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Nano-droplet formation in polymer dispersed liquid crystals

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In this work we analyse the fabrication of Polymer Dispersed Liquid Crystals (PDLCs) using SU8-2002-2007 photoresist and 5CB and E7 Liquid Crystals. Also we report the nonlinear optical behaviour for these materials and for Polymer Dispersed Liquid Crystals with a Twisted Cell (T-PDLC). We found that depending of several parameters, the droplets size varies from nano to micro dimensions. We report for first time, to our best knowledge, the synthesis of a SU8 Polymer Dispersed Liquid Crystal (PDLC) by using the polymer SU8 photoresist and liquid crystals (LC) and also the nonlinear behaviour of T-PDLC. We have characterized the droplets formation from nano to micron size depending of the different variables in the synthesis. We have used this PDLC in microfabrication as planar waveguides of different thickness over Si wafers. Our results also show that PDLCs present low NL optical Kerr coefficient (n_2 about 10^{-9} cm^2/W) and that it is three orders of magnitude larger in T-PDLC. Nevertheless, the fabrication processes of T-PDLCs make impossible their use in microfabrication.

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1 Introduction Liquid crystals (LCs) were discovered more than hundred years ago [1], since then, they have proved to be fascinating materials that often claimed to be a new state of the matter [2]. Their most eye-catching property of these materials is their colourfully dependence. Therein, nowadays they are widely used in displays based on their molecule alignment property. Their temperature sensitivity is another significant characteristic. On the other hand, a polymer is a large molecule composed of identical structural units (monomers), typically bonded by a covalent chemical. The polymerization reaction, required to produce the polymer from the monomer, often requires a short initiator that might be the addition of a chemical initiator or the exposition to high energy UV photons (light). They have interesting mechanical properties, because they combine resistance and flexibility. Both polymers and liquid crystals (LCs) belong to a class of "condensed matter", sometimes called "complex fluids" [3]. Fergason in 1984 [4] introduced a new class of composite materials constituted by small order of magnitude (0.1-100 μm) droplets embedded in a polymeric film. The nowadays term for these kinds of materials is Polymer Dispersed Liquid Crystals (PDLCs). These composite materials are a simply mixture between a polymer and a liquid crystal. The typical aspect of a PDLC, observed by using an optical microscope, is shown in Fig. 1.

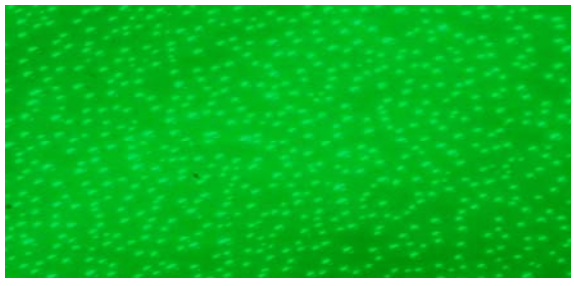

Figure 1 Typical droplet formation in a PDLC. This image was obtained from a 100× optical microscope with an average droplets size of 1 micron.

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In fact, depending on the components percentage, the results are quite distinctive. PDLCs is one the two extremes while Polymer Stabilized Liquid Crystals (PSLCs) are on the other one. PDLCs are characterized by a large percentage of polymer, or polymer network (usually 30-40 wt%), within which the liquid crystal droplets are dispersed in a composite structure. The properties of these composite systems are largely governed by surface interfaces, between the polymer and the liquid crystal, and behave quite different from the liquid crystal on its own. On the other hand PSLCs (also known as gel) have a relatively small amount of polymer (3-8 wt%), which is primarily used for stabilization. In these systems the electro-optic behaviour of the LC is not influenced significantly whereas the mechanical strength is highly increased. These PSLC cells exhibit an anisotropic light behaviour and therein their potential for reflecting displays and telecom applications. Most PDLC and PSLC systems studied to date involve nematic or cholesteric liquid crystals.

