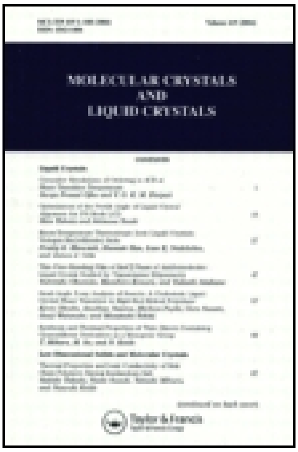

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoinduced Morphological Changes and Optical Writing in a Liquid Crystalline Polymer on the Micron and Sub-Micron Scale

P. Camorani [a], L. Cristofolini [a], G. Galli [b] & M. P. Fontana [a]

[a] Istituto Nazionale per la Fisica della Materia (INFM) UdR Parma, Dipartimento di Fisica, Universitá di Parma

[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universitá di Pisa

To cite this article: P. Camorani, L. Cristofolini, G. Galli & M. P. Fontana (2002): Photoinduced Morphological Changes and Optical Writing in a Liquid Crystalline Polymer on the Micron and Sub-Micron Scale, Molecular Crystals and Liquid Crystals, 375:1, 175-184

To link to this article: http://dx.doi.org/10.1080/10587250210577

Mol. Cryst. Liq. Cryst., Vol. 375, pp. 175-184
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Photoinduced Morphological Changes and Optical Writing in a Liquid Crystalline Polymer on the Micron and Sub-Micron Scale

P. CAMORANI[a], L. CRISTOFOLINI[a], G. GALLI[b] and M. P. FONTANA[a]

[a]*Istituto Nazionale per la Fisica della Materia (INFM) UdR Parma, Dipartimento di Fisica, Università di Parma and*
[b]*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Pisa*

ABSTRACT

In this paper we describe our recent work on optical effects due to photoinduced molecular reorientation in a side chain liquid crystalline polymer, namely azo-polymethacrylate (PMA4). We have studied several kinds of optical effects on space scales ranging from the nanoscopic to macroscopic. In particular, we have built a computer controlled microscope-based apparatus to study photoinduced effects down to the micron scale in thin and ultrathin (Langmuir Blodgett) films of our material. Furthermore we measured the morphology and the photoinduced surface deformation by Atomic Force Microscopy in the submicron scale.

Keywords: azobenzene, side chain polymeric liquid crystals, photoinduced surface relief

INTRODUCTION

Side chain liquid crystalline polymers (LCP) based on the presence in the side chain of the azobenzene moiety have been the subject of intense study in recent years [1]. Of particular interest have been the optical effects due to the photoinduced cis-trans isomerization of the azobenzene. These effects have been studied due to their potential for optical writing applications and more specifically for entirely-optical high-density memories [2].

This class of materials features a rich and complex phenomenology, which makes them very interesting also from a fundamental point of view. Their dynamics is the result of 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 [3]. The relative weight of such processes, and the coupling between side chain and main chain dynamics, depend of course not only on temperature, but it can be also externally influenced by optical pumping with light of the appropriate wavelength, polarization and intensity [4].

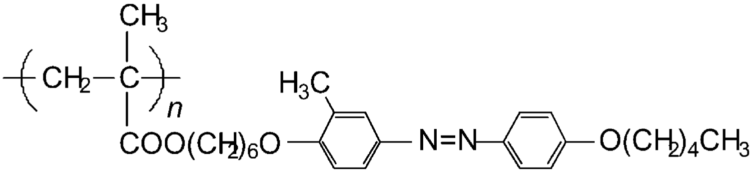

FIGURE 1 Molecular structure of PMA4 monomer.

Moreover, when dealing with ultrathin films, coupling interactions between substrate (imposing a planar ordering to the polymeric main chain) and PLC become relevant. This gives rise- via a purely geometric effect- to an increased stability of the glassy phase upon heating [5], and correspondingly to an increase of the typical times characterising the back-to-equilibrium relaxation process This is of relevance also for the stability of the information optically written onto such thin films of azo-polymer.

