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A New Kind of Photo-Polymerisation Induced Diffraction Gratings in Liquid Crystalline Composite Materials

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Abstract In this paper we report on the first results of a new technique used to obtain good quality holographic diffraction gratings. This technique represents an improvement with respect to the traditional one, the so called polymerisation induced phase separation technique. Gratings are obtained by exposing the initial homogeneous mixture of liquid crystal and monomer molecules to the pattern produced by two interfering UV laser beams. The polymerisation process, which is photo-induced by this pattern, is thus spatially inhomogeneous: It leads to a redistribution of the mixture components and hence to the grating formation.

Keywords Nematic Mixtures; Gratings; PDLC.

INTRODUCTION

Since the first works of Sutherland et. al[1,2] the utilization of Polymer Dispersed Liquid Crystals (PDLC) for obtaining electrically switched diffraction/holographic devices became one of the main items of interest in the area of PDLC-based electro-optical devices. The reason of this interest lies in the possibility of obtaining good and cheap elements for commercial, electrically switchable, holographic devices[1,3,4]. In order to obtain gratings with a high diffraction efficiency and good optical qualities, it is necessary to obtain a sharp and uniform fringe morphology, avoiding the optical inhomogeneities which could be caused by the presence of nematic droplets of the same spatial scale of the fringe spacing. There are two ways of achieving such a result: The first one, utilized by other authors[1-4], consists in reducing the surface tension at the phase interface thus obtaining droplets of size much lower than the fringe spacing. This is just the conventional way for traditional UV curing by means of a spatially uniform radiation intensity; in this case no other intrinsic spatial scale exists but the minimal thermodynamically allowed droplet size. The second way exploits the possibility of obtaining gratings made by an alternation of continuous polymer and nematic stripes, instead of the usual alternation of polymer and PDLC stripes. Such a situation is certainly impossible in traditional PDLC curing by uniform radiation, but in case of curing by an interference pattern of nearly unit contrast (and hence of periodically inhomogeneous degree of polymerization), it
can be obtained under suitable experimental conditions. In this paper we show the main characteristics exhibited by preliminary samples of gratings of this kind.

EXPERIMENTAL

We have used the traditional acrylate-based pre-polymer system SAM-114, diluted in 5CB nematic liquid crystal (both components by Merck). These components are highly soluble in each other (initial weight concentrations of 5CB from zero to 95% appeared to be thermodynamically stable) and lead to a spatially uniform isotropic mixture. Samples were sandwiched between two ITO-coated glass slabs, the 8μm thickness being controlled by proper Mylar spacers. The mixture preparation and cell filling was just common, utilizing no oxygen prevention, and samples were filled and exposed right after the mixture preparation. It has to be noted that, nevertheless such acrylate

compositions are known in general to be oxygen-sensitive, our particular mixture revealed a quite satisfactory (about a month) shelf-life, with no special precautions but preventing a further exposition to UV radiation.

The optical setup for UV curing and diffraction efficiency measurements is presented in Fig.1.

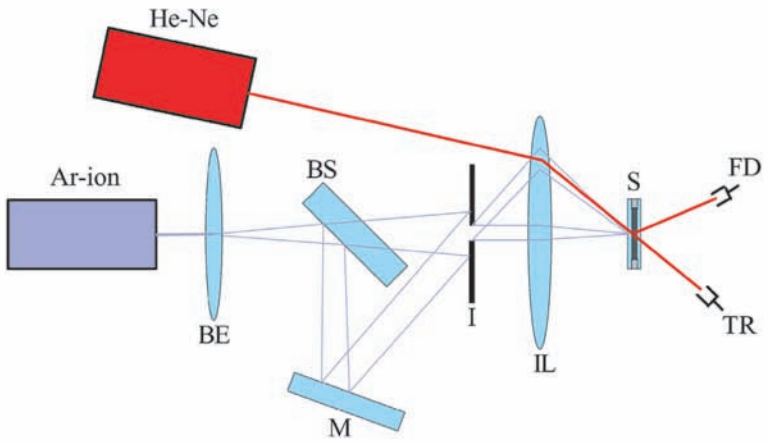

Figure 1. Optical setup for curing and diffraction efficiency measurement. Ar-ion, Argon Ion laser; He-Ne, Helium Neon Laser; BE, Beam Expander; BS, Two-mirror Beam Splitter; I, tunable aperture; IL, Imaging Lens; TR,FD, photo-detectors for transmitted and first-order diffracted beams detection.

