Dynamical Behaviour of Policryps Gratings

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We have studied the dynamical response of a new polymer-liquid crystal composite, realised in a form of a thick grating. This structure, named POLICRYPS, consists in an alternate sequence of homogeneous polymer slides and liquid crystal stripes. Optimisation of response time is an important factor to propose POLICRYPS as basic element in different photonic devices for telecom applications. We analyse the response dependence on the pulse duration and amplitude: we show that both ON and OFF switching times are depending on the applied electric field and propose a phenomenological explanation for this unexpected behaviour. Moreover we outline the possibility to get response times of the order of 100 μs by properly choosing the pulse shape. Results are very interesting for applications and induce to a deeper analysis of the microscopic interaction between liquid crystal and polymer interfaces in POLICRYPS gratings.

I.   Introduction

For many years composite materials containing Liquid Crystal (LC) and polymer have attracted the interest of researchers for their potentialities. In particular the possibility to use Polymer Dispersed Liquid Crystal (PDLC) as recording media for thick, electrically switchable,

holographic gratings makes them very suitable for different applications in photonic devices, especially in the field of optical telecommunications [1]. However, PDLC are still affected by some drawbacks that up to now have limited the real utilisation of these materials. Indeed, the presence of liquid crystal droplets, whose dimension is comparable with the light wavelength, produces a strong light scattering, which affects the overall performance of the device. On the other hand, if droplets are made nano-sized (nano-PDLC), diffusion is strongly reduced but high electric fields are needed to reorient the LC molecules.

A very promising solution to overcome these limits has been recently proposed by the authors from University of Calabria. They have developed and patented a new kind of LC-polymer based diffraction grating, named POLICRYPS, an acronym for Polymer - LIquid CRYstal - Polymer Slides [2]. As suggested by the name, POLICRYPS consist of an alternate sequence of homogeneous liquid crystal layers and polymer films. The absence of a droplet dispersion makes them transparent both in the reoriented and in the non-reoriented state, reduces the electric field necessary for the switching, increases the maximum achievable index difference Δn among adjacent layers, and allows to obtain a morphology with a sharp resolution of the grating fringes; as a consequence, very high diffraction efficiencies can be achieved.

In order to implement their use in photonic devices, POLICRYPS gratings need to undergo a process of optimisation of their main characteristics. This work has already started, and some important static features have been already analysed both in the visible and in the infrared regimes [3,4]. In the present paper, we analyse the dynamical response of POLICRYPS gratings and its relation with some geometrical and morphological factors. Our final goal is to get overall response times in the sub-millisecond range, once a physical understanding of the underlying mechanisms and relevant parameters will be achieved.

II.   Materials

We have characterised two different POLICRYPS transmission gratings, which in the following are referred to as samples A and B, fabricated in the LICRYL at the University of Calabria. The two samples were made starting from the same initial mixture, a solution of 30% liquid crystal (5CB, provided by Merck) in a commercially available pre-polymer (Norland Optical Adhesive NOA-61). This blend was injected by capillarity into a cell realised with two ITO coated glasses separated by Mylar spacers. These samples were heated over the Nematic-Isotropic phase transition temperature of the LC component and cured by a UV laser interference pattern ($\lambda = 351$ nm, $I = 10\text{-}100$ mW/cm^2).

	Pitch Λ [μm]	Thickness d [μm]
Sample A	1.34	8.8
Sample B	0.6	12

Table 1: Sample geometrical parameters.

A detailed description of the POLICRYPS preparation procedure is reported elsewhere [5]. Here we only point out the importance of a good control of vibrations during the curing process, since a better stabilisation results in a cleaner separation between LC and polymer stripes. We know that our samples were produced under a different vibration control: quite rough for sample A, more refined for sample B.

