}}=2.5\,\mathrm{V\,\mu m^{-1}}$). Samples show no particular difference as a function of frequency, being $\mathbf{E}_{\mathrm{driving}}<\mathbf{E}_{\mathrm{d.c.}}$ for every PDLC, i.e. all films are in the quasilinear regime. It should be noted that a larger $\mathbf{E}_{\mathrm{d.c.}}$ value allows a less noisy response as a function of frequency.

As outlined in the introduction, the enhancement of the light modulation in a quasilinear regime is strictly related to the onset of an electric rather than a

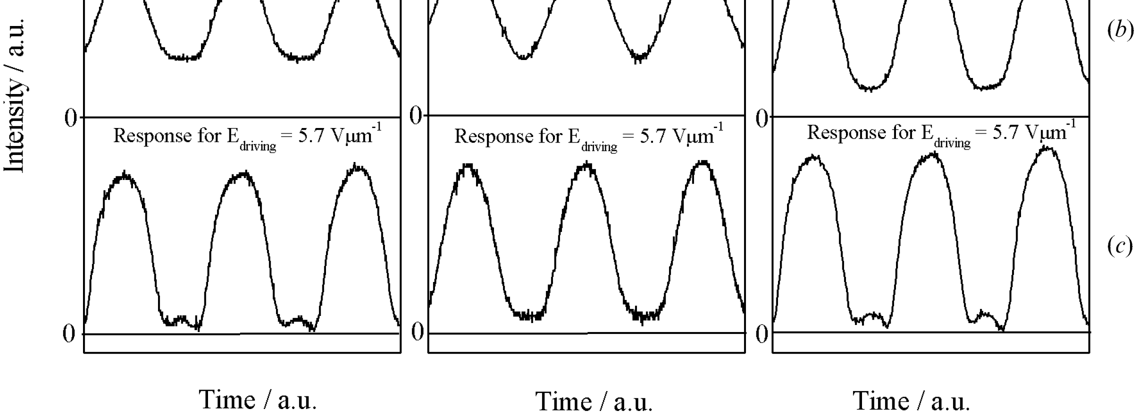

Figure 2. Different electro-optical response of charged PDLC to an effective electric field given by the sum of a driving field, $\mathbf{E}_{\mathrm{driving}}$, and a built-in d.c. field, $\mathbf{E}_{\mathrm{d.c.}}$ (*a*). The electro-optical response is quasilinear if $\mathbf{E}_{\mathrm{d.c.}}>\mathbf{E}_{\mathrm{driving}}$ (*b*) but departs from quasilinearity if $\mathbf{E}_{\mathrm{d.c.}}<\mathbf{E}_{\mathrm{driving}}$ (*c*). The driving frequency is 40 Hz.

