

Diffraction efficiency of polarization holographic gratings recorded in azopolymer thin films coated using different solvents

Blaga Blagoeva¹, Lian Nedelchev*^{1,2}, Georgi Mateev¹, Elena Stoykova¹, Dimana Nazarova¹

¹Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria

²University of Telecommunications and Post, Sofia, Bulgaria

*lian@iomt.bas.bg

ABSTRACT

We present a study of the diffraction efficiencies of polarization holographic gratings recorded in thin films of the azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]). Two series of layers have been prepared using two different solvents – distilled water and methanol. The gratings are inscribed by two plain waves with orthogonal circular polarizations (left and right circular) from a He-Cd gas laser (442 nm) at recording angle 20°, corresponding to grating period 1.3 μm. Higher diffraction efficiency is obtained for the thin film samples spin-coated from the methanol solution for thicknesses below 600 nm. Diffraction efficiency higher than 27% was achieved, as well as surface relief height more than 500 nm.

Keywords: Polarization holographic grating, Diffraction efficiency, Azopolymers, Thin films, Photoinduced birefringence

1. INTRODUCTION

Azopolymers are one of the most efficient materials able to register the polarization state of light. This is achieved through a series of *trans-cis-trans* isomerizations of the azobenzene moieties, leading to their reorientation perpendicularly to the direction of linearly polarized light¹. This effect, known also as Angular Hole Burning (AHB) results on a macroscopic level formation of significant photoinduced anisotropy – birefringence and dichroism. Based on this unique property of the azobenzene-containing materials, they have been used for numerous applications – most often for reversible optical data storage²⁻⁴, tunable surface relief gratings⁵⁻⁷ or diffractive optical elements with unique polarization properties⁸⁻¹⁰. The research on azopolymers during the last decades is also described in some milestone reviews¹¹⁻¹³.

Most of the above-mentioned applications are related with recoding of polarization holographic grating (PHG) in an azopolymer thin film. In some cases beams with orthogonal linear polarizations are used^{14,15}, but more often beams are set to orthogonal circular polarizations (left and right), as this leads to formation of gratings with higher diffraction efficiency¹⁶. As known, together with the polarization grating in the volume of the material, topographic grating is formed on the surface of the azopolymer film, usually denoted as surface relief grating (SRG)^{17,18}. The SRG has the same period as the volume grating and contributes to the increase of the diffraction efficiency.

During the last decades, an azopolymer commonly used for optical applications is the commercially available poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt], often abbreviated as PAZO. An important advantage of this polymer is that it is readily soluble in water, as well as in methanol. Thus, usage of toxic organic solvents can be avoided. In some studies pure water is preferred as solvent^{19,20}, as in other PAZO is dissolved in methanol^{21,22}. In our earlier studies^{23,24}, we have compared thin films of PAZO coated from water and from methanol solution. Higher surface smoothness was reported for the PAZO/methanol layers, as well as better optical quality, even when drying occurs at increased temperature²⁴.

In this study, we present an investigation of the properties of polarization holographic gratings and the concurrently formed surface relief gratings in series of azopolymer thin films with different thickness. One of the series is deposited from solutions of PAZO in methanol, while the other is coated from water solutions of PAZO. Kinetics of the diffraction efficiency as well as height of the surface relief topography are presented and compared.

2. EXPERIMENTAL

2.1 Azopolymer thin films deposition and thickness measurement

In our experiments we use the amorphous azopolymer poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], or PAZO. The polymer is supplied by Sigma Aldrich and is used without further purification. Its chemical structure and spectrum of absorbance are shown in Fig. 1.

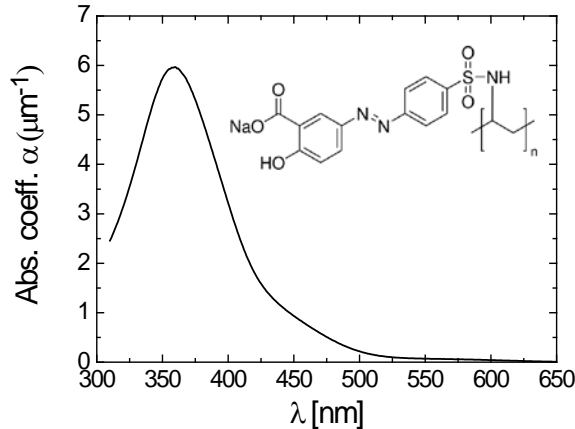


Figure 1. Spectrum of absorption and chemical structure of the azopolymer PAZO (adapted from Ref. 25).

