Recording of Surface Relief in Azobenzene Containing Low Molecular Weight Organic Glasses

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Abstract. One of the used methods to induce mass motion on the surface of azopolymer films is holographic recording using laser wavelength corresponding to the absorption band of the azo compound. The sinusoidal light interference pattern on the surface of the sample leads to a sinusoidal surface patterning - a stable surface relief grating (SRG). As confirmed by atomic force microscopy (AFM), these gratings are found to be very large, with depth up to hundreds of nanometres and they diffract light very efficiently. In this work azobenzene containing low molecular weight organic glass K-RJ-8 was experimentally studied. The compound absorbs at the visible spectrum, holographic recording in this range using different polarization states of the recording beams was done. Diffraction efficiency was measured during the recording of the SRG. The relationship between formation of SRG and photoinduced birefringence is discussed.

1. Introduction
One of the properties of azobenzene containing compounds is that under influence of light the azo compound undergoes trans-cis isomerisation [1] and during this process the moieties may align relative to the electric field vector of light. This leads to anisotropy in the material (which can be observed as dichroism and birefringence), thus making these compounds light polarization sensitive [2]. Another phenomenon which strongly depends on the light polarization is photoinduced mass transport [3]. A well known method how to induce mass motion is holographic recording. By using different polarization states of the two recording beams, different interference patterns can be obtained on the surface of the material and a strong effect on the efficiency of the mass transport can be observed [4].

Mass transport phenomenon allows to create a surface relief directly by light, without the post processing of chemical etching. Materials that possess this ability of direct optical patterning may have potential application in various photoactive devices, optical information storage and the production of diffractive optical elements used in telecommunication (e.g. filters, Bragg reflectors) [5].

As opposed to functionalized azo-polymers, low molecular weight organic glasses containing azobenzene have the advantage of a well-defined molecular structure and they exhibit more uniform physical properties. In this work thin films of azobenzene containing low molecular weight organic glass K-RJ-8 were experimentally studied. We attempt to explain distinctive attributes of photoinduced mass transport in azo compounds by studying photoinduced dichroism and birefringence in K-RJ-8.
2. Experimental

The studied compound K-RJ-8 was synthesized in Riga Technical University by Kaspars Traskovskis [6]. The molecular structure of the compound is shown in figure 1, the absorption spectrum is shown in figure 5. The thickness of the thin film used for birefringence measurements was 0.3 μm, for dichroism measurements and for the holographic recording a thicker sample (0.7 μm) was used to prevent the mass transport from reaching the substrate.

Surface relief gratings were recorded using a holographic set-up shown in figure 2.

Figure 1. Molecular structure of low molecular weight organic glass K-RJ-8.

Figure 2. Experimental set-up for holographic recording. L1 – recording laser (491 nm), L2 – reading laser (653 nm), λ/2 – half-wave plate, Bs – beam splitter, M – mirror, S – sample, PD – photodiode.

For holographic recording 491 nm laser (L1) was used. The laser beam was split into two beams with equal intensities by a beam splitter (Bs). Using mirrors (M) the beams were directed to the sample (S) where they interfere. The period of the interference pattern was Λ=1 μm. Half-wave plates (λ/2) were used to set the polarization states of the recording beams. The intensity of the beams was I_1=I_2=0.18 W/cm². The recording course was monitored by registering the 1st order diffracted beam of 653 nm laser (L2), which is weakly absorbed by the sample, with a photodiode (PD). The diffraction efficiency of the obtained grating was calculated as in (1):

\[ \eta = \frac{I_1}{I_0} \]  

where I_0 is the intensity of the reading laser and I_1 is the intensity of the 1st order diffracted beam.

Experimental set-up for studying the photoinduced dichroism is shown in figure 3. The polarization of 532 nm pump laser (L) was set by a half-wave plate (λ/2), linearity was improved by Glan-Taylor polarization cube (P). The intensity of the pump beam was I =0.07 W/cm². As the probe beam a polarized (A) white light source was used (D). To determine difference of absorption in orthogonal directions, the sample (S) was illuminated with pump beam with polarization parallel or orthogonal to the polarization of the probe beam. The spectra were measured using Ocean Optic HR4000CG spectrometer (PD).

Photoinduced birefringence was measured using experimental set-up shown in figure 4. Birefringence measurements were done using the same wavelength (532 nm) and laser intensity (I =0.07 W/cm²) as in dichroism experiment.
Birefringence was induced by 532 nm laser (L1). The polarization of the laser beams was set using half-wave plates ($\lambda/2$). The linearity of the polarization was improved by Glan-Taylor polarization cubes (P). Probe beam from another 532 nm laser (L2) passes through the sample (S), a part of it is reflected to a photodiode to take into account the changes of transmittance regarding photobleaching but the rest of it passes through an analyzer (A). If a difference between the refractive indexes in orthogonal directions is present in the sample, the polarization plane of the probe beam shifts and a signal appears on the photodiode behind the analyzer. Birefringence then can be evaluated using (2):

$$
\Delta n = \frac{\lambda}{\pi d} \arcsin \left( \frac{I}{I_0} \right)
$$

where $I$ is the probe beam intensity passing through crossed polarizer and analyzer, $I_0$ – probe beam intensity passing through parallel polarisers (with transmittance changes taken into account), $\lambda$ - probe wavelength and $d$ is the thickness of the layer of material.