Our samples differ also in two geometrical parameters, the pitch Λ and the thickness d, that are reported in Table 1; in the volume of the sample, fringes are disposed, in both cases, perpendicularly to the cell glasses. At the operating conditions ($T = 25$ °C and $\lambda = 633$ nm) material refractive indices are: $n_p = 1.53$ for the polymer, and $n_o = 1.53$ and $n_e = 1.71$ for the liquid crystal. These values explain the POLICRYPS operating model, described in Figure 1: it is known that, in the LC fringes, the nematic director is aligned orthogonally to the polymer stripes [4]; when p-polarised light impinges on the sample at a small angle, it experiences a LC refractive index close to n_e, without any applied external field, and close to no, with an applied electric field that fully reorients the LC director. Being $n_p \sim n_o \ll n_e$, by means of the external voltage we can switch from a diffraction state (ON state, when a high index mismatch is achieved between adjacent fringes) to a transmission state (OFF state, obtained when the LC refractive index matches polymer one)[1]. On the other hand, POLICRYPS cannot operate properly with s-polarised light, because in this case, it is the ordinary wave that propagates through the sample and, with or without applied electric field, it sees always the LC ordinary refractive index.
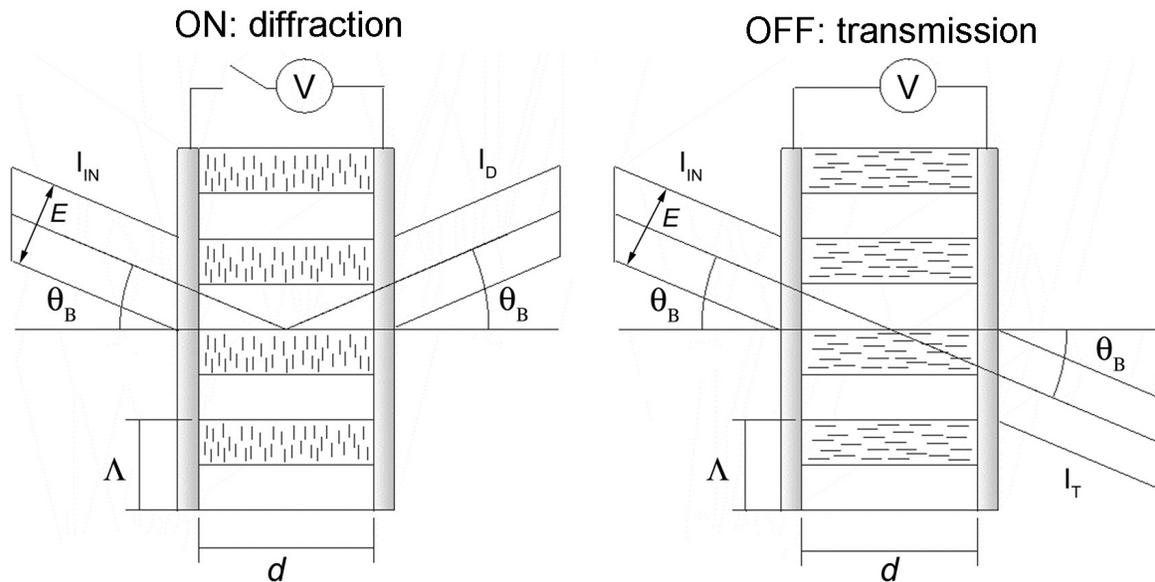

Figure 1: POLICRYPS operating model.

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[1] Please notice that here and in the following ON and OFF states are referred to the effectiveness of the diffraction grating and not to the application of the external voltage.

3

III. Experimental

We illuminated the samples with p-polarised red light from a He-Ne laser (633 nm) impinging at the Bragg angle, i.e. the angle corresponding to the maximum diffraction efficiency (95% for sample A and 93% for sample B experimentally checked). We did not use infrared light, because the pitch of the sample B was too small to allow the Bragg diffraction in the IR; however in a previous work we observed no significant dependence of the response times on wavelength [6]. The operating temperature was fixed at 25 °C by means of a PC controlled hot stage; this was absolutely necessary, the diffraction efficiency showing a pronounced thermal dependence, due to the material choice. In fact, 5CB exhibits a nematic-isotropic phase transition temperature not much higher than room temperature, ~35 °C for pure material, but down to 29 °C in the actual case of LC stripes still containing a non-negligible fraction of polymer and photo-initiator molecules. It is easy to understand that, in practical applications, a different choice of the LC material with a higher clearing point can substantially remove this unwanted temperature dependence.

