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**Mechanism and Model of Laser-Driven Mass Transport in Thin Films of Azo
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by

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13. ABSTRACT (Maximum 200 words) Samples of poly [4'-[(2-(acryloyloxy)ethyl)ethylamino]-4-nitroazobenzene] were used to inscribe surface gratings by optical means, and the Navier-Stokes theory of flow under an applied pressure was used to model the process. Dependence on molecular weight, light intensity, quantum yields of photoisomerization, chromophore free volume, film thickness and bulk modulus was established.			
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MECHANISM AND MODEL OF LASER-DRIVEN MASS TRANSPORT IN THIN FILMS OF AZO POLYMERS

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INTRODUCTION

Polymer thin films incorporating nonlinear optical chromophores are seeing widespread use in a variety of optical devices due to their low cost, ease of preparation and processing, and versatility. One of the most common chromophores for these applications is the azobenzene-based disperse red 1 dye, which is also interesting as it can undergo rapid photoisomerizations between the trans and cis geometrical forms. For these reasons polymer films incorporating azobenzene groups have received much recent attention. Systems studied include amorphous glasses, liquid crystals, and Langmuir-Blodgett monolayer films. By tailoring the molecular structure of both the azo chromophore and polymer backbone, polymers can be prepared and optimized for applications in liquid crystal displays and devices, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and more recently, holographic gratings.

It had been known for some time that volume refractive index gratings could be formed in films of this type by photoinducing birefringence, but it was recently discovered by a number of research groups that these films were also suitable for high-efficiency surface relief holographic gratings. These surface profile gratings are easily formed with an interference pattern created from coherent laser light at a wavelength absorbed by the material, and display high diffraction efficiencies due to large scale modulation of the surface of the films. This is an unusual phenomenon, as grating production implies large scale mass transport in the films well below the glass transition temperature (T_g).

We have used amorphous high T_g azo side chain polymers as materials for reversible optical storage,¹ and have also reported their suitability for the writing of high efficiency surface gratings.^{2,3} Tripathy and Kumar,^{4,5} as well as Hvilsted and Ramanujam,^{6,7} have also produced high efficiency surface gratings from azo side chain high T_g polymers. These groups both observed similar large scale mass transport near room temperature in azo polymer films, and confirmed that the azo isomerization is necessary and that grating formation is highly dependent on the polarization state of the laser beam. As all research groups preclude ablation as a cause, this also concedes the role of bulk viscosity in the polymer films, as there must then be polymer flow well below T_g.

The diffraction gratings can be produced with a variety of polarization states of the writing laser and the depth and spacing of the resulting surface profile can be readily measured. We also have a wide range of polymers displaying various absorption maxima and coefficients, photochemical and isomerization behavior, and bulk viscosities of the films. From examination of the role played by each of these parameters, a mechanism is then proposed for surface grating formation in high T_g azo polymer films, involving the selective photoinduced isomerization of the azo groups and the free volume requirements of this geometrical transformation. It is shown that the creation of free volume for the process where free volume is initially inadequate leads to pressure gradients above the yield point throughout the material, coincident with the light interference grating. The resulting viscoelastic flow in these low viscosity polymers then leads to pressure driven mass transport to form surface profile gratings. A model of polymer flow under the influence of light is derived based on Newtonian fluid dynamics, involving no arbitrary parameters or fitting constants. Predictions from this model are shown to agree well with polymer properties such as photochemical behavior, free volume requirements, bulk viscosity, and molecular weight.

EXPERIMENTAL

The materials studied here are amorphous high T_g polymers containing a substituted azobenzene side group, with the structure of a typical polymer detailed in Figure 1. The polymers were dissolved in THF, spin cast onto clean glass substrates, and heated to 95° to yield dry films of good optical quality and of thickness between 5 and 1000 nm. The gratings were optically inscribed onto the films with a single beam split by a mirror and reflected coincident onto the film surface. A 488 nm beam from an argon laser passed through a spatial filter and expanded to a diameter of 8 mm was used for writing, and the surface profiles of the resulting gratings were recorded by a nanoscope II atomic force microscope (AFM). The irradiation power ranged from 1mW to 100mW. The progression of the grating inscription was monitored by measuring the growth of the first-order diffracted beam over time with a 1mW 633 nm beam from a HeNe laser, also shown in Figure 1.

