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SNOM Imaging of Photoinduced Microstructures in Azo-Polyacrylates

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Abstract Polymer liquid crystals with a photosensitive azobenzene side chain (azo-scPLC) are interesting materials because of their potential in optical switching and high density optical data storage applications. By illumination with blue linearly polarized light, the azobenzene chromophores undergo repeated trans-cis-trans isomerization cycles, resulting in reorientation of the side chains perpendicular to the electric field direction.

We investigate the structural effects due to molecular reorientation in azo-scPLC on the scale of 10-100 nm by using a scanning near-field optical microscope (SNOM). We have selected a SNOM contrast mechanism suitable for domain discrimination by modulating the polarization at the input of the SNOM fiber probe and measuring the sample response with a lock-in technique, since the SNOM optical signal is polarization dependent. We image topographic and optical spontaneous structures of a Langmuir-Schaeffer multilayer of azo-scPLC and photoinduced micron-size patterns previously created by far-field laser illumination.

We also present preliminary results in nanowriting, obtained by a pump and probe technique performed through the SNOM probe.

Keywords SNOM, polarization contrast, azobenzene, polymeric liquid crystals

INTRODUCTION

Liquid crystalline polymers containing azobenzene moieties in the side chain are promising optical material for application in high-density data storage [1]. Illumination with polarized light in the azobenzene absorption region causes a selective trans-cis isomerization cycle of the

cromophores with transition moment parallel to the electric field. The result of such process is a molecular reorientation [2] perpendicular to the pump light polarization direction, as well as an increase of the order parameter. Such effects have been previously studied on a liquid crystalline side chain polyacrylate (PA4) [3] on the macroscopic (millimeter) and mesoscopic (tens of micron) scales with different optical techniques [4]. Such material exhibits a rich phenomenology, which promotes it as a promising candidate for both fundamental studies as well as for applications. In particular, it looks suitable for reversible optical writing, theoretically down to the molecular level, due to its high sensitivity to the optical perturbation and long term stability of the photoinduced effects.

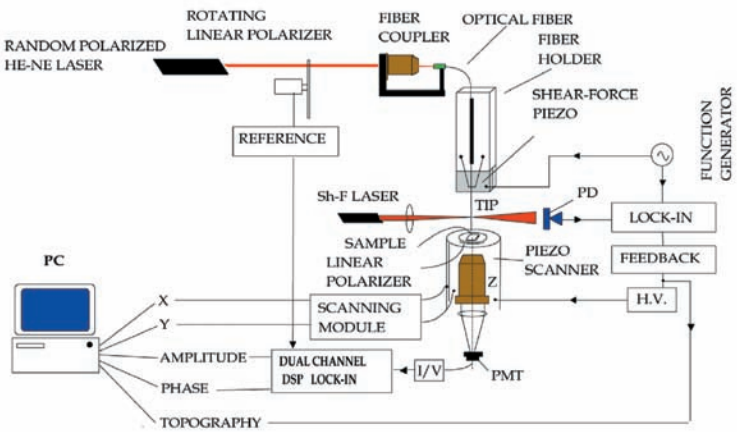

FIGURE 1 SNOM system

In the present work we investigate both the structure of spontaneous optical domains as well as the effects of molecular reorientation on a thin film of PA4 on the sub-microscopic scale (10-100 nm) using a scanning near-field optical microscope (**SNOM**). This technique is suitable for our purposes since the degree of polarization of the near-field is dependent on the input polarization [5] and birefringence has been demonstrated to be preserved in SNOM [6].

EXPERIMENTAL SETUP

In order to be sensitive to the optical anisotropy of the sample we set up a SNOM apparatus working in polarization modulation contrast [7] adapting a homemade instrument [8]. In the system, as shown in Fig. 1, the beam of a random polarized He-Ne laser is coupled to a single mode, metal-coated SNOM fiber probe, with a 50 nm aperture which is approached to the sample surface, within the near-field distance, by means of standard shear-force techniques [9]. The wavelength for optical structure imaging (633 nm) has been chosen to fall well outside both cis- and trans- absorption regions. In the adopted modulation scheme, the input polarization is varied continuously over 180 degrees, and the sample response to the different polarization states at the SNOM tip is