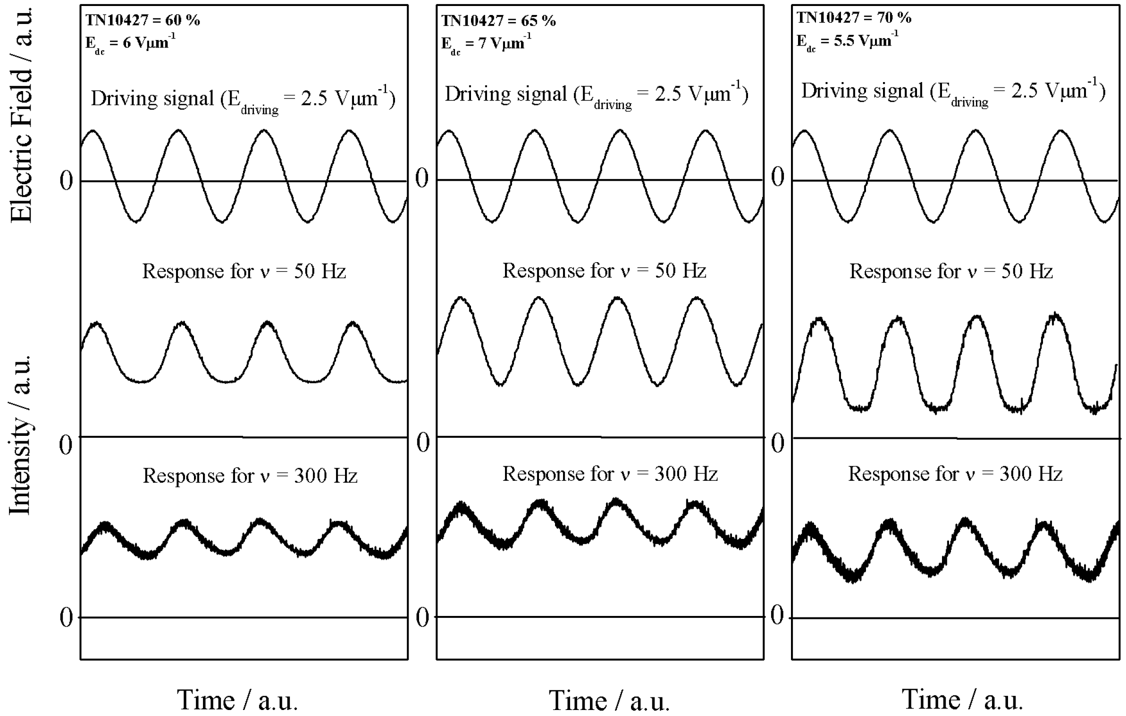

Figure 3. Frequency-dependent quasilinear response of PDLC films with a built-in d.c. field, $\mathbf{E}_{\mathrm{d.c.}}$, for different weight percentages of TN10427. The driving field strength is $\mathbf{E}_{\mathrm{driving}}=2.5\,\mathrm{V\,\mu m^{-1}}$.

mechanical memory state. Every sample with a built-in d.c. field shows, after the charge process, a memory state with a zero-field transmittance between 25% and 35%. In order to determine the amount of 'mechanical' memory, we measured the transmittance of samples when an external field is applied with the same strength as the built-in d.c. field but of opposite polarity. Figure 4 shows the changes in the OFF-state transmittance after such electric 'erasure'; the switching time is only some milliseconds. The effective electric field acting on the liquid crystal droplets is zero ($\mathbf{E}_{\mathrm{effective}}=\mathbf{E}_{\mathrm{d.c.}}-\mathbf{E}_{\mathrm{external}}$) and the residual transmittance is due to the mechanical action of the polymer/liquid crystal interface on the directors. We observe that such a mechanical memory state affects the transmittance value only in the range of a few percent (from 2 to 7%). The light modulation is greater than 90% for a sample with 65 wt% of TN10427. The lower values of light modulation shown by other films may be attributed to both the lower induced $\mathbf{E}_{\mathrm{d.c.}}$ strengths and to higher 'mechanical' memory states.

If the erasing field strengths are lower or larger than $\mathbf{E}_{\mathrm{d.c.}}$, film transmittances vary as shown in figure 5. The two curves for each sample represent the behaviour of transmittance to an external d.c. field which is parallel (upper curve) or antiparallel (lower curve) to the built-in d.c. field. The OFF-state transmittances increase if an external d.c. field is applied parallel to $\mathbf{E}_{\mathrm{d.c.}}$ as the effective field ($\mathbf{E}_{\mathrm{effective}}=\mathbf{E}_{\mathrm{applied}}+\mathbf{E}_{\mathrm{d.c.}}$) allows a better reorientation of liquid crystal directors along a direction parallel to the fields. Transmittances reach a plateau value for an effective field whose strength is the saturation value. By contrast, if the external d.c. field is antiparallel to $\mathbf{E}_{\mathrm{d.c.}}$, transmittances decrease to a minimum value when the effective field acting on the liquid crystal droplets ($\mathbf{E}_{\mathrm{effective}}=\mathbf{E}_{\mathrm{d.c.}}-\mathbf{E}_{\mathrm{external}}$) is zero, i.e. the liquid crystal directors are randomly aligned.

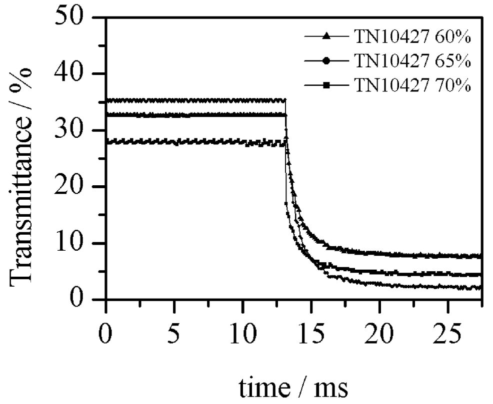

Figure 4. Change in the OFF-state transmittance after the electric 'erasure' of the built-in electric field. The residual transmittance is due to a 'mechanical' memory state.

