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All-optical Manipulation of Azo-dye Molecules

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SUMMARY : A challenging issue in the field of the design of devices for photonic applications is to achieve complete manipulation of the molecular order. Azo-dye aromatic polymers have been shown to offer interesting prospects for material engineering using light matter interactions. Dual-frequency irradiation using appropriate combinations of circular beams polarizations are demonstrated to enable full control of the molecular polar rotation. More recent results on photoinduced surface-relief gratings have also opened the way of molecular translation control using optical fields. Understanding of the relevant parameters of molecular translation processes is a key issue for optimization of such an optomechanical effect : a simple model accounting qualitatively for the essential features of photoinduced surface-relief gratings will be presented.

Introduction

The influence of polarized light on azo-aromatic polymers has been the subject of many studies[1-4]. It is now well established that axial reorientation of molecules occurs following resonant excitation, leading to quasi-permanent birefringence and dichroism. Microscopically, it was evidenced that following resonant excitation and *Cis-Trans* isomerization, molecules tend to align in a direction perpendicular to the exciting light polarization after thermal relaxation and orientation diffusion. Actually, such phenomenon can also be applied to all-optical polar ordering[5,6]. More particularly, we show in the following that dual-frequency irradiation using appropriate combinations of circular beam polarizations enables full control of the molecular polar ordering. Another interesting feature concerns the control of molecular translation. In fact, such mass transport phenomenon was recently observed in holographically inscribed high-efficiency diffraction gratings[7-9]. Although the existence of the competing formation of a birefringence grating was observed[10], atomic force microscopy (AFM) has evidenced that surface-relief gratings with modulation depth as large as twice the film

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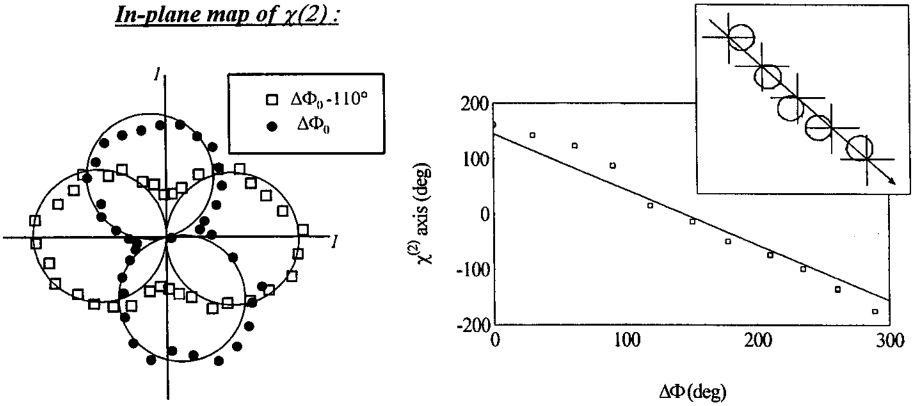
thickness could be induced. Following the first studies of such gratings, we present here complementary experiments aimed at a better understanding of the microscopic origin of such surface-relief grating formation. Theoretical predictions derived from a simple model based on photoinduced azo-benzene diffusion following *Cis-Trans* isomerization show good agreement with the experimental anisotropic features.

Optical manipulation of molecular polar orientation

As it was originally shown in glass optical fibers[11,12)], the coherent superposition of two beams at fundamental and second harmonic frequencies results in a polar field $E=E_{\omega}+E_{2\omega}$. Indeed, the temporal average of the field cube E^3 is nonzero[13)]. In the case of organics, the physical origin of the photoinduced centrosymmetry breaking was identified as a selective excitation of the molecules oriented in one given direction and sense via simultaneous one- and two-photon absorption on the same electronic level[14)]. The orientation selective excitation relaxes thermally inside the polymer. Using appropriate molecules it leads to a quasi-permanent molecular angular redistribution, resulting in the recording of a spatially modulated $\chi^{(2)}$-susceptibility. Optimization of the relative phase and energy between the writing beams at frequencies ω and 2ω permits the achievement of large orientation efficiency in azo-dye copolymers[5)]. A phenomenological model for photoinduced orientation mechanism in dyed polymers was recently proposed and confirmed the importance of parameters such as writing beams relative phase and intensities[5)]. Further study of the all-optical poling dynamics also pointed out that another important seeding condition was the control of the relative weight between molecular mobility inside the matrix and photoinduced reorientation[15)].

