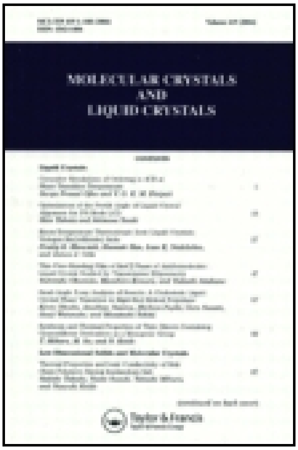

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photofabrication of Surface Relief Gratings Using Photodynamic Polymers

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To cite this article: Sukant Tripathy, Dong-Yu Kim, Xin Li Jiang, Lian Li, Taekseung Lee, Xiaogong Wang & Jay Ant Kumar (1998): Photofabrication of Surface Relief Gratings Using Photodynamic Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 245-255

To link to this article: http://dx.doi.org/10.1080/10587259808042484

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 245–255
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Photofabrication of Surface Relief Gratings Using Photodynamic Polymers

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We present novel observation and detailed investigation of a photodynamic polymer transport process. Surface gratings were photofabricated on various polymer films containing azo groups in the side chain or in the main chain. Effects of the polymer structures on the formation of the surface gratings were investigated. Large surface modulation (>6000 Å) and high diffraction efficiency (>40 %) could be obtained under optimal conditions. Fabrication of various multiple gratings on the same spot was demonstrated. The resulting pattern was a simple superposition of all the interfering recording waves. The surface pattern mimics the light pattern and gradient forces acting on the azo dipoles are responsible for the large scale displacement of the polymers. The relief grating is the result of layer by layer plastic deformation of the polymer surface. Chromophores molecules on the viscous surface layers are plasticized by trans-cis-trans isomerization and are dragged by "optical tweezer" effect of the electric field gradient.

Keywords: azobenzene; polymer; surface relief grating; gradient force

INTRODUCTION

Polymers containing azobenzene groups are widely employed in a variety of research fields. The rigid rod-like azobenzene groups can act as a mesogenic unit and a number of liquid crystalline (LC) polymers with azobenzene groups have been reported[1]. The azobenzene chromophores have also been extensively used over the past decade in designing both third order and second order nonlinear optical (NLO) polymers[2]. Azobenzene-doped, or covalently attached polymer systems have also been studied as optical data storage medium[3]. Photo-induced orientation of azobenzene groups and photophysics associated with the trans-cis-trans isomerization has been explored in a number of other special applications.

Optically induced orientation of azobenzene groups in polymer matrices was first demonstrated in 1984 by Todorov et al.[4]. They also demonstrated reversible holographic phase grating formation using this optically induced birefringence. When the polymer system is irradiated with a linearly polarized laser beam with a wavelength of 488 nm, the optical transmission for light polarized along the polarization direction of the writing beam increased and that for light perpendicular to the direction of the writing beam decreased. Optical dichroism as well as birefringence was induced. The laser induced optical dichroism and birefringence was a result of induced orientation of azo dyes. The mechanism proposed for this phenomenon is related to the trans-cis-trans isomerization process of the azo groups in the polymers[4].

There has been a lot of interest in this area since Eich et al. demonstrated optically induced birefringence and reversible holographic optical storage properties on some LC azo polymer films[5]. The optically induced anisotropic properties of the azobenzene incorporated system have been demonstrated in a variety of matrices; LC polymers, a gelatin film, azo-dye doped polymers, Langmuir-Blodgett films and amorphous azo polymers among others[5-10]. This photoinduced orientation of azobenzene groups has also been employed to produce birefringence gratings by a number of research groups.

We recently reported direct photo-fabrication of large amplitude holographic surface relief gratings on epoxy-based NLO polymer films containing azobenzene groups[11-14]. These surface relief gratings were produced upon exposure to an interference pattern of Ar^+ laser beams at modest intensities without any subsequent processing steps. The gratings were very stable when the polymer was kept below T_g. The gratings could be erased by heating the polymer above T_g. Similar results have been reported by Natansohn and Rochon[15,16]. We have clearly shown that in addition to the photoinduced orientation of azo chromophores in these polymer films there is large scale macromolecular motion leading to the formation of the relief structure.