A single transverse mode beam with s-type polarisation from an Ar-ion laser operating at the wavelength $\lambda_B = 0.33\mu m$ in the power range of 3-100mW (Coherent Innova 90C), is broadened by the beam expander BE up to about a 25mm diameter. It is then divided into two beams of nearly the same intensity ($I_1/I_2 = 0.95 \pm 0.02$) by the beam splitter BS. The two beams intersect in the plane of the tunable aperture I and provide an interference pattern of spatial period $\Lambda = 6.3\mu m$. The tunable aperture is used to cut off the wings of the laser beam intensity profile, so that, within the remaining aperture (2-5mm in diameter), the intensity is uniform with a 4-5% accuracy. In order to avoid Fresnel diffraction, the imaging lens IL produces an image of I at the sample entrance plain. The described setup enables us also to change the diameter of the cured spot without affecting the uniformity of the curing

intensity. The temporal evolution of the diffraction efficiency is measured using a slightly focused probe beam (spot diameter within the sample about 1mm) from a He-Ne laser (λ_R = 0.63μm) of about 1 mW power, which is s-polarized too. Both transmitted (zero order) and first order diffracted beam intensities are detected by photodiodes PD_T, PD_D and visualised at the oscilloscope. Everywhere below, the diffraction efficiency η_N of the N-order diffracted beam is measured by comparing its intensity to the initial transmitted intensity before curing, which is 0.89 of the incident one, due to reflections at the two external interfaces as well as at ITO coatings. The morphology of the obtained gratings is checked by a standard optical polarisation microscope with about 0.5μm resolution.

EXPERIMENTAL RESULTS

Mixtures cured by UV intensities in the range $I_B \approx 1\text{-}10 mW/cm^2$ revealed phase separation only for 5CB concentrations higher than N = 50%. Typical morphologies of the obtained gratings are presented in Fig.2.

Figure 2. Typical morphologies of UV recorded gratings. Nematic concentration is: a) N = 50% ; b) N = 65%; c) N = 90%.

Pictures have been taken with samples placed between crossed polarisers, whose axes are horizontal and vertical with respect to the picture. Here and further, oblique fringes denote therefore a uniform nematic alignment along the fringes, while vertical fringes indicate a stochastic alignment of the droplets director.

It can be seen that for low N values, close to the phase separation threshold, the nematic stripes are narrow (about 1,5μm) and

consist of a single row of droplets, whose director is aligned along the grating fringes. For N ≈ 65% the nematic-containing stripes are broadened up to 3-4μm, droplets being only partially aligned along the stripes (about 70% of total droplets, checked visually by means of a polarisation microscope, Fig. 2b). At higher concentrations (N ≈ 85%, Fig.2c), polymer stripes appear to be linked by nematic droplets; the whole picture appears to become stochastically anisotropic, and the only remaining modulation consists in a change of the average droplet size when going from "hot" fringes to "cold" ones. Such a morphological change is followed by a strong decrease of the diffraction efficiency of the grating, which has been observed in all this kind of experiments[5].

The temporal evolution of the diffraction efficiency η_1 during the curing process is shown in Fig. 3 for different values of the curing UV intensity. We point out that, in those mixtures in which the phase separation occurred during the curing process, the temporal evolution of η_1 shows a monotonous growth and reaches values close to $\eta_1 \approx 20\%$.

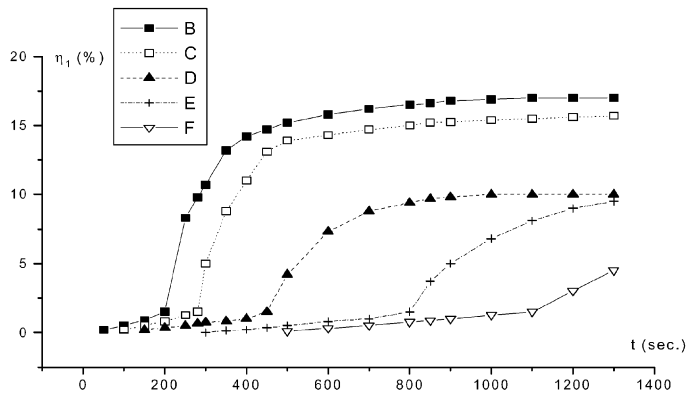

Figure 3. Temporal dependence of η_1 for N = 57.7 % at different values of the curing intensity I_B: B) I_B = 5mW/cm^2; C) I_B = 3mW/cm^2; D) I_B = 2mW/cm^2; E) I_B = 1mW/cm^2; F) I_B = 0,5mW/cm^2.