Interestingly, it was shown that, using appropriate combinations of adequately polarized writing beams at fundamental and second harmonic (SH) frequencies, it is possible to tailor the symmetry of the photoinduced macroscopic polar order, even using one-dimensional molecules. This enables a complete in-plane engineering of the photoinduced polar order[6)].

For linear writing beam polarizations, $\chi^{(2)}$ exhibits axial symmetry along the writing beams polarization direction. $\chi^{(2)}$ magnitude is strongly dependent on the phase difference $\Delta\Phi$ between the writing beams[6)]. For co- and counter-helical writing beam polarizations, $\chi^{(2)}$ magnitude is independent of the phase $\Delta\Phi$ between writing beams. In both cases, variation of the relative phase $\Delta\Phi$ yields in-plane rotation of the $\chi^{(2)}$ pattern by the same angle $\Delta\Phi$. Tensor analysis of the photoinduced $\chi^{(2)}$ was experimentally achieved by studying SH intensity generated along one given polarization direction as a function of the sample in-plane rotation angle δ. The ω-reading beam was linearly polarized along the same direction. $\chi^{(2)}$ tensor polarization results are given in figures 1, and 2, respectively for the co-helical and counter-helical writing beam polarizations at ω and 2ω frequencies.



In-plane map of χ(2) :

Fig. 1 : $\chi^{(2)}$ symmetry for co-helical writing beam polarizations. Left part is the polar representation of the vertically polarized SH amplitude (α $|\chi^{(2)}|$) as a function of the sample in-plane rotation. Two writing beam phase differences ΔΦ are displayed. Solid line is the expected theoretical dependence: $\left|\chi^{(2)}_{\Delta\Delta\Delta}\right| \propto \left|\cos(\Delta k.z + \Delta\Phi + \delta)\right|$, where $\Delta k = 2k_\omega - k_{2\omega}$ is the wave-vector mismatch. Right part of the figure shows that $\chi^{(2)}$ C_1-axis rotates like the writing beams phase difference ΔΦ. Insert is a schematic polar representation of the axis-modulated $\chi^{(2)}$ over propagation.

Experimental data were recorded a few minutes after stopping the preparation process. Samples were spin-coated 0.1 μm-thin films of DR1-MMA 35/65 copolymer. It was obtained by free radical polymerization of a 65/35 molar mixture of methyl methacrylate (MMA) and N-ethyl-N-(metacryloxyethyl)-4'-amino-4-nitroazobenzene, a Disperse Red 1 (DR1) derivative. The source was a Nd-YAG laser delivering 25-ps pulses at 1064 nm with a 10 Hz repetition rate. Second harmonic was obtained after partial frequency doubling in a KDP crystal. Fundamental and second harmonic writing beam fluences were optimized in order to reach maximum poling efficiency.

Using appropriate combinations of the writing beam polarizations, dual-frequency irradiation permits complete all-optical tailoring of the tensor properties of the photoinduced second-order susceptibility $\chi^{(2)}$, using conventional one-dimensional molecules. It enables full control of the molecular polar order. Worth noting is that, in the case of helical polarizations, writing beams phase retardation $\Delta\Phi$ is coded into a $\chi^{(2)}$-pattern rotation by the same angle. As pictured in the inserts of figure 1 and 2, this permits the optical induction of chiral microstructures using achiral molecules.