In this article we will focus on recent exploration of this novel photoinduced macro scale polymer transport process observed in azo polymers. The effects of various chemical structures of the polymers were investigated. The surface grating formation was examined on both polymer films containing azobenzene groups in the side chain as well as in the main chain. We also demonstrated fabrication of complex surface gratings. Based on these results mechanisms for the surface deformation were discussed.

EXPERIMENTAL SECTION

Figure 1 shows chemical structures of some of the polymers on which the surface grating formation was investigated.

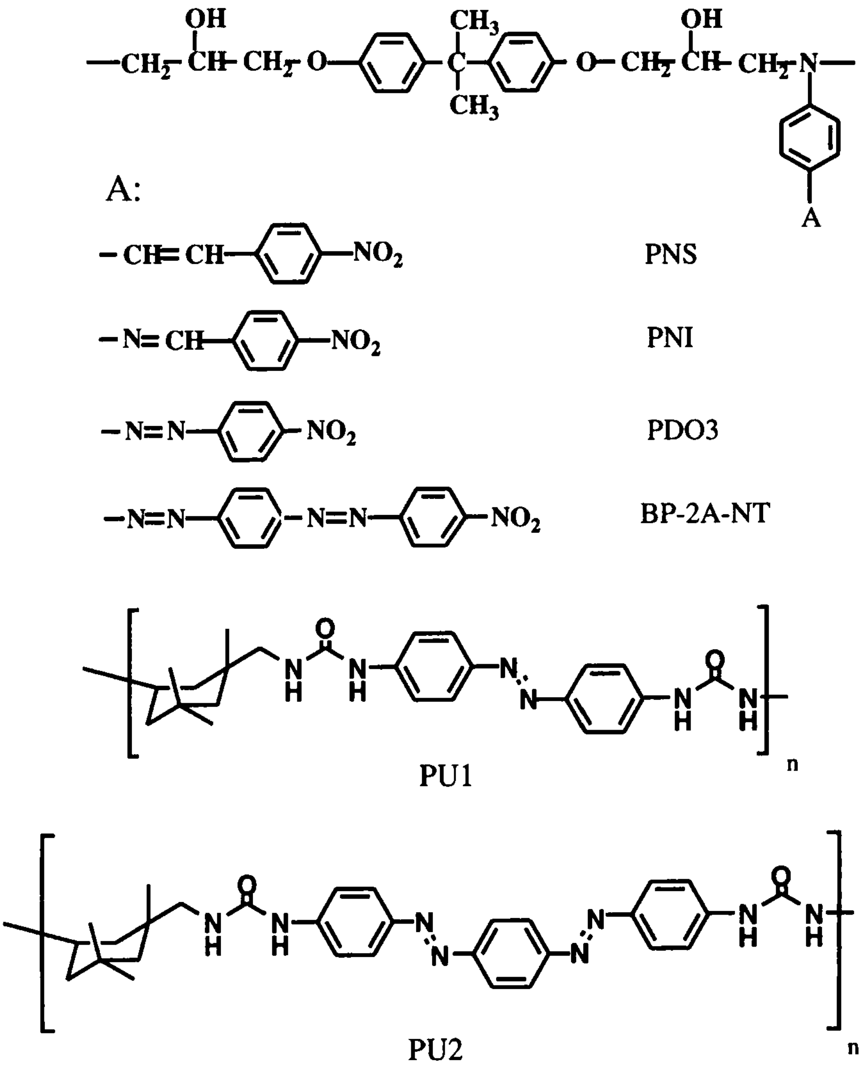

FIGURE 1 The chemical structures of some of the polymers on which the surface grating formation was investigated.

