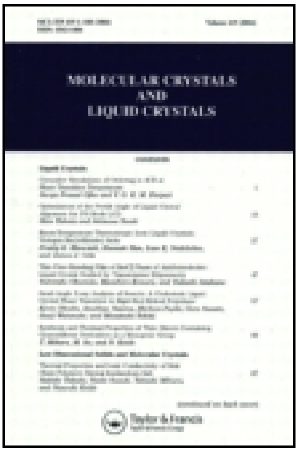

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Enhancement of the Thermo-optical Properties in Dye-doped PDLCs

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A detailed thermo-optical analysis of dye-doped Polymer Dispersed Liquid Crystal (D-PDLC) systems has been performed. A comparison of the optical properties between D-PDLCs and not doped PDLCs based on the same polymeric matrix is addressed. For any D-PDLC composition investigated, the light intensity and the sample temperature are used to control or adjust the nonlinear part of its refractive index.

We investigated the thermal responses of PDLC samples prepared with three different dyes at two dopant concentrations in order to evaluate the contribute of the dopants as a function also of its percentage in the polymeric matrix. Our experimental results demonstrate that self transparency effect, optical hysteresis and thermo-optical modulation are notably affected by the used dye.

We show how the use of dye in preparing PDLC can be useful in order to design thermo-optical devices employing waveguides connected with the considered materials or to realise low cost thermal sensors.

Keywords: liquid crystals; dyes; PDLC; optical switching; thermo-optical characterization; thermal nonlinearities.

INTRODUCTION

One of the most relevant results achieved in the last decades in the field of the *materials science* is the use of dye in preparing materials with special optical properties. The main goal is to obtain materials with optimized performances in order to design optical devices widely employed in different sectors.[1,2,3] The dyes contribute allows to increase the light absorption reducing remarkably the power necessary to induce nonlinear optical effects. Many types of materials, as crystals, liquid crystals, polymers had an improvement of their properties thanks to the use of proper dyes.

PDLCs represent one of the most attractive materials of the last generation owing to their suitability for a variety of applications, ranging from displays to sensors and telecommunication systems.[4,5,6] This range has been greatly widened thanks to the employ of dyes. The preparation of a dye-doped PDLC (D-PDLC) requires a preliminary knowledge of each used material constituting the final sample (polymer matrix, liquid crystal and dye). The refractive index of each components and their matching in the absence of any field represent the necessary conditions to obtain samples of interest for potential applications. In this paper we present experimental results concerning the use of three different dyes, at several concentrations, for preparing PDLC films, an optical characterization, a morphological study, and finally an analysis of some nonlinear optical effects due to the enhancement of the thermo-optical properties in these materials.

Their optical response can be induced both electrically and thermally. Due to the strong optical nonlinearities of the D-PDLC sample subjected to a laser beam, the switch effect from a low to a high transmission can be thermally induced. A nematic-to-isotropic phase transition in the droplets is generated by the laser heating of the sample. Such a thermal effect can form the basis of an optical switch. This is also induced increasing the incident light intensity, so that the initially opaque material becomes transparent. This optical phenomenon, is also termed a *self-transparency* effect.

In this work we show how the laser–induced phase transition are exploited to achieve optical bistability behaviour from PDLCs. In the first part of the experiments a thorough investigation of thermo–optical properties is performed to study the switch effect by increasing the temperature of the samples at a very low input laser power at $\lambda = 514$ nm. In the second part attention is focused onto the bistability phenomenon studying the output light modulation of a probe beam optically induced by a pump beam with several modulation waveforms of different frequencies and at different temperatures of the sample.

A comparison of the optical properties between D-PDLCs and not doped PDLCs based on the same polymeric matrix is addressed. The influence of dye concentration in the D-PDLC on the properties of PDLC films is investigated.

EXPERIMENTAL

Materials

Epoxy-based PDLC samples were prepared with a homogenous prepolymer solution by a polymerisation induced phase separation (PIPS) method thermally initiated. The solution contained: (i) epoxy prepolymer, diglycidyl ether of bisphenol A (DGEBA); (ii) E7 liquid crystal component (40% by weight); (iii) a hardener, methyl–5–norbornene–2,3–dicarboxylic anhydride (MNA); (iv) an initiator (1%wt), 2,4,6–tris(dimethylaminomethyl)–phenol (DMP–30). Uncured epoxy solution was prepared by adding the hardener and the initiator in the epoxy prepolymer. The uncured epoxy solution and E7 were mixed and stirred thoroughly at 70°C to obtain a homogeneous solution. The resulting solution was then spread on a substrate to form a thin film and heated to 130°C in a oven at a heating rate of 2°C/min and hold the temperature for 60 minutes. The sample was cooled down over night by switching off the oven.

