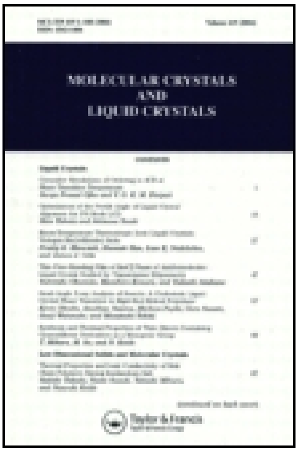

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Optical Bit Stability and Relaxation Processes in a Liquid Crystal Polymer with a Photosensitive Azo Dye Molecule as Side Group

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Version of record first published: 18 Oct 2010

To cite this article: Laura Andreozzi, Paolo Camorani, Massimo Faetti & Diego Palazzuoli (2002): Optical Bit Stability and Relaxation Processes in a Liquid Crystal Polymer with a Photosensitive Azo Dye Molecule as Side Group, Molecular Crystals and Liquid Crystals, 375:1, 129-142

To link to this article: http://dx.doi.org/10.1080/10587250210560

Mol. Cryst. Liq. Cryst., Vol. 375, pp. 129-142

1058-725X/02 $12.00 + .00

Optical Bit Stability and Relaxation Processes in a Liquid Crystal Polymer with a Photosensitive Azo Dye Molecule as Side Group

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We present a study of optically–induced molecular relaxation and optical writing processes in a photosensitive liquid crystalline polymer, containing the azobenzene moiety in the side chain. Linear and non linear ESR spectroscopies, thermal analysis and rheology investigations carried on azo polymethacrylate (PMA) samples subjected to different thermal treatments have allowed to single out a suitable procedure to get stable, homogeneous substrates. Optical studies on micrometer length scale, adopting the selected procedure, have confirmed the stability conditions in both unaligned and aligned samples. The temperature dependence of the bit stability has been determined. The writing threshold power and writing rate have been measured. The results are discussed within the perspective of extension to the nanometer length scale.

Keywords: Polymeric liquid crystal; birefringence; optical recording; non linear Electron Spin Resonance Spectroscopy; structural relaxation.

INTRODUCTION

Side chain liquid crystalline polymers (SCLCPs) have been largely investigated due to their potential application as media for optical information storage [1-3]. In particular, SCLCPs with azobenzene side groups seem very promising for optical nanorecording, optoelectronics applications [4-7]. Stability, relaxation and optical threshold properties represent the key features in optical writing. Moreover, heterogeneity at molecular level affects substantially the bit stability, seriously limiting the effectiveness of the azobenzene-based polymer matrices as erasable storage devices at nanometer length scale. Homogeneity on the microscopic length scale strongly depends on thermal annealing [7].

LCPs conjugate the useful characteristics of low molecular weight liquid crystals with the easy workability and stability of polymer plastics. Azobenzene containing SCLCPs offer the additional advantage of optically-induced molecular reorientation through the *trans-cis* isomerization transition of the azobenzene moiety [1, 8], important for applications to optical writing and information storage down to the molecular level [9]. Another point of interest are fundamental studies of the dynamics which results from the complex interplay between several types of interactions and processes: the mesogenic potential, the conformational main chain transitions, the glass transition, the molecular *trans-cis* isomerization [10].

Homogeneity and bit stability represent crucial parameters in optical data storage media. Diffusion processes can in principle limit the life-time of photoinduced regions in polymeric matrix. Thus it is important to investigate diffusion processes on different time and length scales. Linear (ESR) and non linear (LODESR) Electron Spin Resonance spectroscopies have turned out to be powerful tools to investigate molecular dynamics in simple and complex liquids [11]. The non exponential character of the reorientational correlation function of molecular tracers in supercooled fluids and polymers, can be conveniently investigated by these two spectroscopies. Substantially LODESR spectroscopy provides information of rotational dynamics *inside the molecular cage*, while ESR takes into account the rotational *rearrangement of the cage itself*.