The PDLC Droplets size depends on several variables and size parameters, most of them considered because their physical effect on dispersion. Droplets size is sensitive to polymer type, polymer percentage and curing conditions such as temperature, UV light intensity and time exposure. The size range is from micron to nano dimensions and their shape uniformity and density is a problem that we intend to explore in the future.

PDLC cell does not need surface alignment. These micron-sized droplets scatter visible light and this scattering is independent of the polarization. In the high polymer concentration regime (60-70 wt%), the nanoscale holographic PDLC (HPDLC) droplets are formed [5,6]. Since the droplet size is smaller than the visible wavelength, HPDLC cell does not scatter light. Its response time is faster (aprox 200 μs) and the required LC droplets reorientation voltage is a relatively high electric field (20 $V_{rms}/\mu m$). Other characteristics, such as the the droplets shape and threshold voltaje has been studied.

Although, Liquid Crystals are mainly used in displays, because of the easy alignment of their molecules with an external electric field, they also show interesting and high optical non-linear properties. The first papers on this topic dealt with the characterization and explanation of the the nonlinear behaviour of the different types of liquid crystals [7,8]. However the most recent works dealt with specific nonlinear effects such as Self-focusing [9,10], spatial solitons or nematicons [11] or pattern formation [12], among others. Nevertheless, these nonlinear effects are not exclusive of the pure liquid crystals. They have also been reported in dye-doped liquid crystals [13] and more recently in Polymer Dispersed Liquid Crystals (PDLC) [14-16].

PDLCs have been fabricated using different kind of polymers and liquid crystals. Nevertheless, to the best of the authors' knowledge, the use of SU8 2002-2007 to fabricate PDLCs has not yet been investigated. The use of the photoresist SU8 is not trivial but its widespread use in microfabrication provides a special relevance to the problem. Therefore, It is an attractive idea to explore how the PDLCs nonlinear optical phenomena could be carried out into the microsensors and microdevices realm. In this paper, we characterize the PDLCs synthesis by using SU8 photoresist with 5CB and E7 liquid crystals. They could be used in the microfabrication processes and preliminary results for its nonlinear optical properties characterization, by the well know Z-Scan technique, is shown. A more thorough PDLCs Nonlinear characterizaction will be published elsewhere. We include in this paper the nonlinear optical characterization of a Polymer Dispersed Liquid Crystal confined to a 90° Twisted cell (T-PDLC) [17].

2 Materials synthesis In this section, we will describe the general steps we had carried out to synthesize the materials.

2.1 SU8 polymer dispersed liquid crystals The SU8 2000 is a high index contrast, epoxy-based photoresist. SU-8 has interesting properties that makes it quite an attractive material for a wide range of applications including micro-machining, micro-optics, micro-fluidity and packaging. It is highly transparent to wavelengths larger than 600 nm. It shows heat resistance to temperature higher than 200 °C and it is chemically and mechanically stable. SU-8 exhibits a huge potential for micro-technologies because it can be spin coated to thickness ranging from a few microns to a millimeter and produces very high aspect ratios (1:20).

We are interested in the fabrication of planar waveguides on a Si substrate and PDLCs on a glass substrate. Our objective is to work on light propagation and on Z-Scan experimental setups, but their potential is much wider. For planar waveguides, we numerically determined the thickness of the PDLC, to be deposited on the substrate, Fig. 2.

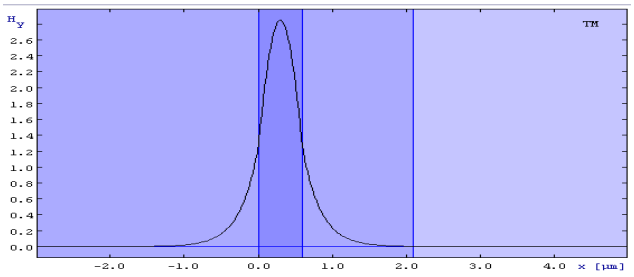

Figure 2 Numerical determination of PDLC thickness on a Si substrate.

