The photoinduced birefringence and mass transport in azo compound K-D-2

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Abstract. Azobenzene containing compounds are among light polarization sensitive materials - the moieties may align relative to the electric field vector of light, leading to anisotropy and birefringence in the sample. Another phenomenon which can be observed in azo compounds under influence of light is macroscopic movement of the material. In this work photoinduced processes in low molecular weight organic glass - bis-azobenzene containing compound K-D-2 were experimentally studied. Birefringence was induced with linearly polarized laser light (473, 532 and 635 nm) and measured at 633 nm wavelength. Polarization holography with recording beam configuration $+45^0/-45^0$ was used to induce mass motion. Dependence of the surface relief depth on the recording laser wavelength in the visible spectrum (375 – 671 nm) was obtained. Formation of the SRG was observed with all used wavelengths and high birefringence values were obtained. Certain correlation between the absorption of the wavelength and photoinduced mass transport and birefringence is yet to be confirmed.

1. Introduction

Azobenzene containing compounds are among light polarization sensitive materials. Under influence of light azo compounds experience *trans-cis* isomerisation process [1]. As a result, the photochrome moieties may align relative to the electric field vector of light, leading to anisotropy in material and thus to birefringence [2]. Another phenomenon which can be observed in azo compounds is macroscopic movement of the material - if a lateral polarization modulation of light is present on the surface of the sample, a mass transport could occur [3]. One of the methods to induce mass motion is holographic recording where a periodical polarization pattern can be obtained at the submicron scale.

The photo-induced mass transport phenomenon allows formation of surface relief directly without chemical etching process. Materials which possess the ability of direct optically induced surface 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) [4].

Low-molecular-weight organic glasses containing azobenzene moieties are the subject of intense current studies [5,6]. In contrast to functionalized azo-polymers, molecular glasses have the advantage of possessing a well-defined molecular structure and they exhibit more uniform physical properties. Recently, SRG formation in amorphous films containing diphenylamine based azochromophores using holographic recording by 532 nm laser has been reported [6]. In this work the efficiency dependence on the wavelength of the laser to photoinduced mass transport and birefringence in low molecular weight organic glass - bis-azobenzene containing compound K-D-2 was experimentally studied.

2. Experimental

The 2-(bis(4-(-(2-bromo-4-nitrophenyl)diazenyl)phenyl)amino)ethanol (referred to as K-D-2) was synthesized in Riga Technical University. The molecular structure of the compound is shown in figure 1. The absorption spectrum of the studied sample is shown in figure 5. The thickness of the film was determined using Veeco Dectak 150 surface profilometer and it was 150 nm.

Surface relief gratings were recorded using a holographic set-up shown in figure 2. Holographic recording was performed with eleven different lasers (L) with wavelengths 375 nm, 405 nm, 448 nm, 473 nm, 491 nm, 532 nm, 561 nm, 594 nm, 635 nm, 650 nm and 671 nm. The set-up was adjusted for each of the laser wavelengths so that the grating period was the same in all cases - 1 μm. 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. Half-wave plates (λ/2) were used to set the polarization states of the recording beams. Two orthogonally at +45/-45 degrees linearly polarized beams were used for recording thus the optimal conditions for surface relief grating formation was provided [7]. One period of the polarization modulation created on the surface of the sample is shown in figure 2. The intensity of the beams was $I_1=I_2=0.18$ W/cm^2 and the duration of the recording was 1 hour thus the dose of illumination received was E=1.30 kJ/cm^2 in all cases. The recording course was monitored by registering the 0th and 1st order diffracted beams of the laser with photodiodes (PD). The diffraction efficiency of the obtained grating was calculated as in equation (1)

$$\eta = \frac{I_1}{I_1 + I_0} \tag{1}$$

where I_0 is the intensity of the 0th order diffracted beam and I_1 is of the 1st order.

The profile of the produced SRG was examined by AFM.

