

CARBAZOLE-BASED AZOPOLYMERS AS MEDIA FOR POLARIZATION HOLOGRAPHIC RECORDING

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Abstract. In this paper we report on direct holographic recording of surface relief gratings in carbazolebased 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 concentration of azo dye and the film thickness were determined. Evolution of the transmittance spectrum upon irradiation with 473 nm laser light clearly demonstrated the photo-induced isomerization of azopolymer sample. 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. The good coincidence of experimental and theoretical values of diffraction efficiency in dependence on 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.

Keywords: Optical recording materials, azopolymer, photo-isomerization, holographic recording, surface relief grating, diffraction efficiency.

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1. Introduction

Since the first observation of surface relief grating (SRG) formation in azobenzene containing photosensitive polymer films in 1995 (Rochon *et al.*, 1995; Kim *et al.*, 1995), 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 and the light intensity distribution (Bian *et al.*, 1999).

The driving mechanism of the SRG formation is the cyclic photo-isomerization of the azobenzene molecules that undergo reversible transition from trans- to cisconformation (Cembran *et al.*, 2004). 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 (Sekkat, 2016). 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 (Yang *et al.*, 2006). Barett et al. (1998) and Bellini et al. (2006) introduced a model based on light-induced pressure. Toshchevikov et al. (2009) 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. The diffraction efficiency measurement probes photo-induced amplitude and phase gratings in the film during holographic irradiation. 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 APP molecules plays an important role in the formation of phase topography.

The main purpose of this work consists in the study of new photosensitive azopolymers for one step relief formation of gratings by using polarization holography. First results on direct SRG formation on these azopolymer films were reported in Meshalkin et al. (2016). 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 diffraction efficiency measurement. Using this method, we compared photosensitive properties of the azopolymer in dependence of azo dye concentration and film thickness at different polarization states of recording beams.

The current work is expected to contribute to understanding the one-step patterning of surface reliefs by measuring the optically photoinduced properties of APP.

2. 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). IR spectra were recorded on a Spectrum 100 FT-IR spectrophotometer (Perkin - Elmer) using the universal ATR sampling accessory. UV spectra were recorded on a Spectrophotometer PerkinElmer LAMBDA 25 UV/Vis. DO 3 is a nonlinear optical azo dye which is well known for its trans \leftrightarrow cis photoisomerization and for its ability to undergo efficient orientation and trigger important polymer movement when it is excited by polarized light (Bockmann & Doltsinis, 2016). The orientation effect is due to the highly anisometric nature of its polarizability tensor (Sekkat & Dumont, 1993). Carbazole-containing polymers were employed as effective recording media for holographic and e-beam recording (Andries *et al.*, 2011).

In our study using modified procedure (Meshalkin *et al.* 2016) azobenzene polymer has been obtained by reaction of 340 mg poly-n-epoxypropyl carbazole (PEPC) (Andries *et al.*, 2011) 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.



Figure 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 20 - 60 weight% of azo dye were carried out as the same method as for described above. The reaction scheme is shown in Fig. 1.

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 a day. The photo of spin-coated poly (PEPC-co-DO) film is shown in Fig. 1.

The thickness of dried films was measured by modified digital interference microscope MII-4 (Meshalkin *et al.*, 2012). The cut of APP film was made by sharp knife down to the glass substrate, inside which the depth between the APP surface and the glass substrate corresponded to the film's thickness. 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. The exposing radiation is an interference pattern produced by the overlapping beams of coherent light on photopolymer. Two polarized beams at wavelength λ of 473nm (actinic light) with equal intensities of 1 W/cm² were used to record the SRG. The grating period Λ corresponding to the interfringe spacing is given by

$$\Lambda = \frac{\lambda}{2\sin\left(\frac{\theta}{2}\right)},\tag{1}$$

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).



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

Diffraction efficiency of grating η in the transmission mode was controlled in real time by measuring laser diode intensity at $\lambda = 650$ 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. The holographic gratings were written using the polarizations of recording laser beams will be given below and leading to intensity and polarization modulation in the interference pattern. In order to evaluate the intensity modulation of the two-beam interference pattern for different polarization configurations, we used parameter called interference contrast K given by expression

 $K = \left| \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \right| * 100\% \text{, where } I_{\text{max}} \text{ and } I_{\text{min}} \text{ are the maximum and minimum of the light}$

intensity in the interference pattern. The interference contrast *K* was calculated for grating period Λ =1.25 µm corresponding to angle between incident beams θ =21.8° at λ =473 nm.

