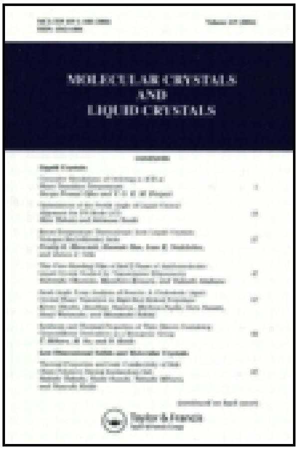

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Electro-optical response of thiol-ene based PDLC

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ELECTRO-OPTICAL RESPONSE OF THIOL-ENE BASED PDLC

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PDLC with micrometer or submicrometer sized droplets have been demonstrated using acrylate syrup as polymer precursor. In this paper the ability of thiol-ene monomere to lead to such PDLC is investigated. Electro-optic response of bulk composite material is measured by an interferometric setup and compared to theoretical model. A morphological study has shown a specific response of submicrometer PDLC. UV laser (355 nm) has been used to record gratings. The weakness of diffractive efficiency seems to show an intrinsic limitation of nanosized PDLC for low spatial frequencies.

Keywords: grating; nanodroplet; PDLC

INTRODUCTION

In polymer-dispersed liquid crystal (PDLC), orientation of liquid crystal clusters is controlled by an external electric field which allows to match the liquid crystal and polymer refractive indexes. When liquid crystal droplet diameters are in the range of a micrometer, devices switch from light scattering to transparent states providing indices are matched. Reducing the size of liquid crystal droplets to sub-wavelength size, leads to isotropic,

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non scattering films with a remaining electro optic coefficient and a polarization insensitivity.

Some papers [1–5] have shown that PDLC with submicrometer sized droplets could be recorded using liquid crystal of the BL series (MERCK) and acrylate monomer. It has been shown in a previous paper [6] that PDLC of micrometer sized droplets could be realized also with thiol-ene monomer and liquid crystal of the BL serie. In this paper we investigate the electro optic behavior of such PDLC when the droplet size is decreased to a sub wavelength scale. Electro-optic response and morphology of homogeneous films are characterized. We show that, under some conditions, holographic grating can be recorded. Measurements of the diffractive efficiency leads to the spatial index variation and can be compared to results obtained on homogeneous films.

FABRICATION

PDLC fabrication using Polymerization Induced Phase Separation (PIPS) is based on two principal chemical monomer series. First, acrylate syrup, including photosensitizer such as Rose Bengal that absorbs green radiations. These films are easy to record using an Ar or a frequency doubled Nd:YAG laser. This system leads to submicrometer sized droplets provided a surfactant is added in order to improve phase separation. Electro-optical devices have been demonstrated [2,7] using this mixture. One of the main issues is reported by Sutherland *et al.* [11] and concerns material ageing which seems to be caused by the surfactant.

Second, thiol-ene syrup, where the curing process is based on free-radical addition of a thiol function on an alcene. The sulphur – hydrogen bond is naturally activated by UV light but coinitiators like Darocure are often added to increase the curing kinetic. Classical micrometric sized PDLC have already been realized with commercial mixture like the Norland series. We have used such a mixture (NOA81 70-w- %) with a typical nematic liquid crystal (BL 24 30-w- %). Films are cured under a UV metal vapor light in ITO coated cells. A IR filtered focalized beam with an intensity between 50 and 300 mW/cm^2 leads to submicrometer sized droplets. This result is coherent with the measurements made by Ren and Wu [8]. It should be noticed that the spectrum of the metal vapor light is broad. Thus, considering that the main active irradiations are in the UV range, a 1 mW/cm^2 tripled Nd:YAG (355 nm) laser beam leads to comparable morphologies.