On the long space/time length scale rheological measurements allow one to get information on the structural relaxation time mainly determined by backbone dynamics. Moreover the decoupling degree between structural and spin probe dynamics, characterizes molecular sites in which the tracer reorients and provides an evaluation of the cooperativity of the dynamics [7].

Diamagnetic systems are often investigated by dissolving very small quantities of suitable paramagnetic tracers in the host matrix. The Cholestane spin probe is an excellent molecular tracer, especially in the study of reorientational processes of liquid crystal polymers [12]. In Figure 1 the formula of the Cholestane spin probe and of the repeat unit of nematic PMA are shown.

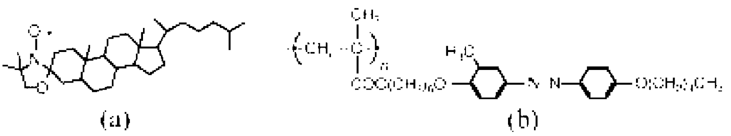
(a) (b)

FIGURE 1 (a) Cholestane spin probe and (b) PMA repeat unit.

The Cholestane spin probe exhibits nearly axial symmetry. Its reorientational dynamics in PMA is characterized by a spinning motion, around its own symmetry axis, and a tumbling motion of the symmetry axis itself, with correlation times $\tau_{||}$ and $\tau_{\perp}$, respectively. By ESR measurements, carried on Cholestane spin probe dissolved in differently annealed PMA matrices [7], the anisotropy $\tau_{\perp}/\tau_{||}$ ratio was found to be essentially independent of temperature. Consequently, in this work only the temperature dependence of $\tau_{||}$ will be shown.

EXPERIMENTAL PART

The SCLCP under investigation is a polymethacrylate (M_w 59000, polydispersity 3.17) containing the (3-methyl-4'-pentyloxy) azobenzene mesogenic unit connected at the 4-position by an hexamethylene spacer to the main chain.

PMA was synthesized following a standard procedure [13]. It forms a nematic phase between the glass transition temperature (T_g = 294 K) and the clearing point (T_{NI} = 353 K).

Differential scanning calorimetry experiments were carried out with a Perkin-Elmer DSC7 apparatus was been calibrated with indium and zinc standards. DSC measurements were performed by firstly maintaining the sample (ca. 15 mg) for 4 hours at a temperature above T_{NI}, and then cooling it to 250 K at a cooling rate of 40K/min. The thermogram, reported in the inset of Figure 2, was obtained with a heating rate of 10K/min. Figure 2 reports an enlarged particular step whose onset occurs at about 320K

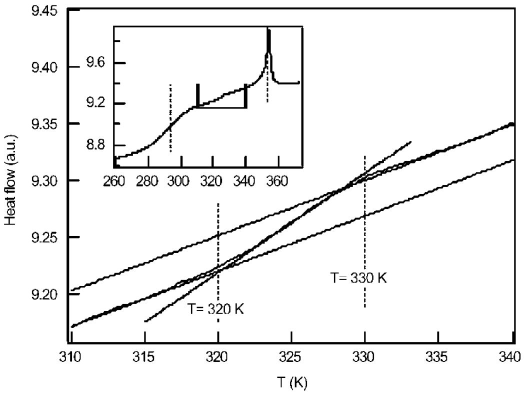

FIGURE 2. Enlarged region of DSC heating scan on PMA sample (10K/min heating rate).

Rheological measurements were performed by using Haake RS150 rheometer: the temperature dependence of the shear flow structural relaxation time is well described by the Vogel-Fulcher law:

$$\tau^{st} = \tau_0^{st} \exp\left(\frac{T_b}{T - T_0}\right) \tag{1}$$

T_0 and T_b are respectively the Vogel temperature and the activation pseudoenergy expressed in kelvin. The VF parameters for the structural relaxation time in PMA hold T_0= 259±5 K, T_b= 1300±50 K and τ_0^{st}=(2.4±0.3)· 10^{-10} s. No differences were found in experiments performed by annealing the sample following the methodology below described.