The side chain polymers, PDO3, PNS, and PNI, were synthesized by reacting diglycidyl ether of bisphenol A and various chromophores[17]. A bisazo polymer, BP-2A-NT, was synthesized by post azo coupling reaction[18]. Synthesis of main chain azo polymers, PU1 and PU2, was previously reported[19]. The thermal properties of the polymers were investigated with a TA Instrument DSC 2910 at a heating rate of 10 °C/min. The UV-vis absorption spectra of the polymers as spin coated films were determined on a Perkin -Elmer Lambda 9 spectrophotometer. Good optical quality polymer films were prepared by spin-casting on glass slides. The films were dried at 70 °C under vacuum for 12 hours. The typical sample thickness of the films was ranging from 0.4 to 1 μm.

The gratings were fabricated using simple interference of the two linearly polarized laser beams at 488 nm or 514 nm from an Ar^+ laser [13]. Laser beams with various polarizations were used. The intensity of the recording beam employed ranged from 3 to 110 mW/cm^2. In most cases, the incident angle θ of the recording beams was selected to be 14°, resulting in grating spacing of about 1 μm. The diffraction efficiency of the first order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He-Ne laser beam at 633 nm. Surface structures on the polymer films were investigated by atomic force microscopy (AFM, Autoprobe Cp, Park Scientific Instruments).

RESULTS AND DISCUSSION

Tgs of the polymers, PDO3, PNS and PNI were 106, 115, and 101 °C, respectively. Tg of the polymer, BP-2A-NT, was 135 °C. Tgs of PU1 and PU2 were 197 and 236 °C, respectively. All these polymers were amorphous.

Surface relief gratings with large surface modulations could be formed on the polymers with azobenzene side groups, PDO3, BP-2A-NT, and on the main cain azo polymers, PU1 and PU2. AFM view of the surface gratings on the polymer showed very regularly spaced sinusoidal surface relief structures with a depth modulation of over 1000 Å. The original film surfaces before exposure to the writing beams were planar with just tens of angstroms fluctuations in the depth without any regular periodicity. The grating spacing could be controlled by changing the angle between the two writing beams and was consistent with the theoretically calculated spacing for the interference pattern. Under the optimum condition[13], surface modulation depth greater than 6000 Å and diffraction efficiency of more than 40 % could be produced on the PDO3 films.

The polymers with stilbene (PNS) and imine chromophores (PNI) were also investigated for the grating formation. UV-visible spectra of the films of PNS and PNI along with the spectrum of PDO3 are shown in Fig. 2.

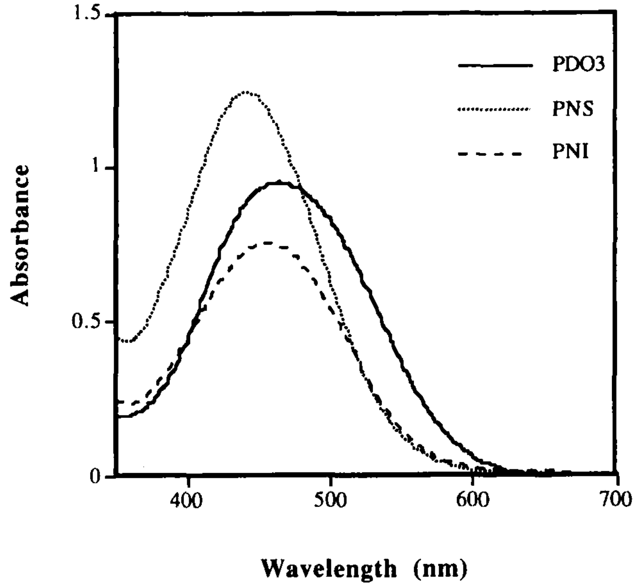

FIGURE 2 UV spectrum of the spin casted polymer films of PDO3, PNI and PNS.