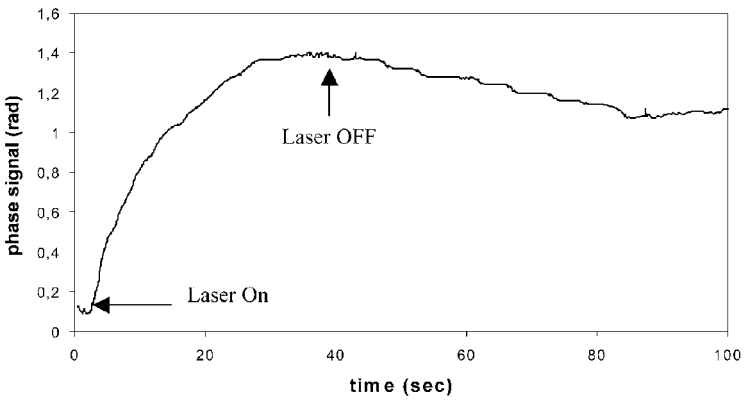

FIGURE 2 Phase signal behaviour during optical pumping in far field.

detected by lock-in techniques. Experimentally, the modulation is realized by rotating a linear glass polarizer (at 70 Hz) which yields a polarization modulation of $\omega/2\pi = 140$ Hz and placing the sample over an analyzer (linear glass polarizer). Light transmitted through the polarizer is collected by means of a photomultiplier and a digital dual channel lock-in amplifier is used for the detection of the optical signal. Acquisition of topography as well as of phase and amplitude of the optical signal is performed simultaneously, since both of them are related to the local nematic axis orientation.

In order to test the degree of polarization of the near-field light, the tip is approached directly to the analyzer and the response is observed on the oscilloscope. The SNOM fiber was looped to compensate the change of polarization due to its anisotropic core structure. The Malus law $\cos^2(\omega t)$ is reproduced fairly well. After the optimization of the modulation depth of such behavior (about 9:1), the fiber was fixed in position.
The polymeric film was prepared by deposition of 30 bilayers with the Langmuir-Schaeffer technique [10]. The thickness of a single layer, measured by ellipsometry [11], is about 20 Å, so that the total thickness of our film is 120 nm.

RESULTS

An alignment of the side chains was induced in the sample by exposition to a 20 mW Ar^+ laser beam at 458 nm. The photoinduced process was monitored using the polarization modulation scheme described above,

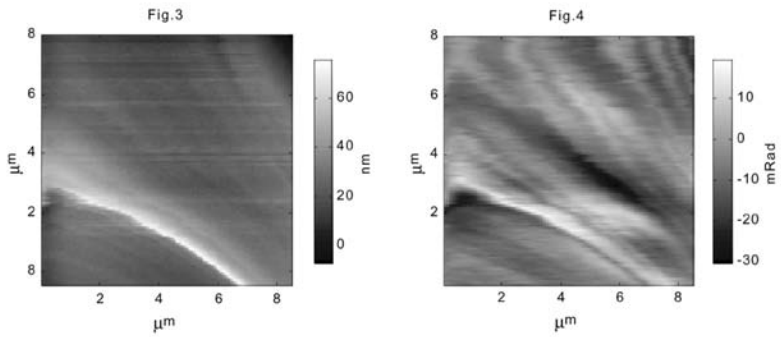

FIGURE 3-4 Topography and phase image of spontaneous structures of our Langmuir-Schaeffer film. The scan size is $8 \times 8\ \mu m^2$.

In Fig. 4 we show the optical phase image of spontaneous structures on a sample region not previously irradiated with blue light. By comparison with the topographic image (Fig. 3) we can infer an influence of morphology on the optical features. For instance, the filament structure noticeable in Fig. 3-4 is due to pressure waves occurring during the sample deposition. On the other hand, photoinduced patterns can be imaged with no such artifacts, since illumination causes a decrease of roughness, as can be directly observed, on a larger scale, by conventional optical microscopy.