Sample preparation [14] and LODESR technique [15] are described elsewhere.

The following measurement protocol was followed: i) maintaining the sample at the annealing temperature T_a, monitoring the system evolution until a stable spectrum was recorded via the acquisition of ESR spectra; ii) Recording spectra on cooling to different predetermined temperatures for an overall measuring time t_r; iii) Re-heating the sample and maintaining it at the annealing temperature T_a during a time t_w; iv)Repeating steps ii), iii) to cover all the temperature range of interest [7]. In ref [7] it was shown that a two δ-like function well characterised the molecular sites distribution in the polymeric matrix. Previous ESR investigations [16], following the thermal procedure above outlined, showed that PMA sample annealed at 383K, well above T_{NI}, turns out to be rich of defects on the nanometer length-scale and unsuitable when envisioning its use as a substrate for optical nanorecording. The PMA sample annealed at 358K, slightly above T_{NI}, appears to be homogeneous at least at temperatures below 334K. LODESR measurements confirm these findings. More precisely, a suitable annealing procedure and a temperature range are specified in which PMA sample seems to provide a good substrate for optical nanorecording.

Finally, an experimental apparatus has been developed wich was optimized for the accurate characterization of the magnitude and stability of photoinduced effects. The apparatus (outlined in Figure 3) is based on a polarizing optical microscope. The writing beam is provided by the 488 nm line of an Argon Ion laser which is focused on the sample trough a microscope with confocal setup, using an objective of magnifying power: 40x and numerical aperture N.A.=0.6. The writing laser spot has a gaussian profile, whose FWHM depends on the size of the confocalizing pinhole. For the measurements described in the following section we typically had a beamsize of FWHM= 2 μm. The intensity and exposure time of the laser beam are controlled by an acousto-optic modulator with switch time of 15 ns. The sample can be observed either in reflection or in transmission mode through cross polarizers.

Besides optical observation, a sensitive CCD (0.0003 lux) camera can be employed to record images also in time resolved mode. To eliminate any influence of the light used for the sample illumination on the molecular orientation in such a sensitive material we have inserted (between the lamp and the sample) a band pass filter centered in the spectral region 550-800nm where our material is not influenced by the radiation. A similar band pass filter was employed before the detector system in order to eliminate the writing beam.

We studied both molecular films produced by the Langmuir-Blodgett technique [17] or thicker films produced by melting the PMA between two microscope glasses spaced by a 10 μm teflon spacer.

The sample was contained in a thermal cell (stability 0.1°C) on a computer controlled motorized XY microscope stage.

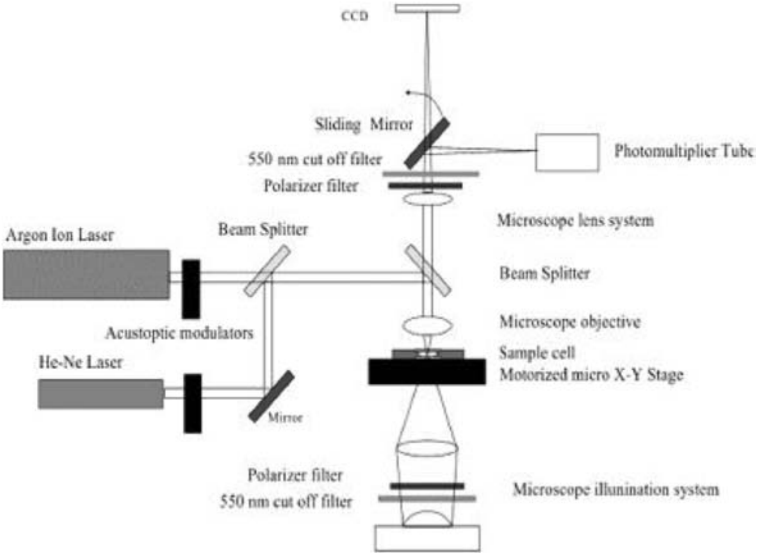

FIGURE 3. Setup for optical characterization.