For these three chromophores, the absorption maxima were relatively closely positioned. The stilbene and imine chromophores are known to be able to undergo trans-cis photoisomerization process as well. However, the amplitude of the surface gratings produced was not appreciable. In addition, photo-induced orientation process was not observed with these polymer films either. It is probably because both stilbene and imine groups require larger free volume (about 224 Å^3) for the photoisomerization compared to the azobenzene groups (127 Å^3)[20]. In these type of moderately high Tg polymer matrix, there may not be enough free volume for the photoisomerization of the stilbene and imine chromophores. Therefore we conjecture that trans-cis-trans cycling is quite an important factor for the surface deformation process. Natansohn et al reported very similar results from acrylate-based side chain azo polymers. They also concluded that azobenzene groups are necessary elements to observe this process. A polymer with bisazo side groups, BP-2A-NT, also showed the formation of large surface relief gratings even though this polymer showed higher Tg.

Surface grating formation was investigated on the film of the main chain azo polyureas, PU1 and PU2. Even though these main chain polymers have very high Tgs, and relatively low absorption at the writing wavelength compared to the side chain polymers, surface gratings could be fabricated. The formation of the surface grating was slower than the side chain polymers probably because the polymers have rigid backbones and the azobenzene groups are bound to the backbone at both ends which restrict the mobility of the chromophores.

Besides the regular simple gratings, we have also fabricated various multiple gratings at the same spot on the film. Fabrication of orthogonal double gratings has been demonstrated earlier[11]. Fig. 3 (a) shows a typical AFM view of a grating with a well defined beat structure. This grating was recorded sequentially with two wavelengths at 488 and 514 nm at a fixed writing angle. In this case the period of the beat was about 19 μm. It is clear that the resulting surface pattern was very close to the simple superposition of the two recording waves. Similar gratings with the beat structure can also be written at two different writing angles at the same wavelength. We also fabricated a Fourier synthesized blazed grating on the polymer film by superimposing two gratings with two different spacing (Λg and 2Λg). Fig. 3 (b) shows a typical three dimensional AFM view of a Fourier blazed grating fabricated on the PDO3 film.. The blazed structure is clearly seen. Two spatial frequency components, one at 1/Λg and the other one at 2/Λg, were observed as expected.

Polarization states of the writing beams significantly influenced the diffraction efficiency and grating formation[12-14]. Under the condition for intensity recording (two s-polarization), very low diffraction efficiency and small surface modulation (<100 Å) were obtained. Furthermore, the surface structures were not uniform in this case. Under the polarization recording condition (two orthogonal polarization), the greatest alternation of the resultant electric field polarization occurs on the film surface. However, very small surface modulation and diffraction efficiency were obtained under this recording condition. This is probably due to the uniform light intensity over the entire irradiated area. Except those two recording conditions, surface relief gratings could be formed with much greater values of surface modulation and diffraction efficiency. This indicates that the existence of both light intensity and resultant electric field polarization variations is essential to the formation of surface relief gratings.

