Influence of thickness and polarization on diffraction efficiency of direct patterned diffraction gratings in carbazole-based azopolymer films

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In this paper we report on direct holographic recording of surface relief gratings in carbazole-based azopolymers. Azo dye Disperse Orange 3 was chemically bonded to oligomer poly-N-(epoxypropyl carbazole) making surface deformation efficient in the presence of optical field gradient. Optimal of the film thickness were determined. Holographic recording at different polarization configurations showed that the P:P polarization of recording beams provides the maximum of diffraction efficiency about 33%. Investigation of the obtained gratings revealed that this value of diffraction efficiency is caused by surface relief modulation (up to 440 nm) during holographic recording. Measured surface profile depth may be the evidence that the main contribution in the value of diffraction efficiency of recorded holographic grating brings the surface relief grating.

Index terms: optical recording materials, azopolymer, photo-isomerization, holographic recording, surface relief grating, diffraction efficiency.

I. INTRODUCTION

Since the first observation of surface relief grating (SRG) formation in azobenzene containing photosensitive polymer films in 1995 [1, 2], a wide variety of novel and highly efficient azobenzene containing photosensitive polymers(APP) have been synthesized focusing on specific applications in the optical data storage, design of diffractive optical elements, photo-patterning of micro- and nanostructures and many more. In addition, it is well known that photoinduced patterns of surface deformations in APP films are determined by the state of the incident light polarization [3].

The driving mechanism of the SRG formation is the cyclic photo-isomerization of the azobenzene molecules that undergo reversible transition from trans- to cis-conformation [4]. The photoinduced patterns appear due to light-induced mass movement of the polymer chains, which in turn is triggered by the photoisomerization of the azo chromophores [5]. Mass transport phenomenon allows creating a surface relief directly by light, without the post processing by chemical wet etching.

A surface relief, which is due to a photoinduced mass movement of the azopolymer, is produced by an interference pattern of light. The polymer mass moves from high- to low-intensity regions in the direction of light polarization, and the trans-cis photo selective isomerization plays an important role in the deformation process. Azo dyes are optical materials that allow us to manipulate their optical characteristics through photoisomerization and following chemical and physical processes initiated by absorption of polarized light. It is possible to form variable patterns of optical constant by irradiating interfering light beams that lead to birefringence, density modulation and surface relief grating. Their properties depend on characteristics of the illumination (intensity, wavelength, polarization, periodicity of the interference pattern) and the parameters of polymers such as molecular structure and weight, matrix type and modes of incorporation (guest–host, side-chained and so on), the substituent of the azobenzene ring and their concentration within the film thickness.

Because of this multi-variability, many aspects of the SRG formation phenomenon are not yet well understood, although several authors proposed theoretical models to describe photoisomerization-induced mass movement in azopolymers. For example, Kumar et al. attributed photomigration to dipoles interacting with the gradient of an optical electric field [6]. Barett et al. [7] and Bellini et al. [8] introduced a model based on light-induced pressure. Toshchevikov et al. [9] proposed a microscopic model that accounts for the internal structure of polymer chains. However, there are no established theories for the unified description of the phenomenon of photomigration.

SRG formation can be controlled during the recording by measuring the kinetics of diffraction efficiency (DE). The term “phase grating” denotes the case of modulation the refraction index and/or the surface profile. The analysis of these phenomena indicates that photoinduced organization of azobenzene molecules plays an important role in the formation of phase topography. [10]

The main purpose of this work consists in the study of film thickness dependence on DE of new photosensitive carbazole-based azopolymers. First results on direct SRG formation on these azopolymer films were reported in [11]. As soon as this technique was reported, a procedure for post-modification of polymer chains of epoxypropyl carbazole-containing oligomer was suggested. In fact, the end- group of oligomer can be transformed into amine substituted azopolymers. New photosensitive azopolymer based on carbazole-containing oligomer and purchased azo dye Disperse Orange 3 (poly(PEPC-co-DO) was synthesized. In this work optical transmission, photo induced and holographic recording properties of the films deposited on glass substrates were studied. Holographic grating formation in different interference patterns (amplitude and phase) were investigated by in-situ DE

measurement. Using this method, we compared photosensitive properties of the azopolymer in dependence of film thickness at different polarization states of recording beams.