In order to study the dynamical behaviour of our samples, we applied alternate electric pulses, generated by a PC driven arbitrary waveform generator and amplified by a suitable external amplifier. We varied both pulse amplitude and duration, in the range $7.5 \div 11.7$ V/µm and $0.1 \div 10$ ms respectively; the pulse time delay was always greater than 30 ms. In all cases we had care to completely switch off the grating. Response time measurements were made by recording the diffracted beam signal detected by a fast photodiode (Figure 2); times, defined as the interval between 10% and 90% values of the maximum signal, were affected by an uncertainty around 5%, especially due to fluctuations in the maximum amplitude of the optical signal.
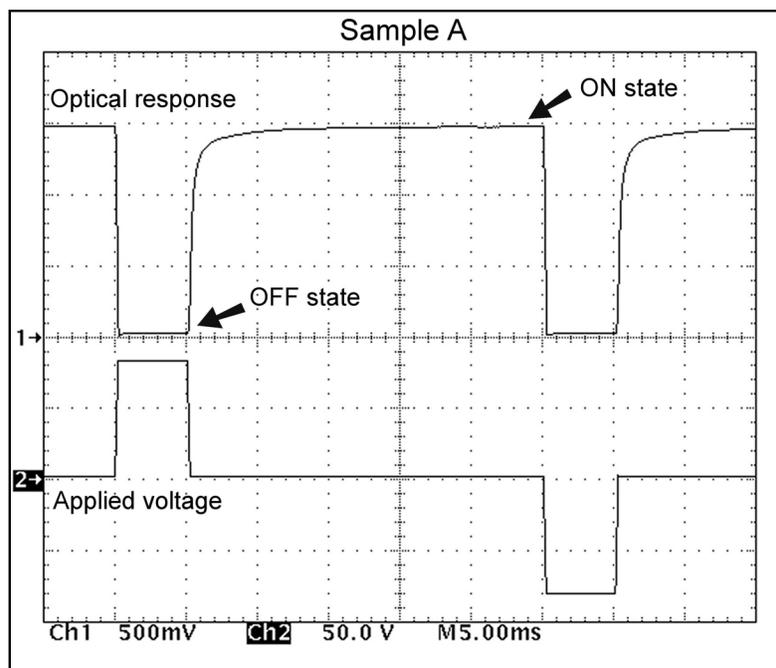

**Figure 2: Oscilloscope snapshot of the applied field (channel 2) and
the diffracted beam optical response (channel 1).**

4

IV.   Results and discussion

In order to understand the dynamical response of our samples it is necessary to refer to their particular structure: inside a POLICRYPS grating, LC molecules are confined both from the polymer stripes and the cell glass walls; however, the first interaction looks much more important, for the double reason that i) the alignment is likely induced by the polymer (glass walls are just cleaned and not further treated) and ii) the distance L between the polymeric walls is much shorter than the cell thickness d. Indeed, in our samples we can assume a thickness of the liquid crystal film not exceeding 30% of the nominal pitch ($L \sim 0.40$ μm for sample A and $L \sim 0.18$ μm for sample B), proportionally to the LC concentration in the mixture. These values for L are theoretical maxima, assuming a complete material separation during the fabrication process; thus we expect shorter actual values.

When we apply an external voltage across the cell, we create an electric field E perpendicularly to the LC director, which is orthogonal to the polymer stripes; thus, the situation is quite similar to the classical configuration for a Fréederiksz transition experiment [7]. We recall that, in the case of strong anchoring, the Fréederiksz threshold field is given by:

$$E_0 = \frac{\pi}{L}\sqrt{\frac{k}{\varepsilon_0 \Delta\varepsilon}}, \tag{1}$$

while the reorientation time constant is

$$\tau_E = \frac{\gamma}{\varepsilon_0 \Delta\varepsilon}\frac{1}{(E^2 - E_0^2)}, \tag{2}$$

