

## Recent advances in polymers for electronics and optics

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**Abstract:** Polymers are increasingly being pushed as new materials for electronics and optics. Necessary elements for this imperative are of course the functional properties but with the added advantage of polymer processability and flexibility in structural design. For optical technology applications polymers with second and third order nonlinearity and photo and electric field driven light emission are of tremendous current interest. In this paper a new photodynamic polymer mass transport process is described that can be used to photofabricate surface relief structures on azo polymer films. This newly developed process can be applied to various azobenzene polymers, including nonlinear optical polymers and conjugated polymers with important electronic and optical properties. The relief grating is the result of layer by layer plastic deformation of the polymer surface. Chromophore molecules in the viscous plasticized (by trans-cis-trans isomerization) surface layers are dragged by "optical tweezer" effects of the electric field gradient. Based on those investigations, possible mechanisms for the optical formation of the surface relief gratings are proposed. A number of device structures will be presented and the nature of optical storage and optical processing using these polymers and the novel photodynamic process will be discussed.

### INTRODUCTION

Over the past decade polymers are finding numerous applications as active materials in electronics and optics. Conjugated polymers for example, have found uses as electronic materials in wide ranging applications as rechargeable batteries, corrosion protection coatings, sensors and actuators, electromagnetic shielding among others. Optical materials have included systems where the index of refraction can be rapidly changed by interaction with light beams or influence of electric fields. Non linear optical polymers for information processing, storage and as light sources are under active research. This paper will focus on one recent novel observation and detailed investigation of a new photodynamic polymer transport process, which presents novel application possibilities in photonics technologies.

We recently reported direct photo-fabrication of large amplitude holographic surface relief gratings on various polymer films containing azobenzene groups in the side chain or in the main chain (ref. 1-4). These surface relief gratings were produced upon exposure to an interference pattern of Ar<sup>+</sup> laser beams at modest intensities without any subsequent processing steps. The gratings were very stable when the polymer was kept below T<sub>g</sub>. The gratings could be erased by heating the polymer above T<sub>g</sub>. Similar results have been reported by Natansohn and Rochon (ref. 5, 6). 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.

Here we will briefly describe recent exploration of this novel photoinduced macro scale polymer transport process observed in azo polymers and its possible applications.

### EXPERIMENTAL

Figure 1 shows the chemical structure of a typical polymer on which the surface grating formation was investigated. Good optical quality polymer films were prepared by spin-casting on glass slides. The typical

typical sample thickness of the films ranged from 0.4 to 1  $\mu\text{m}$ . The gratings were fabricated using simple interference of the two linearly polarized laser beams at 488 nm or 514 nm from an  $\text{Ar}^+$  laser (ref. 1, 2). Laser beams with various polarizations were used. The intensity of the recording beam employed ranged from 3 to 110  $\text{mW}/\text{cm}^2$ . 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).

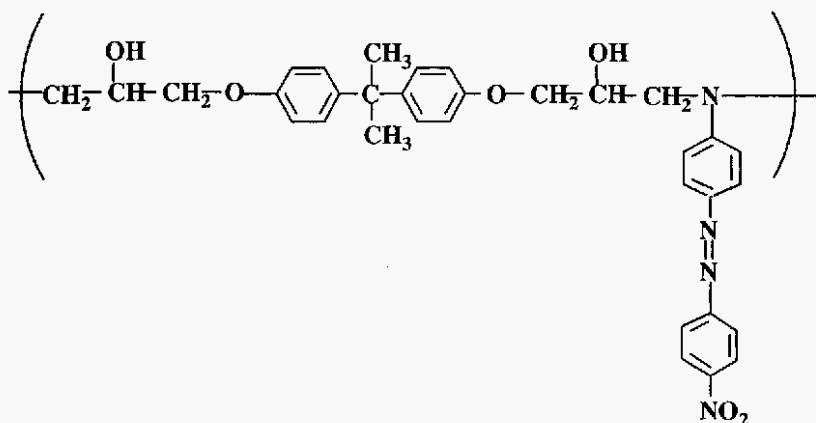


Fig. 1. The chemical structure of a typical polymer on which the surface grating formation was investigated.

## RESULTS AND DISCUSSION

Surface relief gratings with large surface modulations could be formed on the polymers with azobenzene groups. Fig. 2 shows a typical AFM view of the surface gratings formed on PDO3 polymer films. AFM view of the surface gratings on the polymer showed very regularly spaced sinusoidal surface relief structures with a depth modulation of over 1000  $\text{\AA}$ . 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 (ref. 3), surface modulation depth greater than 6000  $\text{\AA}$  and diffraction efficiency of more than 40 % could be produced on the PDO3 films.

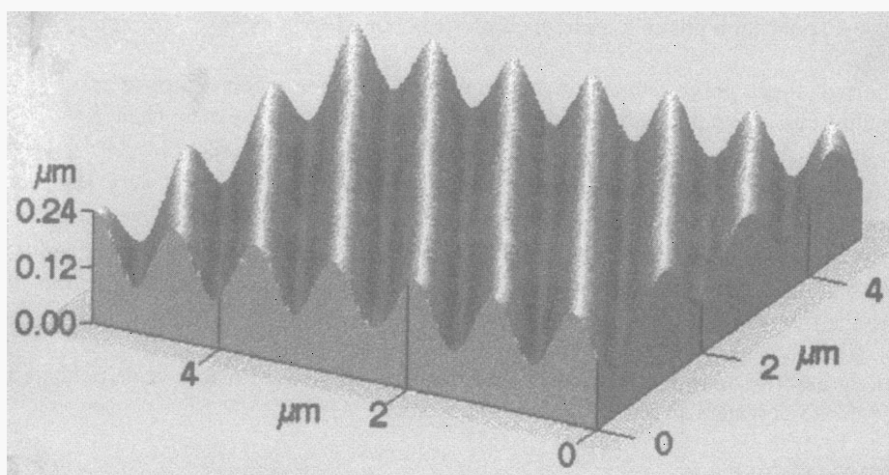


Fig. 2. A typical AFM three-dimensional view of the surface gratings fabricated on a PDO3 film.

Polarization states of the writing beams significantly influenced the diffraction efficiency and grating formation (ref. 3). Under the condition for intensity recording (two s-polarization), very low diffraction efficiency and small surface modulation ( $<100 \text{ \AA}$ ) 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.

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 were investigated as well. When the polymer film is raised to a higher temperature during recording, the grating formation becomes less efficient. At a temperature near to the  $T_g$  of the polymer, the diffraction efficiency was almost zero even under the exposure for a 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.

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 (ref. 6). 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.

## 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  $6000 \text{ \AA}$  and diffraction efficiency greater than 40 % could be achieved into each of the first order Bragg mode. 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.

Photofabrication of surface relief structures employing this new technique eliminates a number of processing steps and reduces material handling. The approach is quite versatile and a number of side chain and main chain azo polymers have been employed to date. Conjugated electroactive polymers including

polydiacetylenes for example, with azobenzene chromophore as side groups have also been photofabricated. The technique may be used to produce complex patterns including optical devices and elements.

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