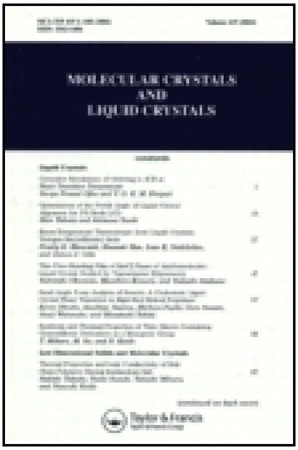

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Jean-Michel Nunzi [a], Céline Fiorini [a], Gabrielle De Veyrac [a], Paul Raimond [a] & Isabelle Maurin [a]

[a] LETI (CEA - Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, CEA Saclay, F-91191, Gif-sur-Yvette, Cedex, FRANCE

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Evidence for Photoinduced Molecular Migration Mediated Surface-Relief Grating Formation in Azo-Dye Polymers

JEAN-MICHEL NUNZI, CÉLINE FIORINI, GABRIELLE DE VEYRAC, PAUL RAIMOND and ISABELLE MAURIN

LETI (CEA – Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, CEA Saclay, F-91191 Gif-sur-Yvette Cedex, FRANCE

Direct and reversible holographic recording of surface-relief gratings in azo-dye polymers was recently evidenced using atomic force microscopy. Irradiation with an interference pattern between polarized laser beams was observed to lead to quantitative mass-transport. The surface gratings have a negative amplitude that can be twice as large as the polymer film thickness. The origin of such photo-driven mass transport is still controversial. We provide here experimental evidence that the chromophores migrate from the high to low the intensity regions. Chain migration in such doped or grafted guest-host polymer systems results from the photoinduced migration of the guest chromophores.

Keywords: azo-dye polymer; holography; photoinduced surface grating; molecular motor

INTRODUCTION

During the past ten years, there has been extensive studies devoted to photoinduced dichroism or birefringence[1-4] and more recently to all-optical poling in azo-dye containing polymers[5]. At the microscopic level, the mechanism was shown to involve a selective axial (or polar) excitation of the molecules, depending on the polarization direction of the optical beams. The orientational redistribution through the repeated *Cis-Trans* isomerization that follows each excitation-relaxation cycle leads to a quasi-permanent alignment or orientation of the dye molecules[3-5]. More recently, the possibility to record holographic surface-relief gratings in similar materials was demonstrated[6-9]. It was shown that irradiation with an interference pattern of coherent light could induce not only an alignment of the chromophores throughout the volume of the material, but also a controlled modification of the film surface, in conjunction with the light interference pattern. Such result was quite unexpected as it implies a substantial mass transport that occurs at temperatures much below the glass transition temperature.

After the first demonstration using amorphous polymeric matrices grafted with azo-dyes, the same observations were also reported in the case of liquid-crystalline polymers[10] and sol-gel matrices[11]. In a typical experiment, the wavelength of the laser was chosen close to the maximum absorption of the chromophores, typically λ=488 nm or 514 nm-lines from an Argon ion laser, with intensities ranging from I = 10-1000 mW/cm^2. Surface gratings have a negative amplitude : the position of maximum height corresponds to light intensity minima. Modulation amplitude of the surface-relief gratings can be as large as twice the film thickness, which corresponds to very high diffraction efficiencies for the visible argon-laser wavelengths. Heating above the glass transition temperature is mandatory for erasure of the surface-relief gratings. Using the same irradiation time, polarization and power efficiency as during the recording phase, we observed that constant illumination of the surface modulation following grating formation, was only leading to a 10 % reduction in grating amplitude. The influence of experimental parameters such as laser intensity, beam polarization, grating spacing have been explored[8,9,12]. Several explanations were proposed such as ablation or swelling but none could explain the latest results, namely the dependence of the grating amplitude on the laser polarization that excludes thermal effects due to light absorption as the main contribution to the process. Indeed, thermal effects are not polarization dependent and *p*-polarized laser interferences were observed to produce surface gratings with a diffraction efficiency at least ten times larger than the *s*-polarized ones. Additionally the process is reversible, which excludes ablation. Different models have been proposed to explain such phenomena[10,12-16]. Indeed, understanding of the relevant parameters implied in the photoinduced mass-transport process is a key issue for the optimization of opto-mechanical effects and further application to the realization of devices for photonic applications such as optical memories or 2D planar photonic microstructures used for instance as filters or couplers.

