

Photoinduced fabrication of complex surface relief structures on azobenzene functionalized polymers

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Abstract. Light induced fabrication of complex surface relief structures on azobenzene functionalized polymers is reported. Large class of side chain and main chain polymers can be utilized to record these relief structures. The recording and erasure process are strongly dependent on the polarization. Possible transport mechanism of polymer chains well below the glass transition temperature due to photoinduced effect is discussed.

Keywords. Azobenzene polymers; surface relief gratings; gradient force.

1. Introduction

Novel synthetic approaches are pivotal for the successful development of materials with optimized performance for various practical applications (Lessard *et al* 1994). Surface relief structures are achieved through holographic recording by periodically modulating the thickness of the samples due to a superposed pattern. Advantages such as ease of fabrication and low cost have an important bearing on applications like large area gratings and other diffractive optical elements.

Here, we describe a recently invented direct single step optical process to fabricate large amplitude ($> 5000 \text{ \AA}$) reversible surface relief structures on azobenzene functionalized polymer thin films (Kim *et al.* 1995; Rochon *et al* 1995; Tripathy *et al* 1998). The structures can be fabricated upon exposure of the film surface to an appropriately polarized single beam or an interference pattern of coherent Ar⁺ laser beams (488 nm) at moderate intensities ($\leq 100 \text{ mW/cm}^2$). We would like to emphasize that this process is completely different from ablation or thermally induced deformation of polymers with high intensity lasers. The direct physical movement employing light beams results in a large-scale transport process and patterning of azo functionalized polymer thin films. This is due to efficient photoisomerization process along with light induced forces acting on the azo chromophore tethered polymeric materials. Strong polarization and fluence dependence indicates that this is a photonic and not a thermal process (Jiang *et al* 1996). We have demonstrated that this approach may be quite suitable for photomanipulation of azo functiona-

lized materials in fabricating complex structures for various applications.

2. Azo polymer thin films

We have synthesized azobenzene chromophore functionalized copolymers through a number of different reaction schemes. Side chain azo polymers were synthesized by reacting diglycidyl ether of bisphenol and various chromophores (Mandal *et al* 1991). The glass transition temperature (T_g) of these polymers ranged from 100–150°C. Azo functionalized poly(acrylic acid) (PAA) with either –COOH or –NO₂ in the azo group is synthesized through a post-azo coupling reaction by modification of high molecular weight (250,000 g/mol) PAA (Nirmal *et al* 1998). The number average molecular weight is $> 500,000$ upon azo functionalization. These PAA based azopolymers are highly soluble in polar organic solvents like DMF and DMSO and are spin coated onto glass slides and vacuum dried to obtain optical quality thin films. The glass transition temperatures (T_g) of the PAA based polymers are 85 and 91°C, respectively. We have also fabricated surface relief structures on thin films of main chain azo polyureas ($T_g = 197^\circ\text{C}$), and rigid rod conjugated polymers such as polydiacetylene, functionalized with azobenzene groups (Sukwattanasinitt *et al* 1998) and poly (azo phenol).

3. Photofabrication of azo polymer film surface

The azo polymers mentioned above can be efficiently manipulated by the photodriven mass transport process to form structured surfaces. Surface relief structures on the azo polymer thin films (thickness: 0.4 to 1 μm)

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photofabricated using either a focused single beam or a two-beam interference pattern were investigated by an atomic force microscope (AFM, Park Scientific). Ar⁺ laser beams with different polarizations were used to study and optimize the grating formation process in the different class of materials. Figure 1 shows a typical three dimensional scan of the SRG photofabricated on high MW azo polymer film. The diffraction efficiency of the transmitted first order diffracted beam from the grating is probed with an unpolarized low power He-Ne laser beam (633 nm). The grating spacing can be adjusted in range of 0.3–3 μm by changing the angle (θ) between the writing beams. The gratings are stable at temperatures below T_g of the polymer and can be erased either optically (Jiang *et al* 1998) or by heating the polymer above its T_g . After erasure, the polymer films may be used to rerecord a surface pattern.

The strong polarization dependence of the induced surface deformation and the phase relationship between the surface relief pattern and the writing beam are demonstrated convincingly in a single beam experiment (Bian *et al* 1998). The horizontally polarized 544 nm He-Ne laser beam with Gaussian intensity profile is focused using a 10 \times spherical lens onto the thin film of poly(azo phenol). The radius of the focused spot is 2.1 μm and the peak intensity is 1 W/cm². A dramatic surface deformation pattern with polymer transport only along the polarization direction is observed although the

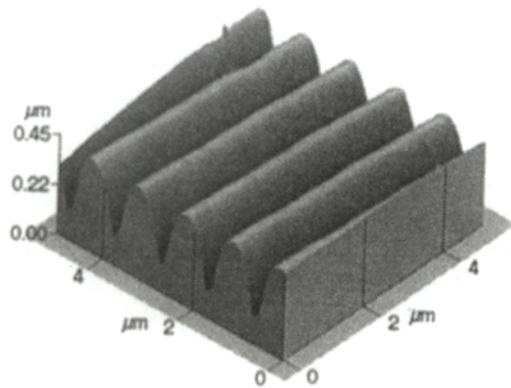


Figure 1. AFM image of the SRG on high molecular weight azo polymer film.