The sample was moved at different velocities, under spot illumination by the writing laser thus allowing for a precise variation of the power density deposited onto the different regions of the sample.

The writing effect obtained by this technique consists of micron sized lines were the molecular orientation is perpendicular to the writing beam polarization direction and whose order parameter is proportional to the absorbed radiation energy. Lines produced on a 10 μm thick film at different power flux densities ranging from 0.65 to

3.15 J/cm^2, are shown in Figure 4, the different interference color of each line depend on the local order parameter.

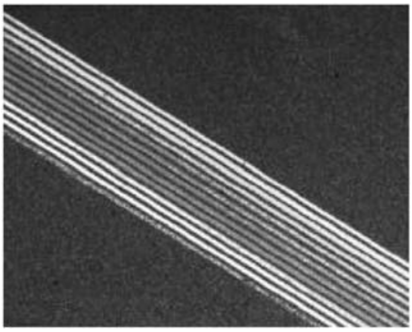

FIGURE 4. Image (1000μm x 850 μm) obtained by polarizing optical microscopy of the writing effect of polarized radiation on a 10 μm thick film of PMA at different energy densities as detailed in the text. The different colours of the lines correspond to different values of the photoinduced order parameter.

These photoinduced effects were quantified as a function of the different energy flux for different sample thickness and their time stability were measured as a function of temperature. The results of such measurements are detailed in the Discussion section.

RESULTS AND DISCUSSION

LODESR measurements have been carried on PMA samples annealed at 383K, 358K and 348K respectively, following the thermal procedure delineated in the previous section. The t_r, t_w and t_a time values are reported in Table 1

The short time dynamics of the dissolved Cholestane spin probe was investigated from about the annealing temperature to about 270K. Moreover, at different temperatures, measurements of the longitudinal relaxation time have been performed along the LODESR spectral lineshape; no dependences on the static magnetic field were found.

T_a (K)	t_a (hours)	t_r (hours)	t_w (hours)
383	2	1	2
358	2	1	2
348	5	1	2

TABLE 1. Values of the annealing temperature (T_a) and annealing (t_a), waiting (t_w) and measure (t_r) times adopted for recording LODESR spectra.

As an example, Figure 5 compares ESR and LODESR spectra, relative to PMA sample annealed at 383K and recorded at 348K. Spectral intensities in the whole range of variation of the magnetic field were normalized. The proportionality between LODESR field swept experiments and ESR lineshapes indicates that a single value of longitudinal relaxation time is obtained when frequency swept LODESR experiments along the spectral profile are carried on. Thus on the short time scale, rotatio nal dynamics turns out homogeneous.

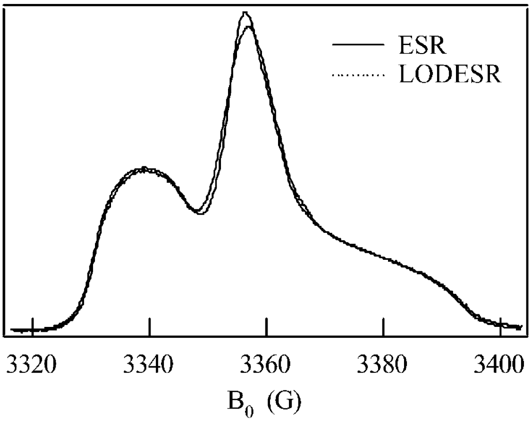

FIGURE 5. A comparison between experimental ESR and LODESR in the field swept configuration lineshapes recorded at 348 K.

The temperature dependences of the spinning correlation times are reported in Figure 6.