Two series of thin film samples were prepared for the holographic experiments using the spin-coating technique. For the first series, PAZO was dissolved in pure distilled water and for the second – in methanol. In order to obtain films with different thickness for both series, we have varied the concentration of the solutions C , as well as the rotation speed R during the spin-coating process. The specific values of C and R for each layer are given in Table 1 in the “Results and discussion” section. All samples are prepared using 200 μL of the solution, the spin-coating time is 30 s and the substrates are preliminary cleaned BK7 glass slides. After drying overnight to ensure that the solvent is completely evaporated, the thickness of the samples is determined by an optical thin films analyzer (Filmetrics F20).

2.2 Recording of the polarization holographic gratings

The optical scheme used to inscribe polarization holographic gratings on the thin film samples is presented in Fig. 2. A He-Cd gas laser (Kimmon Koha) emitting at 442 nm was used as recording laser.

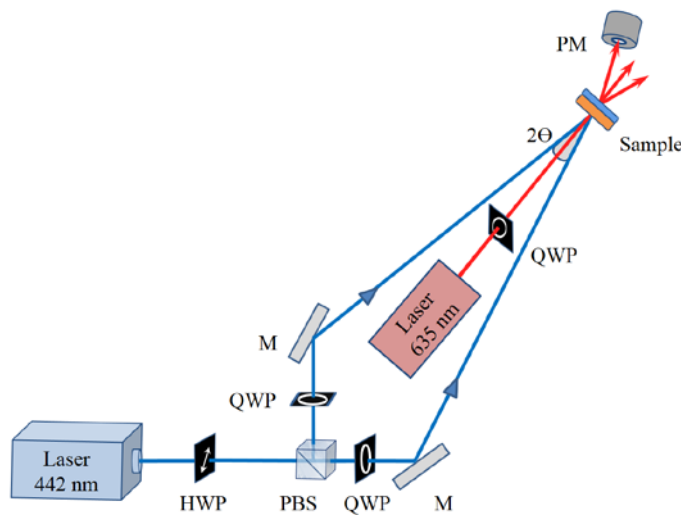


Figure 2. Setup for polarization holographic recording: HWP – half-wave plate, PBS – polarizing beam splitter, QWP – quarter-wave plate, M – mirror, PM – power meter.

This wavelength was selected, as according to our recent study²⁶, highest birefringence ($\Delta n \approx 0.08$) is obtained in PAZO at 442 nm. Furthermore, this laser provides sufficient coherence length required for polarization holography. The beam is split in two beams with equal intensities by a half-wave plate and polarization beam splitter and their polarizations are set to left and right circular using quarter-wave plates. The two beams recombine on the sample at recording angle $2\theta = 20^\circ$, corresponding to grating period $\Lambda \approx 1.3 \mu\text{m}$. Their total intensity is about 1000 mW/cm^2 . A DPSS laser at 635 nm (B&W Tek Inc.) is used as a probe laser, as its wavelength is outside the absorption band of the azopolymer PAZO, as seen in Fig. 1. Its polarization is set to right circular by an appropriate quarter-wave plate. In order to obtain the kinetics of the diffraction efficiency (DE), the diffracted power in the +1 order is measured in real time during the inscription of the grating by a computer operated power meter (PM100D, Thorlabs). The value of DE is given by the ratio of the diffracted power and the power of the probe laser beam incident on the grating.

2.3 AFM analysis of the surface relief gratings

To analyze the surface relief gratings formed during the polarization holographic recording, surface scans of the recorded areas were made using atomic force microscope (MFP 3D Scanning Probe Microscope, Asylum Research). The height h of the surface relief is defined as the vertical distance between the highest and the lowest point of the topographic grating.

3. RESULTS AND DISCUSSION

Two series of samples were prepared according to the procedure described in Section 2.1. For the first series, solutions of PAZO in methanol were prepared with concentrations in the range (25-100) mg/mL. The rotation speed during spin coating was varied from 500 to 1500 rpm and the resulting thicknesses of the samples are in the range (280-1550) nm. The second series of azopolymer thin films was prepared from water solutions of PAZO with $C = (75\text{-}125) \text{ mg/mL}$ and constant rotation speed 1500 rpm. The thicknesses in this series vary from 330 nm to 660 nm.

Using the optical setup described in Section 2.2, we have recorded polarization holographic gratings in the samples from both series. The diffraction efficiency was monitored in real time in order to establish the moment when saturation is reached. The kinetic curves of the DE are shown in Fig. 3 for the samples with highest diffraction efficiency from both series – PAZO/methanol and PAZO/water.