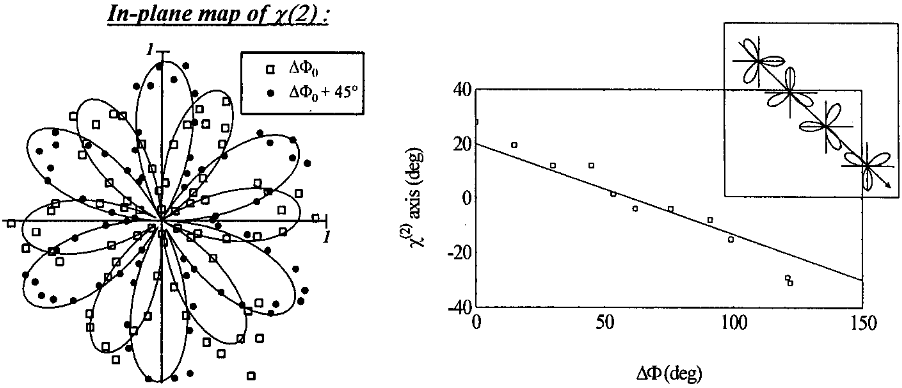


Fig. 2 : $\chi^{(2)}$ symmetry for counter-helical writing beam polarizations. Left part is the polar representation of the vertically polarized SH amplitude ($\propto |\chi^{(2)}|$) as a function of the sample in-plane rotation. Two writing beam phase differences $\Delta\Phi$ are displayed. Solid and dotted lines are the expected theoretical dependence : $\left|\chi^{(2)}_{\Delta\Delta\Delta}\right| \propto \left|\cos(\Delta k.z + \Delta\Phi + 3\delta)\right|$. Right part of the figure shows that $\chi^{(2)}$ C_3-axis rotates as $\Delta\Phi/3$. Insert is a schematic polar representation of the axis-modulated $\chi^{(2)}$ over propagation.

Optical manipulation of molecular migration

Laser-induced gratings were recently evidenced using atomic force microscopy[7-9]. These gratings were obtained when illuminating a polymer thin film containing azobenzene groups with an interference pattern of polarized laser beams. In typical experiments, the wavelength of the laser was chosen to be near the maximum absorption of the chromophores, typically λ=488 or 514 nm of an Argon laser, with intensities ranging from I = 5-100 mW/cm^2. The influence of experimental parameters such as laser intensity, polarization, grating spacing have been explored[8,9]. As shown in figure 3, we also observed surface-relief gratings appearing in real-time holography experiments performed with PMMA films doped with a modified DR1 azo-dye. The surface gratings have a negative amplitude, unlike what was observed in the case of azobenzene liquid crystalline side-chain polymers[16].

As shown in figure 4, modulation amplitude can be as large as twice the polymer film thickness, even in thick film, such as l=0.7 µm with quite high optical density (OD $\approx$ 2.7) at

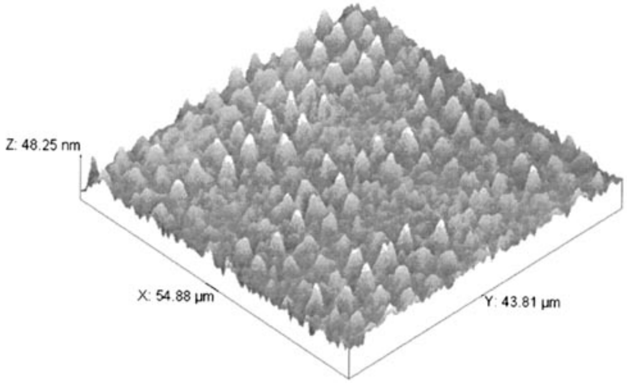


Fig. 3 : Surface-relief grating (inverse image) obtained in a 0.4 µm thickness PMMA film doped with a modified DR1 azo-dye (30% in weight), after irradiation through an array of fibers. We observe a modulation amplitude $\Delta h \approx 60$ nm and it appears that irradiated areas, corresponding to the end of each fiber of the array, are giving rise to pits (inverse image).

the writing beams wavelength $\lambda=514$ nm. These gratings also present very high stability at room temperature.