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) $\pm 45^{\circ}$, when two beams were orthogonally linearly polarized at $\pm 45^{\circ}$ 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 $\pm 45^{\circ}$ and circular RCP:LCP polarizations the interference pattern has a small modulated intensity (4% for 1.25 µm period grating) and periodically modulated polarization states. The theoretical calculation of polarization distribution and interference contrast of the two-beam interference pattern with Λ =1.25 µm for all studied polarization configurations are presented in Table 1.

Therefore, the interference pattern with S:S polarization configuration with 100% of interference contrast ensures best intensity modulation contrast used for standard optical lithography. 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 $\pm 45^{\circ}$ and RCP:LCP polarization configuration where the polarization direction changes periodically, and there is 4% of interference pattern contrast.

In this work, the grating formation is studied using the diffraction efficiency (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.

Polarizatio n of writing beams	Polariza- tion configure -tion	0	Λ/8	Λ/4	3Λ/8	Λ/2	5Λ/8	3Λ/4	7Λ/8	Λ	K, %
s s	S:S	•	1	1	1	1	1	1	t	•	10 0
	P:P	•	t	\$	1	ţ	+	‡	+	•	93
	S:P	1	0	\bigcirc	0	>	0	\bigcirc	0		0
+45 -45	+45°:- 45°	\leftrightarrow	0	\bigcirc	0	1	0	\bigcirc	∂	\$	4
RCP LCP	RCP:LC P	\leftrightarrow			1	1	~	5	1	‡	4

Table 1. Resulting polarization modulation in one fringe period Λ and interference contrast (corresponds to intensity modulation) of the two recording beams for each polarization configuration

In our work during the holographic recording, the linear polarized laser (Ppolarization) 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 $\eta = \frac{I_1}{2I_1+I_0} * 100\%$, where I_I is the light intensity diffracted in first diffraction order, I_0 is light intensity in zero-order diffraction. I_I 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.

3. Optical properties and photoinduced change of azopolymer films

An Specord UV-VIS spectrophotometer was used to make the optical measurements of the transmittance spectra before and after the optically induced changes in the azopolymer film. The transmission spectra of obtained poly (PEPC-co-DO) azopolymer films with different DO content (from 10 to 60 wt%) and the thickness d=1600 nm are presented in Fig. 3. In Fig. 4 the transmission 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.

The maximum of the absorption region for this azopolymer lies at wavelength of ~450 nm, which is characteristic for DO azo dye classified as pseudo-stilbene (Yager & Barrett, 2006). It confirms azo coupling reaction of PEPC with DO. In Fig. 3 the wavelength used for recording (λ =473 nm) and reading (λ =650 nm) of phase grating are shown. The absorbance at wavelength of 473 nm is close to maximum, so this wavelength can be used for recording, whereas red laser at wavelength of 650 nm is in transparent region of spectra. The azopolymer film formation was carried out in the dark to obtain the film in its trans state of isomer.

The optically induced changes in the azopolymer film transmittance 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/cm²) from a 100 mW DPSS single mode laser with linear polarization. This was immediately followed by a transmittance measurement. Trans-cisisomerization can occur by optical excitation into the transisomer absorption band. Thistrans-cisisomerization process is well-known in a number of photochromic dyes including the azobenzene dyes (Cembran *et al.*, 2004).

Figure 5 shows the evolution of the transmittance spectrumupon irradiation with 473 nm laser light, which demonstrates the photo-induced isomerisation of poly(PEPC-co-DO) film with DO content 20 wt% and film thickness d=1600 nm after exposure 4.44 kJ/cm^2 (ca. 100 minutes). The cis-isomer can thermally relax back to the transisomer or this process can occur via optical excitation.

