

In-situ Investigation of Surface Relief Grating Formation in Photosensitive Polymers

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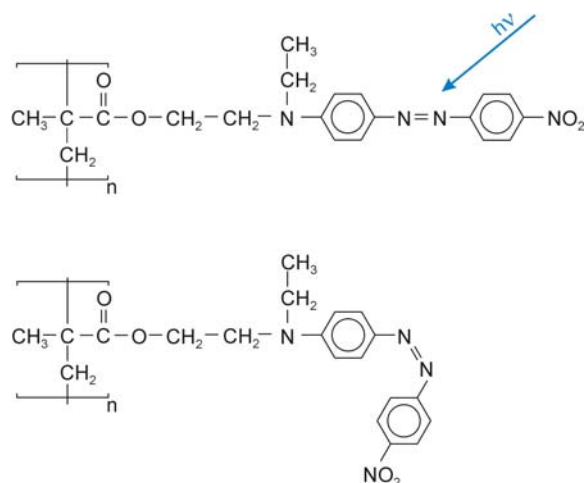
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Photosensitive materials have a huge potential for applications in the computer and telecommunication industry. One example is the use of holographical techniques to store large amounts of data in the volume of a polymer film. This method relies on changes of physical properties induced by optical techniques. Another interesting effect is the movement of bulk photopolymer material with light. The photoorientation of chromophores has been known for almost 100 years [1], but in the mid 1990's it was discovered that material transport may occur at relatively low laser intensity ($<100\text{mW/cm}^2$) [2,3].

At high laser power ($>100\text{W/cm}^2$) thermal melting or evaporation takes place, but material movement at power densities where thermal effects are negligible is totally different. The polymer itself at room temperature is in a glassy state far below its glass transition temperature ($T_g=130^\circ\text{C}$) and therefore should not move at all. But special polymers such as azobenzenes can reversibly change their conformation by absorption of light. Due to a cycling trans-cis-trans isomerization the molecules change their shape (Figure 1), which leads to a movement of mass. Some theories have been developed to explain the phenomenon, but up to now none are able to explain all experimental details [4,5]. In order to gain better insight it is necessary to observe the dynamics, especially at the beginning of grating formation as discussed below.



When light illuminates a periodically varying (electron) density, maxima in scattered light intensity are produced in distinct directions given by Bragg's law ($n\lambda \sim p \sin \theta$). If the development of such grating peaks is recorded, it is possible to observe movement of the polymers forming such grating structures. Up to now only visible light scattering has been performed for in-situ experiments, but visible light has its main sensitivity for large gratings (heights $h > 10\text{nm}$). We have used x-ray scattering at a wavelength of 0.1nm for a more sensitive method to observe gratings with $h < 10\text{nm}$. A second advantage of x-ray scattering is the enhanced range of diffraction orders that characterize deviations from simple (sine-like) periodicity. With a red probe laser at $\lambda = 633\text{nm}$ and a grating period of $p = 1500\text{nm}$ only the first two grating peaks ($n = +1, +2$) are visible, but at x-ray wavelengths Bragg's equation can be fulfilled over 1000 orders.

To produce a periodic structure in the polymer, the intensity or polarisation of the absorbed light has to change periodically. This can be achieved by interference of two blue Ar laser beams ($\lambda = 488\text{nm}$). If we keep one laser beam fixed at normal incidence, we can select the grating period p by adjusting the angle of incidence ϕ for the second laser beam: $p = 488\text{nm} / \sin \phi$ (Figure 2). For different beam polarization the intensity or the direction of the electric field changes over one period. The interference of two circularly polarized waves with opposite helicity yields a rotation of the electric field over one grating period while the intensity is constant. The interference of two linear $p(s)$ polarized waves yields a change of intensity (0 to I_{max}) while the direction of the electric field, the polarization constant. Starting with a flat film this illumination will form a surface grating in several minutes.