The combined action of the cis-trans photoisomerization and the nematic potential lead to collective molecular reorientation, hence to very high sensitivity of the sample to the optical writing beam. However it is not clear-and the subject of current investigation- how the nematic potential determines the collective character (and hence the length scale) of the molecular reorientation, on which the minimum addressable area depends, and hence the maximum information density possibly stored per surface unit. Although the basic microscopic mechanism for the production of optically oriented molecular domains has been amply discussed in the literature and is relatively well established [6], little is known about the propagation to the mesoscopic scale of the single molecule reorientation due to trans-cis-trans cycling under the action of polarized light. This information however is essential to be able to evaluate the potential usefulness of these polymers for micro- and eventually nano-writing applications. What is the role of the nematic potential in propagating the information? To what extent the residual coupling of the side to the main chain is responsible for the extensive memory effects observed? Is the amplification due to collective behavior going to be a problem when trying to rescale the optical effects to the nanoscale?

In this paper we try to address some of these questions, by using a pump-probe digital microimaging technique which allows the visualization in real time of the optical effects induced by the diffraction limited pump beam. The space resolution on the micrometric scale allows us to pinpoint specific domains, or to average over many of them by simply varying the pump beam size. This allows a study on the effects of space non-homogeneity on the kinetics of the formation and propagation of the optically induced domains. The measurements were performed as a function of temperature, energy dose, pump power and polarization, time.

The sample we have studied is PMA4, the synthesis and calorimetric properties of which are published elsewhere [7]. The formula is shown in

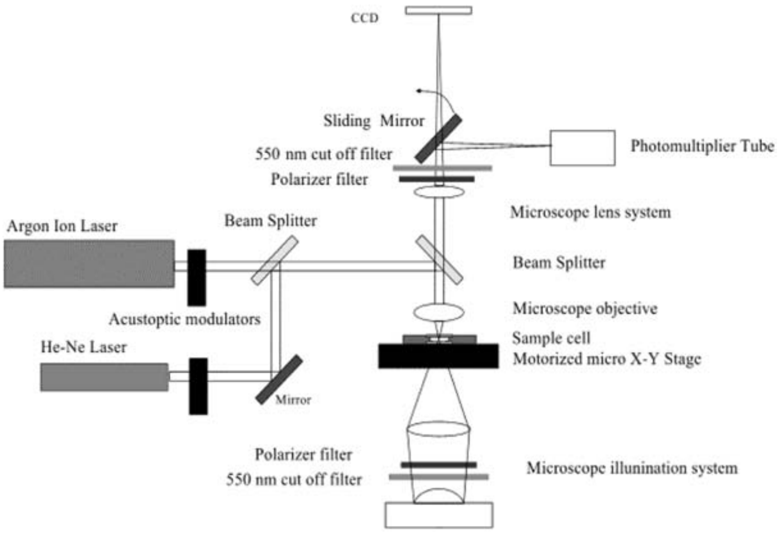

FIGURE 2 Experimental apparatus

fig.1.: the azobenzene moiety is attached to the main methacrylate chain via a polymethylenic "flexible spacer" , whose purpose is to decouple the azo group from the main chain, so that the liquid crystalline phase of the azobenzenes is not frustrated. The clearing point of this material is T_C=85°C while the glass transition temperature is T_g=25°C.

EXPERIMENTAL SECTION

We have developed an experimental apparatus for the imaging characterization of the photoinduced effects. The experimental set up (outlined in figure 2) 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 the microscope objective itself by means of a beam splitter. The Ar^+ beam was focussed onto a pin hole (from 5 to 100 μm size) and collimated by a lens to yield a confocal geometry before entering in the microscope, in order to clean and reduce the Gaussian profile up to beamsize of FWHM = .5 μm (depending on pin hole size and objective magnification employed). The intensity and exposure time of the laser beam is controlled by an acousto-optic modulator with switch time of 15 ns.