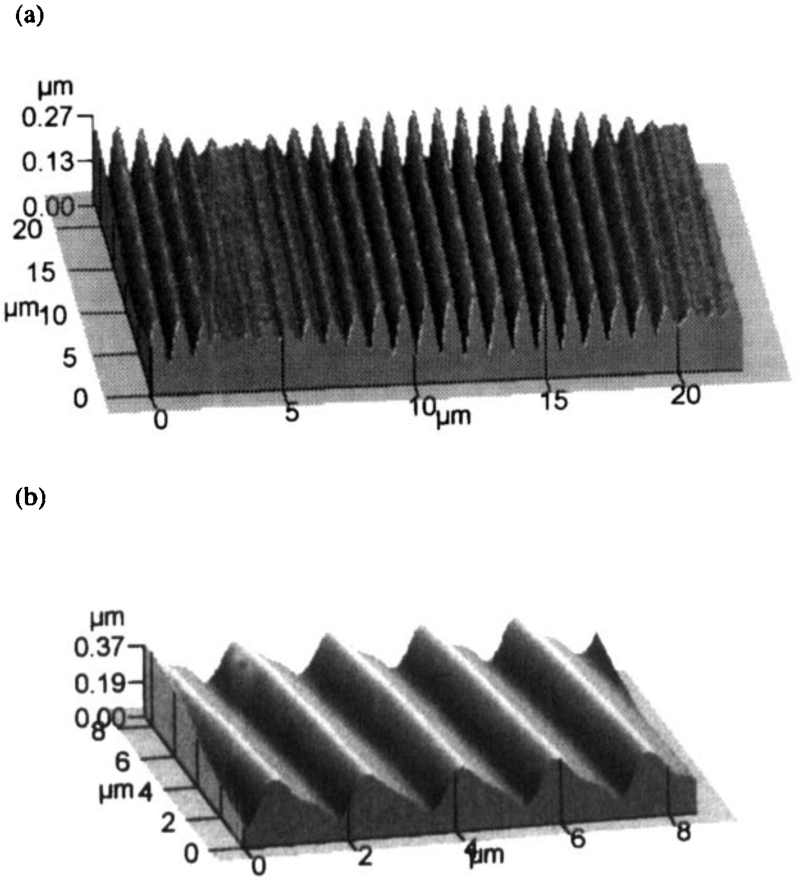

FIGURE 3 (a) AFM 3-D view of the dual gratings sequentially written with the p-polarized beams at 488 and 514 nm. (b) AFM 3-D view of a Fourier blazed grating on the PDO3 film.

Experiments on the formation of surface relief gratings with a constrained layer on top of the azobenzene functionalized polymer films have also been carried out. The restriction layer was obtained by spin-coating a thin transparent film (about 1000 Å) of polyvinylalcohol on the azobenzene functionalized polymer films. The experimental results indicated that even a thin transparent constraining layer almost completely inhibits the formation of the surface relief grating.

To study the phase relationship between the light and surface pattern, the fringe patterns were recorded on the polymer film using near field diffraction from a straight edge with polarizations either parallel or perpendicular to the edge[14]. PDO3 films were used for the studies. Similar to the result of the grating recording with s-polarized beams, no regular pattern of surface deformation was generated on the film when the polarization of the irradiation beam is parallel to the edge. When the polarization of the laser beam is perpendicular to the edge which is analogous to the grating formation with p-polarized beams, a very regular surface relief pattern was recorded. By analyzing the results of the surface relief gratings and the edge diffraction patterns, we have found that there must exist intensity variation in order to produce surface modulation. The grating grooves should be perpendicular to the intensity gradient on the surface. Only when there is an intensity gradient in a direction with nonzero component of the resultant electric field, the surface modulation pattern could be formed in this direction. These results are consistent with the results discussed earlier that both intensity and polarization recordings do not give rise to a surface relief grating.

The time integrated amplitude of the surface profile generated and the resulting diffraction efficiency for a fixed grating period were found to depend only on the energy fluence and not the intensity of the recording beams. This behavior further confirms that the recording process is not a thermal process. These results imply that only the instantaneous recording rates are intensity dependent and the time averaged force responsible for the movement of the polymer chains and the chromophores must be nonzero.

The effects of the recording temperature to the grating formation was investigated as well. Fig. 4 shows the temperature dependence of the writing process. When the polymer film is heated to a high temperature during recording, the grating formation becomes much less efficient. At the temperature near to the Tg of the polymer, the diffraction efficiency was almost zero even under the exposure for longer time. It is probably because the surface deformation cannot be frozen in due to enough mobility at high temperature. These results can be another evidence that this is not a thermal process. It also shows that a highly viscous state is necessary to freeze in the deformation of the surface.

