Relaxation effect of stilbene azobenzene derivatives on their holographic properties

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Abstract. The material relaxation effect on holographic properties of stilbene azobenzene derivatives in the form of glassy films has been experimentally studied. Holographic grating recording with the period of 2 µm was made by a He-Ne laser at 633 nm in the self-diffraction mode. The readout was made simultaneously in order to follow the fast self-diffraction efficiency changes. The existence of the optimal material storage time (6-51 day) is established enabling the most efficient recording. Material relaxation amplitude and the holographic recording efficiency increased when the chromophore concentration was increased, especially above the threshold of about 70 mass %. It is also found that 633 nm recording due to the modulation of refraction and absorption indices is accompanied by the formation of surface relief grating. The conclusion is made that holographic recording in stilbene azobenzene derivatives at 633 nm is due to the chromophore reorientation by linearly polarized light possibly including trans-cis-trans transformations.

1. Introduction
Structure and chemical composition of organic materials can be widely changed so that materials with well defined properties can be produced. Azocompounds are among the most efficient materials for holographic recording [1, 2, 3] which we have studied, also in previous papers [4, 5]. Commonly, blue and green spectrum ranges are used for recording in these materials because absorption spectra of azocompounds have maxima there. In this case trans-cis-trans transformation [1] of material under laser radiation takes place. In the red spectrum range absorption is considerably lower yet the recording is possible [4, 5]. Mechanism of such recording is unclear yet this fact creates motivation for further researches. Discovery of efficient materials for information optical recording in the red part of spectrum will also allow using cheaper equipment and producing volume holographic optical elements with better quality. In this paper we have experimentally studied the material relaxation effect on the holographic properties of stilbene azobenzene derivatives when the recording and readout was made by the red light. It is found that material relaxation has strong and nonmonotonic influence on holographic recording efficiency. Besides, surface relief gratings have been recorded by a red light for the first time, to our knowledge.
2. Samples
Mainly two kinds of stilbene azobenzenes in the form of glassy films were studied: 3-(4-(bis(2-(trityloxy)ethyl)amino)phenyl)-2-(4-(4-nitrophenyl)diazenyl)phenyl)acrylonitrile (sample No1) and 3-(4-(bis(2-(trityloxy)ethyl)amino)phenyl)-2-(4-(2-bromo-4-nitrophenyl)diazenyl)phenyl)acrylonitrile (sample No2). Their chemical structures are shown in figure 1. These are the most effective compounds from whole range that were synthesized and studied in our experiments. Both samples contained NO$_2$ acceptor groups. The only difference between them is the bromine atom (electron donor) connected to phenyl ring in the case of the sample No2. This chemical structure was the most effective for holographic recording.

![Chemical structure of studied samples No1 (a) and No2 (b).](image)

Films were brought on the glass substrates by spin-coating. Chromophore was dissolved in dichloromethane. A drop of the solution was placed on the rotating glass plate where it was distributed rather evenly. After the evaporation of dichloromethane the film has been formed.

The absorption spectra of the samples were measured before the recording. The absorption spectrum for the sample No1 is shown in figure 2. The spectra of the other studied samples were similar differing by the positions of absorption maxima. The wavelength of the second absorption maximum (e.g., $\lambda_{\text{max}} = 516$ nm for the sample No1) is the closest to the wavelength of He-Ne laser light ($\lambda = 633$ nm). Accordingly, it was $\lambda_{\text{max}} = 512$ nm (reddish color) for the sample No2.
Figure 2. Absorption spectrum of the sample No1. All studied azocompounds had similar spectra where an absorption maximum is situated near 633 nm (wavelength of recording).

In order to find the effect of chromophore concentration we have also studied the samples nominally equivalent to the sample No2 with 100 mass % of chromophore concentration (samples No6, 6.1 and 6.2) and samples No7, 8, 9, 10 with the chromophore concentration lower than 100 mass % (see table 1). In the latter case the chromophore groups were dispersed in polivinylpirolidone matrix without the covalent bonding. Besides, sample No11 with CN, NO$_2$ acceptor groups ($\lambda_{\text{max}} = 533$ nm, violet colour), and sample No12 with Br, CH$_3$ donor groups and CN, NO$_2$ acceptor groups ($\lambda_{\text{max}} = 630$ nm, blue colour) were also studied to see the effect of $\lambda_{\text{max}}$.