Δn MEASUREMENT

The main issue to measure the refractive index variation of such layer is the weak optical path variation due to film thickness which is a the range of

30 μm and the electro-optical response in the range of $\Delta n = 10^{-2}$. Thus, optical path variation does not exceed 0.5 μm. Simoni *et al.* [9] used a Mach Zhender interferometer to get the index variation of composite material when an external electric field is applied. In our work, a Michelson interferometer (Fig. 1) allows a double path of the reading beam giving a double optical effect for a same sample thickness. As described on Figure 1, one of the two beams interfering on the CCD detector passes through the sample. A change of the optical path due to the electro-optic material's response leads to a spatial shift of the fringe pattern which is monitored by a photodiode. The CCD camera records simultaneously an ITO coated part of the sample and a non coated part. Doing so, even if the sample moves, the shift between the coated and the non coated part is only due to the electro-optic response of the PDLC. Since we measure an optical path, a good precision on index variation needs a good precision on thickness which is computed from the spectral response of a cavity formed by the ITO coating in the empty cell. Since the electric field may reach 20 V/μm between two 1 cm^2 ITO plane electrodes spaced of 25 μm, the compression of Norland81 film due to electrostatic effect can reach 40 nm leading to a refractive index measurement error of 5%. Introduction of silica spacers in the cell reduces significantly the electrostatic compression of the sample. Measuring the interferogram in both addressed

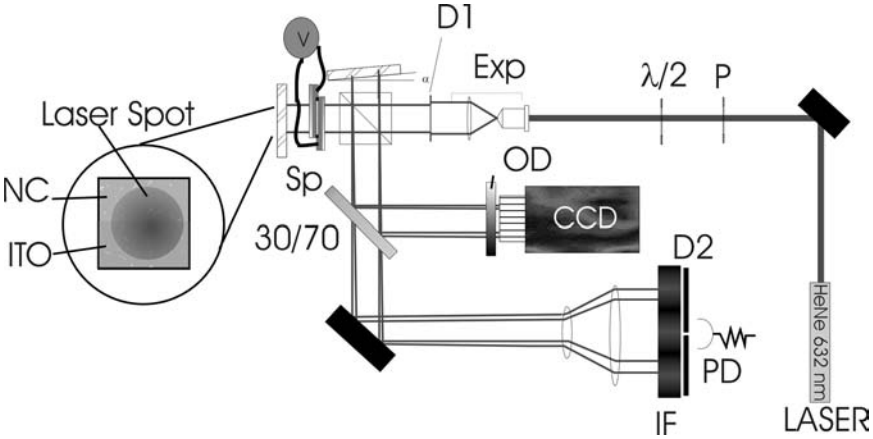

FIGURE 1 Experimental setup: In our Michelson interferometric setup, the laser beam is a non polarized, (P) a polarizer, (D1),(D2) are diaphragms, (Exp) is a beam expander. Interference fringes (IF) are monitored by a photodiode (PD). CCD camera is protected by an optical density (OD). On the schematic view of the sample (Sp) the laser spot crosses both the ITO coated part (ITO) and the non coated one (NC).

and non addressed part, make the measure insensitive to electrostatic effects, cuts off low frequencies vibrations and leads to increased accuracy on the measurement of Δn.

ANALYSIS & RESULTS

Measurement of Δn can be computed from CCD acquisition for each electric field and wavelength. In this paper, we only use an HeNe laser ($\lambda = 633\,\mathrm{nm}$) as indicated on Figure 1. Since liquid crystal orientation is sensitive to $\mathbf{E^2}$ where $\mathbf{E}$ is the electric field, only the rms value of the driving voltage must be taken into account. In our setup, the PDLC is addressed with a 1 kHz square wave. Figure 2 shows a typical record of a fringe shift $\Delta\phi$ linked to the variation of the refractive index by the relation.

$$\Delta n = \frac{\lambda \Delta\phi}{4\pi n e}$$

Where λ is reading wavelength, e the sample's thickness, n the mean refractive index.