In order to test the possible influence of intermolecular cooperative effects, we recorded surface-relief gratings using DR1-MMA copolymers grafted with different concentration of Disperse Red 1 : 15/85, 35/65, 50/50, the first number indicating the molar proportion of grafted MMA monomers. As summarized in table 1, it appears that the relative modulation depth is independent of the chromophore concentration, which indicates that, in such systems, the influence of any cooperative intermolecular movements is negligible in the surface-relief grating formation process.

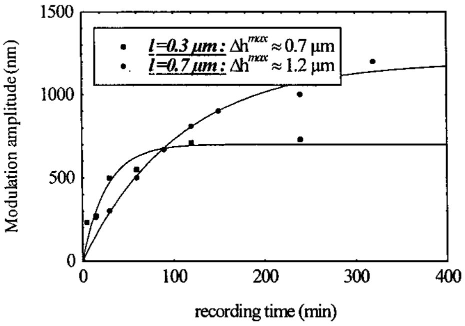


Fig. 4 : Modulation amplitude of the surface-relief grating recorded in two samples with different thicknesses (l), using 45° polarization of the writing beams with $P=50$ mW/cm^2 at 514 nm. Writing beams incidence was adjusted to get about $\Lambda \approx 2$ µm periodicity of the grating.

MMA-DR1 / MMA molar proportions	*Relative modulation depth Δh/2*l*
15/85	34 %
35/65	40 %
50/50	28 %

Tab. 1 : Surface-relief grating relative modulation depth obtained for a given preparation time in systems grafted at different chromophores concentration, using comparable recording conditions (45° polarization, $\lambda = 514$ nm, with P=50 mW/cm^2).

Several explanations were invoked for the photoinduced recording of such surface-relief gratings. Thermal effects due to light absorption are excluded as the main contribution to the process since it was observed that the grating modulation amplitude was highly dependent on the writing beam polarizations9) : *p*-polarized laser interferences produce surface gratings with diffraction efficiency typically 10 times larger than *s*-polarized ones. Additionally, the process is reversible, which excludes ablation. Based on these observations, we have proposed a model with simple assumptions that explains the anisotropic photoinduced diffusion of azo-benzene dyes in polymer matrices17) : as pictured in figure 5, it can be described in terms of caterpillar-like translation motion.

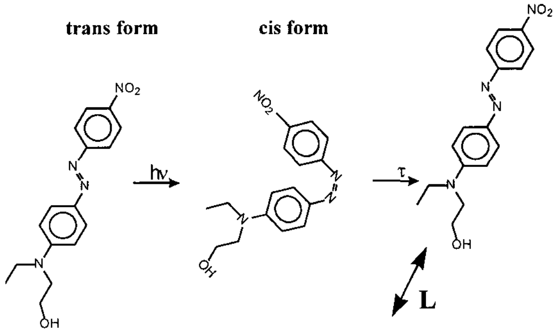


Fig. 5 : Photoinduced isomerization mechanism of the DR1 molecule. In the *cis* form, the molecule is bleached. When it relaxes back to the *trans* form, after orientation redistribution, it has undergone translation by an average amount *L*.

The basic principle of our model is that surface effects are governed by bulk diffusion of the molecules18). In order to understand the formation of the surface-relief grating, we consider the concentration of ground state *trans* chromophores with a dipolar transition moment which is in a element of solid angle around a given angular position, relative to the polarization of the laser beams, at a given position and time. We evaluate then the variation of this concentration after laser irradiation, considering that, after photoexcitation and isomerization in the *cis* form, the molecule relaxes back to the *trans* form after reorientation and translation diffusion by an average amount L (see figure 5). Molecules are thus pushing or pulling the polymer during their migration, giving rise to the surface-relief grating : in our model, surface effects are thus governed by molecular diffusion, azo-dyes molecules playing the role of « molecular motors ». Such description appears totally compatible with the macroscopic description of Barrett et *al.* in terms of a photoinduced viscoelastic flow$^{19)}$. Using this model we have been able to reproduce typical experimental results : for instance, numerical simulations from this model can fairly well predict the influence of the *(s)* or *(p)* polarized light on the grating diffraction efficiency$^{20)}$.