The three dopants used in this work are Dblue 14, Quinizarine from Merck and D4 from BDH; they all are based on the structure of 9,10-anthraquinone. Their molecular formulas are schematically represented in Fig. 1.

SAMPLE	WEIGHT RATIO OF THE COMPONENTS (WT%)
N	DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7 (40)
A	DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/Dblue (39.9/ 0.1)
B	DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/Dblue(39 / 1)
C	DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/D4 (39.9 / 0.1)
D	DGEBA/MNA/DMP-30 (0.53/0.46/0.01) + E7/D4 (39 / 1)
E	DGEBA/MNA/DMP-30 (0.53/0.46/0.01)+E7/Quinizarine(39/ 1)

Table 1 Samples' composition

Epoxy-based dye-doped PDLC (D-PDLC) films were prepared in the same way as the epoxy-based films. The liquid crystal doped with a small amount of dye, prepolymer, crosslinking agent and initiator were mixed under the same experimental conditions described above to obtain the uncured polymerisation mixture. The different compositions of all the investigated samples are reported in Table 1

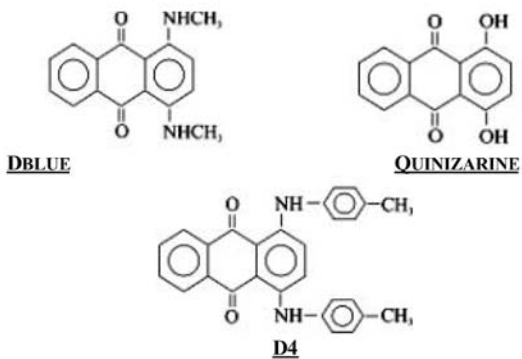


FIGURE 1 Molecular formulas of the dyes employed

Drops of the polymerisation mixture were then introduced in glass cells to form a 30-μm-thick sample. The filled cell was thermally cured under the same curing process employed by the epoxy based PDLCs.

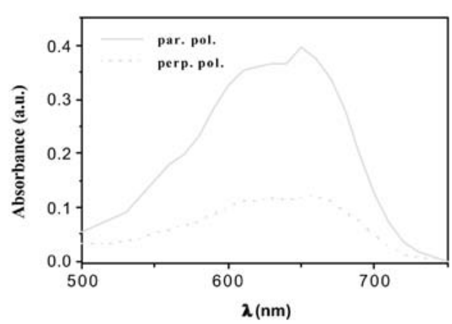


FIGURE 2 Absorption spectrum of D4 dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarisation

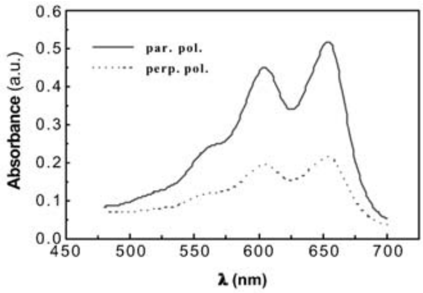


FIGURE 3 Absorption spectrum of Dblue dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarisation

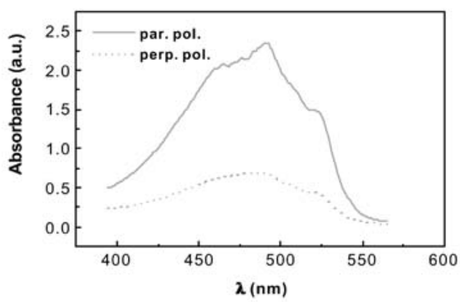


FIGURE 4 Absorption spectrum of Quinizarine dye (1% wt) dissolved in E7 for parallel (continuous curve) and perpendicular (dot curve) polarisation.

Since absorption plays an essential role in both the strong optical nonlinearity in PDLCs and in improving the contrast ratios of PDLC films, we measured the absorption spectrum of the dopants dissolved in the liquid crystal.