Once the thickness was characterized, we selected the type of SU8; SU8-2002 for 2 microns thickness, SU8-2005 for 7-4 microns thickness and SU8-2007 for 14-7 microns thickness respectively. These values were obtained from the fabricant recipe [18], nevertheless, we have to consider that the predicted thickness layer may change because of the mixing of the SU8 and the liquid crystals.

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In order to fabricate the PDLCs, the liquid crystal was mixed into the SU8 polymer directly. In order to fully disperse it, we sonicated the mixture during 30 minutes. The LCs concentration varied from 15% to 40% wt. The mixture was spin coated on a clean 10x10 mm^2 Si substrate. Previously, we had deposited 2 μm SiO_2 layer on the silica wafer by using PCVD. A 2-15-μm -thick layer was spin coated using an experimentally determined curve of thickness versus spin speed. The coated film was then prebaked to evaporate the solvent. The prepared film was exposed to a high UV energy lamp for 2-4 minutes (about 200 mW/cm^2). The UV exposure creates acid radicals, which act as catalyst for the polymerization. Following the UV exposure, the film was postbaked. In this post exposure baking step the crosslinking of the polymer takes place. The layer thickness is the result of several variables such as; polymer-LC mix percentage, polymer density, spin speed and time duration of the spin step. We characterized the samples thickness using different methods, such as SEM images, as can be seen in Fig. 3.

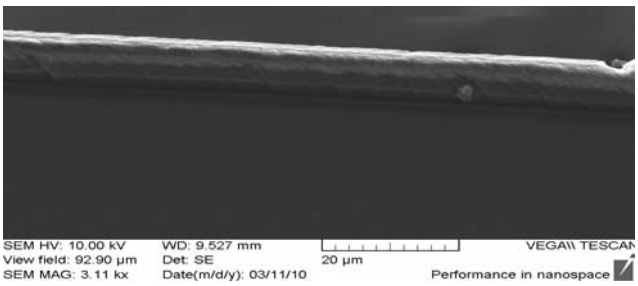

Figure 3 SEM image of a PDLC fabricated with a mixture of 5CB LC and SU8 photoresist deposited on a Si wafer as substrate.

In PDLCs, the droplets size becomes quite an important issue, because it will result in light dispersion if the size of the droplets is comparable with the wavelength. We have found that size droplets have dependence on the polymer cure time and on the UV intensity exposition, among others. Figure 4 shows an image obtained from a 100× optical microscope where we can observe a wide range of droplets size in the same sample (the scale is in microns).

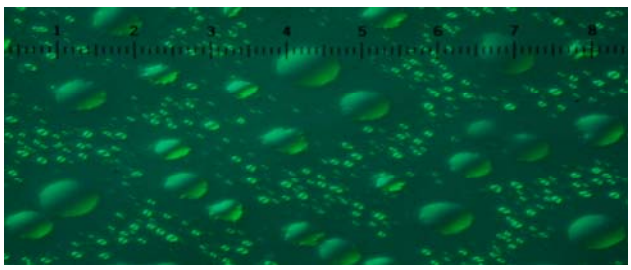

Figure 4 Image obtained from a optical microscope using 100× objective. Different droplets size are observed, where the scale represents 1 micron per line. PDLC was deposited on a Si wafer.

In this work, PDLC was deposited on 2 different substrates; Si wafer and glass. The main goal of this work was to study the possibility of using PDLC on micro-devices and this require Si wafers. We need to obtain the NL optical characteristic of the PDLCs material and therein the use of the Z-scan technique. For this reason we have made some samples using glass as a substrate, Fig. 5.

