Complex Structures of Surface Relief Induced by Holographic Recording in Azo-Dye-Doped Elastomer Thin Films

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ABSTRACT: We report observations of unusual and complex structures recorded on the surface of azo-dye-doped elastomer thin films after irradiation with different interference light patterns. Periodic structures with a variety of topography are inscribed through holographic recording by both intensity light patterns and polarization patterns. Diffraction efficiency of the recorded gratings has been measured. Atomic force microscope measurements confirm the presence of complex structures. For some pattern configurations modulated profiles in two directions (both parallel and perpendicular to the grating wavevector) are observed. The depth and periodicity of the structures are investigated. Analyses of film surfaces after irradiation with a single uniform polarized light beam make evidence of photoinduced micrometer-sized structures depending on the film thickness. Only for linearly polarized light are ordered structures produced; stripes oriented perpendicular to the polarization direction are observed. This last observation suggests that the formation of complex structures by holographic recording can be attributed to the combination of a spontaneous patterning, ensuing from light-induced surface instability, and the large material displacement usually observed on surface relief grating formation in polymer−dye systems, with both intensity and polarization light patterns.

Introduction

Holographic recording in polymer thin film containing azobenzene chromophores has been largely studied in the past years.[1−8] Special attention was devoted to study the one-step photoinscription of surface relief gratings (SRG) in different kinds of guest−host systems, functionalized or grafted. When a film of these materials is exposed to an interference light pattern (either intensity or polarization patterns) with wavelength near the absorption band of the chromophores, its surface undergoes a controlled topographical modification. In some systems, anisotropic gratings due to photoinduced linear and circular birefringence are recorded simultaneously to topographical relief gratings. Depending on both intensity and polarization state of the light, the grating's depth can reach several hundred nanometers. The formation process was found dependent on polarization and has been deduced that thermal effects do not influence surface relief formation if the relief profile is sinusoidal.[7,9] The processes involved in the SRG formation have been largely investigated from both experimental and theoretical points of view, and although various explanations and models of such light-induced mass transport phenomenon have been proposed,[9−12] this question seems at present not properly solved.

The complexity of this question has been underlined by recent results reported in ref 13, where formation of hexagonal surface gratings has been observed in azo-dye polymer film irradiated by a single, uniform polarized, light beam. A preferential direction of the surface features is observed for a linear polarized laser beam exposure, proving that light polarization controls the orientation of the photoinduced structures. Unusual topographic modification of SRG after optical erasures by means of a polarized single light beam has been recently reported.[7] Though these last observations have been done in very recent experiments, periodically structured polymer surfaces induced by irradiation with low-energy laser pulses (below the ablation threshold of the polymer) have already been observed a few years ago.[14] In that work the authors explain the mechanism involving a surface wave, which interferes with the incoming beam.

In our recent work we have observed for the first time SRG formation in an azo-dye-doped elastomer.[15] In these systems deep and regular film surface deformations can be produced, depending on illumination intensity and exposure time. The undertaken study makes evidence of recorded structures having long time stability, probably related to significant interactions between elastomer and azo chromophores. The comparison between layered and mixed samples suggests that the SRG formation is not a mere surface-initiated process, but bulk effects also have to be taken into account.

In the present paper we show complex structures formation by SRG recording on thin film of azo-dye-doped elastomers, never observed in similar systems. Both polarization and intensity holographic techniques have been used. The wide investigation made confirms that these unexpected structures are observed only for few selected mixtures. These structures have a micrometer length scale and show a strong dependence on the light polarization state. Investigations of the surface, after irradiation with only one polarized light beam, show that ordered or not ordered, regular or irregular structures can be induced by means of light irradiation with suitable polarization, when no interference light patterns are present. The influence of a significant parameter as the light polarization was investigated in order to understand these formations, not usual for SRG, in polymeric systems.

Experimental Section

The used materials are an azo-dye (Methyl Red by Aldrich) and a thermoplastic elastomer, polystyrene-*block*-polybutadi-

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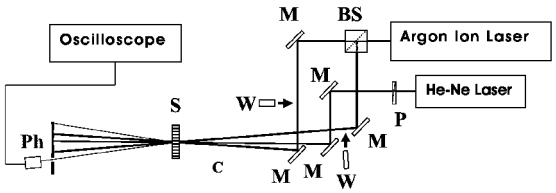

Figure 1. Experimental setup: BS = beam splitter, M = mirror, P = polarizer, W = waveplate, S = sample, Ph = photodiode.