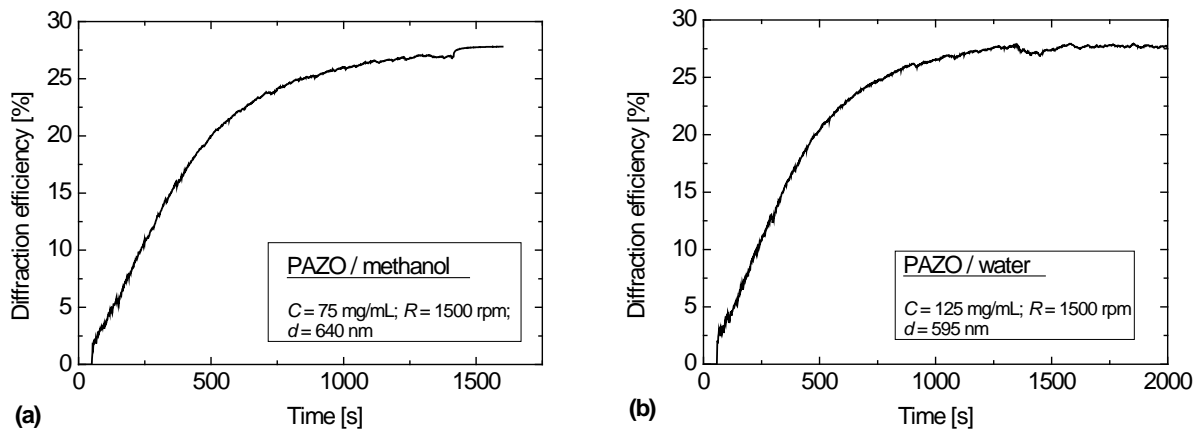


Figure 3. Diffraction efficiency kinetics in the +1 diffraction order during the holographic recording for the thin film samples: (a) PAZO/methanol sample, $d = 640 \text{ nm}$; (b) PAZO/water sample, $d = 660 \text{ nm}$.

As seen in Fig. 3, the kinetic behavior of the DE in the two types of samples is similar. We can define a response time as the recording time needed to reach 80% of the saturated DE. In this case, the response time for the PAZO/methanol sample in Fig. 3(a) is 560 s, and for the PAZO/water sample in Fig. 3(b) it is 520 s. This response time is much higher than the birefringence response time at this wavelength and laser intensity²⁶, which is 15 s. This implies that the volume polarization grating is formed in the initial stage of recording and the rest of the recording time is required for the formation of the surface relief grating.

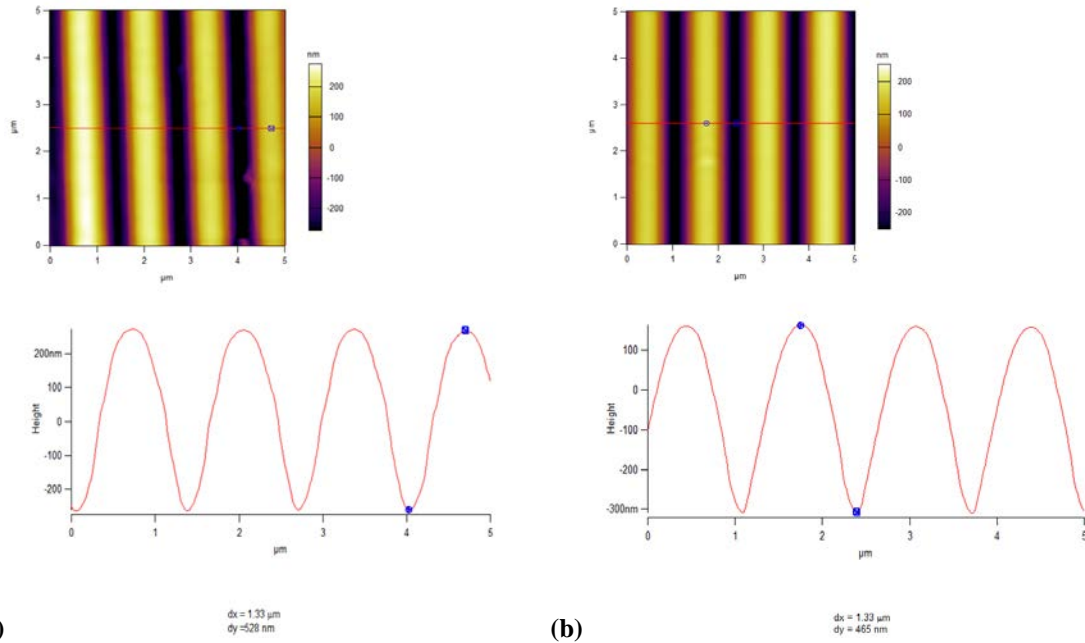


Figure 4. Atomic force microscope (AFM) images of the surface relief gratings formed in the thin film samples: (a) PAZO/methanol sample ($d = 625$ nm), $h = 528$ nm; (b) PAZO/water sample ($d = 595$ nm), $h = 465$ nm.