In Fig. 2-4 the absorption spectra of the Dblue, D4, and Quinizarine (1% wt) dissolved in E7 for two different light polarisations are shown.

The absorbance spectra of the systems show that the systems with Dblue and D4 absorb at the wavelength 632.8 nm.

Quinizarine does not significantly absorb at 632.8 nm but shows a large absorbance at $\lambda = 514.5$ nm.

Morphological analysis

A preliminary investigation on the epoxy-based PDLC system over the composition range 0 - 60 wt % of LC, has been presented in a previous work of the authors. [7]

SEM image of the epoxy-based PDLC (40% wt of LC content) is shown in figure 5; the sample is clearly phase-separated, the LC component forming spherical-like droplets uniformly distributed in the epoxy matrix. Employing software based image analysis[8], the distribution of average diameters of LC droplets appears narrow, ranging from 0.25 to 1.3 μm. However, the main size of LC droplets (exceeding 60% of the droplets) for 40% concentration lies between 0.5 and 0.8 μm.

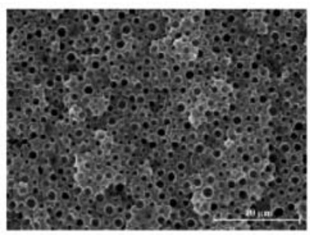


FIGURE 5 SEM image of phase-separated epoxy based PDLC sample

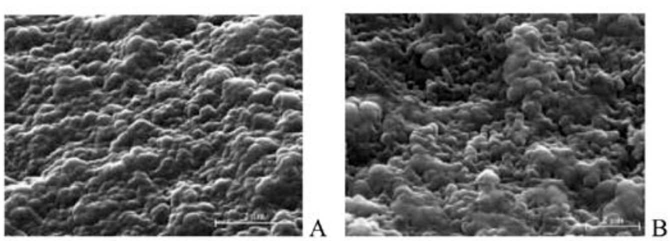


FIGURE 6 High magnification SEM micrographs of the surface of the D-PDLCs: A) Epox/E7 60/39.9 wt/wt + D4 0.1 %; B) Epox/E7 60/39 wt/wt + D4 1 %

Information on the morphology have been obtained by SEM for all the D-PDLC used in this study. In figure 6A-B is shown the high magnification SEM micrographs of the two systems Epox/E7 60/39.9 wt/wt + D4 0.1 % wt and Epox/E7 60/39 wt/wt + D4 1 % wt. The other samples have morphologies quite similar to those presented here.

It is evident from the SEM micrographs that the systems are not clearly phase separated. Despite the undoped epoxy based PDLCs, we don't have in this case a dispersed mesophase in the matrix, instead we observed a co-continuous system that is two continuous interpenetrating phases.

Thermo-optical measurements: Results and Discussion

The experimental set-up, shown in Fig. 7, is used to analyse the thermo-optical properties of both the epoxy-based PDLC (N) and the doped epoxy-based PDLCs (A, B, C, D, E). The sample is heated inside a program controlled thermostatic cell, which allows temperature control to ± 0.1 °C and heating rates as low as 0.1°C/min. The actual sample temperature inside the cell was measured and monitored using a thermocouple connected to a data logger unit.