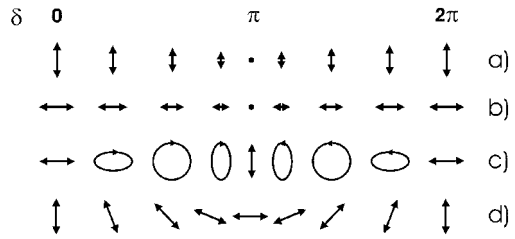

Figure 2. Spatial distribution for the following polarization configurations: (a) s−s; (b) p−p; (c) ±45°; (d) opposite circular. δ is the phase shift along the grating wavevector.

ene-*block*-polystyrene (Aldrich). Among several thermoplastic elastomers, with slightly different amount of styrene, we select the no. 18,287-7 containing 30% styrene. The samples are prepared starting from a solution of polymer and Methyl Red (16% w−w) and then evaporated under vacuum. The film's thicknesses are about 2 and 1 μm; the values have been evaluated scanning a surface scratch by AFM. Dye concentration has been monitored, for all the investigated gratings, measuring the optical density at the Ar ion laser wavelength (λ = 514.5 nm).

The experimental setup is the usual one for holographic recording (Figure 1): two polarized Ar ion laser beams with equal intensities, crossing at $\theta \cong 4.5°$ angle, impinge on the film located in the superposition region. The corresponding spatial periodicity is 6.5 μm. Placing suitable waveplates in the interferometer arms, the following polarization patterns are realized. In the s−s polarized configuration (Figure 2a) the resulting pattern is vertical linearly polarized, and the intensity is largely modulated along the wavevector; for p−p polarizations (Figure 2b) the intensity is largely modulated too, but the polarization is horizontal; for ±45° linear polarized configuration (Figure 2c) the spatial light distribution is almost uniform, but the light electric field takes linear p, elliptical, circular, elliptical, and linear s over one-half period grating; for left and right circularly polarized configuration the light spatial distribution is quite uniform and the electric field is always linear, rotating along the wavevector (Figure 2d). The first two configurations correspond to intensity light patterns, while the last two are polarization patterns. A linearly polarized He−Ne laser beam (λ = 632.8 nm) is used as a probe to investigate the diffracted light fields.

Results and Discussion

Permanent holographic gratings are recorded for all patterns at a light power density of 4 W/cm^2 and exposure time of a few minutes. The diffraction efficiency η, defined as the intensity ratio of the first diffracted beam to the incident one, $\eta_{\pm 1} = I_{\pm 1}/I_0$, has been measured: the obtained values are quite the same, ranging from 3.5% to 4% on all the holographic recording patterns for the 2 μm thickness film.

SRG are probed by AFM, and the topographic images of these reliefs, recorded using the above light patterns, are reported in Figure 3. Although the diffraction efficiencies are nearly the same, the corresponding surface modifications have distinct topographies.

Figure 3a shows the AFM topographic image of a grating recorded with s−s polarization. A modulation depth of 1 μm (maximum peak height) along the *x*-direction (wavevector grating direction) and ∼6.5 μm spatial period appears as expected, but also a modulation of 500 nm depth with a period of ∼2.5 μm along the *y*-direction is found. The spatial periodicities are evaluated on larger areas with respect to those reported in the figures. Figure 3b reports the AFM image for p−p polarization recording; here the topography is quite different: no modulation seems to be evident along the *y*-direction, while the profile looks quite complex along the *x*-direction. High and regular relief grating appears having the same periodicity of the recording pattern (∼6.5 μm) and modulation depth of about 400 nm. Between these reliefs along the grooves, much more irregular and shallow modulations (200 nm), as a ripple structure, are visible. Figure 3c shows the image for ±45° configuration. The topography is unexpectedly similar to the one recorded with the s−s polarization pattern: the periodicity in the *x*-direction has the same value found in that configuration, while in the *y*-direction is a little less, ∼2.0 μm; the modulation depths take values of 700 nm for the *x*-direction and 500 nm for the *y*-direction, which are comparable to the ones measured for the s−s pattern. These two recording configurations, s−s and ±45°, are totally different (deep modulated light intensity in the former and uniform light distribution, but polarization modulation in the latter); therefore, it seems difficult to justify this similarity. Finally, recording by two opposite circular polarizations give a very complex structure of the topography, as Figure 3d shows. The topography shows a formation of reliefs irregularly shaped and distributed, the knowledge of which requires deeper investigations.