If the $\mathbf{E}_{\mathrm{applied}}$ strength is progressively increased, the strength of $\mathbf{E}_{\mathrm{effective}}$ will increase (always along a direction

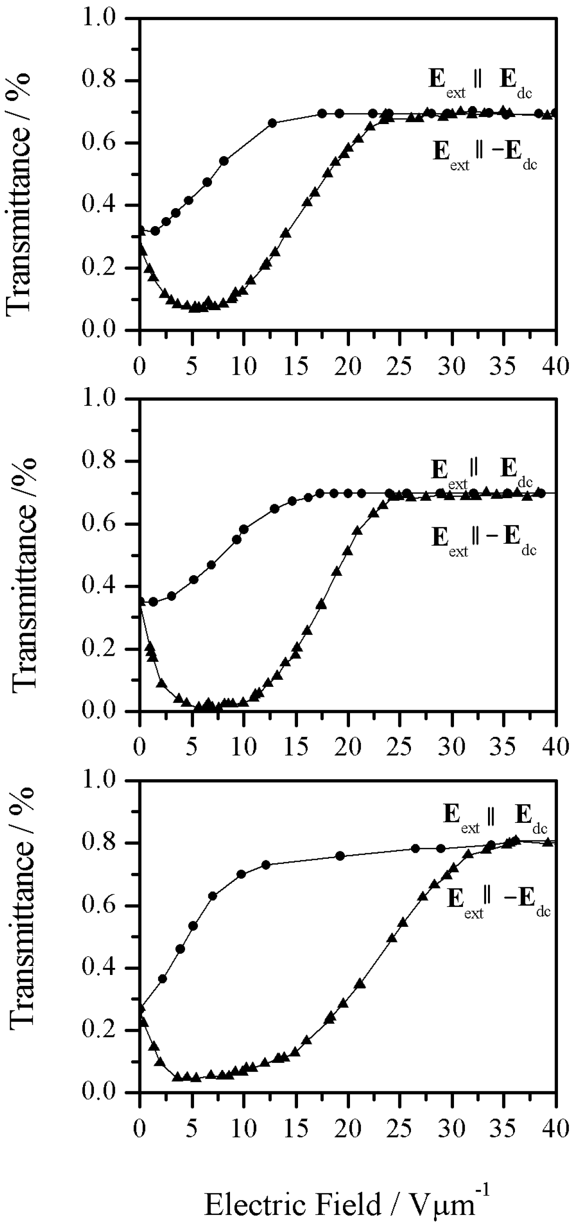

Figure 5. Dependence of the transmittance of charged PDLCs as a function of the external d.c. field strength and direction.

antiparallel to $\mathbf{E}_{d.c.}$) and the liquid crystal directors will align parallel to $\mathbf{E}_{effective}$. It is important to observe that sample transmittance can either increase or decrease as a function of the polarity of the external d.c. field. Consequently, nematic liquid crystal dispersions with a built-in d.c. field may be switched from an almost transparent OFF-state either to a more transparent or to an opaque state by applying an external d.c. field of the appropriate polarity. A transition between the two different ON-states may be achieved by just changing the polarity of the applied field. The contrast ratio between the two different ON-states is reported in figure 6 as a function of $\mathbf{E}_{external}$ strength. It is evident that the maximum modulation is gained when $\mathbf{E}_{external}=\mathbf{E}_{d.c.}$.

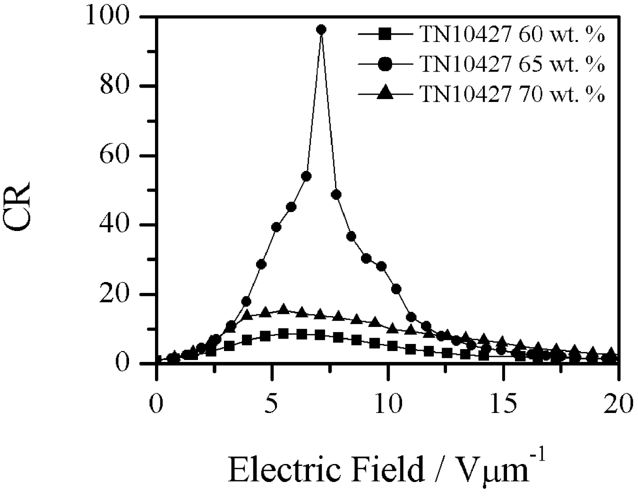

Figure 6. Contrast ratio, *CR*, in PDLCs with a built in d.c. electric field as a function of the external d.c. field strength for different percentages of TN10427.

4. Conclusions

In this work we have studied the change of the electro-optical response in PDLCs after the application of an external electric field as a function of liquid crystal content. We have been able to induce a built-in d.c. electric field over only a narrow range of liquid crystal concentrations because of the polymer matrix viscosity. The built-in field causes the dark state of the devices to appear bright. Driving fields applied to this state are able to modulate the brightness. The main advantage of this switching mode is a quasi-linear response, but the contrast is reduced as the driving frequency is increased. The application of an external d.c. field allows for an increase in the contrast ratios. In particular, samples with 65 wt% of liquid crystal show a light modulation greater than 90%, and consequently, they may be used as devices switchable by a simple change of the external electric field polarisation.

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