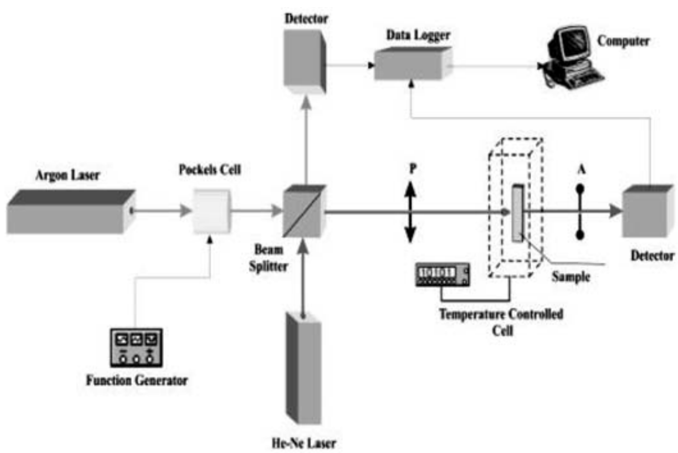


FIGURE 7 Experimental set-up for thermo-optical analysis

Initially, experiments were carried out to measure the temperature dependence of the light transmission of samples for varied input laser power, at $\lambda = 514$ nm incident normally on the sample. Afterwards, an experimental analysis was performed using two unfocused laser beams simultaneously impinging normally on a spot (2.2 mm in diameter) of the PDLC sample. The output light modulation, optically induced by the pump beam, is probed and detected by a weak He–Ne (632.8 nm, 110 μW) when an intense Ar^+ beam (514 nm) propagates inside the material as a pump beam. The power of the input cw Ar^+ laser beam was modulated in the range 0-300 mW at different frequencies and waveforms using a Pockels cell driven by a function generator. A fraction of the input beam was tapped off by a beam splitter and monitored as a reference beam. Behind the sample cell an interference filter was employed in order to stop all the transmitted Ar^+ laser beam and let only the transmitted probe beam reach to the detector. The output modulation and the response of the probe beam induced by an input square wave was monitored and measured using an oscilloscope. In order to get rid of all the possible scattered light from the sample, an aperture (1.5 mm in diameter) was placed behind the sample cell to generate a small collecting angle 2.5° . [9]

Optically self-induced light modulation by an Argon laser has been studied in D-PDLCs using the same experimental set-up where the Argon laser acts as a pump and probe at the same time. Temperature variations of the sample were obtained by increasing and decreasing the input light power. Measurements were carried out changing the modulation frequency at different temperatures.

A comparison of the experimental results of the thermo-optical characterisation of both an epoxy based PDLC (N) and the doped epoxy based PDLCs (A, B, C, D, E) is presented.

In Fig. 8 I-II-III the optical contrast ratio of the doped samples together with the non doped ones as a function of the background temperature at a very low incident power P_{in} = 1.95 mW (λ = 514nm) is reported.

A summary of the thermo-optical characterisations is reported in Table 2. A clear switching effect is observed as the background temperature of the sample is increased in the range from 25°C to 75°C; several features can be obtained from the analysis of the curves in Fig. 8 and from the data reported in Table 2.

(i) The threshold temperature T_{th} is lower for a doped PDLC compared with a non doped system. The temperature shift is due to both

SAMPLE	Tth (°C)	Tr (%)	CR
N (Epox/E7 60/40)	58	94	1400
A (Epox/E7/D-Blue (0.1%wt))	50	83	3500
B (Epox/E7/D-Blue (1%wt))	45	63	3900
C (Epox/E7/D4 (0.1%wt))	48	77	1400
D (Epox/E7/D4 (1%wt))	36	59	2800
E (Epox/E7/Quinizarine (1%wt))	25	38	40

TABLE 2 Transmittance, threshold temperature and contrast ratio values at λ=514 nm for all the samples investigated.

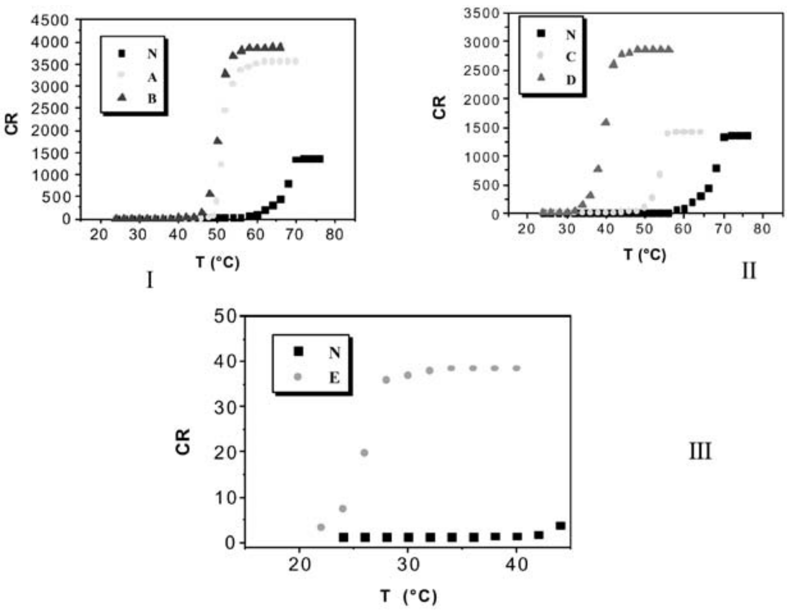


FIGURE 8 Temperature dependence of light contrast ratio at λ = 514 nm for D-PDLCs: I) Dblue-PDLCs; II) D4-PDLCs; III) Quinizarine-PDLCs.

the thermal contribution of the light induced by absorption, greatly enhanced by the presence of the dye, and to the content of dye in the mixture polymer/LC which causes a decreasing of the clearing point.