3. Results and discussion

Diffraction efficiency dependence on time for different polarization states of the recording beams is shown in figure 5.

![Figure 5. Diffraction efficiency dependence on exposure dose for different polarization states of the recording beams. The intensity of the 491 nm laser beams was $I_1=I_2=0.18$ W/cm$^2$.](image)

![Figure 6. Mass transport characterized by $\tan\theta$ (the slope of the linear part of the diffraction efficiency) for different polarization states of the recording beams.](image)
Diffraction efficiency is directly correlated with the depth of the obtained relief and thus to efficiency of mass transport [7]. Recording was done until saturation was reached which indicates that the surface tension forces have overcome the forces of mass transport. There are three parts of the diffraction efficiency curve - nonlinear beginning, linear part and the saturation. To characterize the sensitivity of the material the slope of the linear part is calculated. The slope (tanα) for different polarization states is shown in table 1. The p-polarization is parallel to the grating vector and s-polarization is orthogonal to the grating vector, respectively.

### Table 1. Sensitivity of material for different polarization states of the two recording beams.

| Polarization state | Angle between polarization planes | tanα |
|--------------------|----------------------------------|------|
| s:s (0°/0°)        | 0°                               | 0    |
| +15°/-15°          | 30°                              | 0.12 |
| +30°/-30°          | 60°                              | 0.56 |
| +45°/-45°          | 90°                              | 0.74 |
| +60°/-60°          | 120°                             | 0.75 |
| +75°/-75°          | 150°                             | 0.93 |
| p:p (+90°/-90°)    | 180°                             | 0.31 |

Very strong dependence of holographic recording on polarization state of the recording beams was observed. The correlation is shown in figure 6, by placing the obtained points according to the angle between polarization planes of the two beams. It can be concluded from these experiments that the p-polarization component of light is required for the mass transport to occur. At the same time the best results could be obtained with the polarization states where the polarizations of both beams are almost orthogonal. This can be explained as follows. Two light beams with the same (in this case p:p) polarizations create a light intensity pattern, leaving some places on the surface of the sample not exposed to light treatment at the interference minima. These regions experience no photosoftening effect and therefore are more rigid and less likely to be affected by mass transport phenomenon. This could be improved by using different polarizations for both beams, when the resulting interference pattern exposes the whole area to light - this pattern has the periodical modulation of crucial p component and the periodical modulation of the s component which provides photosoftening without interfering with the main movement of mass.

Figure 7 shows the absorption spectrum of non-irradiated sample and spectra taken while irradiating the sample with polarized 532 nm laser light. Dichroism in the spectra of the K-RJ-8 thin film shows that there is distinctive anisotropy induced by polarised light. If the sample is not illuminated, the moieties are orientated randomly. Strong absorption of the stable trans isomer of the azo compound is observed at 450 nm. During the illumination with polarized 532 nm laser light, a decrease of the absorbance occurs due to photoisomerisation and photoorientation processes [8]. Firstly, a part of the moieties in trans form undergo transition to cis form by absorbing a photon (increase of the absorption of the cis state at 375 nm is observed). Secondly, through this photoisomerisation process the moieties may align relative to the electric field vector of light. That can be observed as a difference between the strength of the absorption in orthogonal directions while the sample is being illuminated - part of the moieties in trans form that absorb in the direction orthogonal to pump light polarization accordingly do not absorb in the parallel direction.
Figure 7. The absorption spectrum of a non illuminated sample and the spectra taken while the sample is being illuminated with linearly polarized 532 nm laser light (intensity I=0.07 W/cm$^2$) with polarization of the probe beam parallel or orthogonal to one of the pump beam.

Figure 8. The photoinduced birefringence in time. Birefringence was induced by linearly polarized 532 nm laser (intensity I=0.07 W/cm$^2$) and measured at the same 532 nm wavelength.

Dichroism in material indicates birefringence and vice versa. Figure 8 shows photoinduced birefringence in K-RJ-8. Birefringence reaches saturation in first seconds and remains constant during the rest of the illumination. After 10 minute time period the pump was switched off and after another time period of 10 minutes the birefringence has dropped significantly. Relaxation of birefringence can be observed contrary to surface relief gratings which are known to be stable [3].

Dichroism and birefringence measurements explains why the holographic recording done with s:s produces no diffracted beam but recording done with p:p or any other polarization state with contains the p component gives far better results. It can be connected to the obvious anisotropy induced by polarized laser light.

4. Conclusions
The studied thin films of compound K-RJ-8 possess very good light sensitivity properties for holographic recording with 491 nm wavelength - large diffraction efficiency (almost 25 %) and recording sensitivity of about 0.9 % cm$^2$/J were obtained. Very strong dependence of holographic recording on polarization state of the recording beams was observed due to the anisotropy of photoisomerisation and photosoftening processes. Distinctive dichroism and high values of photoinduced birefringence (almost 0.12) were observed in K-RJ-8.

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