

# Electro-optical properties of a PDLC based on unsaturated polyester resin

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**Abstract.** An electro-optical characterisation of a polymer-dispersed liquid crystal (PDLC) based on unsaturated polyester (UP) resin, recently prepared in our laboratory, is presented. Transmittance and response times as a function of an electric field applied to the sample, have been measured taking into account also the morphological aspects of various samples. The experimental results confirm the theoretical data previously calculated on the base of the dimensions of the liquid-crystal droplets inside the polymeric matrix. Our analysis on this new material suggests the possibility of employing such a PDLC to realise electro-optical devices.

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In the advanced materials field, liquid-crystal polymer composites have been widely studied in the last two decades because of potential applications such as switchable windows, displays, colour projectors, and other electro-optical systems. This new type of material has been successfully proposed receiving a great deal of attention owing to its electro-optical properties, useful for designing integrated optical structures and electro-optical devices. This composite material is known as polymer-dispersed liquid crystal (PDLC) and is constituted of liquid-crystal (LC) droplets embedded in a polymeric matrix [1]. The most exciting characteristic of PDLCs is their capability to transmit light under the action of an external electric field, whereas in their natural condition they are highly scattering, working as light shutter.

In fact, due to the refractive indices mismatch of LC droplets and of the polymeric matrix, PDLC samples appear opaque, at room temperature and in the absence of any external electric field. In order to exploit the electro-optical properties of such materials, it is necessary to realise a multilayer constituted of a PDLC film sandwiched between substrates having a transparent conducting electrode, such as indium tin oxide (ITO), in order to apply an electric field which can be driven with different frequencies and wave shapes.

Upon application of a voltage across the electrodes of the shutter, it switches from an opaque state (light scattering) to a clear one (transparent state). The applied electric field aligns the molecular director of LC inside the droplets, so that there is an index matching between the LC and the polymeric matrix. As a consequence, this results in a decreasing of the light scattered by the droplets. When the electric field is removed the film of PDLC returns to the scattering state. The response times of such materials, which are the times to switch from one state to the other one when an alternating voltage of amplitude  $V$  is applied, depend on their morphology [2]. To be useful for a broad range of application the PDLC films must operate with a switching time fast enough. Since their use depends on response times to an applied electric field, it is necessary to measure the electro-optic performance of the samples [3–5].

In this article we present experimental results on the electro-optical properties of PDLC samples, prepared in our laboratory, consisting of nematic liquid-crystal droplets in a polyester resin binder [6].

The easy preparation of our PDLC sample represents one of the main advantages of such a material. Furthermore the polymerisation-induced phase separation by ultraviolet (UV) exposure of LC/monomer solution guarantees the possibility to control the LC droplets' size which play an important role in the electro-optical properties of PDLC such as their response times.

Our unsaturated polyester is a good basic polymeric material for realising PDLC and it does not require a particular equipment in preparing the samples. Furthermore, the cost of this material is very low.

Our experimental results demonstrate the possibility to employ these materials for realising electro-optical devices such as light modulator and optical switches.

## 1 Materials

Several methods to dispense the LC droplets in the polymer matrix were reported with regards to methods of:

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- (a) Polymerisation-induced phase separation (PIPS), where the LC is dissolved into the monomer, which is subsequently polymerised either thermally or photochemically.
- (b) Thermally induced phase separation (TIPS) in which the LC and a thermoplastic polymer form a homogeneous solution above the melting point of the polymer. The phase separation is obtained by rapid cooling of the melt.
- (c) Solvent-induced phase separation (SIPS), in which the LC and the thermoplastic polymer are dissolved in a common solvent. Controlled evaporation of the solvent results in the phase separation of the LC component.

The unsaturated polyester prepolymer was obtained by a condensation reaction between propylene glycol, maleic anhydride, and isophthalic anhydride in the molar ratio 0.50/0.45/0.05. The polyester prepolymer had a number average molecular weight,  $\bar{M}_n$ , of  $2.4 \times 10^3$ , a weight average molecular weight,  $\bar{M}_w$ , of  $8.0 \times 10^3$ , and an average number of unsaturations per chain of 9.5. The formulation used in the present contribution contained 35 wt % of styrene as co-reactive monomer; therefore the initial molar ratio between styrene and polyester unsaturations was 1.1.