(ii) The maximum transmittance is lower than that of the non doped sample N. This decreasing can be ascribed to an increased scattering because of morphological changes, but is mainly due to the absorbance of the dye, which determines a lowering of the light intensity as a function of the sample thickness. For the same reason the contrast ratio of the doped samples (A, B, C, D) is higher than the sample N one. In fact, the OFF state in the former case is strongly scattering so that the transmittance is minimised and the denominator in the contrast ratio, too.

(iii) As it is expected, the content of the dye in the liquid crystal affects the transmittance, the contrast ratio and the threshold temperature: a higher dye content results in a lower transmittance, a higher contrast ratio and a lower value of the clearing temperature.

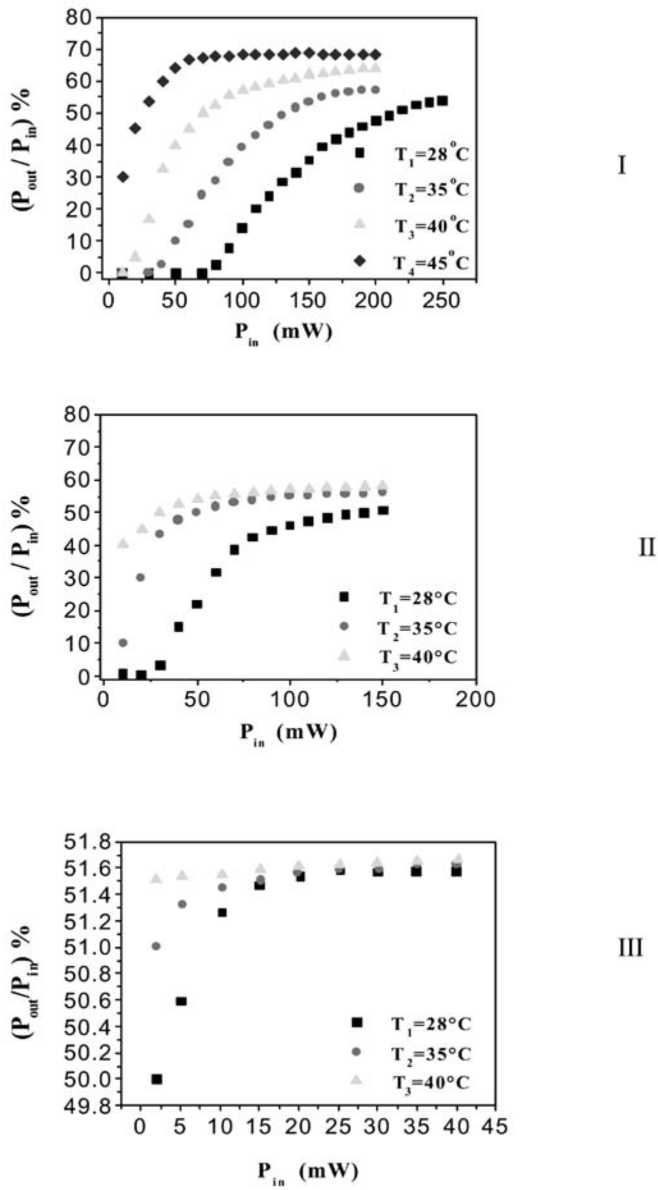


FIGURE 9 Dependence of transmittance at $\lambda = 514$ nm on the varied input power at different background temperatures for D PDLCs: I) Dblue-PDLCs (sample B); II) D4-PDLCs (sample D); III) Quinizarine-PDLCs.

Laser-induced Thermal Nonlinearities

The *self-transparency* effect has been studied for increasing values of the incident power with constant temperature of the sample.

In Fig. 9 I-II-III we report the dependence of light transmittance (λ = 514 nm) on the varied input power of light at different background temperatures, for D-PDLCs .