At this stage, we want to underline that in any case, even if we do not obtain a final phase-separation, a weak initial grating with about 1% diffraction efficiency is observed. Furthermore, in all cases in

which the phase separation does not take place, this weak grating (we call it "pre-grating"), if examined microscopically, appears as a quite isotropic phase grating with no visible evidence of distinct interfaces (Fig.4a). The evidence of a phase nature of this grating is brought by the fact that it is not visible at the microscope unless this one is slightly defocused from the layer plane, thus allowing the phase modulation to change into an amplitude one.

As for the long-term stability of the final phase-separated grating, the situation is the following. If the pre-syrup around the cured spot is additionally cured (by a UV lamp) within about half an hour after the curing of the grating itself, the final grating morphology appears to be stable at least within a month time scale. Otherwise, if the surrounding pre-syrup is left "raw", within few hours a degradation of the grating takes place, which starts from the spot edge (Fig.4b)

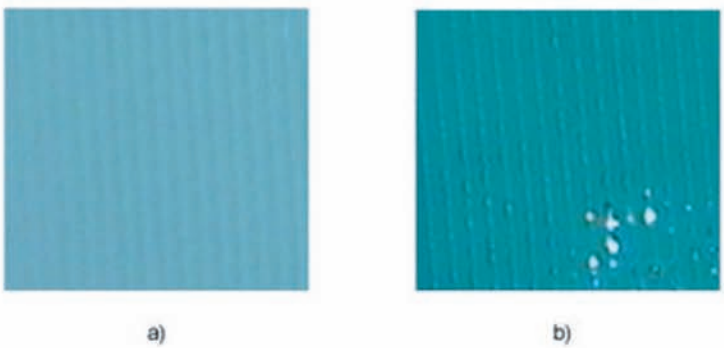

Figure 4. a) pre-grating (no polarisers, microscope slightly defocused); b) partially "dissolved" grating, polarisers partially de-crossed (70° between axes). In this case, some residual nematic droplets are visible.

Going back to Fig. 3, we notice a further feature in the temporal evolution of η_1: the phase separation, evidenced by a discontinuity in the derivative of the plots, always starts at the same breakdown value of η_1, which is about 1.5%. This value weakly depends upon the LC concentration (from 1% up to 1,7% in the range from 50 to 70%) but does not depend upon the curing intensity. Data concerning samples with a LC concentration N = 50% (presented in Fig.5) reveal an even more straightforward evidence of this feature: In the two cases in which

the phase separation takes place, the "breakdown" value of the diffraction efficiency is just independent of the curing intensity.

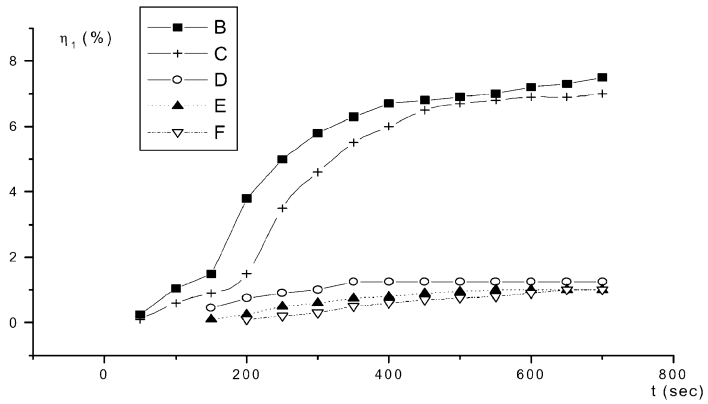

Figure 5. Temporal evolution of η_1 for samples with LC concentration N = 50% but cured at different UV intensities: B) I_B = 10mW/cm^2; C) I_B = 5mW/cm^2;D) I_B = 2,5mW/cm^2; E) I_B = 1,5mW/cm^2;F) I_B = 0,5mW/cm^2.

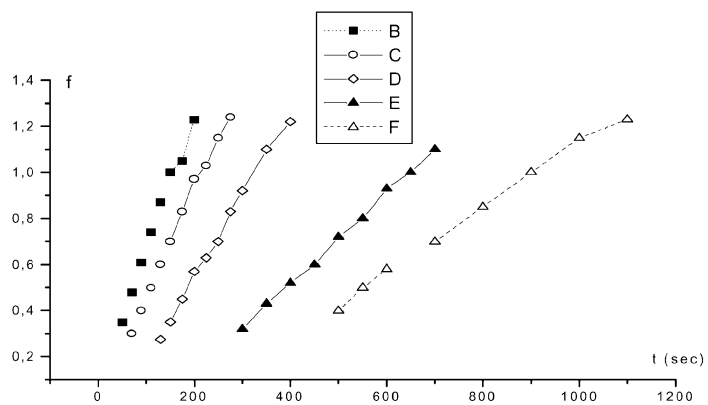

Figure 6. Temporal evolution of the pre-grating force for different values of the curing UV intensity: B) I_B = 5mW/cm^2; C) I_B = 3mW/cm^2;D) I_B = 2mW/cm^2; E) I_B = 1mW/cm^2; F) I_B = 0.5mW/cm^2. For all samples, the LC concentration is N = 57.7%.