The LC component was a eutectic mixture of four liquid crystals, commercially available as E7. The glass transition temperature of this mixture, as evaluated by differential scanning calorimetry (DSC), is  $-65^\circ\text{C}$ , whereas the nematic-isotropic transition occurs at  $58^\circ\text{C}$ .

The PDLC samples based on unsaturated polyester resin were prepared by mixing the appropriate amounts of E7 into the uncured resin at  $70^\circ\text{C}$ , obtaining a visually transparent, homogeneous solution. 1.0 wt % of the UV curing agent, 1,2 diphenyl-2,2-dimethoxyethane-1, was added and the formulation was poured between two glass plates separated by Teflon spacers of different thickness, according to the type of measurement to be performed on the specimen. The assembly was placed under an UV lamp and irradiated for 5 min.

## 2 Morphology

Optical microscopy shows evidence of a separate LC phase in the form of birefringent droplets at compositions higher than 10 wt %.

These morphological features have been investigated in deeper detail by scanning electron microscopy (SEM), after an etching treatment with methanol, which selectively removes from the specimen's surface the LC phase. In Fig. 1 are shown the etched surfaces of an UP/E7 60/40. At this magnification, we note an interconnected texture characteristic of a two-phase system, in which irregularly shaped holes left behind by removal of the LC phase are evident. This type of texture is completely absent in the neat UP resin cured in the same conditions and etched accordingly. Image analysis has been performed also on this type of micrograph, and the results are reported in the histogram of Fig. 2. In this case the particle size distribution is considerably narrower, with most of the domains ranging between 0.1 and  $0.6\ \mu\text{m}$ . The peak of the statistical distribution (exceeding 30%) is located between 0.2 and  $0.3\ \mu\text{m}$ .

As reported in literature [5, 7], the size of the LC droplets plays a fundamental role in determining the thermo- and electro-optical response of a PDLC system. In particular it

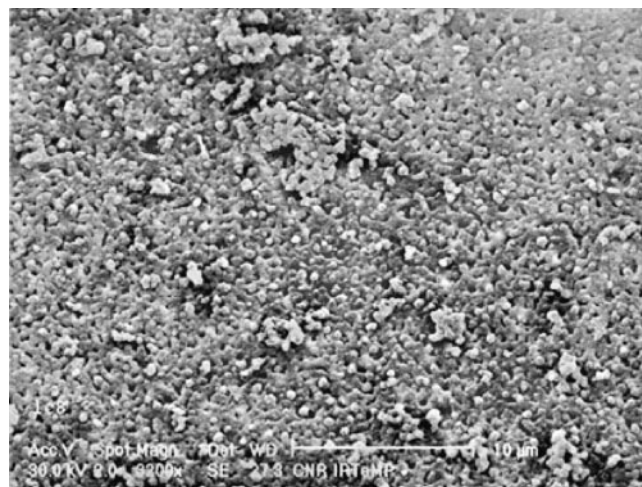


Fig. 1. High-magnification SEM photo of the etched surface of the 60/40 PDLC composition after curing

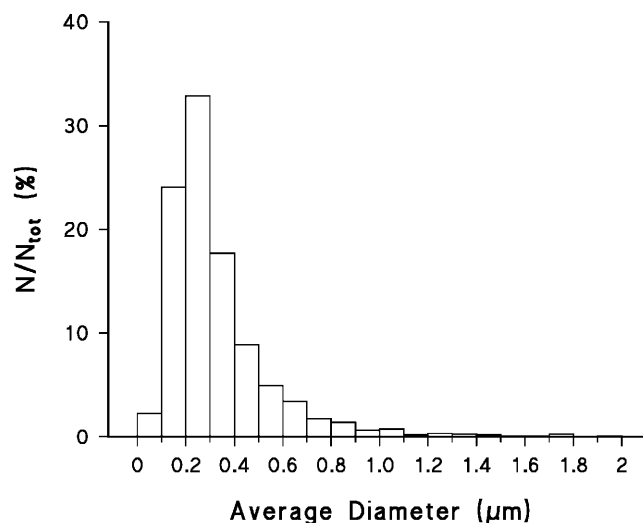


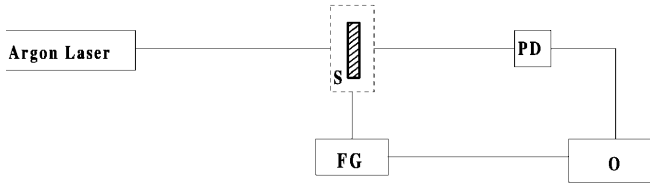
Fig. 2. Histogram of the particle size distribution inside the polymeric matrix. This distribution was evaluated by computerised image analysis from several SEM micrographs

