

High photoinduced birefringence in thermally treated layers of the azopolymer PAZO with significantly changed absorbance spectrum

Georgi Mateev^{1,2*}, Deyan Dimov^{1,2}, Dimana Nazarova^{1,2}, Elena Stoykova¹, Keehoon Hong³ and Lian Nedelchev^{1,2}

¹Institute of Optical Materials and Technologies–Bulgarian Academy of Sciences, Acad. G. Bonchev Str, Bl. 109, Sofia 1113, Bulgaria

²University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd, Sofia 1756, Bulgaria

³Electronics and Telecommunications Research Institute, 218 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

Abstract. In this experimental work we present the effect of thermal treatment of azopolymer thin films on their absorbance spectra and how that influences the photoinduced birefringence of the azopolymer. The azopolymer we use – PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]) is commonly investigated material for polarization holography because it is easily accessible and has well pronounced photoanisotropic properties. In a recent study it was discovered that its absorbance spectrum gradually changes upon heating to 250°C and as a result the absorbance in the range 400-600 nm is increased. That raises the question is it possible to increase the photoinduced birefringence for wavelengths that are far away from the peak of absorbance of the azopolymer PAZO, located approximately at 360 nm. For example, there are powerful lasers at 532 nm, which could be used for optical recording instead of traditionally used lasers in the blue and UV range. To answer this question, we investigated thin film samples of PAZO deposited on quartz substrate and measured continually their spectra of absorbance while heating the samples from room temperature to 250°C. We also measured the photoinduced birefringence using pump laser at 532 nm before and after the thermal procedure. Thus, we report significant increase of the birefringence at 532 nm after the thermal treatment and mention some potential applications.

1 Introduction

Azopolymers are well-known media for many optical applications mainly in the polarization holography [1-3] but also in other areas like in advanced fabrication [4], where the authors are imprinting nanopatterns of flexible substrate or for solar-thermal energy conversion and storage [5]. With all of these optical or optically related applications it is very important to analyze properly the spectra of these materials and how you can change and influence them. Usually, the influence of the temperature is analyzed with relation of the highest laser fields illuminating the azomaterials [6-7] or other indirect ways like with thermogravimetric analysis [8-9]. There are also examples of studying the influence of temperature in other materials in polarization optics. Recently Suzuki et al. analyzed how the temperature influences the diffraction efficiency of polarization gratings recorded in liquid crystals by circularly polarized beams [10]. In that work the authors report that the increase of the temperature leads to increase of the diffraction efficiency. Earlier we studied how the temperature influences the formation of photoinduced birefringence and the investigated material was the azopolymer P_{1,2} [11]. It was shown that if you increase the temperature of the sample and then start to illuminate

it, the maximal birefringence decreases its value. However, none of these shows whether heating azopolymer films could bring structural changes which can eventually improve their optical properties. So, in recent years there have been reported works when azopolymers were directly heated with the idea of checking how the chemical structure [12] or the absorbance spectra [13] will change. For example, Mateev et al. report a noticeable change of the absorbance spectra of PAZO and significant increase specifically in the range 400-600 nm [13].

That is important because of the reorientation processes of the azomolecules which are in the core of every photo induced polarization effect – converting thin films from isotropic into anisotropic, inducing chirality and creating surface relief gratings [1-3]. When a thin film of azomaterial is illuminated with linearly polarized light from the absorbance band the azochromophores start to reorient with respect to the orientation of the polarization.

So, an increase of the absorbance in the range 400-600 nm could potentially mean that the most effective pump wavelength can shift towards larger wavelength. Nedelchev et al. investigated the spectral dependence of the birefringence [14] and found that the highest values for PAZO were achieved for pump laser with

* Corresponding author: g_mateev@abv.bg

wavelength 442 nm, while around 532 nm the photoinduced birefringence (Δn) is significantly smaller which decreases the potential application using lasers at this wavelength. On the other hand, there are very powerful lasers at 532 nm like 12 W laser “Verdi” which could be used for making large optical elements if the process of photoorientation becomes more efficient. And that is the main objective of the present work. We investigate whether or not we can increase the photoinduced birefringence for pump laser at 532 nm via increasing the absorbance of PAZO at 532 nm after thermal treatment of our samples.

2 Experimental methods and results

2.1 Preparation of the samples

We have prepared our samples of PAZO with spin coating procedure using methanol as solvent. The concentration of the solution for this work was 175 mg/ml. The solution was sonicated and a magnetic stirrer was used. That provided us with samples with good optical quality and 2800-2850 nm thickness which were used for the investigation of the birefringence. Additionally, another series of samples of PAZO was made with concentration of 30 mg/ml and 200 nm thickness. The use of that samples will be discussed in the following subsection.

2.2 Spectral investigation

As pointed out in the introduction, it is reported already that heating thin films of PAZO can lead to a significant change in the absorption spectra [13]. We decided to investigate the dynamic change of the spectra while heating with thermal system THMS600 (Linkam Scientific, Salfords, UK) from room temperature to 250°C with constant rate of 1°C/min (Fig. 1). Spectral measurement was performed by a high-resolution spectrometer HR4000 (Ocean Optics, Orlando, USA).