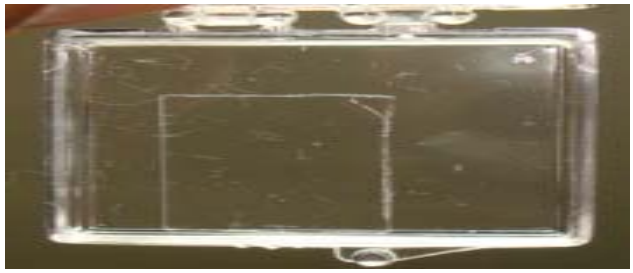

Figure 5 A transparent plastic container with a PDLC sample deposited on a glass substrate (small rectangle).

2.2 Polymer dispersed liquid crystals in a twisted cell Unlike the traditional PDLC cell, polyimide-buffed substrates are rubbed in orthogonal directions, similar to a 90° twisted nematic cell. Due to the larger refractive index mismatch, the T-PDLC not only preserves the advantage of polarization independence but also exhibits a higher light scattering efficiency.

In order to fabricate the samples, we mixed UV-curable monomer NOA65 in a nematic LC host (E48, $\Delta n = 0.231$ at $\lambda = 632.8$ nm with a nonlinearity of $n_2 \approx 1.49 \times 10^{-7}$). The concentration of NOA65 is in the 15%-50% range. The LC/monomer mixture was injected into an empty 90° twisted cell in the isotropic state. The pre-tilt angle of the LC cell is; 3° and the cell gaps are 8 microns. For comparison, a conventional PDLC cell, i.e. the indium-tin-oxide (ITO) glass substrates without alignment layer, was also prepared under the same conditions ($d = 8$ μm). In our experiments, the UV exposure intensity is $I = 60$ mW/cm^2 and the curing time for both cells is 15 minutes at $T = 20$ °C. Figure 6 shows a sample fabricated with this process.

Figure 6 An 8 μm thick polymer dispersed liquid crystal in a twisted cell (T-PDLC) sample next to a pen as a size reference.

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3 Experiments and results Once the different samples were fabricated, we implemented different experimental setups, in order to obtain the nonlinear optical characterization.

3.1 The Z-scan technique The basic experimental setup for the Z-scan technique is shown in Fig. 7. In our case, it was implemented by using a nonpolarized 800 mW Ti:Sa laser beam. The direction and the power of the incident polarization to the sample were controlled by means of two linear polarizers mounted on a rotatory stage. The polarized laser beam was then focused on the sample by using a positive lens (f = 5 cm). The sample was attached to a translation stage of 4.5 cm of travel distance. A large area Si-photodetector was located at a distance L = 1 m, much larger than the Rayleigh distance (z_0 = 3 mm) from the focusing lens. A 1mm diameter aperture was placed in front of the detector to measure the on-axis intensity changes. A beam splitter is located after the sample; it projects the beam to a second large area Si-photodetector without aperture in order to measure the non linear absorption. A third photodetector registers the input variations intensity to the reference signal. All three photodetectors signals were registered with a digital oscilloscope and recorded on a computer.

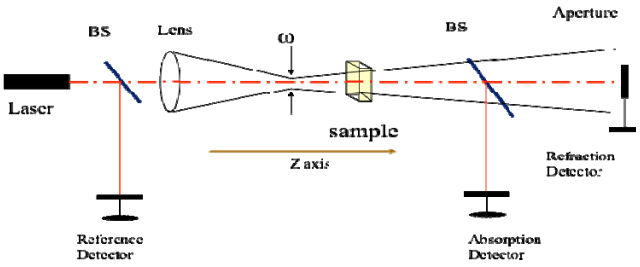

Figure 7 Z-scan basic experimental setup.

The Z-scan experiments were done for several samples, studying a wide range of parameters variations such as; LC wt percentage, UV intensity exposure, UV time exposure and type of LC used. Figure 8 plots a result obtained for SU8-2007 and 5CB LC at 33% wt on glass. The sample was 10 microns thick and the laser intensity was 20 mW. The behaviour is a focusing nonlinearity.