The experimental data for all samples prepared and recorded within this experiment are summarized in Table 1 below. The dependence of the maximal (saturated) diffraction efficiency on the thickness of the sample is graphically presented in Fig. 5 for both PAZO/methanol and PAZO/water thin film series. A spline curve is plotted through the experimental data points to better illustrate the trends.

Table 1. Summary of the prepared azopolymer thin films and parameters of the gratings, inscribed in them.

| N ^o | Concentration C [mg/mL] | Rotation speed R [rpm] | Film thickness d [nm] | Diffraction efficiency DE [%] | SRG height h [nm] |
|-----------------|------------------------------|-----------------------------|----------------------------|----------------------------------|------------------------|
| PAZO / methanol | | | | | |
| 1 | 25 | 500 | 280 | 7.0 | 175 |
| 2 | 50 | 700 | 350 | 13.1 | - |
| 3 | 50 | 600 | 450 | 25.7 | 169 |
| 4 | 50 | 500 | 625 | 25.5 | 528 |
| 5 | 75 | 1500 | 640 | 27.8 | 321 |
| 6 | 100 | 1400 | 1550 | 27.8 | - |
| PAZO / water | | | | | |
| 7 | 75 | 1500 | 330 | 9.0 | - |
| 8 | 100 | 1500 | 450 | 18.3 | - |
| 9 | 125 | 1500 | 595 | 27.7 | 465 |
| 10 | 125 | 1500 | 660 | 25.9 | 139 |

As seen, for lower film thicknesses the DE value is higher for the PAZO/methanol series, however a convergence is observed for thickness above 600 nm. It should also be noted, that the DE of the sample with highest thickness from the PAZO/methanol series ($d = 1550$ nm) is the same as the DE of the thinner layer ($d = 640$ nm). This indicates that for the given setup this is the highest achievable diffraction efficiency.

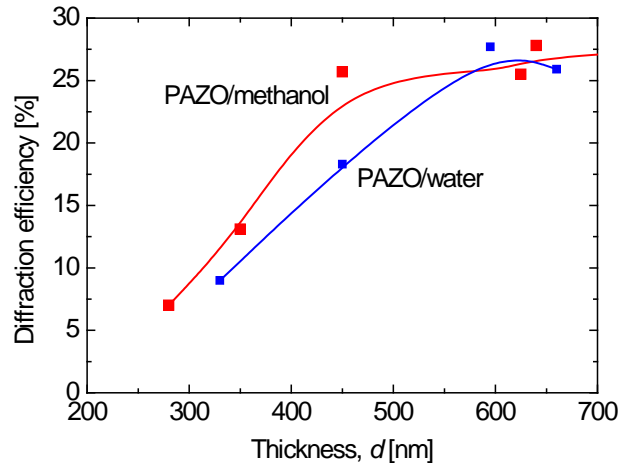


Figure 5. Dependence of the diffraction efficiency on the thickness of the azopolymer thin films for the series – PAZO/methanol and PAZO/water.

4. CONCLUSIONS

Two series of thin film samples were prepared from the azopolymer PAZO – one using methanol as a solvent, and second using pure water as solvent. Polarization holographic gratings were recorded in these samples with beams with orthogonal circular polarizations (RCP and LCP) at angle $2\theta = 20^\circ$ and 442 nm wavelength of the recording laser. Diffraction efficiency of 27.8% was obtained. Our experiments indicate that for thickness of the sample below 600 nm, the diffraction efficiencies of the PAZO/methanol series is higher compared to the samples from the PAZO/water series. Surface relief gratings with significant height have been obtained in both series. More specifically, $h = 528$ nm has been reached, comparable with the sample thickness ($d = 625$ nm). In addition, higher DE values have been obtained compared to our previous work²⁷, where under similar conditions ($2\theta = 20^\circ$, $\lambda_{\text{rec}} = 442$ nm, $d = 850$ nm), the maximal value of DE was 9.8%.

5. ACKNOWLEDGEMENT

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