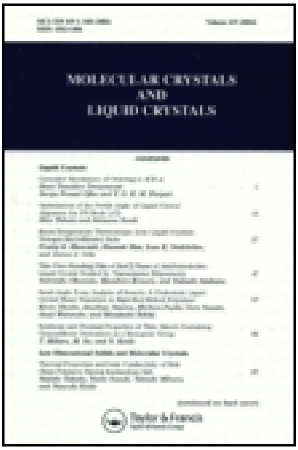

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Investigation of Photorefractive Effect in Dye Doped PDLC: TBC Experiments and Photoinduced Currents Measurements

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Investigation of Photorefractive Effect in Dye Doped PDLC: TBC Experiments and Photoinduced Currents Measurements

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Results are reported on the wave mixing characterisation of dye-doped dispersion of liquid crystalline droplets in a polymer matrix (PDLC) by means two beam coupling experiments and experimental observation of photoinduced DC current, which arise in these materials under cw laser-beam illumination. We determine the TBC gain by means of the asymmetric energy transfer measurements and the amplitude and the phase shift of the phase grating and amplitude grating by means the TBC translation technique measurements. The experimental results of this first characterisation reveal the nonlocality of the effect: the gratings obtained are essentially the phase gratings spatially shifted of $\pi/2$ respect to the interference pattern. The photoinduced currents reveal transient behaviour, i.e. a relaxation to zero value after an initial increase. A qualitative discussion of the obtained results is reported. The observation and the results of the experiments evidence the photorefractive nature of the light-induced diffraction gratings, which were earlier observed in these materials.

INTRODUCTION

The photorefractive effect is commonly known to be due to redistribution of photogenerated charge carriers when a material is illuminated in a non-uniform way. These charge carriers produce a non-uniform space charge field; and this field induces a modulation of the refractive index of the material through an electro-optic effect [1,2,3]. This effect is characterised by a spatial modulation of the refractive index, induced by a light intensity pattern spatially shifted with respect the intensity pattern. Usually the materials that exhibit this effect combine different properties as photinduced charge generation, transport, trapping and electro-optic response.

In this paper we report a detailed investigation that prove the presence of photorefractive effect in an optical storage effect observed in dye doped polymer dispersed liquid crystalline materials (PDLC)[4,5,6].

In these materials in fact it is possible to produce permanent diffraction gratings when exposed to a non-uniform illumination (interference pattern). A complete characterisation of these gratings is reported in our previous papers [4,5,6], in these papers we shown that the gratings are due essentially to the orientation of the liquid crystal inside the droplets. The results of two beam coupling (TBC) experiments show that the permanent gratings produced in these materials are essentially phase gratings and are phase shifted by π/2 respect to the writing interference pattern.

In photorefractive materials, this phase shift take place when the refractive index modulation is due to photocarriers diffusion [7], in the absence of external applied electric field as in our experimental conditions.

These results are an evident proof that the formation of permanent gratings observed in dye doped PDLC can be attributed to processes of photoinduced charge generation, transport and trapping in these materials. The electrooptic effect involved is the orientation of liquid crystal by means the spatially modulated static electric field induced by the charge distribution.

We report the photocurrent measurements made on a film of dye doped PDLC illuminated by a cw Ar^+ laser beam. In our samples the presence of the dye, which has maximum absorption near the laser wavelength, produces a non-uniform illumination along the direction of the laser beam during the irradiation.

In the first section we describe the materials, the components and the preparation methods. In the second section the TBC experiments and the related results are discussed. In the third section the experiments to measure the photoinduced current is explained and a qualitative explanation of the results is proposed.

MATERIALS

The PDLC samples were prepared using two phase separation techniques, one induced by polymerisation (PIPS) and the other one induced by temperature (TIPS) [8]. The samples used have been realised with two kind of polymers (epoxy resin and polymethyl methacrylate), two kinds of dye and a nematic liquid crystals In the case of epoxy resin the phase separation is induced by polymerisation, while in the case of poly-methyl methacrylate (PMMA), which is a thermoplastic polymer, polymerisation is induced by cooling (TIPS). The first kind of samples was prepared starting from a mixture of nematic liquid crystal (E7 by MERCK), epoxy resins (Epon 815 by Shell Chem., MK107 by Wilmington Chem. and Bostik B by Boston), an initiator (Capcure 3-800) and a dye (the azo-dye D2 or the anthraquinone D37, both by MERCK). The second was obtained starting by a mixture of thermoplastic polymer (PMMA) at high temperature, liquid crystal (E7) and dye (D2 or D37). The structures of the two types of samples are quite different, since the former is made by a crosslinked polymer while the latter by a linear chain polymer. The chosen weight concentrations were 35% of liquid crystal including 0.1% of dye, and 65% of the pre-polymer mixture for the PDLC with epoxy, while for PDLC with PMMA the concentrations were 50% of liquid crystal including 0.1% of dye and 50% of the polymeric mixture.