A clear switching effect is observed and there are different thresholds of the input power (P_{th}) corresponding to the different temperatures, respectively. Below the threshold power, P_{th}, there is no switching effect, and the sample is in the OFF-state. The ON-state is achieved when the input power is above P_{th}. Furthermore, as the background temperature of the sample approaches that of the isotropic phase, the threshold value P_{th} reduces and the slope of the transmittance becomes smaller. Since the background temperature pre-heats the whole sample and reduces the index difference between the liquid crystal droplets and the polymer matrix, a lower power of the incident light is necessary to induce the transition.

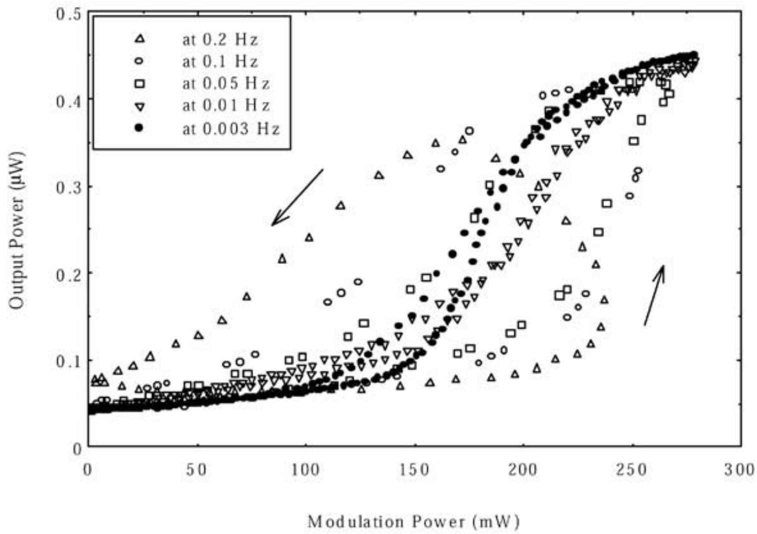
Our experimental results on the optically induced light modulation in epoxy-based PDLCs using a pump-probe configuration are presented in Fig. 10. These results have been described in all details in some previous works of the authors. [10,11]

Optically self-induced light modulation by an Argon laser has been studied in D-PDLCs using the experimental set-up shown in Fig. 7. Measurements were carried out by changing the modulation frequency at different temperatures. In Fig. 11 light transmission as a function of the input power at T = 25°C, 30°C, 35°C (nematic state), 40°C (isotropic state), respectively, is shown for the D4 doped sample (sample D). The results show that the effects obtained are quite similar for the three different samples. It is quite clear that the increasing background temperature leads to a decrease of the threshold power P_{th} as expected.

Furthermore, the actual local temperature of the samples can also be varied by changing the frequency of the pump beam. [12] The threshold shifts to a higher value and the hysteresis loop becomes larger with increasing modulation frequency at a fixed background temperature.

Our data show (Fig. 11) that more power of the input laser beam is required to induce switching at higher frequencies, because the local temperature rise is lower than with a lower frequency. Therefore, a larger hysteresis loop is achieved when the power of the input pump is increased linearly at higher frequencies.

Basically, when the input beam impinges on the sample normally, the absorbed energy from the laser beam is non-radiatively transferred into



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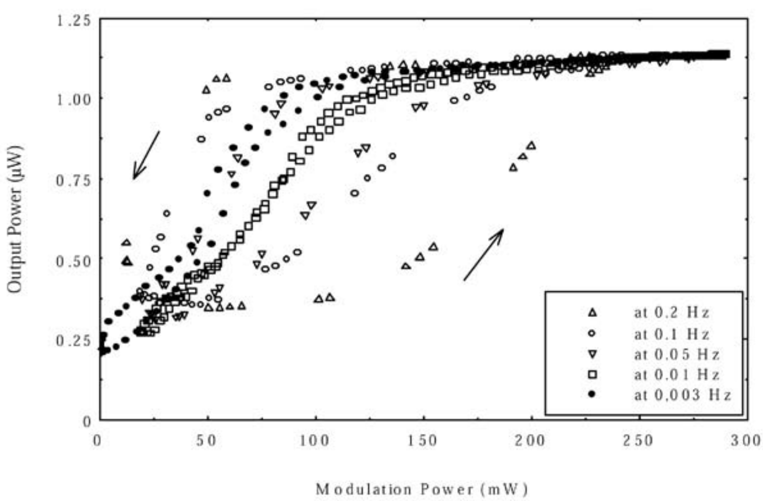

II

FIGURE 10 Light transmission (Probe beam) as a function of the input power (Pump beam) at different modulating frequencies (0.003 to 0.2 Hz) for a PDLC: (I) 55°C (nematic state), (II) 61.5°C (isotropic state).