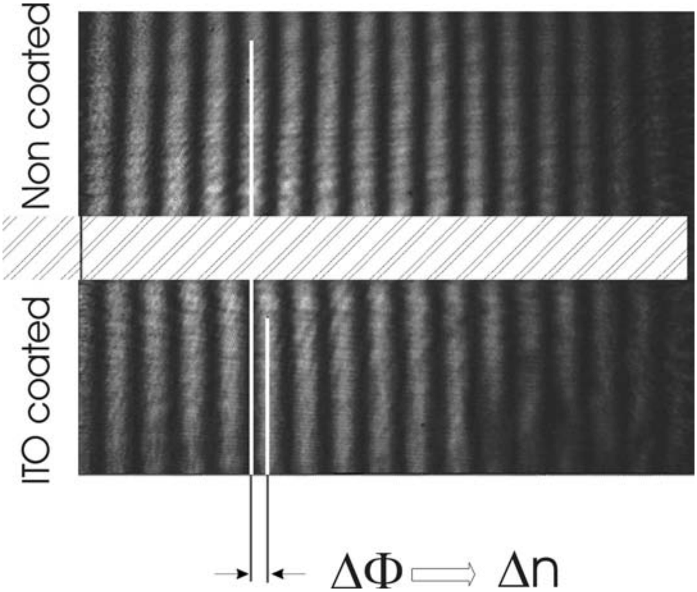

FIGURE 2 Typical view of CCD camera. The shift ΔΦ between the coated part and non coated one is due to the refractive index variation of the electro-optic composite material. Providing the sample thickness is known, index variation can be calculated.

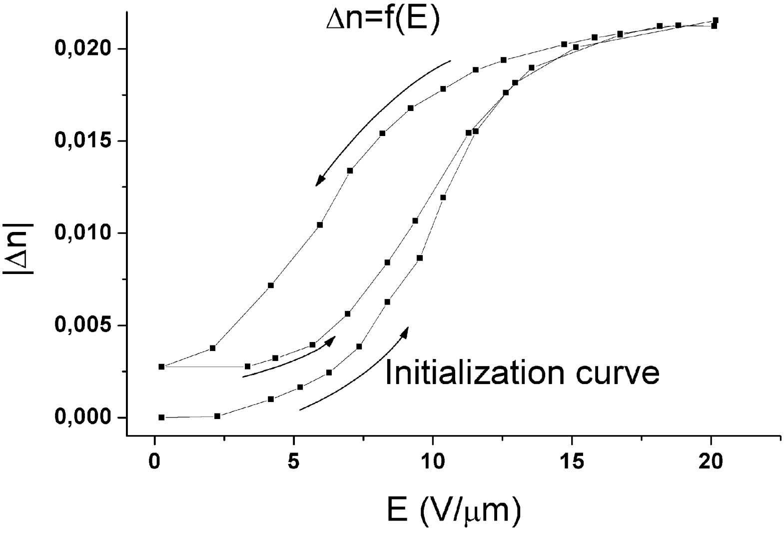

FIGURE 3 Electro-optic response of a bulk submicrometer sized PDLC. Initialization curve and hysteresis cycle are characteristic of such materials.

The first results on Figure 3 confirm the typical hysteresis effect observed on micrometer PDLC and the fact that the hysteresis cycle is stable only after a first ramp of applied voltage. The molecular orientation of liquid crystal molecules is invariant in the sample's plan whether an electric field is applied or not. So, theoretically, for a normal incidence beam no polarization effect should be observed. We have confirmed this insensitivity using 2 linearly polarized beams. As shown on Figure 4, no birefringence has been detected under a large range of voltage.

It is also interesting to compare the maximum measured variation of refractive index of the composite material $\Delta n_{\max}^{measured} = 0.019$ with the birefringence of pure liquid crystal $\Delta \mathrm{n} = \mathrm{n_e} - \mathrm{n_o} = 0.2042$. It can be considered that the droplet size is small compared to wavelength because no scattering is observed. This assumption is validated by the SEM microscopy Figure 5. Therefore the Maxwell Garnet theory of effective index can be applied. n_{Eff}, the mean index of the material can be calculated.

$$n_{Eff} = \sqrt{\chi_{Vol}^{CL} n_{CL}^2(\theta) + (1 - \chi_{Vol}^{CL}) n_p^2}$$

Where χ_{Vol}^{CL} is the volumic concentration of liquid crystal, n_p the polymer refractive index and $n_{CL}(\theta)$ the mean liquid crystal refractive index for a given orientation of molecules. When no voltage is applied on the sample (off stat), liquid crystal molecular orientation is isotropic so $n_{CL} = \frac{n_e + 2n_o}{3}$.