The sample can be observed in transmission mode through cross polarizers by a highly sensitive CCD camera (0.0003 lux) and the images can be acquired in time resolved mode by the computer. To remove the pump light spot from the images a band pass filter (550-800nm) was inserted after the analyzer. The same type of filter, which selects a spectral region where the azobenzene does not adsorb, was placed between the lamp and the sample in order not to influence it by the radiation. Moreover birefringence can be accurately determinate by the measurement of the depolarization ratio of a He-Ne laser (λ=633nm, power W=1 mW) impinging on the sample collinearly with the writing beam and with plane of polarization rotated by 45° with respect to that of the writing beam. In this case a photomultiplier tube in photon counting mode is used for the accurate evaluation of the delivered light.

We investigated the surface morphology and its photoinduced modifications by atomic force microscopy (AFM, Autoprobe CP-Research, Thermomicroscopes) using both intermittent contact (IC) and non-contact (NC) modes. We selected Ultrasharp-Noncontact silicon cantilevers (Silicon-MDT Ltd, Russia) with typical resonance frequency in the range 110-150KHz, vibration amplitude about 50 nm and used a large area scanner (100 μm max sweep) with optical feedback. UV sample illumination was provided *in-situ* by a high pressure mercury lamp whose light was filtered (λ=365nm) so that it could effectively induce trans to cis isomerization processes. We could then follow the photoinduced, as well as the thermally induced morphological changes and film dewetting processes. We note in passing that the cis-to-trans back-relaxation in dark takes place over a time scale of several hours at room temperature for this material [3,5].

RESULTS AND DISCUSSION

We studied the microscopic mechanism of domain reorientation by imaging the photoinduced changes of the optical texture using the microscope based apparatus described above. A sample was prepared by placing the PMA4 between two glass plates pressed toghether and spaced by a 10 μm thick spacer. The sample was molten at 100°C (20°C above his clearing point) for one hour and then slowly cooled (1°C/min) to room temperature . A region of the sample was illuminated by blue light employing the microscope reflection mode lamp as optical pump source and observed the light transmitted through crossed polarizers set at 45° with respect to the writing beam polarization (the geometery of the experiment is sketched in figure 3a). We reduced the light power so that the photoinduced dynamics developed over a timescale of several seconds. The pristine sample (figure 3b) exhibits at room temperature the nematic Schlieren texture [8] with points defects of strength ±1. After the optical pumping (figure 3e), the irradiated area became a monodomain containing disclinations lines (strength ±½). The photoinduced reorentation, creating an optical axis, decreases the symmetry of the system and a 'topological' transition occurs from the initial point defects (monopoles) to disclinations lines.

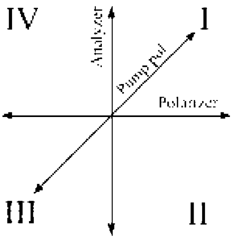

FIGURE 3a

FIGURE 3a Experiment geometry
FIGURE 3b Sample before irradiation
FIGURE 3c,d,e Texture evolution under illumination

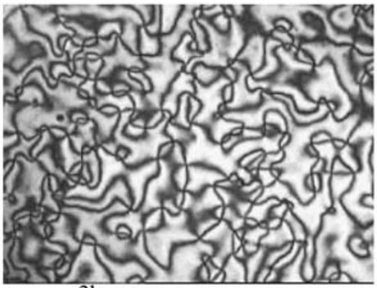

FIGURE 3b

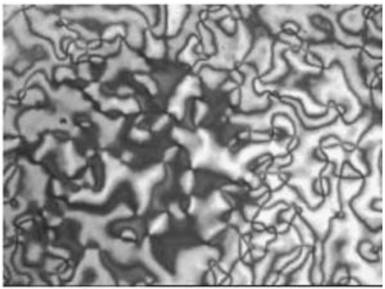

FIGURE 3c

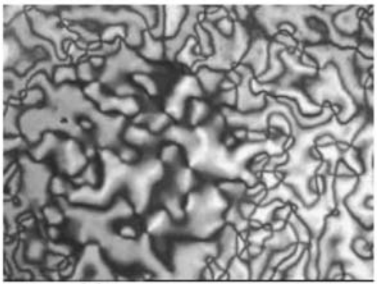

FIGURE 3d

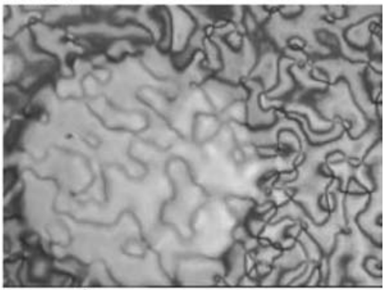

FIGURE 3e

The created disclinations join together the former monopoles. Let us consider the possible director orientations divided in four cartesian quadrants (see fig.3a). The collective molecular reorientation process takes place in 3 steps:

1. A nematic to isotropic phase transition occurs in the regions of I and III quadrant where the nematic axis is initially predominantly parallel to the pump beam polarization, as it can be seen by comparing Figures 3b and 3c: these regions become dark between crossed polarizer.
2. The domains oriented in the II and IV quadrant, oriented predominantly in the perpendicular plane, grow at the expense of the isotropic regions until they finally fill the whole area (fig3d) . A disclination line is created when to domains of opposite quadrant meet. Furthermore, a detailed analysis performed on the time resolved

digitized microscopic images pointed out that the growth is faster in the directions perpendicular to the induced nematic axis.

3. Finally when the nematic director is oriented along the same direction in all the sample, the order parameter starts to grow, as it can be deduced by the increase of the integrated birefringence shown in Figure 3e.

The imaging of morphological change indicates that the photoinduced mechanism strongly depends on the initial system state, the nematic potential play an important role in the propagation of reorientation and that a photoinduced nematic-to-isotropic (N-I) phase transition is an important step in the process.

The occurrence of molecular reorientation or phase transition as final results of irradiation, depends on whether the order propagates in the disorder area or viceversa, respectively. What actually happens appears to be driven by many factors as temperature, pump power and wavelength. In particular we have found for a similar compound, a polyacrylate with the same side chain, [9] a macroscopic power-temperature P-T phase diagram in which the photoinduced N-I transition occurs upon heating at a critical temperature which decreases with increasing pump power. This indicates that for a given temperature, there is a critical pump power density above which the collective effects which are responsible for the macroscopic reorientation of the nematic director are destroyed by the poisoning of the nematic potential.

The observed anisotropy in the growth of oriented domains, which proceeds more rapidly in the direction perpendicular to the local director, indicates that at the boundary between isotropic and oriented regions the nematic potential tends to attract and align the molecules from the isotropic region.

Our result strongly supports one of the models employed to explain the mass transport which originates the surface reliefs observed after space resolved optical pumping in many azobenzene compounds [10]. These observations indicate thus the importance of space-resolved studies of sample morphology as evidenced by topographic or optical birefringency probing of the photoinduced effects over an extended range of length scales.

Therefore we investigated then the effect of light on the surface morphology by AFM microscopy. A report of studies in which we used the birefringency probe with SNOM microscopy, both for optical perturbation and for imaging, is in preparation [11]. In figure 4 we report the topographic images showing the progressive evolution of the surface, from the homogeneous pristine surface of the LS multilayer (10 monolayers) through the formation of holes which grow both in size and in number as the dewetting of the polymeric film from the silicon substrate takes place under the action of UV illumination. Here it must be recalled that the main effect of UV light is that of converting most of the ***trans***-azobenzenes to the ***cis*** conformer, whereas illumination with blue light induces, as described above, a more complex phenomenology, due to the simultaneous optical absorption of the ***trans*** and