The peak at about 450 nm corresponds to the trans form of isomer, which increase upon irradiation. The series of spectra presented correspond to the 473 nm laser light photoisomerization of the trans isomer into the cis. The inset shows the change of transmittance at wavelength 450 nm (in %) vs exposure. The appearance of a second

peak at ~360 nm (indicated by arrow) can be attributed to the cis-isomer absorption (Tamai & Miyasaka, 2000). As it can be seen, the used wavelength λ =473 nm is close to the trans-isomer peak absorption coefficient; hence, photo-induced changes from trans-cis isomerization are expected to be faster than those that could occur if a longer wavelength was used. We show in the Fig. 5 that the absorption change increases with exposure and it saturates at exposure 4.44 kJ/cm². The saturation is likely to appear due to equilibrium between optically induced trans-to-cis-isomerization by exciting into the trans-isomer band peaked at wavelength of 450 nm and thermal relaxation from the cisto-trans-isomer (Tamai & Miyasaka, 2000).



Figure 3. UV-Vis transmission spectra of poly (PEPC-co-DO) films (the film thickness d=1600 nm) with different DO content. The blue (473 nm) and red (650 nm) lines mark the wavelength used for recording and reading of phase grating, respectively.



Figure 4. UV-Vis transmission spectra of poly (PEPC-co-DO) films with different film thickness. DO content is 30 wt%.



Figure 5. Photoinduced spectra changing of poly(PEPC-co-DO) film with DO content 20 wt% and film thickness d=1600 nm

4. **Results and Discussion**

The dependence of DE on recording time and exposure for all of the studied polarization configurations is shown in Fig. 6. 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, diffraction efficiency versus time has increased and eventually reached a relatively steady state during the exposure.



Figure 6. 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 azo dye concentration in polymer and film thickness. To do it holographic recording using P:P polarization configuration was carried out in poly(PEPC-co-DO) films with different concentration of azo dye DO simultaneously measuring the DE. The dependence of DE on recording time and exposure using P:P polarization configuration during holographic recording in poly (PEPC-co-DO) film with thickness 1600 nm and azo dye concentration from 10 to 60 wt% is shown in Fig. 7.

As it can be seen in Fig. 7, the optimal concentration of azo dye in the synthesized azopolymer poly (PEPC-co-DO) is about 30% by weight, i.e. 1: 3.5 to the weight of the polymer matrix PEPC. A further increase in the concentration to 60 wt% leads to a decrease in the DE, which is possibly due to scattering into the film, which is also observed in the transmission spectra in Fig. 3. This can be caused by a content of undissolved azo dye in the solution and film.



Figure 7. 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 thickness 1600nmand azo dye concentration from 10 to 60 wt%

The effect of film thickness on DE was experimentally studied. In Fig. 8 the growth kinetics of DE during the recording on poly (PEPC-co-DO) films of different thicknesses (concentration of azo dye 30 wt%) using a P: P polarization configuration is shown.



Figure 8. 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 from Fig. 8, the optimal thickness of the film exists, which gives the highest value of DE η =33%, and which is close to the theoretical maximum DE limit for thin sinusoidal phase gratings equal to 33.8% (Goodman, 1996).

The films with thickness over 1600nm show scattering of light due to presence of small bubbles after drying. The origin of the bubbles is vapor of solvent which presents in film volume. So samples with thickness over 2160 nm were not measured for DE.

It is important to notice, that the DE in this readout scheme can results from both the anisotropic grating formed in the volume of the layer, and the surface relief grating induced on the surface of the film. The amplitude grating due to absorption coefficient changes $\Delta \alpha$ is out of readout wavelength λ =650 nm and hence the DE was not affected by light absorption modulation. Diffraction gratings made by two-beam interference that leads to a sinusoidal profile of intensity/phase in the film with the modulation direction being in the film surface plane. This can results in a periodic modulation of the refractive index as well as periodic modulation of film thickness. The phase delay magnitude of such type of grating can be written as $\Delta \varphi = \frac{2\pi}{\lambda \cos \alpha} \cdot (h \cdot (n-1) + d \cdot \Delta n)$, where λ is the probe wavelength, h -amplitude of surface modulation, n is the refractive index of azopolymer, d is film thickness, and Δn is the maximum change in the refractive index, α is a angle of diffraction for the probe wavelength. Using a probe beam at normal incidence, the first-order DE of thin sinusoidal diffraction grating is given by

$$\eta = J_1^2 \left(\frac{\Delta\varphi}{2}\right),\tag{2}$$

where J_1 is a Bessel function of the first kind, $\Delta \varphi$ represents the peak-to-peak amplitude of phase delay in grating (Goodman, 1996). According to Eq. (2), the largest possible DE into one of the +1 and -1 diffraction orders is the maximum value of J_1^2 and is equal 33.8%.