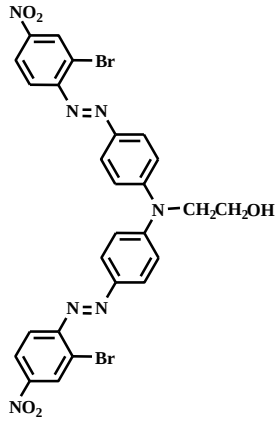

Figure 1. Molecular structure of low molecular weight organic glass K-D-2.

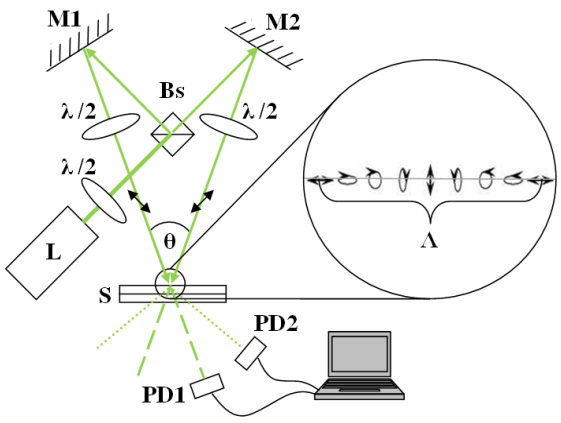

Figure 2. Experimental set-up for holographic recording. L – pump laser, λ/2 – half-wave plate, Bs – beam splitter, M – mirror, S – sample, PD - photodiode.

Photoinduced birefringence was measured using experimental set-up shown in figure 3. Experiments were carried out with three different lasers as pump lasers (L1) with wavelengths 473 nm, 532 nm and 635 nm to induce birefringence in the sample (S) and it was measured at 633 nm by a probe laser (L2). The polarization of the laser beams was set using half-wave plates (λ/2). The linearity of the polarization was improved by Glan-Taylor polarization cubes (P). Probe beam passes through the sample, 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 formula (2)

$$\Delta n = \frac{\lambda}{\pi d} \arcsin\left(\sqrt{\frac{I}{I_0}}\right) \quad (2)$$

where I is the probe beam intensity passing through crossed polarizer and analyzer, Io – probe beam intensity passing through parallel polarizers (with transmittance changes taken into account), λ - probe wavelength and d is the thickness of the layer of material.
The intensity of the pump beam was I =0.12 W/cm^2 and the duration of the measurement was 1 hour thus the dose of illumination received in these experiments was E=0.44 kJ/cm^2. The intensity of the probe beam was much smaller compared to that of the pump beam to exclude its interaction with the material during the experiment.

A quarter-wave plate was used to determine whether the birefringence is negative or positive by using a phase shift compensating method.

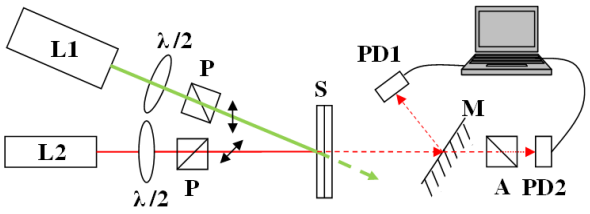

Figure 3. Experimental set-up for photoinduced birefringence measurements. L1 – pump laser, L2 - probe laser, λ/2 – half-wave plate, P - polarizer, A - analyzer, M – semitransparent mirror, S – sample, PD - photodiode.

3. Results and discussion

Figure 4 shows diffraction efficiency dependence on time for recording done with 653 nm, 405 nm and 375 nm lasers. The diffraction efficiency has not yet fully reached saturation after receiving the dose of 1.30 kJ/cm^2. Figure 5 shows the obtained values of modulation depth along with the absorption spectrum of the sample. It has to be mentioned that the modulation depth obtained with 491 nm, 532 nm, 561 nm and 594 nm lasers are likely not the maximal possible because the 300 nm exceed the thickness of the sample by 2 times, which simply means that there is not enough material to transport. AFM profiles of the obtained relief show that the substrate is already reached in these cases.