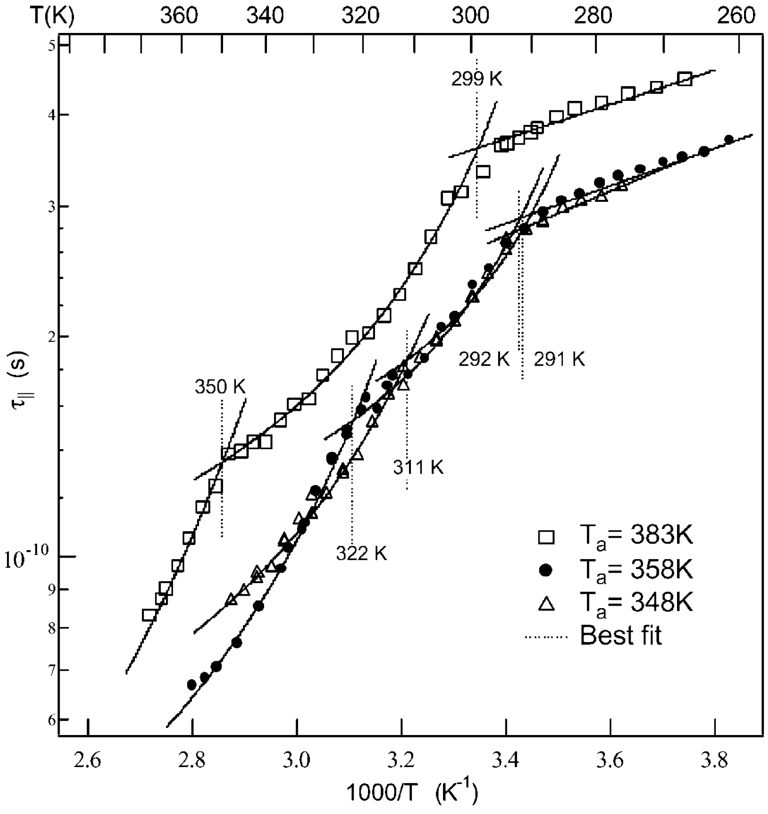

FIGURE 6. Spinning correlation time of Cholestane spin probe dissolved in PMA matrix after an annealing procedure at different temperatures.

Three temperature regions can be identified. In the low temperature regions, the crossing to activated regimes nearly coincides with glass transition. The temperature dependences of the spinning correlation time in high and low temperature region are well described by a Vogel-Fulcher law:

$$\tau_{\|} = \tau_{\|_0} \exp\left(\frac{T_b}{T - T_0}\right) \qquad (2)$$

where $\tau_{\|0}$ and T_b depend also on the spin probe. The values of the fit parameters are reported in Table 2.

The T_0 value obtained with rheological measurements coincides, within the experimental errors, with those reported in Table 2 .Therefore in both high and intermediate regions the spinning correlation time behavior can be expressed by a fractionary law of the structural relaxation time τ^{st}:

$$\tau_{\|} \propto \tau^{st}(T)^{\xi} \qquad (3)$$

where ξ, the fractional exponent, may vary between 0 and 1. $\xi=1$ corresponds to a complete coupling of the probe dynamics to the structural relaxation of the host matrix.

T_a(K)	T.R.	$\tau_{\|_0}$(s)	T_b(K)	T_0(K)
383	HT	$(5.4\pm0.4)10^{-12}$	300±15	257±3
383	IT	$(5.9\pm0.3)10^{-11}$	78±5	256±7
358	HT	$(1.4\pm0.1)10^{-11}$	152±5	259±2
358	IT	$(7.3\pm0.3)10^{-11}$	50±3	256±4
348	HT	$(2.9\pm0.2)\cdot 10^{-11}$	100±5	258±5
348	IT	$(9.6\pm0.7)\cdot 10^{-11}$	35±2	259±8

TABLE 2. Fit parameters for the temperature dependence of the tracer spinning correlation times in the different temperature regions (T.R.): higher temperature (H.T) and intermediate temperature (I.T.).

ξ is the ratio of the activation pseudo-energy of the VF law relevant to the short time dynamics over the value of the activation pseudo-energy of the structural relaxation time τ^{st}.