II. MATERIALS AND METHODS

All used solvents and reagents were of reagent quality and used without additional purification. 4-[(4'-Nitrophenyl)azo] aniline, Disperse Orange 3 (DO 3) with dye 90% purchased from Sigma-Aldrich. Analytical TLC plates were Silufol® UV-254 (Silpearl on aluminum foil). UV spectra were recorded on a Spectrophotometer Specord M40 UV/Vis. DO 3 is a nonlinear optical azo dye which is well known for its trans ↔ cis photoisomerization and for its ability to undergo efficient orientation and trigger important polymer movement when it is excited by polarized light [12]. The orientation effect is due to the highly anisometric nature of its polarizability tensor [13]. Carbazole-containing polymers were employed as effective recording media for holographic recording [14].

In our study using modified procedure [11] azobenzene polymer has been obtained by reaction of 340 mg poly-*n*-epoxypropyl carbazole (PEPC) [14] with 34 mg of DO in boiling toluene (2 ml) during 3 hours. The resultant solution of carbazole-based 4-[(4'-nitrophenyl)azo]aniline-labeled azopolymer called as poly(PEPC-co-DO) was filtered, determined by UV-Vis absorption and used for thin film deposition. The reaction scheme is shown in Fig. 1.

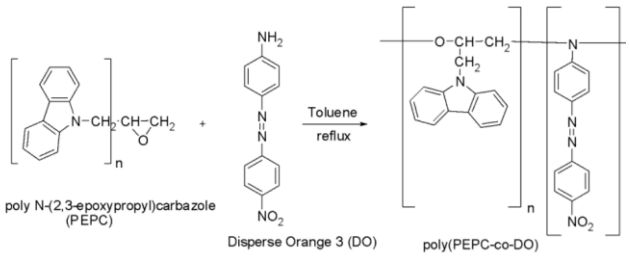

Fig. 1 The reaction scheme of poly(PEPC-co-DO) and the picture of obtained thin film on glass substrate.

The synthesis of poly(PEPC-co-DO) with 30 weight% of azo dye were carried out as the same method as for described above. This concentration was selected as optimal and will be shown in other work[12].

In order to obtain films with different thickness resultant solution was diluted with different amounts of toluene. Thin azopolymer films were obtained in equal conditions by spin-coating of initial and diluted solution under 500 rpm for 30 sec and dried at room temperature for 8 hours. The modified interferometric microscope MII-4 measured film thickness. Microscope magnification is 490x. The miscroscope was equipped with a Logitech HD Webcam C310 1280x720px. A specially developed software OpticMeter was used to determine film thickness[15]. A number of films with thicknesses 250, 400, 800, 1600 and 2160 nm were obtained.

The experimental arrangement for polarization holographic recording of the SRG is schematically presented in Fig. 2.

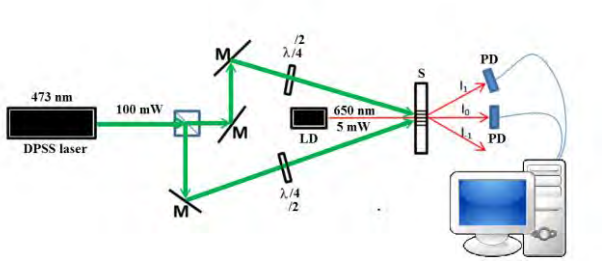

Fig. 2 Experimental set-up for polarized holographic recording and in-situ readout of diffraction efficiency.

The exposing radiation is an interference pattern produced by the overlapping beams of coherent light on photopolymer. Two polarized beams at wavelength λ of 473 nm (actinic light) with equal intensities of 1 W/cm^2 were used to record the SRG. The grating period Λ corresponding to the interfringe spacing is given by (1), where λ is the wavelength of laser and θ is the incidence angle between the writing beams onto the sample. The recording interbeam angle θ was set to 21.8°, resulting in a grating period of 1.25 μm, according to Eq. (1).

$$\Lambda = \frac{\lambda}{2\sin\frac{\theta}{2}} \quad (1)$$

DE of grating η in the transmission mode was controlled in real time by measuring laser diode intensity at λ= 650 nm (no actinic light and low power of 5 mW) in the first and 0 diffractive orders. The polarization states of the two writing beams were individually controlled by half and/or quarter wave plates.