where L is the distance between the anchoring surfaces, k is the elastic constant (in our geometry, the bend one, $k = 8.4\times10^{-12}$ N), $\Delta\varepsilon$ is the LC dielectric anisotropy ($\Delta\varepsilon = 11.5$), ε_0 is the vacuum dielectric constant and γ the viscosity ($\sim 10^{-2}$ Pa·s). Putting Equation 1 into Equation 2 and setting $E = 0$, the expression for the relaxation time constant is obtained:

$$\tau_r = \frac{\gamma L^2}{k\pi^2}. \tag{3}$$

Note that in the previous formulae τ is the usual exponential time constant, that is related to the experimentally measured 10-90% response time by means of the relation $t_{10\text{-}90} = 2.2\ \tau$.

Of course, our situation is much more complicated than in the simple homeotropic LC cell, because we cannot observe directly the director reorientation, but only the effect produced by the reorientation on the optical response of the grating. Nevertheless, these formulae are useful to understand the experimental behaviour of our samples.

We start by analysing the switching off dynamic, ruled by the electrical reorientation of the liquid crystal director. First, we experimentally determined the minimum voltage required to obtain a complete switching off; then we increased stepwise the voltage up to reach a saturation in the fall time curve (Figure 3). As expected, due to the different thickness of the LC layers, the complete switching off field for sample A was lower than for sample B. For both samples, we found quite obviously that a higher electric field corresponds to a faster response time, but in sample B the response dependence on the applied field was much more important than in sample A. For the former we measured a variation in the range 50 ÷ 650 μs, while for the latter we observed times within the narrower interval 30 ÷ 170 μs (see Table 2).
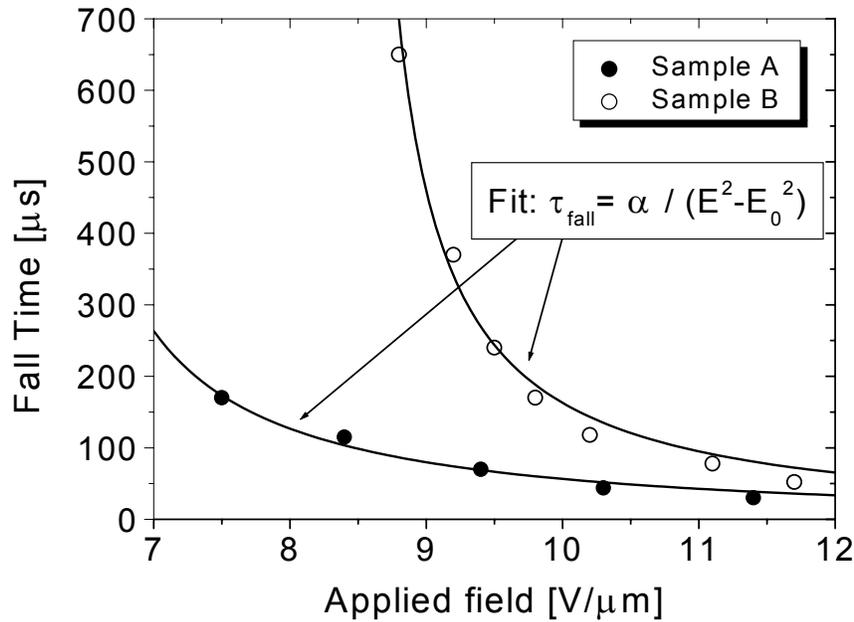
Figure 3: Fall time dependence on the applied field, experimental points and fit.

	Fall time [µs]		Rise time [µs]	
	min	max	min	max
Sample A	30	170	180	1040
Sample B	50	650	130	280

Table 2: Response time ranges.