Finally, in Fig.6 the temporal evolution of the so called "grating force" $f = (\eta_1(t))^{1/2}$ is reported for cases in which phase separation does not take place. We note that the rate of f depends on the curing UV intensity. Fig. 7 shows indeed that, within the experimental error, the squared rate of f linearly depends on the curing intensity I_B.

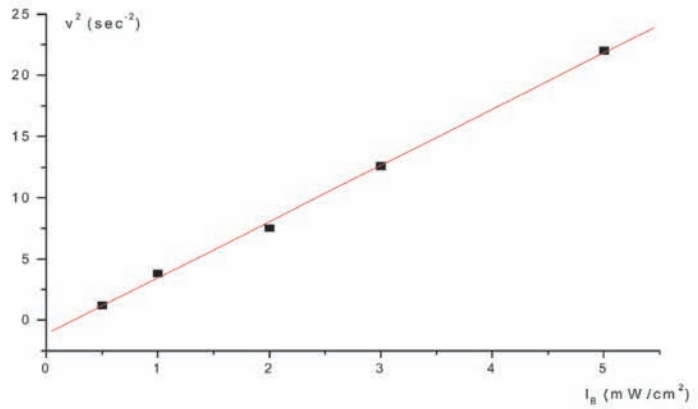

Figure 7. Dependence of the squared rate of f, $v^2 = (\partial f/\partial t)^2$ on the curing intensity.

UV CURING BY MPTIPS TECHNIQUE

From the above discussion, it is evident that between a pre-grating and a real grating (a grating in which the phase-separation process already occurred) there are essentially two main differences:

- the pre-grating morphology is quite sharp and regular, since neither phase transition nor UV scattering are involved in the curing process;
- the diffraction efficiency of pre-grating is low and non-switchable due to the absence of a nematic order.

A new technique which induces nematic order in pre-gratings after curing has been therefore developed, in order to obtain the high diffraction efficiency of PDLC based gratings, but avoiding the formation of nematic droplets, responsible for high scattering losses. In this way we have obtained a new class of holographic diffraction gratings of good morphology and high values of the diffraction efficiency. The detailed illustration of this technique, called MPTIPS,

cannot be given here, since it is under patenting, but first results are reported as an example for mixtures with LC concentration in the range N ≈ 50% - 70%. The new morphology can be observed in Fig. 8.

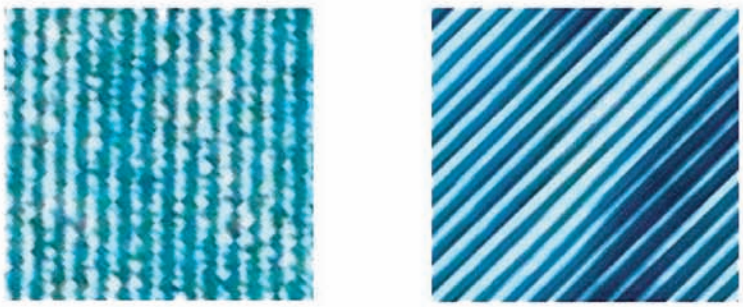

Figure 8. Grating morphologies obtained in samples with N = 60% and 5 mW/cm^2 curing intensity: a) traditional PIPS technique; b) MPTIPS technique.

Both gratings have been obtained in samples with N = 60% and cured with the same UV intensity I_B= 5mW/cm^2, but the first picture (Fig.8a) shows a typical PDLC based grating, with stochastically aligned droplets, while the second one (Fig.8b) represents a MPTIPS grating and reveals perfectly aligned and sharp-edged stripes of a continuous nematic phase. Analysis of the samples at the polarisation microscope revealed no presence of nematic droplets nor micro-structures of any kind in the nematic stripes of the second grating. The use of the SAM114-5CB mixture revealed however some technical problems. Namely, the N-I transition temperature for the liquid crystal in the mixture is at about 25°C (the pure 5CB transition is at 37°C), thus too close to the room temperature to allow detailed morphological studies. We changed therefore the liquid crystal inside the mixture choosing the BL036 (by Merck), which exhibits a N-I transition at 90°C when it is used pure.