has been reported that optimum results have been obtained with submicron particle dimensions; therefore, in this respect the morphology of the system under investigation is at least partially satisfying.

The above-described morphology was found suitable to evaluate the response times of our PDLC sample and to estimate the electro-optical properties.

## 3 Electro-optical properties

The first step to the characterisation of such a material has been the evaluation of the refractive index  $n_p$  of the polymeric matrix, at  $\lambda = 514\ \text{nm}$ , using the Abbe refractometer. The measured value for  $n_p$  is 1.551, whereas, for the liquid crystal (E7), as reported in literature, the ordinary refractive index  $n_o$  and that extraordinary one  $n_e$  are respectively:  $n_o = 1.522$  and  $n_e = 1.746$  (at the same wavelength).



**Fig. 3.** Experimental set-up. S: PDLC Sample, PD: Photodiode, FG: Function generator, O: Oscilloscope

These values allow us to estimate previously, the optical behaviour of the analysed sample by the indices mismatch. A good index matching determines high transmittivity of the material under action of the electric field as it is shown in the curve reporting the transmitted signals as a function of the applied voltage.

In order to measure the response times of the PDLC sample, we used the experimental apparatus shown in Fig. 3.

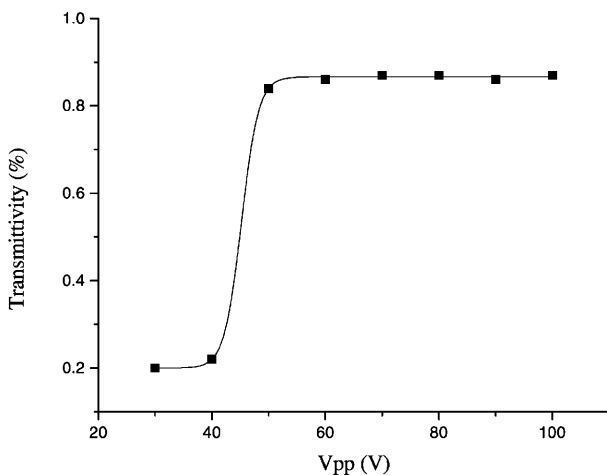
We calculated the rise time ( $\tau_{ON}$ ) and the decay time ( $\tau_{OFF}$ ) as a function of the applied electric field, and measured also the transmitted light vs. the electric voltage, which was applied to the ITO films used as transparent conductive electrodes.

The applied voltage was driven by a function generator which allows different wave shapes, amplitude, and offsets. Different sets of measurements were performed in order to evaluate the best condition to obtain the fastest response times by varying the frequencies and the driving voltages.

We analysed the output polarisation states: the light propagating inside the sample doesn't change its polarisation plane when the electric field is applied.

In all the tested configurations the field was driven by a square-wave applied voltage. The output signal was detected by a photodiode and monitored by an oscilloscope together with the driven signal. The transmitted signals, monitored at the oscilloscope, were photographed.

As a first approach to the electro-optical characterisation of the PDLC samples, we measured the threshold voltage at which the output signal passes from the OFF level (scattering state) to the ON one (transmission state). The curve in Fig. 4 reports the transmittivity as a function of the driving voltage. As shown in this figure the threshold voltage corresponds to



**Fig. 4.** Transmittivity as a function of the applied voltage

about 40 V, whereas the contrast ratio is not so high because of the refractive index of the used polymer.