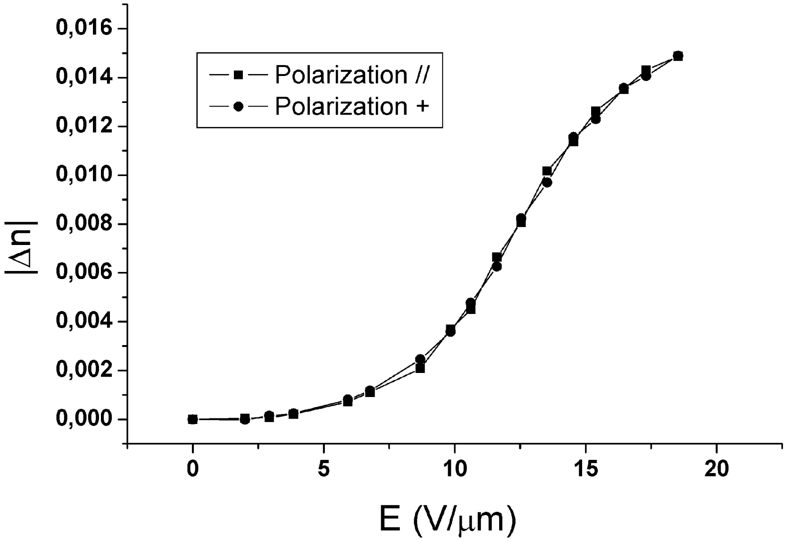

FIGURE 4 Symmetries of the liquid crystal molecules orientation what ever the external voltage is, leads to a polarization insensitive electro-optic response for bulk composite materials.

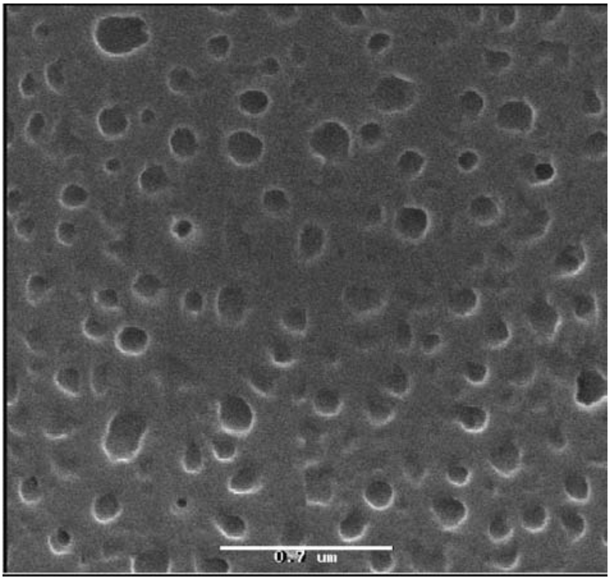

FIGURE 5 SEM microscopy of a bulk composite material. Droplets can be distinguished and their size measured. On this view droplet size is clearly below 100 nm and does not scatter visible light.

In the on state, the orientation is supposed to be parallel to the electric field so $n_{CL} = n_o$. If we assume that all liquid crystal molecules can rotate freely, the calculated variation of refractive index of the composite material is $\Delta n_{\max}^{theoretical} = 0.02$ which is very close to the measured value $\Delta n_{\max}^{measured} = 0.019$. Though it is commonly accepted that in PDLC the phase separation is usually not complete and that some liquid crystal remains in the matrix, the previous result shows that nearly all liquid crystal could be electrically oriented in this sub micrometer sized PDLC.