The employment of this new technique has shown interesting features of the recorded gratings. In general, they exhibit values of the diffraction efficiency higher than 20% for any fringe spacing utilised within the range Λ = 6.3 μm - 0.22 μm. In addition, we have observed a

diffraction efficiency dependence on the curing intensity, as shown in Fig.9.

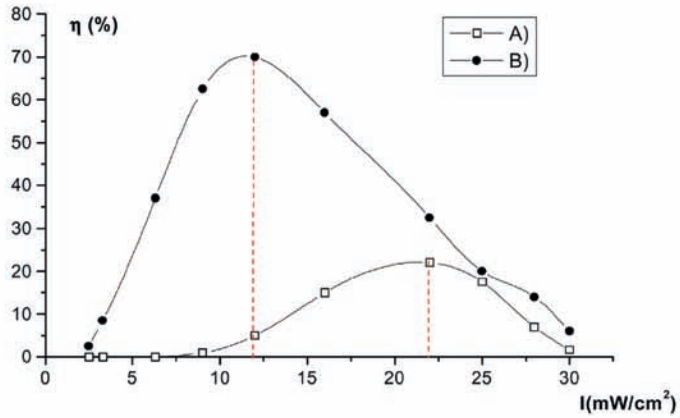

Figure 9. Dependence of the diffraction efficiency on the curing intensity for the SAM-BL mixture and different fringe spacing: A) $\Lambda = 0.31\mu m$; B) $\Lambda = 1.8\mu m$.

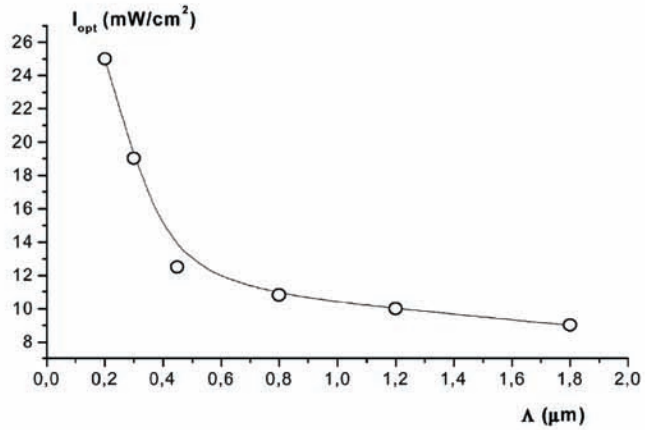

Figure 10. Dependence of the optimal curing intensity I_{opt} on the fringe spacing for SAM-BL mixture.

It is evident that, for each fringe spacing, an optimal intensity I_{opt} of the curing radiation exists, at which the diffraction efficiency has a maximum. The value of I_{opt} depends, in its turn, on the fringe spacing (Fig.10). Finally, Fig.11 shows that the biggest reached value of the diffraction efficiency strongly depends on the grating fringe spacing.

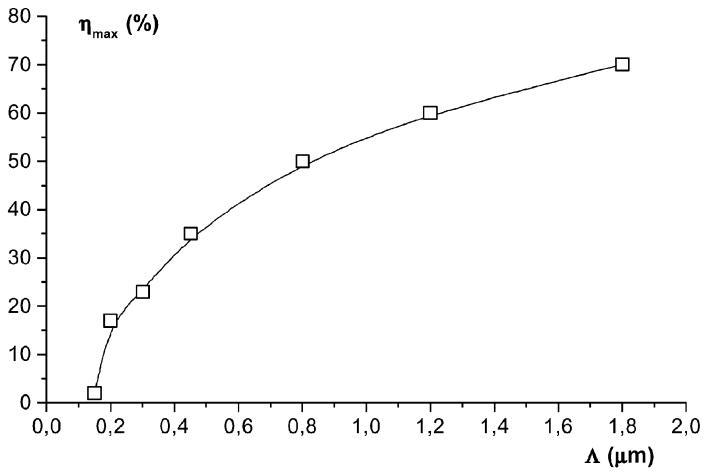

Figure 11. Dependence of biggest diffraction efficiency on the fringe spacing for the SAM-BL mixture.

CONCLUSIONS

In conclusion, in this paper we have reported a first, preliminary characterisation of diffraction gratings recorded in liquid crystalline composite materials by means of a new UV curing technique (MPTIPS). The setup of this technique has been suggested by a detailed experimental characterisation of the so-called "pre-grating", a sort of gratings previously obtained under particular conditions that do not allow the realisation of phase separation between liquid crystal and polymer molecules. Our results show that the use of the new technique noticeably reduces scattering losses and improves the morphological and optical quality of obtained grating.

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