The strong decoupling degrees from structural relaxation time must to be mainly ascribed to the of time character of the heterogeneity [7] met in the polymeric matrix, when tested buy the LODESR spectroscopy. On the other hand, we may note the progressive decreasing of the activation pseudo energies on lowering the annealing temperature. This points out the augmented segregation degree of the spin probe from side groups, driven by the

increased mesogenic order in a more homogeneous polymeric matrix. Lower activation pseudoenergy values, as signaled in previous ESR investigations [7], correspond to molecular sites farther from polymeric main chain. So it would appear reasonable to localise the molecular sites relevant to the lowest activation pseudoenergy values along the mesogenic side chain near the terminal alkyl tails of the repeat unit.

The crossover from high to intermediate dynamical regions must be taken back to different physical mechanisms. In the 383K annealed sample the decoupling from high temperature dynamical regime occurs at 349K, a temperature slightly below the T_{NI}. It is to ascribe to the onset of nematic order in the matrix; the delayed response in the temperature scale, observed through LODESR, is due to the local character of the spectroscopy.

The dynamical variations in 348K and 358K annealed samples signal instead the effect of the onset of conformational disorder on the probe molecules embedded in differently soft environment. In the thermogram, reported in Figure 2 the onset of conformational disorder is located at 320K.

The substantial coincidence of spin probe dynamics in the temperature region below 311K is of particular relevance for optical applications.

The suitability of the material for optical memories application was evaluated by the optical measurements described in the previous section; here we outine the principle of the data analysis. The measured quantity is the ratio $R=I_{\perp}/I_{||}$, where $I_{\perp}$ and $I_{||}$ are the intensities of light polarized respectively perpendicularly and parallel to the impinging probe beam (which in turn is rotated by 45° from the writing beam polarization plane). Neglecting depolarization effects arising from multidomain-structure or sample inhomogeneities, which are excluded in our case, R is a periodic function of the sample thickness d:

$$R = \tan^2\left(2\pi \cdot \Delta n \cdot \frac{d}{\lambda}\right) \quad (4)$$

where Δn is the birefringence and λ is the probe wavelength. In our case, only the first period of the function was explored as molecular films were employed. The photoinduced birefringence as a function of the deposited energy on a 220 nm thick film is shown in Figure 7.

A large saturation value of birefringence (Δn=0.1) was obtained at quite small energy density. Photo-lithography also employing bitmap schemes was performed at room temperature in a similar manner on several samples prepared with the same thermal treatment as outlined above and with the same pumping power i.e. the minimum energy required for the saturation of the photoinduced effect. The stability of the optically written information was probed by heating the samples for 24 hours to different temperatures. The degree of degradation of optical information due to thermal effects was evaluated by time lapse imaging of the lithography. The images acquired as a function of time were compared to the first image of the lithography by 2 dimensional cross correlation algorithm and we found that the optical information is stable after 24 hour at 45° C.

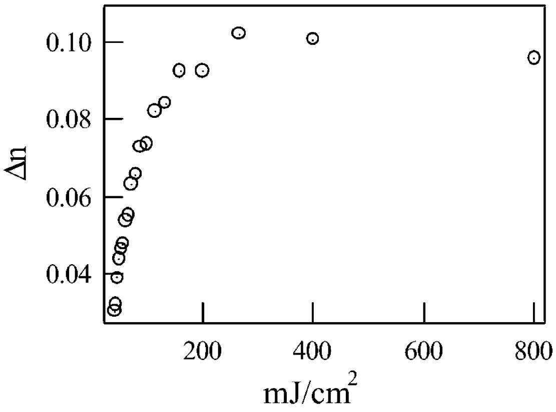

FIGURE 7. Photoinduced birefringence (Δn) as measured from images such as that in Figure 4, as a function of the deposited energy.

In conclusion our results indicate that, given the proper sample treatment procedure, PMA can be a quite sensitive and stable material for optical writing applications. Furthermore, both the magnetic spin probe and the optical microwriting data show that the extention of optical storage to the submicron scale might be feasible.

Acknowledgements
We gratefully acknowledge CIPE for financial support of the project P5W5.

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