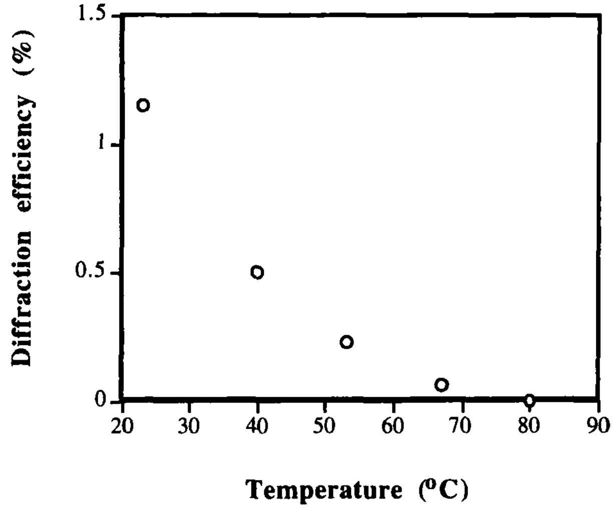

FIGURE 4 *Diffraction efficiency of PDO3 film with different recording* temperatures. Diffraction efficiency was measured after exposure to a wavelength of 488 nm with 50 mW/cm^2 for 10 min.

A model for the formation process is proposed. This model can explain the observed experimental data which are summarized below: 1) only azo functionalized polymers show large amplitude surface relief structures; 2) the surface profile is proportional to gradient of the light profile; 3) intensity and polarization recordings do not record appreciable surface relief grating; and 4) the recording process is not a bulk process and needs an unconstrained surface. Thus the time average force leading to displacement of chromophores and polymer chains should be nonzero even though relatively small in magnitude.

The spatially varying optical field would give rise to a force due to the induced polarization of the chromophores. For polymers functionalized with azobenzene chromophores the gradient force in the direction of the grating vector is nonzero only for polarizations having a p-component. Thus polymer chains which have a component of induced polarization in the field gradient direction experience a force in that direction. Polymer chains that are not extensively entangled behave as viscous medium and can be displaced under these optically induced forces. The forces experienced by the chromophores when compared to the forces such as a d.c. space charge field are small due to the smaller magnitude of the optical field and the induced polarization.

However, such optical gradient forces[21] have been known to exert forces that trap and move latex microspheres in fluids.

It has been observed that immediately after shining light on the polymer films in the absorption band of the azobenzene chromophores these films tend to soften. The softening of the azo polymers was detected by the indentation of the AFM tip before and after irradiation with light at a constant force. This "light induced plasticization" of polymer surface presumably due to the efficient optical trans-cis cycling may be the critical factor allowing the motion of the azo-polymer chains. High molecular weight would also lead to the inhibition of the polymer chains due to extensive entanglement as observed by Natansohn et al.[16]. Since the gradient forces are small and position dependent, extensive entanglement will not allow movement of the polymer chain. This gradient force based model is also consistent with the observed fluence dependence of the surface modulation in azo functionalized polymers. Since the time averaged force density is proportional to the gradient of intensity the time integrated displacement of polymer chains should be just proportional to gradient of the fluence. The polarization dependent writing efficiency of these gratings can be also explained by this model. Circular polarization and linear polarization with the plane of polarization at 45 degrees to the plane of incidence seem to the most efficient because they not only provide a nonzero gradient force but the most efficient trans-cis trans cycling of the chromophores.

CONCLUSION

Novel photo-fabrication of surface relief gratings on polymer films has been demonstrated. Large amplitude surface relief patterns could be obtained on various polymer films containing azobenzene groups in the side chain or in the main chain. Under the optimal recording conditions, surface modulation larger than 6000 Å and diffraction efficiency greater than 40 % could be achieved into each of the first order Bragg mode[13]. The surface pattern mapped the negative first derivative of the beam intensity distribution. The relief gratings are the results of layer by layer plastic surface deformation under the optical gradient force. This small force is assisted by light induced plasticization due to trans-cis cycling of azobenzene groups. We have demonstrated the formation of various complex gratings on the same spot by simply controlling the writing wavelength and the writing angle. The resulting surface pattern was a simple superposition of all the interference recording beams regardless of the sequence of the recording. This one step surface grating fabrication process opens up new possibilities of fabrication of complex surface optical elements and devices.

Acknowledgments

Financial support from the ONR and NSF is gratefully acknowledged.

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