Diffraction gratings in poly(PEPC-co-DO) films were recorded in five different polarization configurations:

1) S:S, when two beams were linearly polarized with electric field vectors perpendicular to the incidence plane;

2) P:P, when two beams were linearly polarized with electric field vectors parallel to the incidence plane;

3) S:P, when two beams were orthogonally polarized with respect to each other, one is S and the other is P to the incidence plane;

4) ±45°, when two beams were orthogonally linearly polarized at ±45° with respect to the incidence plane;

5) RCP:LCP, when two beams were orthogonally circular polarized with respect to each other, one is right-circular polarization (RCP) and the other is left-circular polarization (LCP).

The interference pattern of two coherent waves with parallel linear polarizations has a periodically modulated intensity, but a polarization state is constant. In case of orthogonal linear polarizations S:P the interference pattern has a constant intensity, but a polarization state that is periodically modulated. In case of orthogonal linear ±45° and circular RCP:LCP polarizations the interference pattern has a small modulated intensity (4% for 1.25 ⌈m period grating) and periodically modulated polarization states.

Therefore, the interference pattern with S:S polarization configuration with 100% of interference contrast ensures best intensity modulation contrast used for standard intensity holography. Contrary to it, S:P polarization configuration has no intensity modulation but interference resulted polarization varies periodically between linear, elliptical and circular forms. For the case of ±45° and RCP:LCP polarization configuration, the resultant

polarization becomes a linear polarization where the polarization direction changes periodically, and there is 4% of interference pattern contrast .

In this work, the grating formation is studied using the DE measurements. The DE measurement probes the photo-induced changes, namely surface relief modulation, amplitude and phase grating formation in the film during recording. Using the wavelengths of reading beam from the non actinic transmission region of APP we can study the phase grating formation and non consider the amplitude grating formation. Therefore, this method is feasible to observe local changes in the film polymer topography as a function of polarization state or the intensity distribution of light electrical field.

In our work during the holographic recording, the linear polarized laser (P-polarization) at wavelength of 650 nm was directed to the sample at normal incidence to serve as the probe beam. The zero-order and first-order diffraction intensities of sample were monitored in situ to diagnose the kinetics of grating formation. First-order of DE η is defined as:

$$\eta = \frac{I_1}{2I_1 + I_0} * 100\% \quad (3)$$

where I_1 is the light intensity diffracted in first diffraction order, I_0 is light intensity in zero-order diffraction. I_1 and I_0 intensities were measured with a two silicon photodiodes equipped with amplifiers. Since this wavelength is outside the absorption region (see Fig. 3), only a phase holographic recording was considered by DE measurement. The higher diffraction intensity implies the larger phase modulation of recorded grating.

After the completion of recording the grating, the Atomic Force Microscopy (AFM) was employed to measure the surface relief of recorded structure.

III. Optical Properties and Photoinduced Change of Azopolimer Films

An Specord UV-VIS spectrophotometer was used to make the optical measurements of the absorption spectra before and after the optically induced changes in the azopolymer film. In Fig. 3 the absorbtion spectra of obtained poly(PEPC-co-DO) azopolymer films with different film thickness (from 250 to 2160 nm) and the DO content 30 wt% are presented. Also are shown dependence of absorption

The maximum of the absorption region for this azopolymer is at wavelength of ~450 nm, which is characteristic for DO azo dye classified as pseudo-stilbene [16]. It confirms azo coupling reaction of PEPC with DO.

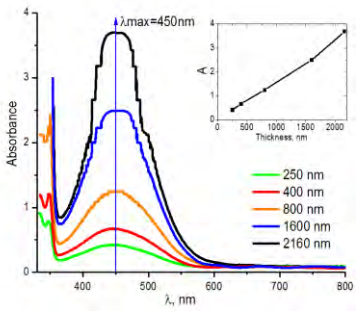

Fig.3 UV-Vis absorption spectra of poly(PEPC-co-DO) films with different film thickness. DO content is 30 wt% and dependence of thickness on the value of absorption.