The ratio between the DE's due to the volume and the surface relief grating can be determined by measuring not only the intensity, but also the polarization of the first diffracted order (Holme *et al.*, 1997). Up to now in our experiment no evidence of polarization changing of the first diffracted order was observed, but such study will be the subject of our future work.

According to Eq. (2), the DE can be rewritten using $\Delta \varphi$:

$$\eta = J_1^2 \left(\frac{2\pi}{\lambda \cos \alpha} \cdot (h \cdot (n-1) + d \cdot \Delta n) \right).$$
(3)

It is well known that the cis molecules are not stableat room temperature and the cis-trans isomerization is very rapid (King *et al.*, 1997). In our experiment the recording gratings were stable and measured value of DE after the grating formation was nearly constant during long storage (at least one month) at room temperature. Moreover, exposure of obtained grating by linear polarization light leads to insignificant DE change. Hence, based on the present experiments, we can presume that the main contribution for the increase of the DE is from surface relief grating.

Let's consider the DE dependence only on surface relief modulation. Thus the Eq. (3) could be transformed in

$$\eta = J_1^2 \left(\frac{2\pi}{\lambda \cos \alpha} \cdot \left(h \cdot (n-1) \right) \right), \tag{4}$$

where h is amplitude of surface modulation, n is the refractive index of azopolymer.

In the Fig. 9, the kinetics of experimental measured 1st order diffraction efficiency at 650 nm for the poly (PEPC-co-DO) film during P:P polarization recording (blue curve) and kinetics of computed theoretically 1st order DE according to Eq. (4) (shown as a red curve) are presented.



Figure 9. The kinetics of experimental measured 1st order diffraction efficiency at 650 nm for the poly (PEPC-co-DO) film during P:P polarization recording (blue curve) and kinetics of computed theoretically 1st order DE according to Eq. (4) (shown as a red curve)

The coincidence of experimental and theoretical curves at the first part of curves is good evidence that surface relief grating recording occurs in linear mode and after the grating relief depth reaches 300 nm the material feedback for the recording becomes nonlinear.

It is possible to estimate h from Eq. (4) using the first-order DE. As shown in Fig. 9 (red curve, blue star) that at η = 30% we estimate that *h*=430 nm from Eq. (4). To prove this estimation the holographic grating was recorded by P:P polarization up to 30% of DE (Fig. 9 (blue curve, red star) and the surface of the obtained grating was observed with AFM. The AFM analysis revealed the creation of a surface relief modulation. The h of such modulation (peak-to-peak amplitude) of the obtained grating (see Fig. 10) was measured to be about 440 nm. Despite sinusoidal distribution of intensities during holographic recording the profile of grating is not sinusoidal. Possible reason for that is nonlinear response of polymer on intensities as proved by Fig. 9. The good coincidence of experimental and theoretical estimated value of surface modulation amplitude means that DE analysis of the recorded holographic gratings in poly (PEPCco-DO) film can be performed by assuming the surface relief grating dominates in DE with slight influence of scalar refractive index gratings. The above-mentioned approach is valid for our polarization holographic recording. The study of the mechanism and origin of such a relief modulation is beyond the scope of the present work while its experimental and theoretical study is in progress and corresponding results will be reported soon.



Figure 10. AFM image (a) and cross-section (b) of surface relief grating recorded in poly (PEPC-co-DO) film (thickness 1600 nm, azo dye content 30 mass%) in P:P polarization configuration up to DE 30% measured at 650 nm

5. Conclusions

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 concentration of azo dye 30 wt% and 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%. Investigation of the obtained gratings revealed that the value of DE is caused mainly by surface relief modulation during holographic recording. The good coincidence of experimental and theoretical values of DE in dependence on surface profile depth may be the evidence that our explanation is reasonable. The above-mentioned approach is valid for the polarization holographic recording.

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.