The main experimental method for photoinduced surface-relief grating characterization has mainly consisted in diffraction efficiency measurement or Atomic Force Microscopy (AFM) study. Raman spectroscopy was also developed to monitor the photoinduced changes following surface-relief formation at the molecular level[9]. Although such measurements provided interesting information about the dynamics of some relevant parameters of the process, no clear insight into the microscopic origin of the process could be evidenced. In this article, we report on experiments based on optical and confocal microscopy analyses which show that photoinduced surface-relief grating formation is inherent to the formation of a concentration grating created by molecular migration between regions of different light intensity. This is in good agreement with our recently developed model of photoinduced translation diffusion of azo-dyes.

EXPERIMENTS

In order to record surface-relief gratings, we made use of the now classical Lloyd mirrors set-up developed by Rochon and coworkers[6] : the incident expanded beam from an argon laser (λ=514 nm ; P=100 mW/cm^2) is divided into two parts : first half is directly incident onto the sample and second half reflects first onto a metallic mirror rigidly held at 90° to the sample. This permits invariance of the interference grating with respect to mechanical instabilities throughout the recording process (a few dozen of minutes). The incident angle is approximately 7°, corresponding to a 2 µm-periodicity of the grating. Samples were spin-coated films of the azo-dye Disperse Red 1 [4-(N-(2-hydroxyethyl)-N-ethyl-)amino-4'-nitroazobenzene] (DR1) in poly(methyl-methacrylate) (PMMA). Experiments were performed both in a grafted or in a guest-host system using identical experimental conditions and sample thicknesses ($l \approx 250$ nm). Because of phase segregation effects, concentration in the guest-host system is limited to 10% in weight. For this purpose, DRPR, a DR1 derivative showing enhanced solubility was synthetized, enabling up to 30 % dissolution. The copolymer studied (DR1-MMA 35/65) was obtained by free radical polymerization of a 65/35 molar mixture of methyl methacrylate (MMA) and N-ethyl-N-(methacryloxyethyl)-4'-amino-4-nitroazobenzene (DR1 derivative). The glass transition temperature T_G, measured by differential scanning calorimetry was found to be comparable in each system : T_G=105°C for the doped systems and T_G=130°C for the grafted DR1-MMA 35/65 system.

RESULTS AND DISCUSSION

A modulation amplitude of up to 500 nm (peak to valley) was measured in the DR1-MMA 35/65 grafted system using atomic force microscopy. A much weaker modulation (about 20 nm peak to valley) was measured in the case of the 30%-weight DRPR guest-host system. No modulation could be detected in the other low concentrated 10%-weight DR1 guest-host system. Grafting of the azo-dye chromophore to the polymeric matrix is thus not a mandatory parameter for surface-relief grating formation, as it could be claimed previously. However, it appears that the process efficiency is much larger in the grafted than in the doped system. Surface-relief gratings were also recorded using DR1-MMA copolymers grafted with different concentrations of Disperse Red 1. The relative modulation depth $\Delta h/(2*l)$ measured with AFM, where Δh is the height difference between peaks and valleys and l is the film thickness, was found independent of the chromophore concentration. This shows that, unlike the case of liquid-crystalline systems[10], the influence of any cooperative intermolecular movements is negligible in the surface-relief grating formation process with such systems[17].

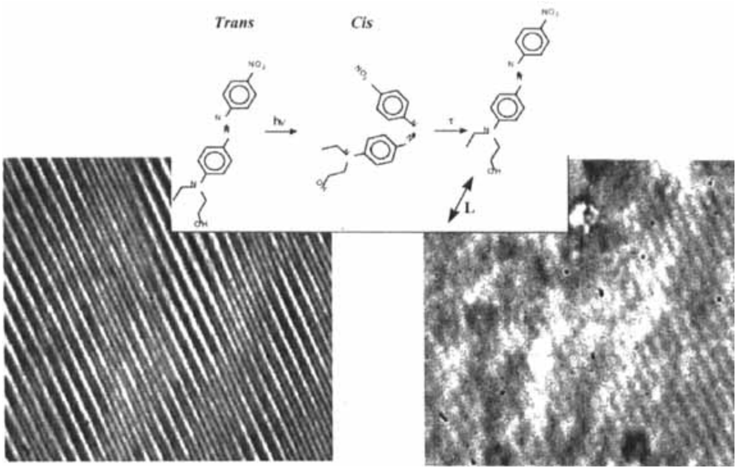

FIGURE 1 : White light optical microscopy analysis of the surface-relief gratings recorded in two spin-coated PMMA based thin films. Both cases correspond to an identical surface-relief grating recorded 30 minutes with λ=514nm and I=100mW/cm^2. Writing beam polarization was set at 45° from the incidence plane. Left : DR1-MMA 35/65-copolymer. A relative modulation $\Delta h/(2^*l)\approx 100\%$ was measured using atomic force microscopy (AFM), with Δh the height difference between peaks and valleys and l, the film thickness. Right : PMMA doped with Disperse Red 1 (10 %-weight). No surface modulation was detected using AFM. Insert is a schematic representation of the photo-induced translation motion of DR1 molecules following isomerization.