Figure 4 shows the AFM topographic image of a grating recorded with s−s polarization for 1 μm film thickness, at the same experimental condition. At lower thickness value of the film is observed the same *x*-periodicity, related to the interference pattern, but also spatial periodicity along the *y*-direction of ∼1.5 μm. This result suggests that the *y*-spatial periodicity could depend on the sample thickness.

The main results of these investigations can be listed as follow. (1) For the first time complex structures are observed in azo-dye-doped elastomer by holographic recording. (2) The materials used in the experiment have been selected between different elastomer and dye mixtures; only for few materials belonging to the same class of polymers the above-described topography modification are observed, indicating that polymer−dye interactions are important other than relevant polymer parameters as viscosity, density, surface tension, etc. (3) Observations of light-induced modifications on thinner films seem to indicate a length scale dependence from the film thickness. (4) Surprisingly, very similar topographic modifications are observed for two different configurations of holographic recording. (5) Looks evident that a relevant parameter in the mechanisms inducing the different topographical modifications is the light polarization state.

To elucidate this last aspect, analysis of the film topography after illumination with a single laser beam, having different polarization states, has been performed; the intensity value is kept comparable to the total intensity used for the gratings recording. The film does not present ordered structures on micrometer and submicrometer scales before the irradiation. Figure 5a reports the AFM topographic image of the film surface

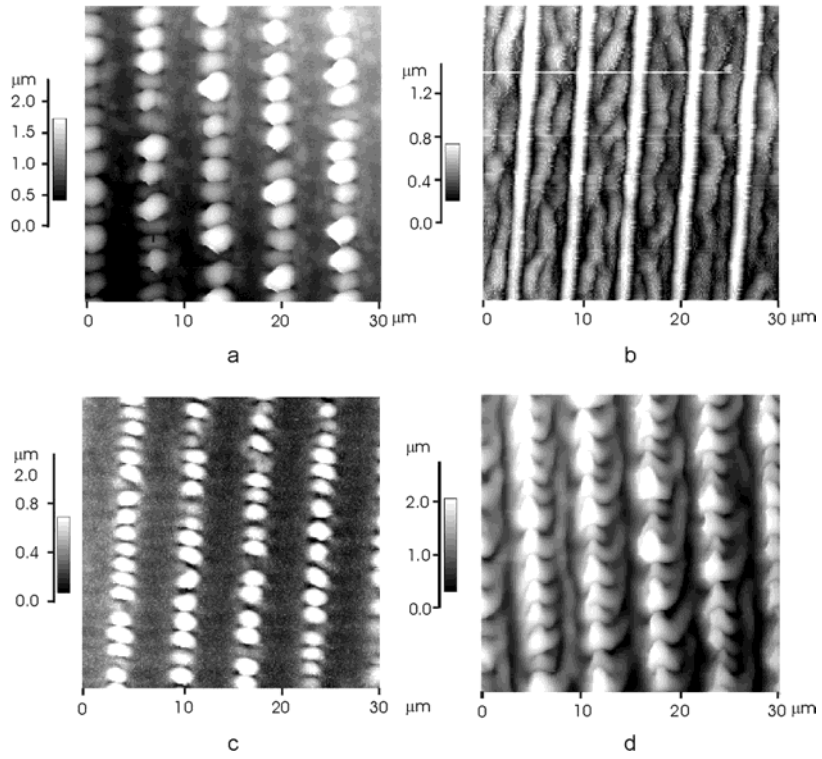

Figure 3. AFM images (30 μm × 30 μm) of surface reliefs recorded using the following polarization patterns: (a) s−s; (b) p−p; (c) ±45°; (d) opposite circular. The film thickness is 2 μm.