The induced phase separation lead to a dispersion of liquid crystal droplets embedded in the polymeric matrix with droplet size ranging from 0.1 to 1μm.

The cells were 36μm thick and made of ITO coated glasses. The experiments were performed in fully cured samples.

TWO BEAM COUPLING MEASUREMENTS: RESULTS AND DISCUSSION.

A peculiar features of the photorefractive effect is the nonlocality[1-3], therefore the signature of this phenomenon can be obtained by measurements of two beam coupling (TBC). One kind of experiment is based on the direct measurement of energy transfer between two beams that interfere inside the material and prove only the nonlocality. Another method is the grating translation technique [9], which allows a more extended characterisation than the former one. In facts this technique allow to distinguish between phase gratings (modulation of the refractive index) and amplitude gratings (modulation of the absorption coefficient). Moreover, it is possible to get direct measurements of the spatial phase shift between the grating and the optical interference pattern (we define this quantity ϕ_P for phase grating and ϕ_A for amplitude grating).

For these reasons the experimental results are important to prove the onset of the photorefractive effect.

The experimental set-up used for the first kind of measurements is a standard one reported in our previous paper [5]. The angle (2θ) between the two interfering beams in the sample was about 3° producing a grating period Λ of $10\mu m$, the sample being normal to the bisector of the writing beams. The condition $\Lambda^2 >> d\lambda$ holds, being d the sample thickness and λ the light wavelength, hence a Raman-Nath type interaction was realised (thin grating); however because of the low efficiency under this condition only the first order diffraction beams could be observed at the exit of the sample.

An asymmetric transfer of energy from one beam to the other has been measured through the TBC experiment. The experiment was performed by chopping one beam and monitoring the transmitted intensity of the other. A gain was measured in one beam and a loss in the other. The TBC gain is evaluated using the formula [3]:

$$\Gamma = \frac{1}{d/\cos\theta}\left(\ln(\gamma m) - \ln(m+1-\gamma)\right), \text{ where } m = \frac{I_1(0)}{I_2(0)} = 1, \text{ and } \gamma = \frac{I_{\text{with pump}}}{I_{\text{without pump}}} \quad (1)$$

The TBC gain measured for all type of samples and for p polarisation of the writing beams is reported in table 1.

As mentioned, the translation grating technique give us measurements of the amplitude of the phase grating P and the amplitude grating A and the relative phase shift ϕ_P and ϕ_A respect to the intensity pattern. After the grating formation at steady state, the sample was translated in the parallel direction to the grating vector moving the grating with respect to the interference pattern.

The measured signal have been recorded using the intensity of one of the two beams lower than the one necessary to write the grating, in order to avoid rewriting during translation. In our case, due to the presence of threshold intensity, the speed of translation does not affect the measurements.

In our geometry $I_1(0)=I_2(0)=I(0)$, $\theta_1=-\theta_2=\theta$, for low diffraction efficiency the intensities at the output beams are given by the equations [9]:

$$I_1(d) = I_1(0)\exp(-\alpha d/\cos\theta)\left[1 - 2A\cos\phi_A - 2P\sin\phi_P\right] \quad (2a)$$

$$I_2(d) = I_2(0)\exp(-\alpha d/\cos\theta)\left[1 - 2A\cos\phi_A + 2P\sin\phi_P\right] \quad (2b)$$

Where $A=\frac{\Delta\alpha d}{4\cos\theta}$ and $P=\frac{\pi\Delta n d}{\lambda\cos\theta}$, α is the absorption coefficient, Δα is its modulation and Δn the modulation of the refractive index.

The obtained results for A, P, ϕ_P and ϕ_A are reported in table 1.