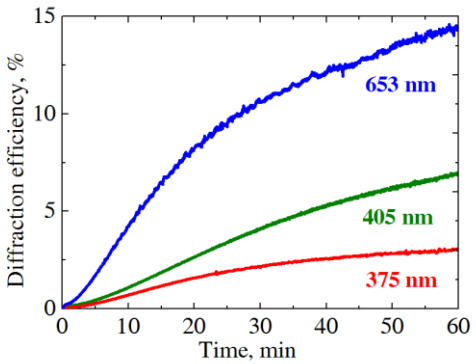

Figure 4. Diffraction efficiency in time for recording done with 653 nm, 405 nm and 375 nm lasers. The intensity of the beams was I_1=I_2=0.18 W/cm^2.

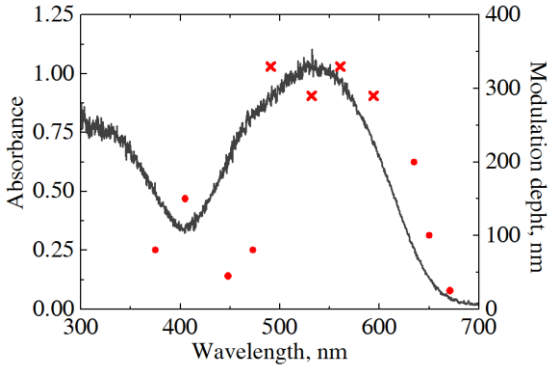

Figure 5. The absorption spectra of the sample (line) and modulation depth obtained with different recording laser wavelengths (points) at received dose of illumination E=1.30 kJ/cm^2.

Diffraction efficiency values correlate well with modulation depth, i.e., the gratings with deeper relief diffract better.

It can be seen in figure 5 that there is a correlation between the absorption of the wavelength and the efficiency of mass transport induced by this wavelength. Most likely it is related to the *trans-cis* isomerisation process of the azo compound and the corresponding absorption of each isomer [8]. It cannot be certainly concluded from these experiments whether particularly the stable *trans* configuration or the metastable *cis* configuration or the cycling process between the both of them is responsible for the mass transport.

Figure 8 shows the photoinduced birefringence measurements in time. It can be seen that there is a rapid change in the refractive index of the sample in the first seconds of the irradiation. That means the most of the moieties quickly orientate in presence of the light electric field thus making the material anisotropic. Birefringence values obtained in this sample are high - almost 0.2 and the birefringence was determined to be negative. It cannot be certainly concluded from these experiments whether there is a correlation between birefringence and surface modulation depth induced by one wavelength.

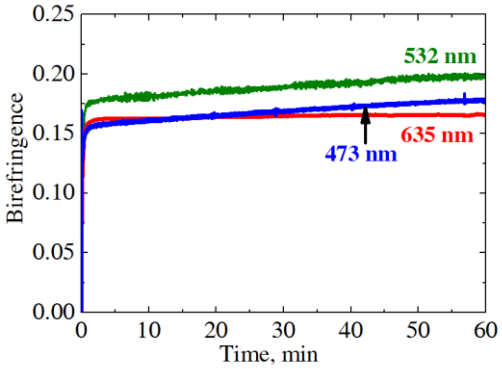

Figure 8. Birefringence values at 633 nm, induced by 473 nm, 532 nm and 635 nm lasers with beam intensity I =0.12 W/cm^2.

4. Conclusions

Formation of the SRG was observed with all used recording laser wavelengths with depth determined by AFM to be even greater than the thickness of the sample. Dependence of the surface relief depth on the recording laser wavelength in the visible spectrum was obtained but certain correlation between the absorption of the wavelength and the efficiency of the photoinduced mass transport is yet to be confirmed. High birefringence values were obtained in the sample with all laser wavelengths used to induce the anisotropy. Birefringence was concluded to be negative in all cases. Also certain correlation between the photoinduced mass transport and birefringence is yet to be confirmed.

Acknowledgements

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