3. Experiments

Scalar transmission holographic gratings (HG) with the period of $\Lambda = 2\mu$m were recorded by two symmetrically incident linearly TE-polarized He-Ne laser beams of equal power ($P_S = P_R$, figure 3). Laser of ЛГН-222 type (Ukraine) was used for the recording and readout at $\lambda = 632.8$ nm $\approx 633$ nm. Diffraction efficiency (DE) could not be measured directly due to the fast power changes of diffracted beams observed during the exposure. Therefore, self-diffraction efficiency (SDE) was measured in real time according to figure 3 by Gentec Solo power meter (Canada) connected to PC. SDE was determined according to the formula:

$$SDE = \frac{P_d(k=-2,l=-1)}{P_S},$$  \hspace{1cm} (1)

where $P_d(k=-2,l=-1)$ is the light power of the beam corresponding to the first diffraction order of the $P_S$ beam and to the second diffraction order of the $P_R$ beam (see figure 3), $P_S$ is the incident readout light power.
Figure 3. The scheme of recording process. $P_S$ and $P_R$ – incident laser beams, $\Theta_1 = \Theta_2$ – angles of incidence of the beams, $k$ – diffraction orders of the $P_R$ beam, $l$ – diffraction orders of the $P_S$ beam, $\Lambda = 2\mu m$ – period of holographic grating, $\Delta$ – grating shift due to the photoinduced processes and/or holographic setup instability.

Using thin hologram theory [6] one can find that

$$SDE = DE_{(-1)} + \frac{P_R}{P_S} DE_{(-2)} + 2 \left( \frac{P_R}{P_S} DE_{(-1)} DE_{(-2)} \right)^{1/2} \cos(\Phi_S - \Phi_R + \Phi_{S(-1)} - \Phi_{R(-2)}) , \quad (2)$$

where $P_R$ and $P_S$ are the incident light beam powers, $DE_{(-1)}$ and $DE_{(-2)}$ are the minus first order and the minus second order diffraction efficiencies, $\Phi_S$ and $\Phi_R$ are the phases of the $P_S$ and $P_R$ beams, $\Phi_{S(-1)}$ is the phase of the $P_S$ beam diffracted into the minus first order, $\Phi_{R(-2)}$ is the phase of the $P_R$ beam diffracted into the minus second order. For pure phase grating $\Phi_S - \Phi_R$, SDE can be either larger or smaller than $DE_{(-1)}$. We have estimated that in our experiments the SDE values were in the range from 0.5 $DE_{(-1)}$ to 1.6 $DE_{(-1)}$. These changes were due to the grating shift $\Delta$ with respect to the recording interference pattern $[\Phi_S - \Phi_R = (2\pi/\Lambda)\Delta]$ occurring due to the photoinduced processes and/or holographic setup instability.

The SDE exposure time dependences were measured. The maximal values of SDE ($SDE_{\text{max}}$) were found and the corresponding specific recording energy values, $W_{\text{max}} = I_{\text{max}} / SDE_{\text{max}}$, were calculated where $I = 4(P_R + P_S)/\pi d_0^2$ was the recording light intensity, $t_{\text{max}}$ was the exposure time corresponding to the $SDE_{\text{max}}$. $d_0 = 1.93 \text{ mm}$ was the $1/e^2$ laser beam diameter.

Apart from holographic measurements the surface relief of the sample No1 was studied with the scanning atomic force microscope (AFM) of SPM III VEECO type (USA). Absorption spectra were also measured after the recording with the “Ocean Optics” spectrometer HR400 with a 200 $\mu m$ fiber probe. To see the effect of annealing on the material relaxation two samples were annealed at 100°C during one hour in the ambient atmosphere before the recording (sample No2 and sample No12 with Br, CH$_3$ donor groups and CN, NO$_2$ acceptor groups; $\lambda_{\text{max}} = 630$ nm, blue color, the structure similar to shown in Fig.1). Some HG self-enhancement [7] measurements have been made too.
4. Results and discussion
Experimental results are shown in figures 4 - 8 and table 1. The surprising conclusion can be made from these data that fresh samples are not the best as it is usually expected [1, 8]. Rather for the most efficient recording (maximal $SDE_{\text{max}}$ and minimal $W_{\text{min}}$) optimal storage time of sample $t_{\text{opt}}$ exists. This optimal storage time is very sensitive to many factors because even for the same composition (samples No2, 6, 6.1, 6.2) it varies from 6 days to 51 day. The SDE measurements of annealed samples after 50 days did not reveal noticeable differences compared to the nonannealed ones. The annealing procedure was not optimized.

![Figure 4. SDE exposure time dependences for different ages of the sample No1. Recording process was more effective for older sample.](image-url)
**Figure 5.** SDE exposure time dependences for different ages of the sample No2. Recording process was more effective for older sample.

**Figure 6.** SDE exposure time dependences for two ages of the sample No6. Recording process was less effective for older sample.
As table 1 shows recording efficiency increases when the chromophore concentration is higher. There exists the concentration threshold at about 70 mass % after which steady increase of the recording efficiency takes place. Both the recording efficiency and the relaxation effect are the best for pure chromophores (100 mass %). Interestingly, the samples with $\lambda_{max}$ values closest to 633 nm (No1, $\lambda_{max}$=533 nm and No12, $\lambda_{max}$=630 nm) were much less efficient than samples No2, 6, 6.1, 6.2 ($\lambda_{max}$=512 nm). Thus we have measured $SDE_{max}=0.08\%$, $W_{max}=20860$ J/(cm$^2$%) for the sample No11, and $SDE_{max}=0.04\%$, $W_{max}=14301$ J/(cm$^2$%) for the sample No12. At the end of recording these samples were almost completely bleached.