	Epoxy resin+E7+Dye		**PMMA+E7+Dye**	
	D2 (dye)	D37 (dye)	D2 (dye)	D37 (dye)
Γ (cm^{-1})	130	170	70	60
Δn_Γ	5×10^{-4}	7×10^{-4}	3×10^{-4}	3×10^{-4}
A	7.5×10^{-3}	1.5×10^{-3}	3.0×10^{-3}	2.7×10^{-3}
P	7.5×10^{-2}	7.4×10^{-2}	5.2×10^{-2}	4.6×10^{-2}
ϕ_a	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$
ϕ_P	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$
Δn_P	3×10^{-4}	3×10^{-4}	2×10^{-4}	2×10^{-4}

Table1.TBC measurement results for different kind of samples.

For all samples the grating is essentially a phase grating with a spatial phase shift of π/2.

The observed behaviour (phase shift equal to π/2) is similar to the one known in photorefractive media where the photoinduced index change occurs by diffusion of the photocarriers without externally applied electric field [7].

As can be deduced by table 1, we observe also the presence of weaker amplitude grating. The results of the spatial phase shift of these amplitude gratings show that they are shifted by π/2 respect to the intensity pattern, as the phase grating. This result can be explained if we suppose that the dichroic dye can reorient along the director orientation by the same internal field, producing a small modulation of the absorption having the same spatial shift. The values of Δn calculated by the results of TBC gain

(Δn_Γ) and the results of the translation technique (Δn_P), reported in the table 1 agree within the experimental error.

In conclusion these experimental results support our hypothesis of the photorefractive effect occurrence.

PHOTOCURRENT MEASUREMENTS: RESULTS AND DISCUSSION.

In order to provide an additional evidence of the photorefractive origin of the optical storage effect observed in our materials, photocurrent measurements have been performed.

These kind of measurements have the following aims: to find out whether a non-uniform longitudinal illumination may originate a photocurrent by a charge diffusion process and to characterise photocharges generation and transport.

The experimental set up is sketched in fig.1, the cell is connected to a picoammeter (model 486 Keithley) and is illuminated by a cw Ar^+ laser beam (λ=514.5nm) that impinges at normal incidence. The picoammeter output signal is acquired and analysed by a digitising oscilloscope (Tektronix TDS 784A). The photoinduced current measurements are made only in one kind of sample, in particular the one made with epoxy resin, E7 liquid crystal and D37 dye.

A gradient of the intensity along the propagation direction of the light, as shown in fig.1, is produced by the absorption of the dye at the laser wavelength; the measured absorption coefficient at λ=514.5nm is $80cm^{-1}$.

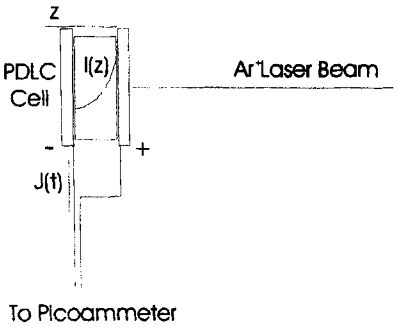

Figure 1. Experimental set-up to measure the photocurrent.

This gradient enables the investigation of charge photogeneration and diffusion by means of photocurrent detection. The dark-state resistance of the samples was about 5MΩ value.

Figures 2 show the time dependence of the current when the PDLC (fig.2b) sample is illuminated by a 74W/cm^2 intensity step (fig.2a). The current in fig.2 shows a sharp peak at the beginning of the irradiation, with a rise time of about 2-3s, followed by a slow depletion (tenths of seconds) with the inducing laser beam still present, until the measured photocurrent become negligible.