Lucchetti and Simoni [10] concluded for larger sized PDLC that the volume of droplet remains constant: the reduction of the droplet diameter would be compensated by an increase of the droplet density. We have carried on this study for diameter less than 100 nm and found (Fig. 6) that only 5% of the volume are filled by droplets containing typically 17% of the initial liquid crystal molecules. Taking into account that $\Delta n_{\max}^{theoretical} \approx \Delta n_{\max}^{measured}$, it seems that the liquid crystal molecules trapped in the solid matrix conserve a certain ability to be oriented when an external voltage is applied. As a conclusion it seems that for sub micrometer

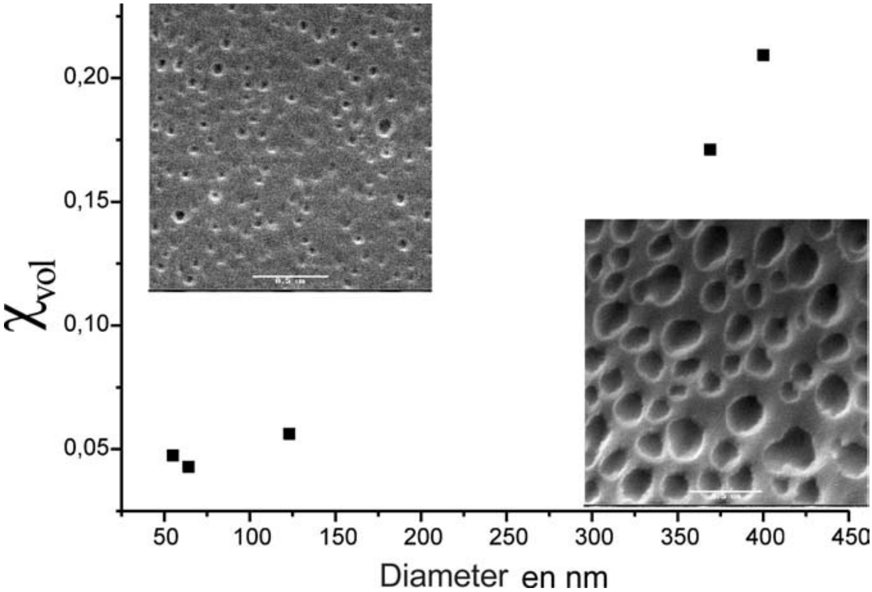

FIGURE 6 Volume fraction of LC in PDLC. Morphological analysis is performed using SEM microscopy. Droplet size and density can be measured and the volume fraction χ_{vol} can be computed. Bulk materials are cured with different droplet size by varying illumination intensity. It can be noticed that for a given sample droplet size distribution seems to be relatively homogeneous.

PDLC the electro-optic effect is not only due to droplets orientation but also to the one of the liquid crystal molecules dispersed in the matrix.

GRATINGS

As shown by Ren and Wu [8], droplet size is a function of light intensity used during the curing process. Therefore, gratings with various size of droplets can be recorded. Some devices have already been recorded using a typical two beam interference setup. In order to improve stability, a cell with initial syrup is sticked on an refractive index grating with a $\Lambda = 5\,\mu\text{m}$ µm step. A UV laser (355 nm) is focused on this device so that the two first diffracted orders (+1, −1) interfere in cell leading to a spatially modulated intensity. A SEM microscopy shows the recorded grating on Figure 7.