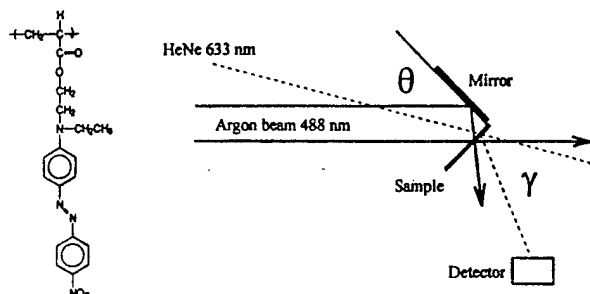


FIGURE 1. Polymer structure of PDR1A and inscription geometry.

RESULTS and DISCUSSION

Irradiation of the films as described produces a highly efficient grating written on the timescale of minutes. Figure 2 displays the growth of the first order diffracted beam for a sample of PDR1A so irradiated.

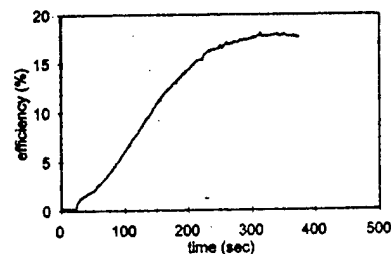


FIGURE 2. Growth of first order diffracted beam for PDR1A.

There is an initial and rapid growth (on the order of seconds) of efficiency to about 1% corresponding to production of the reversible volume birefringence grating, then a slower process (on the order of minutes) dominates up to high efficiency. The efficiency in these gratings ranges from 5% to 45%, far beyond what can be achieved for solely a birefringent volume grating of these samples, and has been found to be due to a modulation of the surface of the film as AFM reveals a regularly spaced and sinusoidal surface relief grating coincident with the light intensity interference pattern. Depths from peak to trough of nearly 1000 nm have been achieved on samples whose initial film thickness was 1000 nm, and the phase relationship between the surface and volume gratings coincides the light intensity maxima with the surface profile minima. A typical grating profile is presented in Figure 3. The efficiency is over 42% and the depth is near 900 nm.

Once written, the grating profile is stable over time and not photoerasable, but can be erased thermally by heating the polymer film beyond the T_g. The film can then be subsequently irradiated to produce a grating then again erased repeatedly. Once a grating is written the writing geometry can also be altered and another grating inscribed coincident with the first, either sharing the same

fringe axis, or rotated at an angle to the first. In this manner up to 10 coincident gratings have been stored, with good resolution of all 1st and higher order diffraction spots for large spacing, and also resolution of all argon laser fundamentals if so irradiated. As an example, Figure 4 displays the AFM surface profile of two such gratings written on a film of PDR1A rotated 90 degrees between inscriptions. The depth and efficiency of the written gratings appear to depend on the polarization, power, and geometry of the incident light, mobility and free volume requirements of the azo chromophores, and bulk viscosity of the polymer matrix.

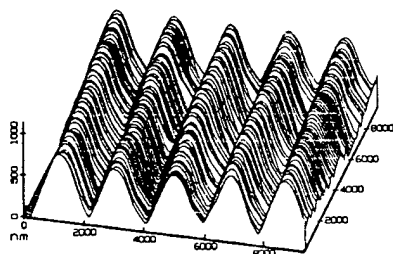


FIGURE 3. AFM surface profile of a laser-inscribed grating.

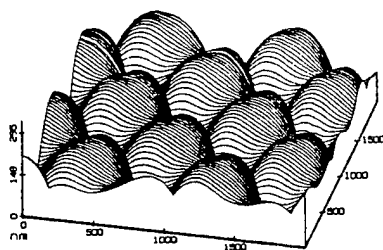


FIGURE 4. AFM surface profile of two gratings laser-inscribed consecutively after sample rotation of 90 degrees.