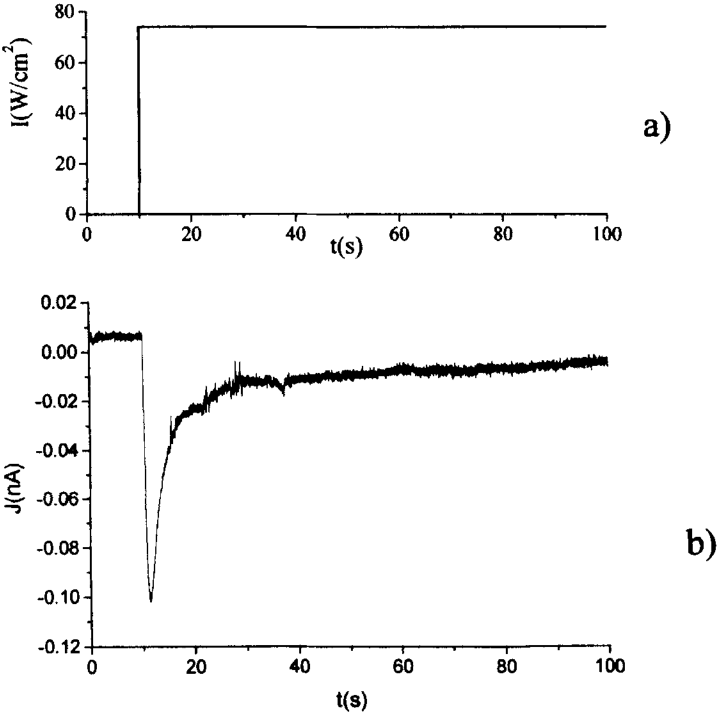

Figure 2. Time dependence of the photocurrent for a PDLC sample (b) when illuminated by a 74W/cm^2 temporal intensity step (a).

In fig.3 we present the peak current values versus the incident laser beam intensity.

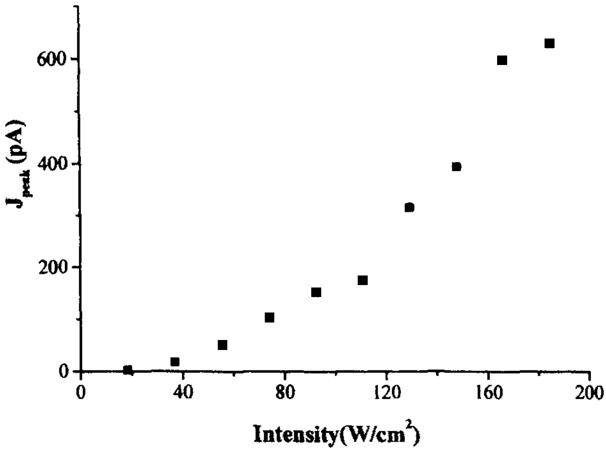

Figure 3. Peak current values versus the incident laser beam intensity for PDLC samples.

Numerical fit of the photocurrent peak value versus the intensity reveals a clear quadratic behaviour of this dependence.

In order to investigate the current amplitude signal during the irradiation of the sample by a chopped Ar^+ laser beam, we report in fig.4 the time evolution of the synchronous signal for different chopping frequencies, measured by using the set-up sketched in the fig.4 inset.

The photocurrent amplitude modulation shows a cut-off frequency at about 100 Hz, which indicates a characteristic response time higher than 10 ms for the diffusion process over the cell thickness.

During the photocurrent measurements other observations, described below, allowed us to get additional information about the process. A sequential illuminations onto the same region show a peak current reduction that is more evident when the time between