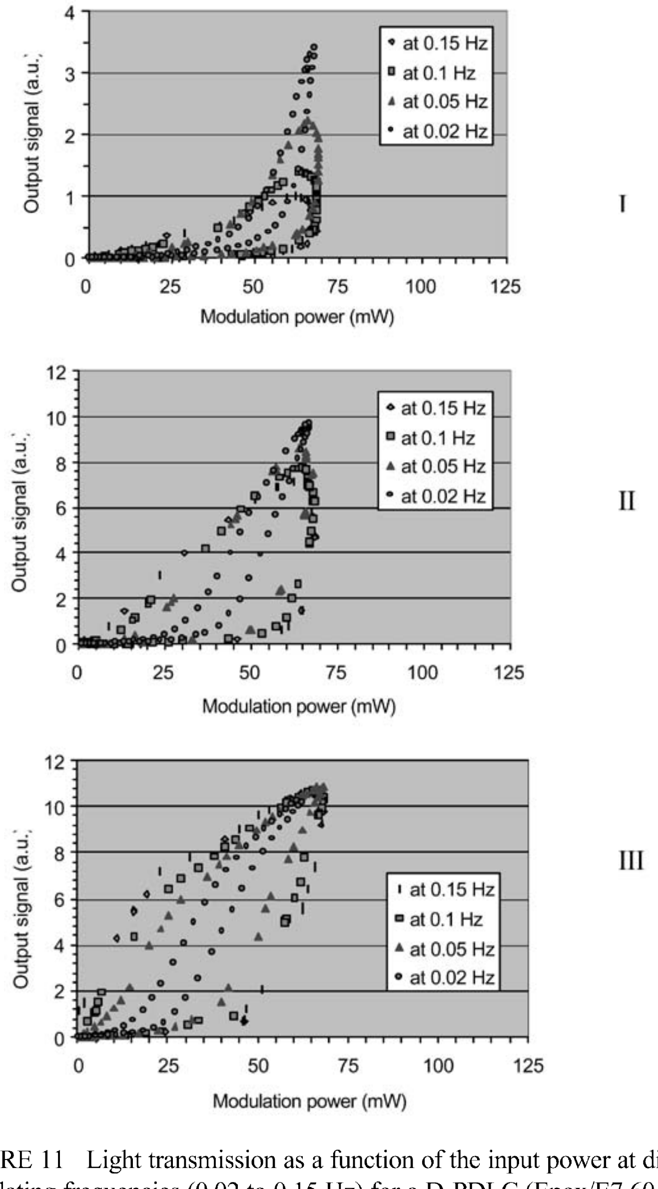

FIGURE 11 Light transmission as a function of the input power at different modulating frequencies (0.02 to 0.15 Hz) for a D-PDLC (Epox/E7 60/39 wt/wt + 1%wt D4): (I) 25°C, (II) 35°C, and (III) 40°C.

heat thus inducing a local temperature rise of the sample. If the laser beam is modulated or chopped, the heat flow equation shows that there is a difference between the local average temperature and the local instantaneous temperature. This difference is strongly dependent on the beam modulation parameters. Because of the relatively slow material response of the D-PDLC samples, their optical properties are affected only by the average temperature increase and not by the instantaneous one. This leads to the experimental observation that a higher threshold power is obtained for higher modulation frequencies of the laser beam.

CONCLUSIONS

Our research confirms that the use of dyes in PDLC samples can enhance their thermo-optical properties. Taking into account different dyes at several concentrations we prepared PDLC films in order to analyse the spectral responses, the morphology, the thermo-optical behaviour and nonlinear optical effects.

The experimental results were compared with those obtained from pure PDLC samples. They demonstrate that the use of dyes allows to reduce remarkably the light power necessary to reach the threshold for passing from an opaque state to a transmission state.

Finally we presented experimental evidence of very high contrast ratio in D-PDLCs during the optical switch from the OFF state to the ON state.

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