Unlike the birefringent volume gratings, the inscription of surface profile gratings is power dependent, and surface modulation is most pronounced when the intensity or phase interference pattern leads to alternating regions of low and high trans-cis-trans isomerization of the azo groups. This, combined with the fact that the process was enhanced when bulky substituents were added to the azobenzene rings (requiring greater free volume to undergo photochemical isomerization), suggested that this process driving the mass transport is linked to the isomerization of the azobenzene groups. Although elevated temperature in regions of high absorption and isomerization may help the process, it has been shown by all groups that the phenomenon isn't temperature driven.^{3,5,6} The mechanism proposed here for this phenomenon involves pressure gradients as a driving force, present due to different photochemical behaviors of the azo chromophores at different regions of the interference pattern. The phase addition of the two beams in the interference pattern leads to regions of high trans-cis-trans isomerization by the absorbing azo groups, bordered by regions of low isomerization. As the geometrical isomerization requires free volume in excess of that available in the cast films, the photochemical reaction in these areas produces a laser-induced internal pressure, which can be shown to exceed the yield point of the material.³ It is proposed that the resulting viscoelastic flow from these high pressure areas to lower pressure areas leads to the formation of the regularly spaced sinusoidal surface relief gratings that were observed by all of the research groups working with these materials, and previously unexplained.

This photo-transport mechanism is further supported by the observation that the rate and extent of grating formation are strongly dependant on the length of the polymer chains in the material (molecular weight). For samples of increasing molecular weight from MW = 4000 g/mol (40 units long) to MW = 11700 g/mol (117 units long) the inscription rate is significantly

decreased. Samples with molecular weight greater than this become entangled in bulk, and no modulation of the surface of the polymer film can be induced.

In order to quantify this process, and make testable predictions as to the influence of polymer properties on inscription rates, a model was derived based on the Navier-Stokes equation (1), the basic relation of Newtonian fluid dynamics under an applied pressure.⁸ This expression relates the time dependent motion V in directions x and y in the bulk polymer resulting from an internal pressure $P(x)$ in a viscous medium with density ρ and viscosity η . An approach of this nature had been reported previously to successfully model flow in a viscous oil film under laser-induced thermal gradients.⁹

$$\frac{\partial V_x}{\partial t} + V_x \frac{\partial V_x}{\partial x} + V_y \frac{\partial V_x}{\partial y} = \frac{-1}{\rho} \frac{\partial P(x)}{\partial x} + \eta \frac{\partial^2 V_x}{\partial y^2} \quad (1)$$

Applying appropriate boundary conditions allows an exact solution of the resulting differential equation, which then relates the height $h(x,t)$ of the film surface during laser modification at a given time and position, as a function only of variables relating to the laser light pattern, chromophore, and bulk polymer matrix (2).

$$\frac{\partial h}{\partial t} = \frac{-h^3 \cdot I_0 \cdot B \cdot [\text{cis}]}{6 \cdot C \cdot \text{MW}} \cdot \left(\frac{FV_{\text{cis}} - FV_{\text{trans}}}{FV_{\text{trans}}} \right) \cdot \frac{16\pi^2}{\lambda^2} \cdot \text{Sin}^2 \theta \cdot \text{Cos} \left(\frac{4\pi}{\lambda} \cdot \text{Sin} \theta \cdot x \right) \quad (2)$$

With no integration constants or arbitrary fitting parameters, predictions from this model can be compared directly to the experimentally determined dependence on light intensity, quantum yields of the photoisomerization, chromophore free volume, film thickness, molecular weight, and bulk modulus. With a series of azobenzene polymers available with a wide range of properties, each property corresponding to a variable in Equation (2) was isolated and tested independently by experiment. In this fashion, the grating inscription rates were measured while varying the light intensity and polarization, substituents on the azo chromophore, film thickness, and molecular weight while keeping all other variables constant. Good agreement is observed between this pressure-driven laminar flow model and experimental the results.

CONCLUSIONS

Surface profile holographic gratings could be inscribed in azo polymer thin films by low power laser irradiation. The mechanism for the high efficiency photoinduced surface gratings appears to be isomerization driven mass transport, with grating depths of up to $1 \mu\text{m}$ achievable with films of an initially similar thickness. A fluid dynamic model constructed based on this proposed photo-transport mechanism agrees well with results of experiments performed varying the nature of the writing laser, free volume requirements of the chromophores, and bulk viscosity of the polymer matrix.

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