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References

- Andries, A., Abaskin, V., Achimova, E., Meshalkin, A., Prisacar, A., Sergheev, S., ... & Vlad, L. (2011). Application of carbazole-containing polymer materials as recording media. *Physica status solidi* (A), 208(8), 1837-1840.
- Barrett, C.J., Rochon, P.L., & Natansohn, A.L. (1998). Model of laser-driven mass transport in thin films of dye-functionalized polymers. *The Journal of chemical physics*, 109(4), 1505-1516.
- Bellini, B., Ackermann, J., Klein, H., Grave, Ch., Dumas, Ph., Safarov, V. (2006). Lightinduced molecular motion of azobenzene-containing molecules: a random-walk model. J. *Phys. Condens. Matter.*, 18, S1817-S1835, doi:10.1088/0953-8984/18/33/S04.

- Bian, S., Williams, J. M., Kim, D. Y., Li, L., Balasubramanian, S., Kumar, J., & Tripathy, S. (1999). Photoinduced surface deformations on azobenzene polymer films'. J. Appl. Phys, 86, 4498-4508 doi:10.1063/1.371393.
- Böckmann, M., Doltsinis, N.L. (2016). Towards understanding photomigration: Insights from atomistic simulations of azopolymer films explicitly including light-induced isomerization dynamics. *The Journal of Chemical Physics*, 145(15), 154701.
- Cembran, A., Bernardi, F., Garavelli, M., Gagliardi, L., & Orlandi, G. (2004). On the mechanism of the cis- trans isomerization in the lowest electronic states of azobenzene: S0, S1, and T1. *Journal of the American Chemical Society*, 126(10), 3234-3243.
- Goodman, J.W. (1996). *Introduction to Fourier Optics*, 2nd ed.; McGraw-Hill Inc: New York, NY, USA, pp.81-83.
- Holme, N.C.R., Nikolova, L., Ramanujam, P.S., & Hvilsted, S. (1997). An analysis of the anisotropic and topographic gratings in a side-chain liquid crystalline azobenzene polyester. *Applied Physics Letters*, 70(12), 1518-1520.
- Kim, D.Y., Tripathy, S.K., Li, L., & Kumar, J. (1995). Laser-induced holographic surface relief gratings on nonlinear optical polymer films. *Applied Physics Letters*, *66*(10), 1166-1168.
- King, N.R., Whale, E.A., Davis, F.J., Gilbert, A., & Mitchell, G.R. (1997). Effect of media polarity on the photoisomerisation of substituted stilbene, azobenzene and imine chromophores. *Journal of Materials Chemistry*, 7(4), 625-630.
- Meshalkin, A., Abashkin, V., Prisacar, A., Triduh, G., Andries, I., Bets, L., Achimova, E. (2012). High precision interferometric thickness analysis of sub-micrometers spin-coated polyepoxypropylcarbazole films. *Sensor Electronics and Microsystem Technologies*, 3, 62-69.
- Meshalkin, A., Robu, S., Achimova, E., Prisacar, A., Shepel, D., Abaskin, V., & Triduh, G. (2016). Direct photoinduced surface relief formation in carbazole-based azopolymer using polarization holographic recording. *Journal of Optoelectronics and Advanced Materials*, 18(9-10), 763-768.
- Rochon, P., Batalla, E., Natansohn, A. (1995). Optically induced surface gratings on azoaromatic polymer films. *Appl. Phys. Lett.*, *66*, 136-138 doi:10.1063/1.113541.
- Sekkat, Z. (2016). Optical tweezing by photomigration. *Applied Optics*, 55(2), 259-268.
- Sekkat, Z., Dumont, M. (1993). Photoinduced orientation of azo dyes in polymeric films. Characterization of molecular angular mobility. Synthetic Materials for Non-Linear Optics and Electronics, 373.
- Tamai, N., Miyasaka, H. (2000). Ultrafast dynamics of photochromic systems. Chemical Reviews, 100(5), 1875-1890.
- Toshchevikov, V., Saphiannikova, M., & Heinrich, G. (2009). Microscopic theory of lightinduced deformation in amorphous side-chain azobenzene polymers. *The Journal of Physical Chemistry B*, 113(15), 5032-5045.
- Yager, K.G., Barrett, C.J. (2006). Novel photo-switching using azobenzene functional materials. *Journal of Photochemistry and Photobiology A: Chemistry*, 182(3), 250-261.
- Yang, K., Yang, S., & Kumar, J. (2006). Formation mechanism of surface relief structures on amorphous azopolymer films. *Physical Review B*, 73(16), 165204.