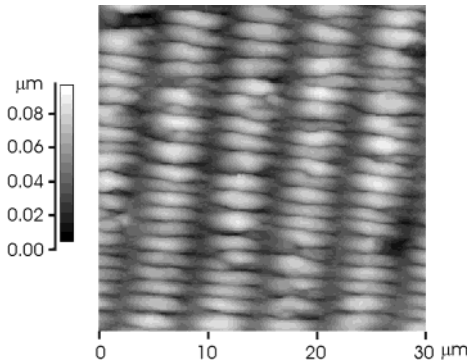

Figure 4. AFM image (30 μm × 30 μm) of surface reliefs recorded using the s−s polarization pattern. The film thickness is 1 μm.

after irradiation with one circular polarized light beam, while Figure 5b shows the AFM image of the film after irradiation with a linearly polarized beam. For both cases the irradiation has been done at normal incidence. Topographic modifications on micrometer length scale are evident in both cases: irregular structures for circular polarization and regular oriented stripes for linear polarization. The stripes widths are around 2 μm in size, and the groove's depth is ∼400 nm. The presence of these oriented ripples structure proves that the linear polarization controls the orientation of the photoinduced structures. In particular, the stripes orientation is orthogonal to the polarization direction, indicating that the orientation of the chromophores induced by light[1] play an important role in the linear polarization case. Figure 6 reports the AFM image of a thinner film (1 μm thickness) irradiated with a single linearly polarized laser beam. The length scale of the photoinduced structures is found to be about 1 μm, i.e., smaller than the one found in Figure 5b, as expected. In this figure close inspections show that superimposed on the

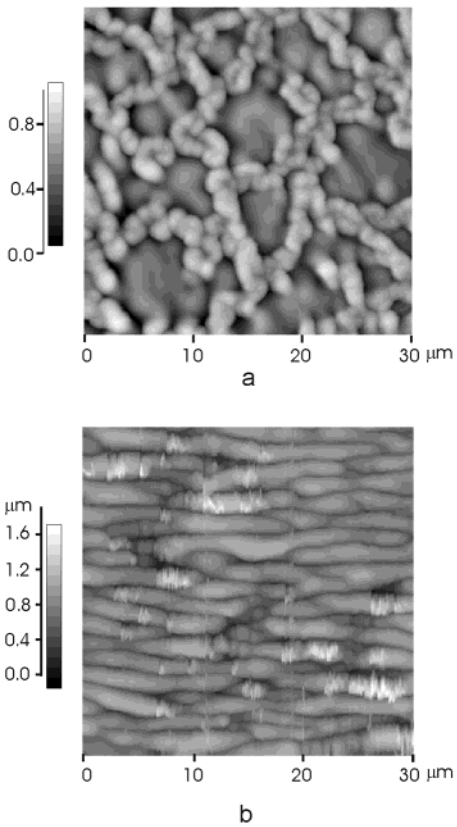

Figure 5. AFM images (30 μm × 30 μm) of the film surface after irradiation at 4 W/cm^2 intensity with a single beam: (a) circular polarized and (b) linearly polarized. The film thickness is 2 μm.

stripe pattern are smaller structures (∼0.5 μm) that do not form any pattern.

The presence of smaller structures is reminiscent of spontaneous patterning obtained by light-controlled

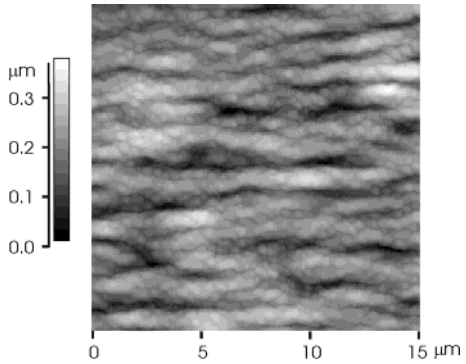

Figure 6. AFM image (15 μm × 15 μm) of the film surface after irradiation at 4 W/cm^2 intensity, with a single linearly polarized beam. The film thickness is 1 μm.

mass transport driven by polarization, as in ref 13, where hexagonal structures having characteristic length scale related to the light wavelength, i.e., 0.5 μm are observed. Nevertheless, when irradiated with a vertical polarized light beam, the polymer film shows significant differences compared to ref 13. Contrary to Figure 6, ordered hexagonal structures are clearly visible in Figure 2a of ref 13; elongated structures could also be observed, but at an angle of about 45° respect to the light polarization direction. In that paper the authors claim that the spontaneous patterning develops mainly at normal incidence, giving a good indication of a feedback mechanism. No incidence angle dependence of the ripple periodicities is observed in our experiment. This means that the measurements performed at incidence angles different from zero show the same topographical structures and scale length, as Figure 5 shows. These results support that other kinds of laser-assisted periodic structuring in polymers, related to the interference between incident and scattered radiation,[14] are unlikely.