The optically induced changes in the azopolymer film absorption were studied by comparison of non-exposed and exposed films. An initial transmittance measurement was made, and then the film was exposed to an expanded 473 nm laser beam (diameter 3.4 mm, intensity 740 mW/cm^2) from a 100 mW DPSS single mode laser with linear polarization. This was immediately followed by a transmittance measurement. Trans-cis isomerization can occur by optical excitation into the trans-isomer absorption band. This trans-cis isomerization process is well-known in a number of photochromic dyes including the azobenzene dyes [4].

IV. Results and Discussions

The dependence of DE on recording exposure for all of the studied polarization configurations is shown in Fig. 4. Holographic recording was performed on poly(PEPC-co-DO) film with thickness 1600 nm and concentration of azo dye 30 wt%. As it can be seen in the figure 6, the DE strongly depends on the polarization configuration. The best performance is reached at P:P polarization configuration. For all polarization configurations except S:P and S:S polarization, DE versus time has increased and eventually reached a relatively steady state during the exposure.

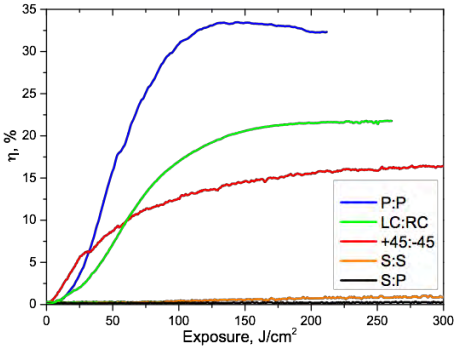

Fig.4 The dependence of diffraction efficiency in transmission mode on recording time and exposure for the all studied polarization configurations using poly(PEPC-co-DO) film with thickness 1600 nm and concentration of azodye 30 wt%.

Since the best polarization configuration was determined, the next step was holographic characterization to find the optimal film thickness. To do it holographic recording using P:P polarization configuration was carried out in poly(PEPC-co-DO) films with different film thickness simultaneously measuring the DE(Fig.5).

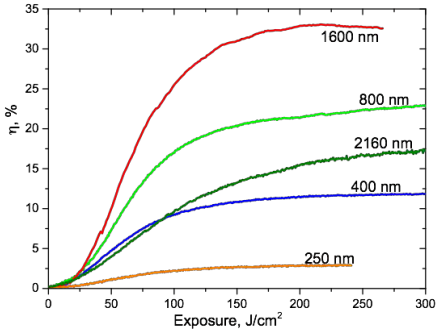

Fig.5 The dependence of diffraction efficiency in transmission mode on recording time and exposure using P:P polarization configuration during holographic recording in poly(PEPC-co-DO) film with film thickness from 250 to 1600 nm.

As it can be seen in Fig. 5, the optimal thickness of the film exists. It gives the highest value of DE η=33%, and is close to the theoretical maximum DE limit for thin sinusoidal phase gratings equal to 33.8% [17].

The surface of the obtained grating was observed with AFM. The AFM analysis revealed the creation of a surface relief modulation. The depth of such modulation (peak-to-peak amplitude) *h* of the obtained grating was measured by AFM to be about 440 nm.

The films with thickness over 1600 nm show more scattering of light (see fig.3), which may be result of presence of small bubbles after drying. The origin of the bubbles can be vapor of solvent which presents in film volume.

V. CONCLUSION

New synthesized photosensitive azopolymer (poly(PEPC-co-DO) is able to be medium for one step polarization holographic recording. Holographic gratings with high DE more than 30% can be recorded in poly(PEPC-co-DO) azopolymer films by polarization holography. Optimal film thickness 1600 nm were determined. Irradiation of this azopolymer films with a single beam at 473 nm into the trans-isomer band that is centered ~450 nm leads to a structural transition to the cis-isomer and a concomitant reduction in the trans-isomer band absorption coefficient. Holographic recording at different polarization configurations showed that the P:P polarization of recording beams provides the maximum of DE about 33%.

Thus, we have shown that synthesized poly(PEPC-co-DO) azopolymer can be applied for using as a recording media for direct SRG formation with high DE.

Acknowledgments

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