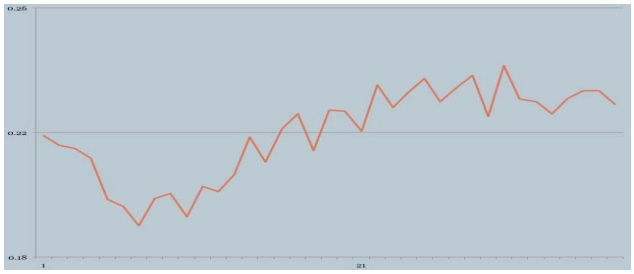

Figure 8 Positive nonlinear behaviour of PDLC for SU8 2007-5CB LC mix.

3.2 T-PDLC Z-scan The nonlinear responses on Polymer Dispersed Liquid Crystals on a Twisted Cell (T-PDLC) are also measured by the Z-scan technique. In this case, we used the same experimental setup than that for the PDLC. Figure 9 plots the result obtained for a T-PDLC for the nonlinear refraction index (close aperture), while Fig. 10 shows the corresponding nonlinear absorption (open aperture).

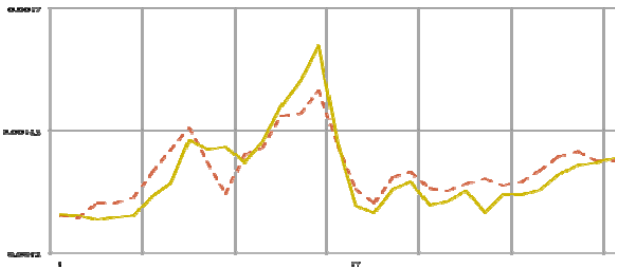

Figure 9 Close aperture Z-scan for a T-PDLC 8 microns thick sample. The dotted line is obtained by applying 20 Vrms.

We must remember than a T-PDLC requires rubbed twisted substrates. In our case, the front face has the same polarization than laser beam. Figure 9 shows a defocusing behaviour that is lightly modified when an AC voltage is applied to the sample. A Nonlinear absorption behaviour is also founded in the T-PDLC sample, Fig. 10.

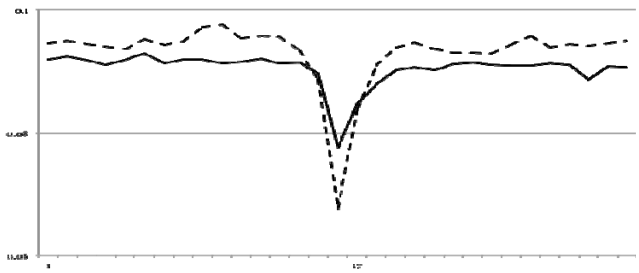

Figure 10 Open aperture Z-scan for a T-PDLC 8 microns thick sample. The dotted line were obtained by applying 20 Vrms.

3.3 Discussion The optical Kerr coefficient can be determined from the corresponding peak to valley heights of the Z-scan curve, by using equation [19]

$$\Delta T_{p\text{-}v} \cong (0.406)(1-S)^{0.25}\Delta\Phi_0 \qquad (1)$$

where $S = 1-\exp(1-2r_a^2/w_a^2)$; r_a is the linear radius of the iris, and w_a is the beam radius at the iris in the linear region. The phase distortion $\Delta\Phi_0$, is defined as

$$\Delta\Phi_0 = \frac{2\pi}{\lambda}\Delta n_o \frac{1-\exp(-\alpha_o d)}{\alpha_o d} \qquad (2)$$

where λ is the laser wavelength; α is the linear absorption coefficient and *d* is the thickness of the sample. The on fo-

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cus and on axis refraction index change Δn_o is linearly related to the optical Kerr coefficient n_2 by

$$\Delta n_o = n_2 I_o \tag{3}$$

where I_o is the intensity of the laser beam at the focal point.