By means of a fitting procedure, we also verified that the fall time dependence on the electric field is well described by Equation 2. From the fit we can calculate the rotational viscosity γ, according to Equation 2, and obtain the values 0.17 ± 0.02 and 0.22 ± 0.02 Pa·s for the sample A and B, respectively. These values differ by one order of magnitude from the value provided in literature for 5CB: γ should be $\sim 10^{-2}$ Pa·s. This difference can be due to the presence of impurities, like polymeric clusters that affect the LC domains. For the threshold fields E_0 in the two samples, we found the values 5.9 ± 0.3 V/µm and 8.37 ± 0.04 V/µm, respectively. The ratio of these fields, 1.4, is quite different from the value of 2.2, calculated by using the maximum allowed width of the LC layers. In fact, if we put our E_0 fitted values in Equation 1, we get for the width L of the LC stripes, the values 0.15 µm ($=0.11 \cdot \Lambda$) and 0.11 µm ($=0.18 \cdot \Lambda$), both much less than 30% of the grating pitch Λ.

Even adopting a simplified model, it seems reasonable to infer that the pitch fraction really occupied by the liquid crystal is strongly dependent on the fabrication procedure; in particular, the different result in the two samples can be related to the different control of the set-up mechanical stability ensured during the curing process: larger vibrations producing wider irradiated areas and broader polymer layers.

6

Unlike the switching off, the switching on process is not ruled by the electric field, but only by the elastic torque induced by the surface anchoring; this torque drives the relaxation of the LC director towards the zero-field orientation. Nonetheless, contrary to an intuitive expectation, also the rise time was found to depend on the pulse shape: in Figure 4, the non linear dependence of the rise time on the pulse duration is shown for different amplitudes; in Figure 5, the same experimental data are reported versus the pulse amplitude for different pulse durations, showing an almost linear behaviour. In this case, that is for switching ON, the sample A showed the largest variation of the response time (180 ÷ 1040 µs), while sample B rise time changed only in the range 130 ÷ 280 µs (Table 2). Hence, our experimental results indicate that some kind of "memory" of the electric field that has been applied remains also when only the elastic restoring torques are effective. In our opinion, the observed behaviour can be explained by assuming that a partial anchoring breaking and restoring, ruled by a surface viscosity, happens at the LC-polymer interface. Indeed, we don't expect that the interfacial region is very thin, i.e. of the order of few molecular layers. At the contrary due to the curing process, a fraction of the LC molecules remains partially embedded in the adjacent polymer stripes, close to the border, still retaining a reduced mobility. Moreover, the curing interference pattern has not a rectangular profile, but
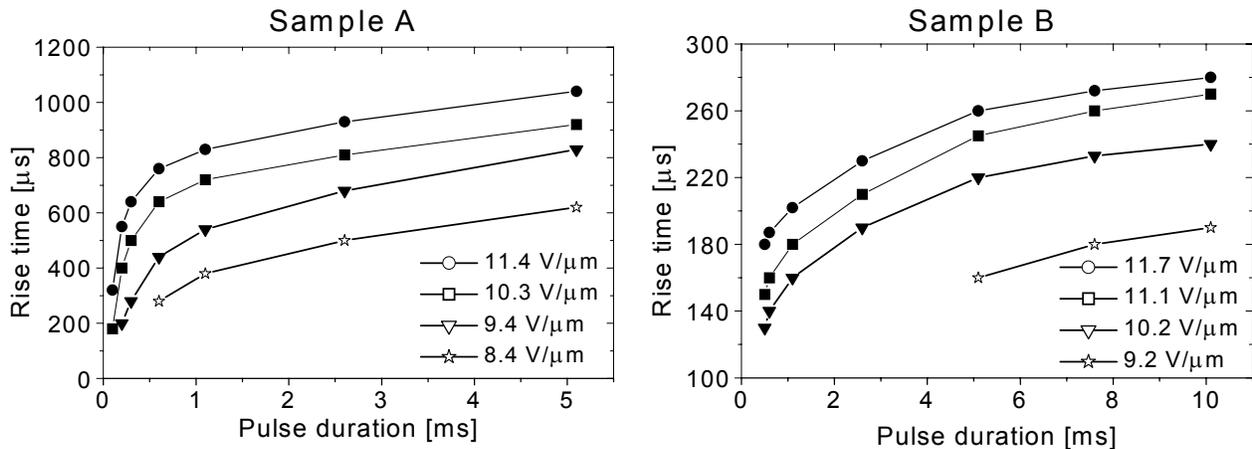