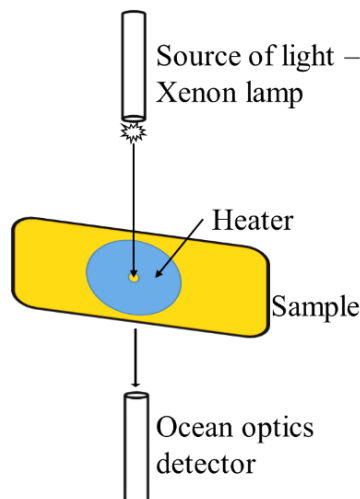


Fig. 1. Optical scheme for real-time absorbance measurement during the heating of the sample.

Heating to higher temperatures is undesirable because the polymer starts to degrade. The spectra of absorbance from 250 to 1000 nm were measured at a rate of one spectrum per minute. We are showing several spectra of absorbance corresponding to different temperatures for a sample with 200 nm thickness in Fig. 2. The sample was thinner than the samples used later for the birefringence measurement because for thicker samples there was the possibility of reaching saturation of the signal for the important range 350-600 nm where we have significant absorbance. For samples with that thickness (200 nm) we are sure that we can get reliable data.

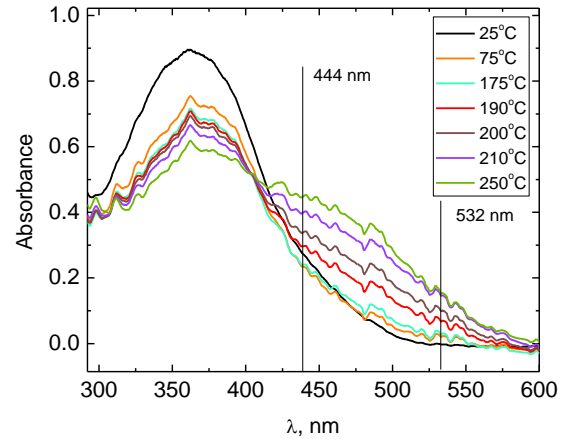


Fig. 2. Absorbance spectra of PAZO thin films with 200 nm thickness taken while heating the sample from room temperature to 250°C.

With the black curve we see the sample before the start of the heating procedure. By heating the sample, we see how the peak of absorbance at 359 nm starts decreasing while in the range between 425-600 nm the absorbance increases. Two vertical lines indicate the wavelengths of our two pump lasers (444 and 532 nm). The results correspond with previous reports [13].

2.3 Birefringence measurement

For measurement of the birefringence, we have used a well-known optical setup with polarimeter (Fig. 3). The sample is irradiated by vertically polarized pump beam.

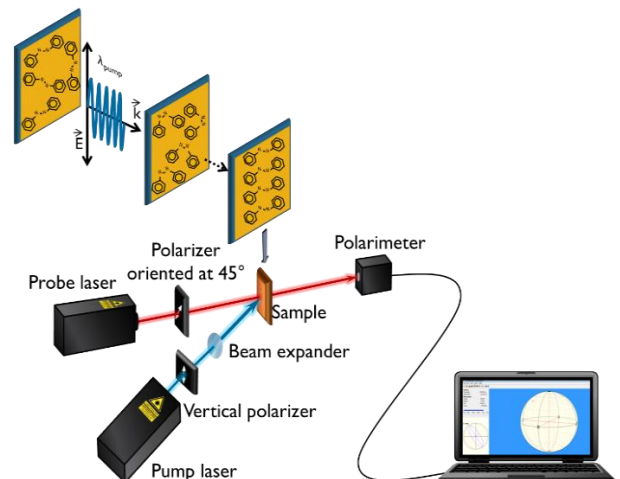


Fig. 3. Optical setup for birefringence measurement.

For our study we have applied two different pump lasers – DPSS laser at 444 nm and 12 watts DPSS Laser “Verdi” at 532 nm. As explained in the Introduction section, the second laser is very powerful but its wavelength is on the edge of the absorbance band so without the suggested thermal treatment the process of reorientation of the azomolecules is not effective. Meanwhile through the illuminated area passes also a probe beam at 635 nm (DPSS laser), linearly polarized at 45° before the sample. Its polarization after the sample is measured by polarimeter Thorlabs PAX57. Throughout the experiments we measure the background (the signal before the start of the irradiation with the pump beam) of the probe laser for several seconds. Thus, we can be sure that in the beginning of the experiment the sample is isotropic. Then we turn on the pump laser and the reorientation of the molecules begins. The process has saturation and when reached we turn off the pump laser again and record several minutes of relaxation. The intensity of the pump laser with 444 nm is approximately 125 mW/cm². Similarly, the intensity of the 532 nm pump laser is 300 mW/cm². The value of Δn in time is determined by the following formula:

$$\Delta n = \frac{\lambda}{2\pi d} \operatorname{atan} \left(\frac{S_3}{S_2} \right), \quad (1)$$

where with S_2 and S_3 we denoted the Stokes parameters and λ is the wavelength of the probe laser (635 nm).