Fig 1: The absorption of a blue photon ($\lambda = 488\text{nm}$) leads to change of the azobenzene conformation in the photosensitive polymer (pDR1M). By multiple absorptions the molecule can cycle through a stretched trans (top) and a curved cis (bottom) conformation

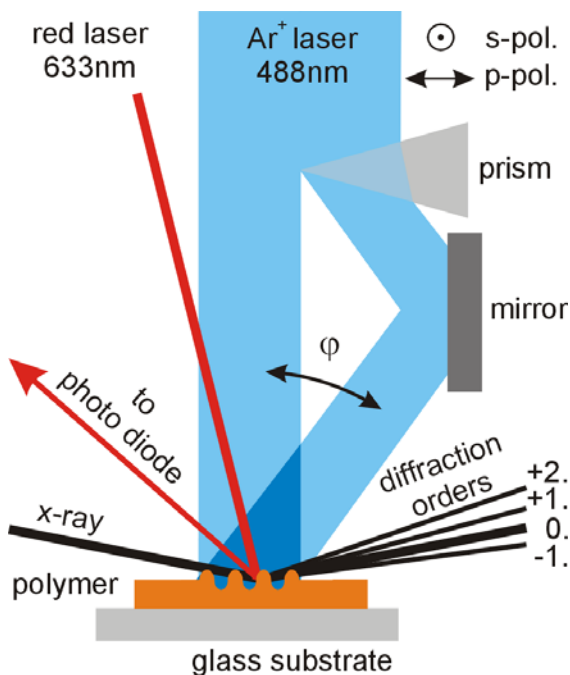


Fig 2: An expanded Ar-laser beam is split by a prism and made to interfere at the polymer film on a glass substrate. An initial flat polymer forms a surface grating, which can be probed by red laser light and X-ray scattering.