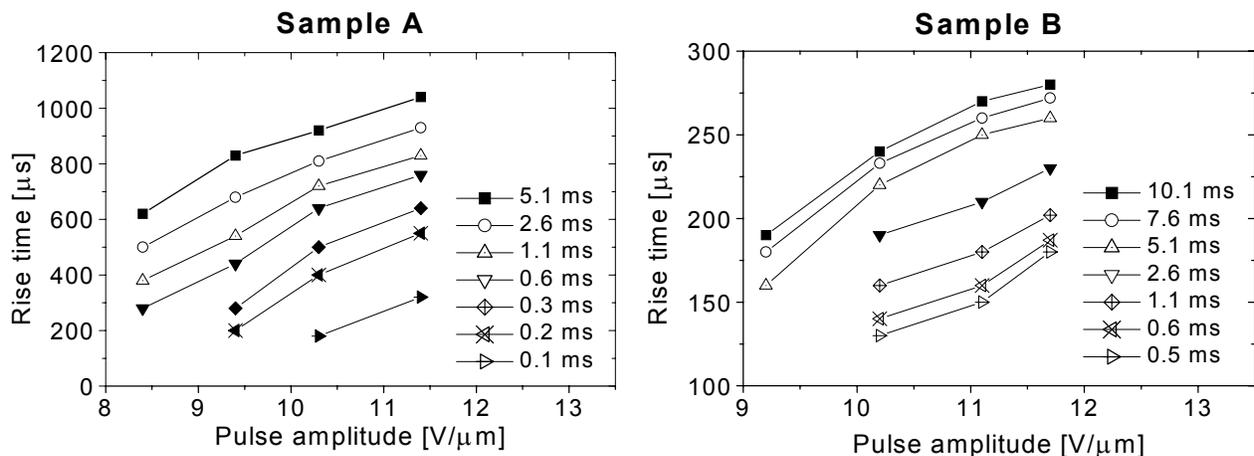**Figure 4: Rise time dependence on the pulse duration for different pulse amplitudes.**

Figure 5: Same experimental points as in Figure 4; here rise time is reported versus pulse amplitude for different pulse durations.

7

instead a $\cos^2$ one, thus we expect a reduced number of polymeric links close to the LC-polymer border. Finally, the degree of spatial stability of the pattern does certainly affect the width and softness of the interfacial region. Therefore, let us depict the consequent scenario. When the electric field is switched on, surface and bulk molecules reorient with a different viscosity, corresponding to different time constants. Bulk response is faster and is responsible for the strong reduction of the diffraction efficiency; the response of the surface layer is slower but its influence on the optical signal is almost negligible because this layer is much thinner. When the electric field is switched off, the boundaries play the main role in the reorientation process, thus in determining the response dependence on the pulse shape. Short and/or weak electric pulses are not able to affect significantly the reorientation of the director in the surface layer; only bulk molecules reorient and both ('on' and 'off') transitions are ruled by a simple Fréederiksz transition model with strong anchoring, according to the Equations 2 and 3. Putting in the last equation the data obtained from our fit, we obtain for the elastic relaxation time of the two samples the values 110 ± 20 µs and 68 ± 7 µs respectively, which could be considered as limiting values in the case of a perfect interface and infinite anchoring energy. Latter values are obviously smaller than the smallest measured relaxation times.

For long and/or strong pulses, also the molecules in the interfacial region are partially reoriented. These molecules are affected by a higher surface viscosity and need more time to resume the initial orientation than the bulk ones. At the removal of the electric field, the molecular director in the bulk undergoes a first quick reorientation towards the intermediate orientational state held by the director at the surface; then, with a slower time constant, the director at the surface will relax towards the unperturbed state and the bulk director will follow it adiabatically. The final result is that the overall relaxation time is a mix of the bulk and surface time constants, which depends on the intermediate state of reorientation reached by the director at the surface under the effect of the electric field.