The AFM images of the single-beam irradiations and the thickness dependence of the length scale of the structures suggest that besides photoinduced orientation effects a nonnegligible thermal effect concurs to the light-induced mass transport. The presence of the dye, having its maximum absorption peak near the laser wavelength, indicates the presence of a significant temperature gradient in the film.

Although pattern formation processes caused by convective effects, as Rayleigh−Benàrd and Benard−Marangoni convection seems to be dubious due to the high viscosity of the fluid, instabilities of thin polymer films caused by temperature gradienthave been recently reported.[16] The authors of that paper consider a new interfacial (polymer/air) instability, supposing an interfacial radiation pressure, originating from the heat flow. Even if the experiments are not directly comparable, in both cases the variation of the structures length scale depends on the temperature gradient that in our experiment is established by the film thickness. When the film is irradiated with linear polarization, the photoinduced chromophores orientation occurs, and anisotropy is induced in the originally isotropic medium. By consequence, different destabilizing forces, related to different driving mechanisms,[9−12,16,17,18] can be induced both at the surface and into the bulk producing ordered stripes. Anisotropic interaction between the chromophores, as well instabilities induced by the temperature gradient in an "anisotropic" viscoelastic fluid, could be considered at this stage.

The observed structures in holographic recording could be justified considering the occurrence of the above effects when the illumination pattern becomes more complex. The nonsinusoidal relief profiles support thermal effects involvement. For the intensity light patterns, a transverse gradient temperature should also be considered. For p−p configuration recording (Figure 3b) the ripple's structure induced by the linear polarized light (Figure 5b) is evident in the grooves. In the illuminated regions, in fact, the light polarization is p, i.e., along the grating wavevector, and the ripples grow perpendicular to the wavevector direction. The topography examination of Figure 3b indicates that the large material displacement, due to the periodic light distribution, occurs from the illuminated regions to the dark regions, as expected.[17,18] In the s−s configuration, the ripples structure induced by light polarization should align along the grating wavevector, the same direction of the material displacement; here no ripples are observed in the grooves. Nevertheless, the periodicity along the *y*-direction matches to the ripples width, indicating that this periodicity can be due to the ripples structure induced by the linear polarization direction. These observations could be described as follows. Contrary to the p−p configuration, where the two phenomena (material displacement due to light distribution and the light polarization effect) act along orthogonal directions producing any coupling, for the s−s configuration the two directions match; thus, the coupling is able to produce the structures observed in Figure 3a.

The polarization pattern represented in Figure 2c has a uniform spatial light distribution; therefore, the temperature gradient is just along the film thickness. If the gradient force due to the different orientation of the chromophores were neglected, the polarization light pattern should produce regions with ripples structure along the wavevector alternating with regions with orthogonal oriented ripples. The resulting structures, similar to that produced by the intensity patterns in s−s configuration, are a clear indication that the gradient force due to the anisotropic interaction between the chromophores[10] plays a relevant role in the effect. In fact, the coupling between the anisotropic interaction of the chromophores (generally responsible for SRG formation[10]) and the destabilizing forces[16] at the surface (liable to the micrometer-sized ripple structures) can produce the observed topography. It is reasonable to expect that the opposite circular polarizations light pattern, represented in Figure 2d, would give a more complex structure.

Conclusions

We report observations of complex structures inscribed on azo-dye-doped elastomer films by means of holographic recording. The surface modifications are permanently recorded, and their topography depends from the light pattern configurations. The length scale of the structures seems to be dependent on the film thickness. Investigations of the film surface irradiated with a single polarized light beam support the thickness dependence and suggest that the complex structures formation can be due to a coupling of different mechanisms. Light-induced surface instability related to the temperature gradient and the usual material displacement, observed during the holographic SRG formation in polymer−dye systems, could be the most important involved processes. Although these hypotheses seem to

be plausible, further investigations should be done. Detailed and quantitative analyses of the different topographies, together with studies of the dynamics, are in progress.

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