The nonlinear refraction index and absorption coefficent were determined by our experimental setup. The results obtained in the Z-scan experiment were consistent with the reported no optical Kerr coefficient of pure PDLC materials [16]: the Kerr coefficient for the PDLC samples is $n_2 \approx 3.45x10^{-9}\,\mathrm{cm}^2/\mathrm{W}$, while the T-PDLC Kerr coefficient was $n_2 \approx 1.12x10^{-6}\ \mathrm{cm}^2/\mathrm{W}$. These results were obtained for not oriented droplets; therefore we should expect a random orientation. We will publish elsewhere the oriented droplets results.

The open aperture Z-scan technique is used to calculate the nonlinear absorption of the sample. The graphs obtained from the Z-scan also determine the existence of the NL absorption, for the PDLC and T-PDLC cases. The T-PDLC shows an applied voltage dependence that, however, it is also small compared with those of pure LC or dye doped LC materials.

3.4 Planar waveguide The goal of this section is to analyze the propagation of the light through a waveguide. In particular, we are interested in the self-focusing effect. We cut the sample input and output faces sides and we launch a laser beam into the planar waveguide, fabricated in Section 2.1, by using a very simple experimental setup. As we can see from Fig. 11 no self-focusing was observed under a wide range of beam intensities, even for samples that showed focusing NL behavior, i.e. Fig. 8.

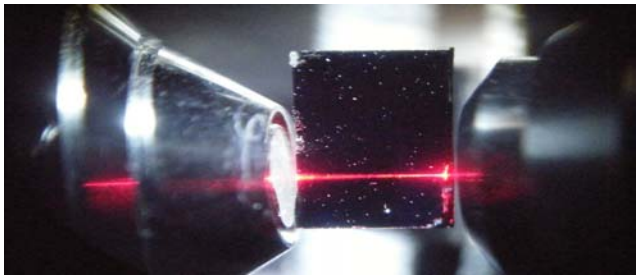

Figure 11 Propagation experiment in a PDLC planar waveguide. The Light input is at the right hand side. The PDLC characteristics are the same than in Fig. 7 except for the substrate, which is a Si wafer, in this case, with a 2 μm SiO_2 layer.

4 Conclusions This paper introduces the possibility of fabricating a new type of polymer dispersed liquid crystal (PDLC). These materials were deposited as thin layers on two different substrates; Si wafers and glass. The aim of manufacturing the first kind of samples is their potential use in microfabrication, while the second kind is meant for different experimental photonics use. We report the nonlinear optical behaviour of both materials; the new PDLC and a Polymer Dispersed Liquid Crystal with Twisted Cell (T-PDLC), previously reported [17]. Particularly, we were interested to determine the optical Kerr coefficient n_2 and for that purpose we used the Z-scan technique.

Depending on the different physical parameters, the liquid crystal droplets in PDLC varies from nano-sized to micro-sized. For the T-PDLC case; the authors reported nano-sized droplets. In either cases, we worked with droplets size sufficiently small (less than wavelength) and then the scattering of light from these droplets can be ignored. Experimental results indicate that the non oriented PDLC film have a small optical Kerr constant, n_2. We found that n_2 is in the range of $n_2 \approx 3.45x10^{-9}\,\mathrm{cm}^2/\mathrm{W}$, this very low value agrees with previous reports that found zero Kerr coefficient value for pure PDLCs [16]. The optical Kerr constant n_2 of the T-PDLC film was three orders of magnitude larger, but still very low for practical applications. We have to consider that T-PDLCs also require some specific conditions in their fabrication, which make impossible their use in microfabrication. In order to fabricate the PDLCs, we used 2 different kind of Liquid Crystals (5CB and E7) mixed with SU8 photoresist, which to our best knowledge was not reported previously. These was proposed because is use in processes. Even the small the Kerr coefficient found for the non-oriented LC composite of this microfabrication material, we strongly believe that SU8 and LC mix is suitable for practical optical nonlinear applications in microfabrication. The inclusion of dyes into the PDLC or new schemes can increase in several orders of magnitude the NL coefficient, as it had been reported previously in others PDLC materials [17].

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