Figure 1 shows the optical transmission images obtained under white illumination, both in the case of a doped and of a grafted system. As it is well known from photoinduced dichroïsm measurements, following excitation and *cis-trans* isomerization, molecules preferentially reorient in a plane perpendicular to the exciting light[3,4]. In order to take this effect into consideration, optical transmission analyses were performed using different reading beam polarizations. Whatever the reading beam polarization, the same modulated transmission spectrum was observed, evidencing the existence of regions with different chromophore concentration. Such transmission modulation can be observed both in the grafted and in the doped systems, the contrast between regions with high and low chromophore concentrations being only reduced in the case of the doped systems. This shows that surface modulation is caused by chromophore migration, the molecules presumably pushing or pulling the polymeric host when diffusing from the high to the low intensity regions. This is in good agreement with our model of photoinduced translation diffusion of azo-dyes[14,15]. As illustrated in the insert of figure 1, we indeed assume that following excitation and isomerization from *trans* to *cis*, molecules relax back to their stable *trans* form after an average translation L along their molecular axis.

In-situ dynamic studies of the chromophore-concentration grating formation was also performed using confocal microscopy. In such experiment, irradiation of the sample was performed using one single focused beam at the argon laser wavelength λ=514 nm. Following the results in figure 1, a concentration grating was expected in conjunction with the Airy diffraction rings formed at the beam focus. Figure 2 shows the different cases of horizontal (upper part) and nearly vertical (lower part) recording beam polarizations. In both cases, recording of the confocal microscopy transmission image was made at different recording times using the same experimental recording parameters (P= 400 nW/μm^2, λ=514 nm). As we see in figure 2, transmission is larger at the beam center, which confirms that molecules migrate from the high to the low intensity regions. Importantly, the concentration grating is only formed along the direction of the recording beam polarization, evidencing the strong polarization dependence of the surface-relief grating formation. This is in good agreement with the photoinduced surface deformation recently observed by S. Bian and coworkers[18] using a similar single-beam irradiation.

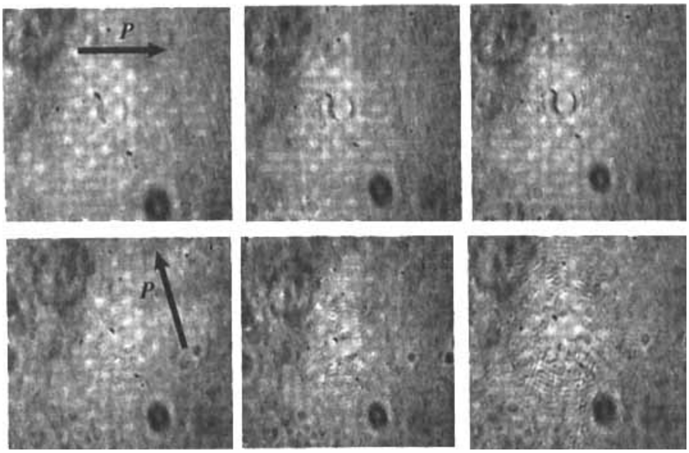

FIGURE 2 : In-situ dynamic recording of the confocal microscopy transmission images of the DR1-MMA 35/65 copolymer film following single beam irradiation at the beam focus (I=400 nW/μm^2 at λ=514 nm). The 3 different pictures on a line (from left to right) correspond to increasing recording times from a few seconds to about one minute. As indicated on the left pictures, the polarization direction ***P*** of the recording beam was set horizontal in the upper 3 pictures. It was set nearly vertical in the lower 3 pictures.

CONCLUSION

We have given experimental evidence that together with the surface-relief grating formation, a concentration grating which could be evidenced optically was also built simultaneously. Such result shows that surface-relief grating formation obviously follows molecular migration from the high intensity to the low intensity regions, the photoinduced molecular movements inducing the polymer chain migration. This is in good agreement with our model of photoinduced translation diffusion of the azo-dyes[14,15,19]. Most interesting is that it opens the way to molecular translation control using optical fields. A deeper understanding of the relevant parameters of the molecular translation process is now a key issue for the optimization of such opto-mechanical effect. One challenging issue in an aim to design devices for photonic applications would indeed be to achieve a complete manipulation of the molecular order. In this respect, those photo-powered molecular-motor actions represent an interesting route toward the nano-structuring of devices. A more extensive study of the photoinduced molecular movements should enable an optimization of the molecular structures which are the most efficient as molecular-motors. A control of the relative weights between photoinduced translation and rotation[20] should also be an important issue in order to optimize the fabrication of optically patterned microstructures.

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