This hypothesis can also account for the quite complex shape of the relaxation optical signal.
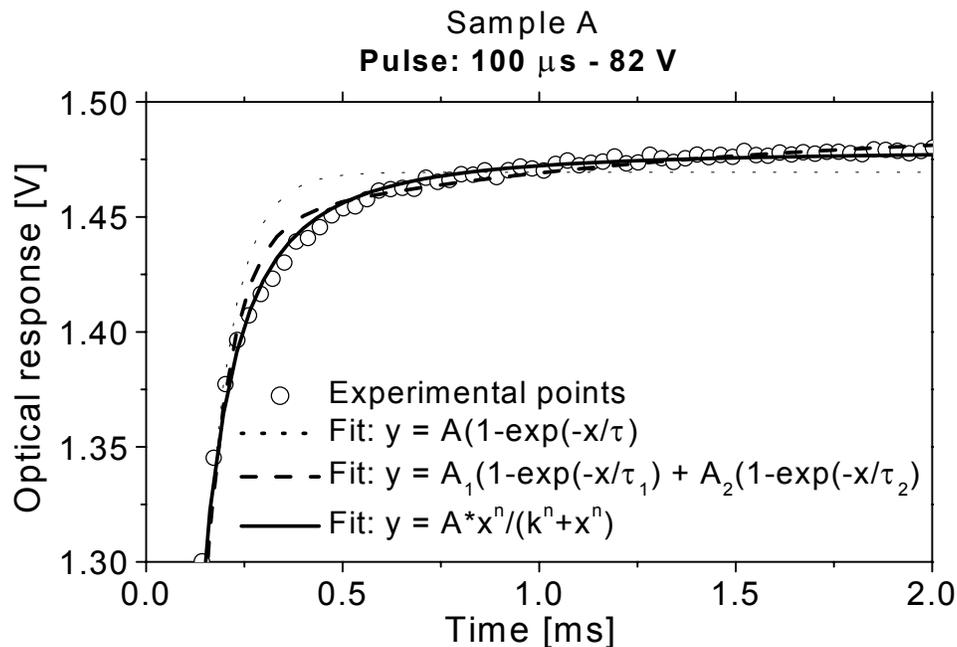

Figure 6: Diffracted beam optical signal (circles) during the off-on transition; lines show different fitting curves.

As shown in a previous work [6], experimental curves cannot be described by a single exponential function. A good fit is obtained only by using a double exponential or some kind of sigmoid curve (Figure 6). At the present stage, we are not able to infer a direct physical meaning for the parameters entering in these mathematical models. Probably, they are just a good approximation of the real behaviour. Anyway, all these functions have a common general shape, with a fast growing part, followed by a very slow saturation tail. We guess this can be connected to the different bulk and surface viscosity values. We are planning further systematic analysis, both from theoretical and experimental side, in order to fully confirm our idea.

Finally, from an application point of view, we underline that, by choosing short driving pulses and a proper voltage, it is possible to get simultaneously both response times in the range $50 \div 150 \, \mu s$. Furthermore, as mentioned above, the large value of the bulk viscosity found in the LC stripes determines the limiting values for achievable response times: optimisation of the fabrication process will have a positive effects also in lowering the viscosity, hence on the switching dynamics.

V.   Conclusions

In this work we have analysed the dynamical behaviour of two samples of POLICRYPS gratings. We showed how both switching off and switching on times strongly depend on amplitude and duration of the applied electric pulses. This was not expected for the elastic off-on transition and has been explained by assuming an essential role of the interfacial region between the LC and the polymer stripes, without a well-defined and sharp border, exhibiting a surface viscosity higher than the LC bulk one.

Though both rise and fall response times can change in a wide range, it was already possible for those first batch and not-optimised samples, to get values in the range $50 \div 150 \, \mu s$, by means of a proper choice of the driving pulse shape. These results are very attractive for many possible applications of a key component, like a fast switchable Bragg grating, in telecom devices. Moreover, they can be the starting point for fundamental studies on bulk and surface elastic interactions in liquid crystalline composite materials.

VI.   References

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