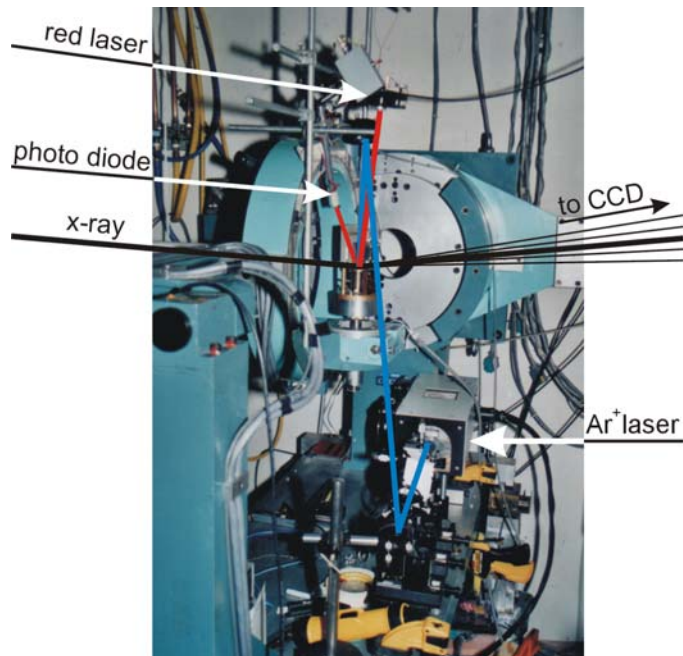


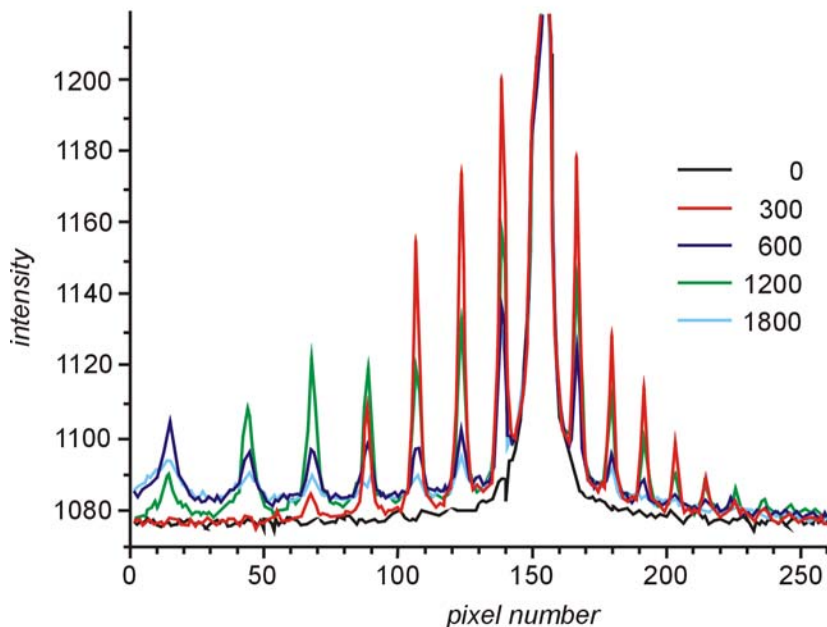
Fig 3: Holography setup used to investigate photopolymer dynamics with simultaneous visible light and X-ray scattering at CHESS C-line. A blue laser creates a grating that is monitored simultaneously by a photo diode recording diffraction of red laser light from the surface and by a CCD-camera recording many x-ray scattering peaks.

To see what happens during polymer movement, the grating must be written on the goniometer of the x-ray diffractometer. During holographic laser illumination any vibration of the system would cause destruction of the interference condition. Therefore no motor motions are allowed and the diffractometer must be isolated from vibrations caused by vacuum pumps, etc. Many beamlines at different synchrotron light sources were checked for suitable conditions, but our best results have been achieved with a heavy Huber diffractometer and a damping system at CHESS C-line (see Figure 3). To our knowledge this is the first time a hologram was written and investigated with synchrotron radiation.

Figure 4 shows a typical x-ray CCD image after 600 second of exposure with the blue laser. A line scan through the CCD image very clearly shows each diffraction order.

With the CCD-camera we recorded the development of this grating with time resolution of 0.6 seconds and with up to 16 diffraction peaks detected simultaneously.

Fig 4: CCD image (top) of the X-ray diffraction pattern recorded after 600s of writing with the blue laser of 5mW/cm² and two counter circular polarized beams. Below are the integrated intensities of each row for 5 different illumination times (0, 300, 600, 1200 and 1800s). Beside the specular peak (at #155) are the grating peaks.



The intensity of corresponding pixels in each grating peak has been integrated to give the time development of the diffraction orders shown in Figure 5. While the red probe light signal increases slowly, the time development of each x-ray diffraction order is different. In particular the first order X-ray diffraction peak has a maximum near 120 seconds and decreases afterwards.