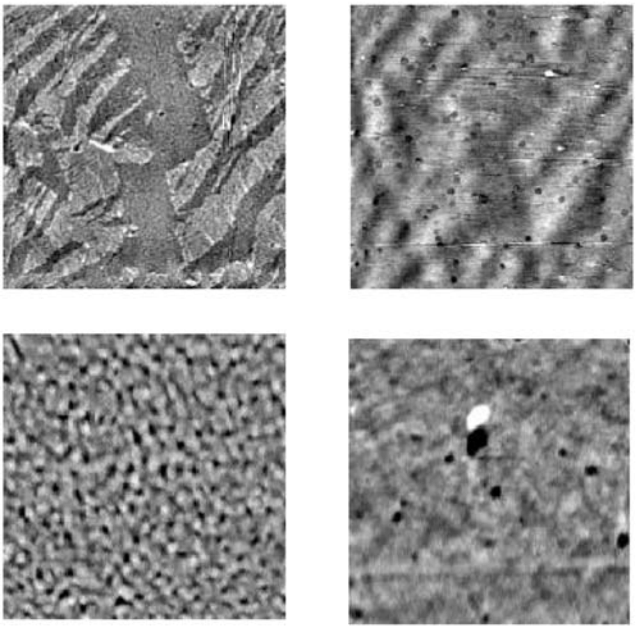

FIGURE 4 AFM topographic images showing the progressive dewetting of the polymeric film from the silicon substrate. The lateral size of the images is 6x6μm^2, except for the bottom right image, which is 1x1 μm^2. In the vertical scale, the full white-to-black contrast corresponds to 2nm for the first image, and to 6nm for the others. The top left image is the LS film as deposited, top right after 1 hour ofHg exposure, bottom left same after 14hours Hg exposure, while the bottom right is a detail of the previous topography with enhanced resolution.

cis conformers. The lateral size of all the images is 6x6μm^2, except for the bottom right image, which is 1x1 μm^2 .

In the vertical scale, the full white-to-black contrast corresponds to 2nm for the first image (top left panel) , in which the flat morphology of the as-deposited LS film can be evaluated. The only structures we can observe in this image are the terraces due to the incomplete coverage of the upmost molecular layer only, and correspond to a root mean square (RMS) roughness of about 18-20Å. The second image, in the top-right panel, of lateral size 6nm, vertical scale for white-to-black contrast 6nm was taken after 1 hour of exposure to the Hg lamp. Here we note two processes: first, some holes start to form in the film (black circular spots in the image), and second the roughness due to the terraces is reduced. We note that independent X-ray reflectivity measurement on similar samples have

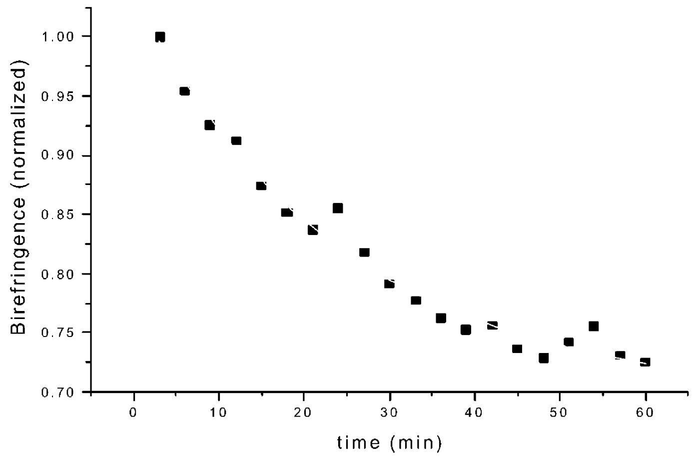

FIGURE 5 Photoinduced birefringence after UV exposure

confirmed this effect, with a photoinduced reduction of the RMS roughness to about 10Å [12,13]. This effect can be ascribed to increased fluidity of the polymeric material as the cis fraction grows and can be related to the observation of

higher optical compliance after UV irradiation, as reported later in this same section. The third image, on the bottom left panel was taken after 14 hours of Hg lamp exposure. Here the terraces structure has completely disappeared, and the holes have grown in density and in size, at the level at which they cover almost half of the sample surface. Finally in the bottom right panel is a detail of the previous topography with enhanced resolution (lateral size 1x1 μm^2).