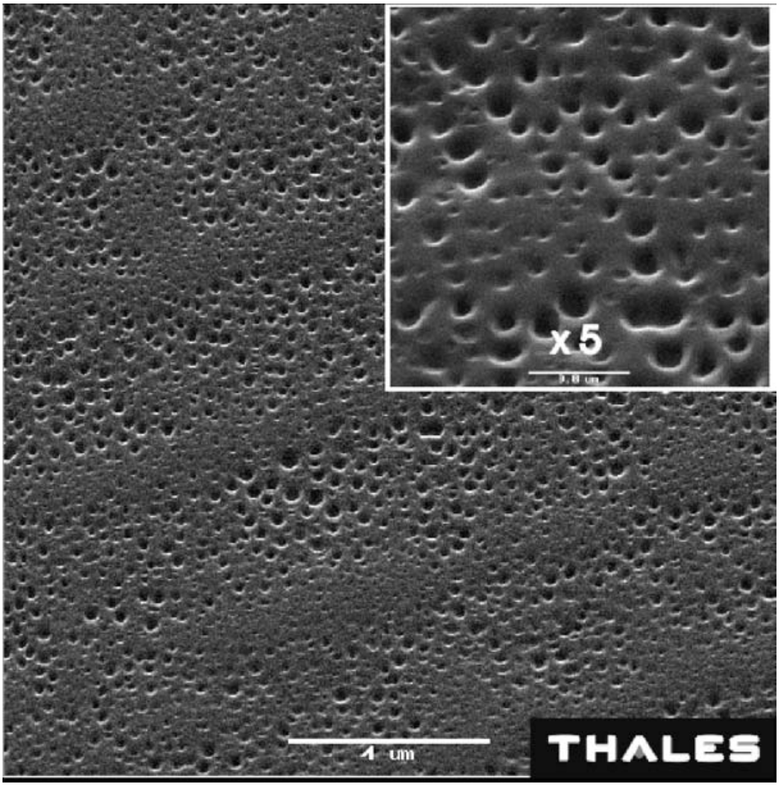

FIGURE 7 Grating Morphology. SEM microscopy shows spatial modulation of droplet size. Grating step is 5 µm. Direct measurements on picture must be corrected taking into account a sample tilt.

Morphology analysis allows the computation of the specific volumic fraction of droplet in each area. On the one hand, small droplet with a typical size of 120 nm leads to 5.5 – v-% of droplet and, on the other hand, big droplet with a typical size of 350 nm leads to 17.5 – v-% of droplet. Effective index has been calculated using Maxwell Garnet theory and leads to the same spatial variation of index $\Delta n = 0.004$ for both on and off state which is fortuitus. Theoretically, for a sinusoidal grating, such an index modulation leads to a diffraction efficiency of $\eta = 11\%$ for the first order. Experimentally, measurements of this efficiency confirms that Δn modulation is the same in the off state than in the on state although diffraction efficiency remains under 1%.

Considering the results on bulk materials, we can assume that for each area, liquid crystal is trapped either in droplet or in the polymer matrix. Liquid crystal droplet size is sub-wavelength throughout the sample in spite of size modulation shown on Figure 7. Therefore, the diffraction efficiency can not arise from transmission modulation. Then, the weak measured diffraction efficiency suggest that the liquid crystal concentration is nearly homogeneous on the sample surface. Crawford and Sutherland [2,4] reported diffraction efficiency as large as 90% in Bragg setup. Such a diffraction efficiency can only be reached if the refractive index contrast between liquid crystal and polymer domains is high, which implies that the diffusion length of the liquid crystal molecules is comparable to the grating step. Previous results legitimate the introduction of a "locality scale". In our case, low spatial frequency of the illumination pattern leads to a local response where the structure modulation is recorded but where the diffusion length is much smaller than the grating step forbidding high refractive index modulation. In our setup, light frequencies $f = 1/\Lambda = 200 = 200\ 000\,\mathrm{m}^{-1}$ is obviously larger than the cut off frequency of the system.

CONCLUSION

Nanosized PDLC devices based on acrylate syrup have been demonstrated. We have shown in this paper that thiol-ene syrup is also a good candidate for submicrometer structuring. Bulk composite materials can be cured up to 25 μm with refractive index variation up to $\Delta n = 0.02$. Morphological analysis and electro-optic measurement have shown that the liquid crystal induce the same variation of refractive index whether they are in droplet or in the solid matrix. Gratings have been recorded and show that spatial modulation of the droplet size is not sufficient to ensure a good diffractive efficiency in the case of submicrometer sized droplet. A phenomenological analysis of the diffusion process lead to the notion of "locality scale". Under a low cut off spatial frequency recording submicrometer PDLC is inefficient to achieve good diffraction efficiency. On the contrary, high spatial frequency leads to a non local response where liquid crystal diffusion allows high index modulation. This non local response seems to be the most promising set point. Further studies should be pursued in order to determine the highest recordable spatial frequency.

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