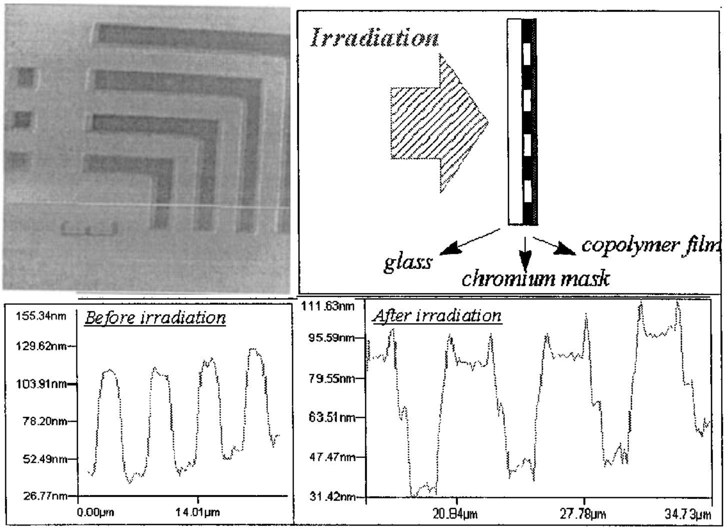


Fig. 6 : Surface-relief gratings recorded after 1 hour irradiation through 3-µm periodicity binary chromium mask. The copolymer film was about 300 nm thick. Irradiation was performed with P=50 mW/cm^2 at λ=514 nm using a 45° polarization of the beam.

In order to get the order of magnitude of the maximum total diffusion length after recording of the surface-relief grating, we performed some experiments through binary chromium mask. As schematically illustrated in figure 6, in order to avoid diffraction effects over propagation after irradiation through the mask, the azo-dye PMMA-DR1 copolymer was directly spin-coated onto the mask, AFM measurement being performed on the back side of the film. The result obtained after one hour irradiation of a 0.3µm-thick film is given in figure 6. As shown in the AFM scan before irradiation (left part of figure 6), the square modulation is mainly due residual surface modulation of the copolymer film following extra-thicknesses due to partial chromium deposition. In fact, photoinduced surface modulation is thus limited to the small pits and peaks appearing at places of intensity changes : intensity modulation being step-like, we may thus deduce that the maximum diffusion length corresponds to the width of these photoinduced pits and peaks, which is of the order of 400 nm.

Conclusion

Using appropriate combinations of laser beam polarizations, optical interactions enable full control of the molecular order : using azo-dye polymers, photoinduced polar rotation of dye molecules was achieved using dual-frequency beams irradiation and molecular translation was observed from holographic mono-frequency interferences. Indeed, our model of photoinduced translation diffusion of azo-dyes accounts qualitatively for the essential features of photoinduced surface-relief gratings, photoinduced molecular movements leading to polymer chain migration.

Understanding of the relevant parameters of photoinduced molecular translation and rotation processes is a key issue for optimization of such molecular optomechanical effect and further application to the realization of devices for photonic applications such as frequency converters, real-time holography, optical memories, or 2D planar photonic microstructures used for instance as filters or couplers21). Control of the relative weight of the translation and rotation processes appears now as an important step to control such optical microstructures patterning22). A more extensive study of photoinduced molecular movements should enable optimization of the molecular structure. Besides azo-dyes with *Cis-Trans* isomerization, molecules with Twisted Intramolecular Charge Transfer (TICT) could for instance reveal as an alternative possibly exhibiting propeller-like motion. Another interesting issue for microstructures optical patterning would also be to achieve a unipolar diffusion process : in this respect, dual-frequency interferences, leading to polar excitation, could be an interesting route.

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