Table 1. Holographic recording efficiency dependence on the chromophore concentration in polymer and sample age for 3-(4-(bis(2-(trityloxy)ethyl)amino)phenyl)-2-(4-(2-bromo-4-nitrophenyl)diazenyl)phenyl)acrylonitrile.

| Sample | 6 days from sample preparation | 7 days | 66 days from sample preparation |
|--------|--------------------------------|--------|--------------------------------|
| Concentration, % | 100 | 100 | 95 | 70 | 35 | 20 | 0.23 | 0.35 | 0.04 | 0.03 |
| $SDE_{max}$, % | 15.8 | 5.05 | 9.79 | 0.07 | 0.11 | 0.06 | 5175 | 4506 | 144 | 161 |
| $W_{max}$, J/cm$^2$% | 57 | 265 | 162 | 22651 | 13692 | 30068 | 0.51 | 0.74 | 0.89 | 0.90 | 0.98 | 1.01 |
| $I$, W/cm$^2$0.51 | 0.74 | 0.89 | 0.90 | 0.98 | 1.01 |

The HG recorded in the samples with the chemical structure as shown on figure 1 (No1, 2, 6, 6.1, 6.2, 7.1, 8, 9, 10) were quite stable during more than two months. Small effects of coherent and relaxational HG self-enhancement [7] have been observed in contrast to the previously studied azobenzene oligomers [4, 5]. AFM studies of the sample No1 (figures 7, 8) have revealed the surface relief grating (SRG) with the maximum thickness variation amplitude of $d_{max}=62$ nm. To our knowledge, this is the first time when SRG in azobenzene materials have been recorded in the red spectral range.

It is believed [9] that SRG can be recorded only due to the trans-cis-trans transformations enabling the mass transfer. The measurements of the absorption spectra in the irradiated and unirradiated areas of the samples No1, 2, 6, 7 have shown noticeable optical density increase of the irradiated area in the 600-1100 nm spectral range corresponding to cis-absorption thus giving evidence in the favor of trans-cis transformation [10]. Unfortunately, the measurements in wider spectral range were not technically possible. Therefore, the question about the trans-cis-trans transformation by 633 nm light should be studied further.
We have calculated the SRG first-order diffraction efficiency according to the formula for TE polarization [11]:

$$\eta = \frac{1}{3} \tau \frac{\pi(n-1)d_{\text{max}}}{\lambda \cos \theta_i}^2,$$

where $\tau$ is the average transmittance of HG, $n$ is the average refractive index, $\theta_i$ is the readout beam incidence angle inside the medium. In the case of the sample No1 $\tau = 0.178$, $n = 1.5$, $d_{\text{max}} = 62$ nm, $\lambda = 633$ nm, $\cos \theta_i \approx 1$ and $\eta = 0.14\%$. The experimental SDE value was 0.5%. It is considerably larger even if the difference between SDE and $\eta$ is taken into account. This means that photoinduced modulation of refraction and absorption indices takes place simultaneously with surface relief modulation.

HG recording in stilbene azobenzene derivatives is accompanied by characteristic aperiodic surface roughness changes as seen also from figures 7 and 8. Initially there are approximately 250 nm deep craters with a diameter of about 2.8 μm and with small particles inside them. There are no craters after the recording. Instead, oval $\sim 4 \times 2.5 \times 0.43$ μm$^3$ particles arise.
5. Conclusions
Holographic recording efficiency in stilbene azobenzene derivatives is a nonmonotonic function of the sample storage time. The optimal recording time exists after the sample preparation enabling the maximum efficiency. This optimal recording time is not uniquely determined by the chemical composition because even for the same composition it can be considerably different. Most probably, the nonmonotonic storage time effect on the recording efficiency is due to the peculiarities of the structural relaxation of stilbene azobenzene derivatives consisting of pure chromophores having large free volume.

Holographic recording efficiency in stilbene azobenzene derivatives strongly depends on the chemical composition and chromophore concentration. The best composition was that with Br donor and NO₂ acceptor groups (sample No2 and its equivalents). Steady efficiency increase takes place for the chromophore concentrations exceeding 70 mass %.

It is found for the first time that holographic recording in azobenzene materials in the red spectral region is accompanied by a periodic surface relief modulation. The maximum surface relief modulation amplitude was 62 nm. Characteristic aperiodic surface roughness changes take place as well.

In our opinion, the holographic recording in stilbene azobenzene derivatives at 633 nm is due to the chromophore reorientation by a linearly polarized light accompanied by the changes of refractive and absorption indices, and by the mass transfer. Some spectral evidence has been got in favor of trans-cis-trans transformation. However, the final conclusion remains to be drawn.

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