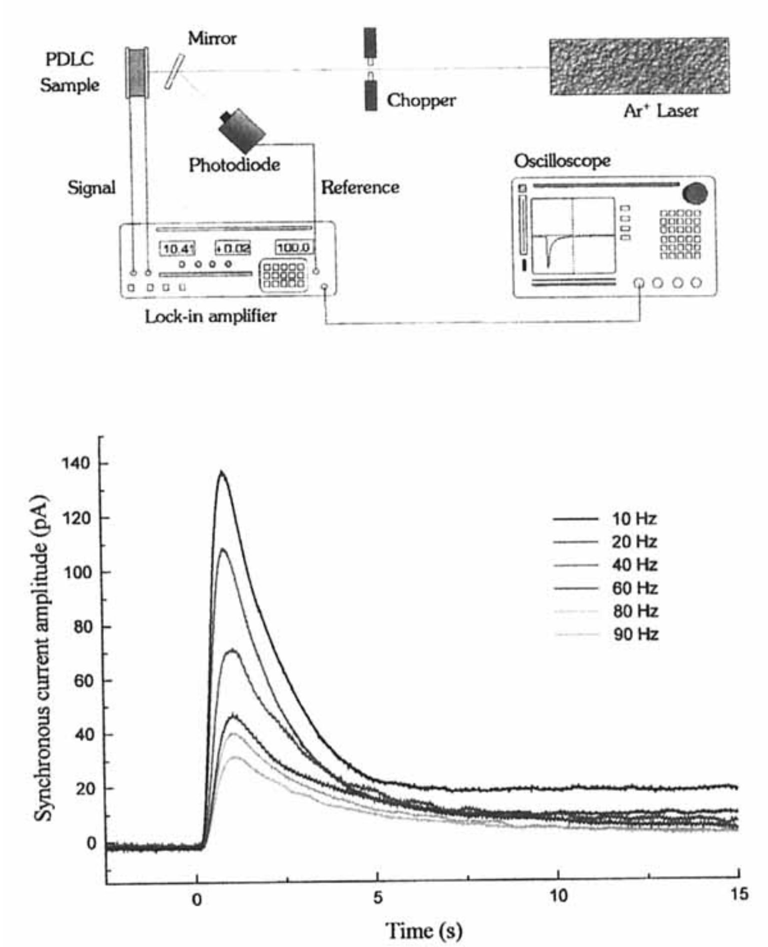

Figure 4. Photocurrent time dependence for different light modulation and experimental set-up.

two exposures become shorter. Beside the presence of a photovoltage detected at the sample electrodes immediately after the illumination, this observations indicates that as a result of the laser irradiation, the charge diffusion due to the concentration gradient gives rise to an internal electric field in the direction of the illumination. Since the current becomes negligible after few tenths of seconds, the current reduction seems to be due to processes leading to the depletion of the photogenerated carriers.

The observed sign of the current means that the current direction coincides with the diffusion flux, which is due to the intensity gradient consequent to the laser beam absorption. This is certainly the only reason of the current rise, since the medium itself is nearly isotropic and, at any rate, centrosymmetric. Thus we conclude that the sign of mobile carriers is positive. The estimations of the carrier density (n^+) from experimental current values across the sample provide $n^+ \approx 10^{17} cm^{-3}$ (by given value of diffusion coefficient $D \approx 10^{-7}$ cm^2/s, typical for moderately crosslinked polymers). Meanwhile, the concentration of dye dopant (N) is 0.1% by weight, which corresponds to 2×10^{19}molecules·cm^{-3}.

Some features mentioned above suggest that possible processes involved can be sketched in the following way:

$$\begin{tikzcd}
 & & & d \\
d \arrow[r, leftrightarrow, "h\nu_0"] & d^* \arrow[r] & d^*_T \arrow[ru] \arrow[rd, "h\nu_0"'] & \\
 & & & d^- + p^+
\end{tikzcd}$$

The sign of the detected current indicates that the carriers involved could be positive charge (probably holes). The dye molecules (d) are excited by the illumination in a long living triplet state (d^*_T), and negative immobile ions of dye are produced. The negative sign of the latter is just conventional for dyes, usually having highly electronegative halogen or oxygen atoms in the central part of the molecule.

Therefore the carriers are originated through excitation of already excited long-living triplet state, in agreement with the quadratic dependence of the current peak versus the intensity, as shows in fig.3. In fact within the above scheme the concentration of the excited molecules is $d^*_T \propto N \cdot I$, where I is the local intensity of light. As a consequence the rate of growth of positive carriers will be $w_c = \alpha N I^2$, where α represents a combination of rate constant (absorption cross sections and quantum yields for light induced ones) of elementary stages depicted in the above scheme.

The rather high value of the n^+/N ratio estimated suggests the dye depletion as possible reason for the current decrease after the peak. Moreover the relaxation to zero supports that this depletion can occur via trapping by long-lifetime traps (neutral molecules), which prevents "recycling" of the dye molecules, i.e. recombination of negative immobile ions of the dye.

CONCLUSIONS

In conclusion the reported results confirm the presence of the photorefractive effect in the optical storage observed in dye doped PDLC.

The first investigation supports the already demonstrated nonlocality of the effect by means of the characterisation of the holographic grating produced in different kind of samples.

In the last section we show that a non-uniform longitudinal illumination may give rise to a photocurrent due to a charge diffusion process and a photovoltage at the sample boundaries.

The mobile carriers appeared to be of positive sign and their concentration depleting to zero after the initial rise. The amplitude of the peak current appears to be proportional to the square of the illumination intensity. A qualitative discussion of the obtained results and a scheme of the involved processes are reported.

These results show that our materials exhibit properties as photoinduced charge generation, transport and trapping, necessary for the photorefractive effect. The electro-optic effect involved in this case is the usual nematic liquid crystal director orientation induced by the light-induced electric field.

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