Figure 2. Surface deformation of the poly(azo phenol) exposed to horizontally polarized single Gaussian laser beam.

incident intensity pattern is radially symmetric (figure 2). The lateral size of the induced surface deformation is approximately equal to the diameter of the Gaussian beam.

The versatility of fabricating complex surface relief structures in the azo polymer films is demonstrated by the well-defined beat structure shown in figure 3. The grating was recorded at the same spot sequentially with two wavelengths (488 and 514 nm) at a fixed writing angle; the beat period was 19 μm . The surface pattern is very close to the simple superposition of two recording waves. Surface relief hexagonal array diffraction gratings have also been produced by a three-beam coherent exposure. Other surface relief structures with practical applications include orthogonal gratings and Fourier synthesized blazed grating. Fresnel zone plates were also efficiently fabricated (Tripathy *et al* 1998). The results mentioned above along with further experiments discussed elsewhere (Kumar *et al* 1998), indicate the necessity for an optical field gradient and induced anisotropy for the surface deformation process in the azo polymer films.

4. Optical gradient force driven mass transport

Polarization states of the writing beams significantly influence the diffraction efficiency and the grating formation process (Jiang *et al* 1996). In cases where there is a simultaneous variation of both light intensity and the resultant polarization field on the film, large amplitude and high efficiency SRGs could be formed. The surface modulation appears to be due to the lateral migration of the polymer molecules from the valleys to the ridges driven by the time averaged optical gradient force $\mathbf{P} \cdot \nabla \mathbf{E}$ acting on the “plasticized” polymer surface (Kumar *et al* 1998). The SRG formation is a result of layer by layer movement of the locally plasticized polymer surface material and depends on the nature of the polymer surface.

5. Surface initiated mechanism

A constrained surface, where chains are entangled inhibits grating formation. A systematic study was carried out to firmly establish the role of the surface layers and to

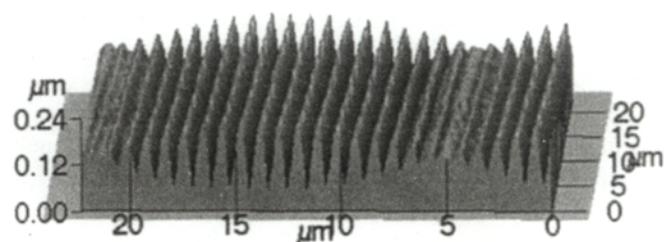


Figure 3. AFM image of the dual grating beat structure.

experimentally verify the surface initiated grating formation mechanism in azo polymer films (Nirmal *et al* 1998). The approach is based on a novel technique of forming ultrathin polymer layers through an alternate layer by layer electrostatic deposition of oppositely charged polyelectrolytes. Multilayers of polycation and polyanion are formed on top of the azo polymer (containing ionizable groups) film by repeated dipping in solutions. The transparent polyion bilayers are expected to restrict the surface initiated material movement. Even an ultrathin (30 Å thick) overlayer strongly impedes the material transport and SRG formation. Thicker the overlaid film, more difficult it is to move the material and efficiency of SRGs decreases.

6. Conclusions

A large class of azobenzene functionalized polymers can be optically manipulated to form complex surface structures. Large scale movement of polymer chains can be achieved well below the glass transition temperature. Polarization dependence of the recording process implies that the optically induced force on the polymer chains is due to time averaged gradient forces. It is important to have a free unconstrained surface to obtain the surface relief structures. Even an ultrathin (30 Å) layer of trans-

parent polymer overlaid on the azobenzene functionalized polymer film severely inhibits polymer chain movement.

References

- Bian S, Li L, Kim D Y, Williams J, Kumar J and Tripathy S K 1998 *Appl. Phys. Lett.* **73** 1817
- Jiang X L, Li L, Kim D Y, Shivshankar V, Kumar J and Tripathy S K 1996 *Appl. Phys. Lett.* **68** 2618
- Jiang X L, Li L, Kim D Y, Kumar J and Tripathy S K 1998 *Appl. Phys. Lett.* **72** 2502
- Kim D Y, Li L, Kumar J and Tripathy S K 1995 *Appl. Phys. Lett.* **66** 1166
- Kumar J, Li L, Jiang X L, Kim D Y, Lee T S and Tripathy S K 1998 *Appl. Phys. Lett.* **72** 2096
- Lessard R A, Changkakoti R and Manivannan G 1994 *Holographic recording materials* (New York: Chapman & Hall)
- Mandal B, Jeng R, Kumar J and Tripathy S K 1991 *Makromol. Chem. Rapid Commun.* **12** 607
- Nirmal K Viswanathan, Balasubramanian S, Li L, Kumar J and Tripathy S K 1998 *J. Phys. Chem.* **B102** 6064
- Rochon P, Batalla E and Natansohn A 1995 *Appl. Phys. Lett.* **66** 136
- Sukwattanasinitt M, Wang X, Li L, Jiang X L, Kumar J, Tripathy S K and Sandman D J 1998 *Chem. Mater.* **10** 27
- Tripathy S K, Kim D Y, Li L and Kumar J 1998 *Chemtech.* **28** 34