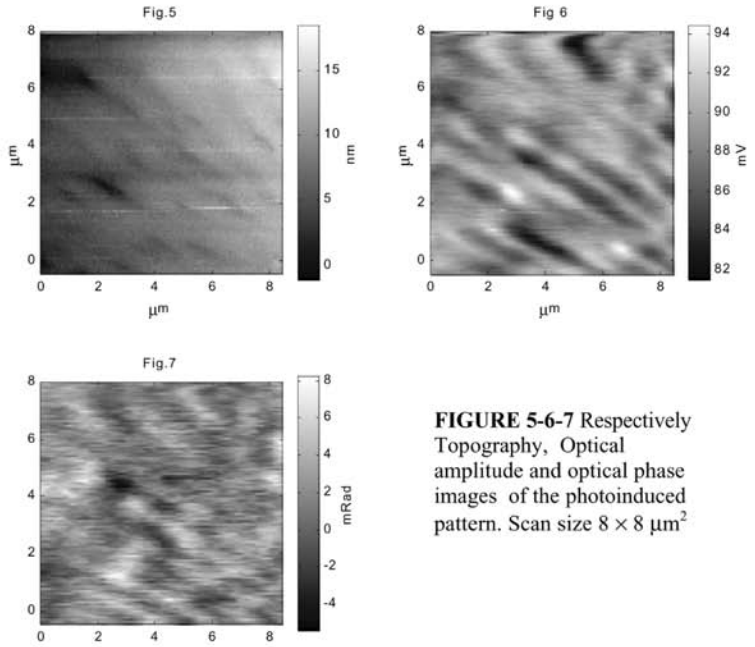

FIGURE 5-6-7 Respectively Topography, Optical amplitude and optical phase images of the photoinduced pattern. Scan size $8 \times 8\ \mu m^2$

In order to obtain the best contrast for the written pattern, the sample was oriented with the grating vector at 45° respect to the analyzer axis.

Images of amplitude (Fig. 6) and phase (Fig. 7) of the irradiated sample show the expected micron-size photoinduced structure. The simultaneously acquired image of Fig. 5 shows that the exposure to the optical lattice, responsible of the writing of the lines shown in the optical

images, has slightly influenced the morphology of the surface as well, as independently observed by other groups [13]. Nevertheless, the contrast visible in the optical images is clearly due to modulation of the optical activity of the sample and not by topographic artifacts or thickness variations of the film. This is evident by the lack of one-to-one correspondence between topographic and optical features, as well as by the more pronounced contrast of the optical images themselves. These measurements confirm the ability of our technique to image the optical anisotropy on the near-field scale.

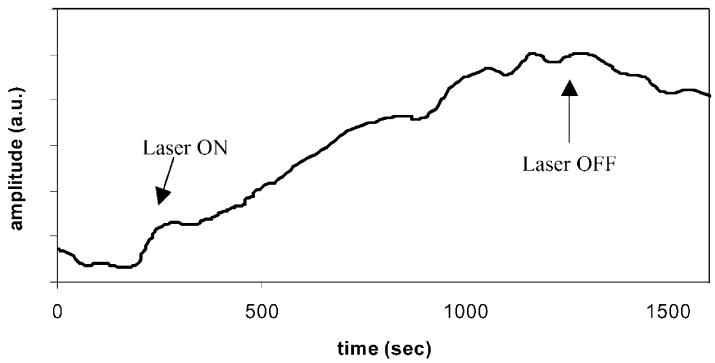

FIGURE 8 Optical amplitude signal in the pump and probe experiment performed through the SNOM fiber tip.

A different method of optical micro-patterning was used and subsequently checked by SNOM. The pattern was created by illuminating the sample with blue light through a copper TEM mask, namely a square grating composed by 20 μm square apertures and 5 μm wide stripes. The shadow pattern could be observed by both SNOM and conventional optical microscope.

In the last part of our work, we have performed the same pump and probe experiment previously described by coupling both the writing and reading beams to the SNOM fiber probe at the same time, with the aim of producing a localized change in the sample. The variation of the optical signal, reported in Fig. 8, is in agreement with the result obtained on the macroscopic scale.

CONCLUSIONS

We have selected a SNOM contrast mechanism suitable for the discrimination of the orientation of the local director in a photosensitive liquid crystalline polymer (PA4). Tests have been performed by measuring micron-size patterns created by far-field laser illumination on a 120 nm thick film prepared with the Langmuir-Schaeffer technique. We have shown that PA4, prepared with such technique, is suited for application in high density optical data storage because of both the reduced roughness of the film and the possibility of controlling the film thickness under the near-field depth, down to the double layer size (~4 nm), that would ensure nanometer size spatial resolution. Finally, we have presented preliminary nanowriting results by performing a pump and probe experiment on the near-field scale. The demonstration of the induced birefringence change on the nanometer scale by SNOM techniques confirms the potential of this class of liquid crystalline polymers for high density optical storage.

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