The sample after UV treatment appears black in polarizing optical microscopy because of the presence of non mesogenic cis molecules which poisons and destroys the nematic phase. We found by UV-Vis absorption spectroscopy that in our sample 15 min UV irradiation causes an almost complete trans to cis transformation. This exposure time in any case is not sufficient to cause the dewetting phenomena described above. The back isomerization to the more stable trans form takes place then in the dark with a characteristic time of several hours, a time much longer than our experiment. This allows us to probe the properties of the material as a function of cis-isomer concentration. We evaluate the writing efficiency by illuminating with Ar^+ laser micron sized areas at constant power density (~1 W/cm^2 for 200 ms) as a function of time after the UV exposure. As already stated, the light at 488 nm induces both isomerization processes which yield an oriented region from isotropic phase. We find an increase of about 25% in the optical birefringence, due to the fluidification effect.

FIGURE 6a: 50x50 mm AFM image of photoinduced surface relief

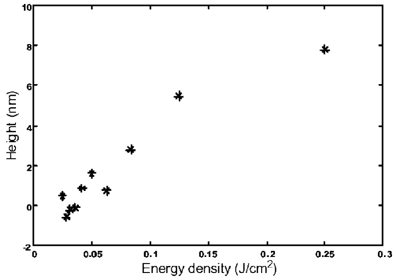

FIGURE 6b Heigh of relief in figure 6a as a function of energy density.

In the graph in Fig.5 we show the exponential decrease of efficiency after UV irradiation, the asymptotic value is reached before the complete back-isomerization time since the cis concentration is the equilibrium value at this pumping power density.

We further investigated surface deformation producing some lithographs with the microscopic setup and probing them by AFM. The lithographs were produced by moving the sample under spot illumination. We found that this induces a surface relief only when the sample is moved perpendicularly to the pump light polarization. This confirms the previous observation that the realignment process proceeds mainly in the direction perpendicular to the nematic axis.

We produced some lines moving the sample at different speeds in order to fine tune the energy deposited on sample per line and we imaged them with AFM (fig.6a) .

We found , from the measurement of the height of the reliefs (Fig.6b), a threshold energy density of 0.06 J/cm^2 under which no photodeformation is induced.

CONCLUSIONS

We have studied the mechanism of domain reorientation in the nematic phase of a typical liquid crystalline polymer on the mesoscopic scale through detailed birefringency microimaging. We have demonstrated the presence of an intermediate isotropic phase as an important step in the overall reorientation process. This was ascribed to the photoinduced fluidification of the nematic side chain fluid, which was confirmed by AFM microscopy data. Finally, we have demonstrated the possibility of using such effects to produce images on the submicron scale.

REFERENCES

1. S.Kumar, Chem. Rev. **89**, 1915, (1989)
2. S.Hvilsted, F. Adruzzi, C. Kulima, Siesler-H.W. and P.S. Ramamujan, Macromol. **28**, 2172-2183 (1995)
3. L. Cristofolini, P. Facci, P. Camorani, M. P. Fontana, J. Phys.: Condens. Matter., **11,** A359-366(1999)
4. L. Cristofolini, M. P. Fontana, M. Laus B. Frick - Phys. Rev. E, 64, in press (2001)
5. L. Cristofolini, S. Arisi, M. P. Fontana - Phys. Rev. Lett. **85,** 4912. (2000)
6. T.G. Pedersen , P.M. Johansen - Phys. Rev. Lett. **79,** 2470. (1997)
7. A.S. Angeloni,D.Carretti,C. Carlini , E. Chiellini, A. Altomare, R. Solaro M.Laus
   Liq. Cryst., **4,** 513, (1989)
8. P.G. DeGennes, The physics of Liquid crystal , Oxford Uniniversity Press (1974)
9. S. Arisi, P. Camorani, L. Cristofolini, M.P. Fontana, M. Laus - Mol. Cryst. Liq. Cryst., in press (2001)
10. N.C.R. Holme, L. Nikolova, P.S. Ramanujam, S. Hvilsted, Appl. Phys. Lett. , **70**, 1518, (1997)
11. M.Allegrini, P. Camorani, M. Labardi, M.P. Fontana (in preparation)
12. L. Cristofolini, T. Berzina, M. P. Fontana, O. Konovalov this iussue
13. L. Cristofolini, M. P. Fontana, O. Konovalov, Philos. Mag. B in press (2001)