As known, the threshold voltage  $V_{th}$  depends on the size of the LC droplets inside the sample and is a linear function of a reciprocal size of the droplets  $R$  according to

$$V_{th} \cong \frac{d}{R} \left[ \frac{K(w^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \right]^{\frac{1}{2}}, \quad (1)$$

where  $d$  is the film thickness,  $R$  the droplet radius,  $K$  the effective elastic constant,  $\Delta \varepsilon$  the dielectric anisotropy,  $w$  the aspect ratio of elongated droplet and  $\varepsilon_0$  the vacuum dielectric constant. Considering the following values for our case:  $d = 30 \mu\text{m}$ ,  $R = 0.2 \mu\text{m}$ ,  $K = 1.71 \times 10^{-11} \text{ N}$ ,  $\Delta \varepsilon = 6.49$ ,  $w = 1.1$ , and  $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ , the calculated threshold voltage  $V_{th}$  is 37.5 V, which is in good agreement with the experimental value.

The response times were measured directly from the traces shown at oscilloscope. In Fig. 5 we report the photograph of the traces of the driving signal (lower curve) at a frequency of 200 Hz and voltage of 60 V, and of the output signal (upper curve), respectively. In this situation, we measured a rise time 0.8 ms and a decay time of 80  $\mu\text{s}$ . We compared the results with the expected values for  $\tau_{OFF}$  and  $\tau_{ON}$  by the following formulas:

$$\tau_{OFF} = \frac{\gamma a^2}{K(w^2 - 1)}, \quad (2)$$

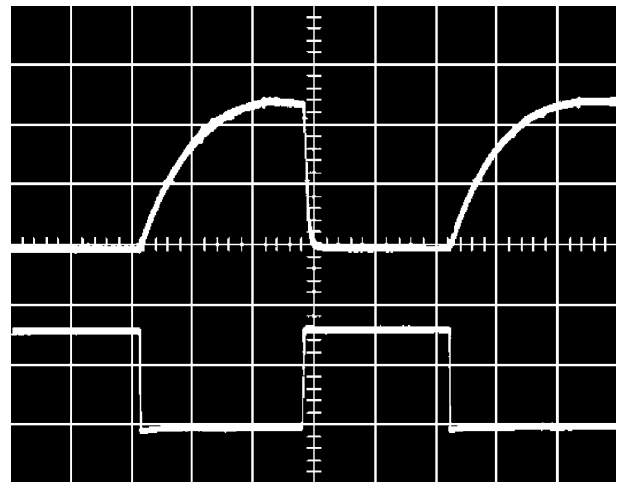
and

$$\tau_{ON} = \frac{\gamma}{\Delta \varepsilon \times E^2}, \quad (3)$$

where  $\gamma$  is the viscous torque,  $a$  is the length of the semi-major axis of the droplets, and  $E$  is the electric field.

The calculated values for  $\tau_{OFF}$  and  $\tau_{ON}$  are 73  $\mu\text{s}$  and 0.77 ms, respectively. These results are in good agreement with the measured values.

At the frequency of 200 Hz, we varied the driving voltage in order to measure the variations of the response times,



**Fig. 5.** Optical response of our sample (upper trace). In the lower trace is shown the driving voltage whose frequency is 200 Hz. The time scale is 1 ms/cm; the output voltage scale is 1 V/cm; the driving voltage scale is 50 V/cm

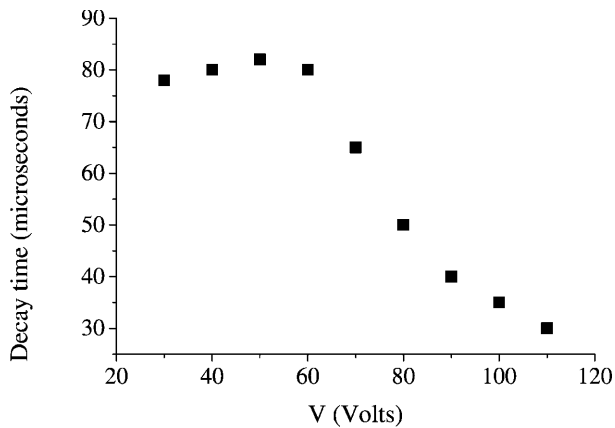


Fig. 6.  $\tau_{\text{OFF}}$  as a function of the driving voltage at a frequency of 200 Hz