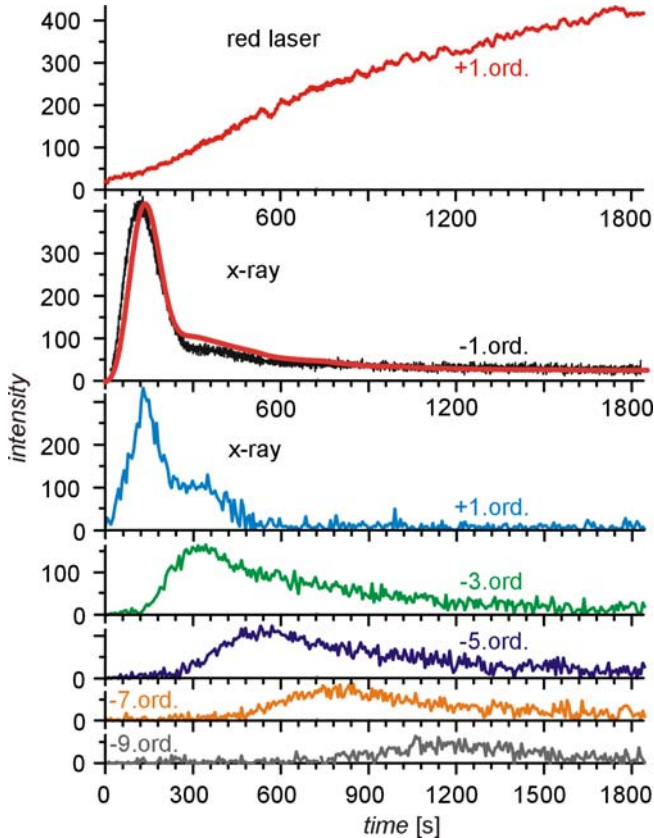


Fig 5: Development of grating orders for laser light (top curve) and X-ray (lower curves) scattering. The interference of blue laser for 1800s leads to a grating formation. The red laser light diffraction increases slowly with growing grating height. X-rays are most sensitive for small grating height and show an intensity maximum after some seconds. For the -1. order we simulated the diffraction (red line).

A theoretical analysis shows that an ideal sinusoidal grating without any fluctuations will give a Bessel functional behaviour. The intensity of each grating order I_n develops with the height of the grating h like the square of a Bessel function of order n as: $I_n \sim J_n^2(q \cdot h)$, with $q = 2\pi/\lambda$ [6]. Due to the Gaussian laser profile, the grating develops faster in the center of the illuminated area than at its borders and this causes the oscillation to blur. A simulation shows very good agreement between experiment and theory. This is illustrated by comparing the red and black curves (-1. order) in Figure 5.

If we change the polarization direction of the Ar-laser we get different time dependence for the grating development. The fastest growth can be obtained by interference of two counter rotating circularly polarized beams (Figure 6). Writing with two p-polarized beams

leads to slower growth of the surface grating and interference of two s-polarized beams produces a very weak grating structure.

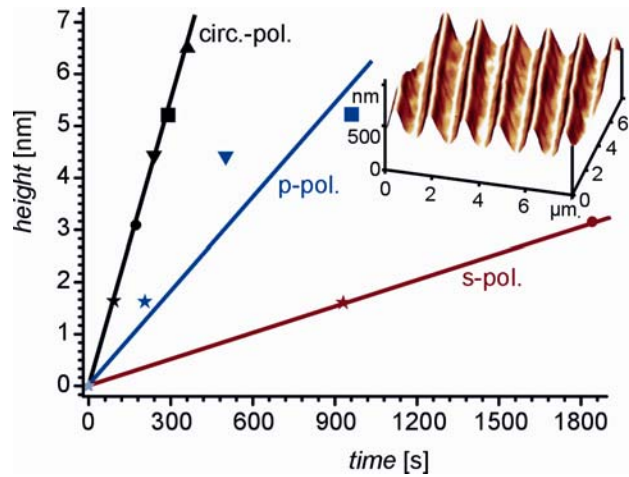


Fig 6: The grating formation depends strongly on the polarization of the Ar-laser. It is fastest with two circularly polarized beams. Inset: Atomic force image of a surface grating.

The behavior illustrated in Figure 6 is explained as follows. To form a surface grating the polymer has to move, in the horizontal plane of Figure 2, from the positions of minimum to maximum. If the electric field of the blue laser is perpendicular to that direction (s-polarization) there is only a very slow grating formation. The movement is faster, when the electric field is along the direction of polymer movement (p-polarization), but interference of two p-polarized beams leads to areas of very low intensity. This can be avoided by interference of two counter circular polarized beams. We have thus revealed an important role for the direction of the electric field in polymer movement.

In conclusion, our research shows that CHES x-ray beams have been very useful in monitoring polymer movement in thin polymer coatings as the gratings form in response to optical laser energy. These permanent gratings seem suitable for future holographic storage of information, and the industrial opportunities are just now being explored.

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