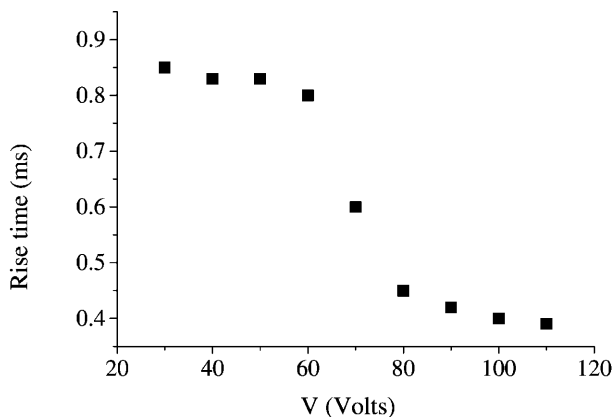


Fig. 7.  $\tau_{\text{ON}}$  as a function of the driving voltage at a frequency of 200 Hz

which, as known, depend on the applied electric field as  $V^{-2}$ . In Figs. 6 and 7 we report the experimental results which indicate, as expected, the decrease of  $\tau_{\text{OFF}}$  and  $\tau_{\text{ON}}$ , respectively, after the threshold value of the applied voltage ( $V_{\text{th}} = 40$  V).

We noted that at higher frequencies the PDLC sample is not able to follow the driving voltage. This is ascribed mainly to the material preparation and to the used curing which affects the droplets dimensions, as recently reported in literature [7, 8]. A further advance is in progress in order to obtain samples with faster response times and higher contrast ratio in the transmittivity curve.

#### 4 Discussion

The experimental results reported in this article could be qualitatively compared with those obtained by Lackner et al. [9]; even if in the present paper we devoted our attention to the response times of PDLC samples, whereas the other authors, in

their article, were interested much more in the correlation between the liquid-crystal droplets' size and selected characteristics of PDLC. However, our measurements on the response times are very satisfactory and this encourages us to improve the curing in order to obtain lower threshold values of the applied electric field and higher contrast ratio.

#### 5 Conclusion

In this communication we presented experimental results on electro-optical properties of PDLC samples prepared in our laboratories, consisting of nematic liquid-crystal droplets in a polyester resin binder. We estimated the rise time and the decay time as a function of the applied electric field and measured also the transmitted light vs. the voltage.

The experimental results exhibit an interesting electro-optical behaviour of our material and confirm the theoretical predictions. In particular, the value of the threshold voltage ( $V_{\text{th}}$ ) theoretically expected, has been experimentally verified and confirmed. For a driven signal of 200 Hz and voltage of 60 V, the rise time is 0.8 ms and a decay time is 80  $\mu\text{s}$ .

The expected values by a theoretical calculation were  $\tau_{\text{ON}} = 0.77$  ms and  $\tau_{\text{OFF}} = 73$   $\mu\text{s}$ . These data are in good agreement with those obtained experimentally.

Our results were correlated with the sizes of the droplets and demonstrated the validity of the theoretical indications presented in literature. From our analysis we can conclude that, after a further improvement of the employed polymeric material (*i.e.* higher contrast ratio), this new PDLC can be used to realise electro-optical devices such as light modulators working in a low frequency-regime.

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#### References

1. L. Bouteiller, P. Le Barny: *Liquid Crystal* **21**, 157 (1996)
2. H.-K. Jeong, H. Kikuchi, T. Kajiyama: *New Polym. Mater.* **5**, 103 (1998)
3. M. Mucha: *J. Appl. Polym. Sc.* **43**, 175 (1991)
4. B.-G. Wu, J.H. Erdmann, J.W. Doane: *Liquid Crystal* **5**, 1453 (1989)
5. G. Chidichimo, G. Arabia, A. Golemme, J.W. Doane: *Liquid Crystal* **5**, 1443 (1989)
6. P. Mormile, L. Petti, M. Abbate, P. Musto, G. Ragosta, P. Villano: *Opt. Commun.* **147**, 269-273 (1998)
7. S.-C. Peng, J.-W. Yu, S.-N. Lee: *J. Polym. Sci. - Polym. Phys.* **35**, 1373 (1997)
8. H.-K. Jeong, H. Kikuchi, T. Kajiyama: *New Polym. Mater.* **5**, 103 (1998)
9. A.M. Lackner, J.D. Margerum, E. Ramos, K.C. Lim: *SPIE Liquid Crystal Chem.: Phys. Appl.* **53**, 1080 (1989)