The samples were investigated before and after thermal treatment (or annealing) which represents heating for 2h from room temperature to 190°C in oven. After reaching the desired temperature the oven holds it for another 0.5 h and then the sample is slowly cooled to room temperature again. Immediately after reaching room temperature the sample is prepared for measurement of its birefringence once at 532 nm pump laser and once at 444 nm. The results for the pump laser at 532 nm shown in Fig. 4 reveal a very significant (almost 70%) increase of the birefringence for the thermally treated sample.

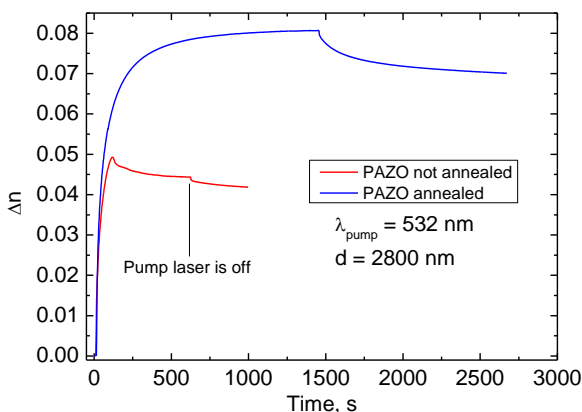


Fig. 4. Birefringence kinetics of both annealed and not-annealed sample with pump laser at 532 nm.

Even further the highest birefringence has larger value than the highest reported values of birefringence for non-treated PAZO films in any wavelength of pump laser and 635 nm for probe laser. This confirms our initial hypothesis that thermal treatment can make lasers

around 532 nm more efficient for pump. And considering the existence of very powerful lasers at 532 nm that opens the possibility of creating larger polarization-selective optical elements.

It is also worth mentioning that the birefringence curve for the not-annealed sample, shown in Fig. 4, doesn't reach saturation. After a brief period of increase, the birefringence starts to decrease so the relaxation doesn't start at the highest value of the birefringence. Similar behavior was previously reported exactly for pump laser at 532 nm [14].

In Fig. 5 we are showing also the annealed and not-annealed samples when the pump laser is 444 nm.

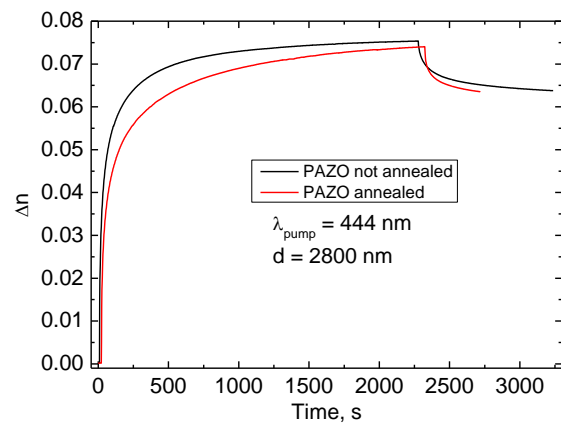


Fig. 5. Birefringence kinetics of both annealed and not-annealed sample with pump laser at 444 nm.

In this case we do not observe significant change of the birefringence curve after the annealing procedure.

3 Conclusions

We have investigated the change of the absorbance spectra of thin films deposited from the azopolymer PAZO after thermal treatment of the samples from room temperature to 250°C. As a result of the annealing, we observe higher absorbance at the range 400-550 nm which leads to significant increase of the birefringence with almost 70% when using laser with $\lambda = 532$ nm. That allows much wider use of lasers at that range for pumping PAZO for different applications as recording of polarization-selective diffractive optical elements, for digital polarization holography, digital storage of information, etc.

Acknowledgements: This work was supported by the Institute of Information & Communications Technology, Planning & Evaluation (IITP), grant No. 2019-0-00001. The authors are grateful for the funding from the European Union–NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project BG-RRP-2.004-0002, “BiOrgaMCT”. Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science, was used in this investigation.

References

1. L. Nikolova, P S. Ramanujam, Polarization holography, (Cambridge: Cambridge University Press, 2009)
2. X. Wang, Azo Polymers: Synthesis, Functions and Applications, (Springer-Verlag. Berlin Heidelberg, 2017)
3. Emoto, E. Uchida, T. Fukuda, Optical and physical applications of photocontrollable materials: Azobenzene-containing and liquid crystalline polymers, *Polymers* **4**, 150-186 (2012)
4. Y. Bowen, C. Feng, H. Shuai, Y. Haifeng, Athermal and Soft Multi-Nanopatterning of Azopolymers: Phototunable Mechanical Properties, *Angewandte Chemie International Edition* **59**, 4035-4042 (2020)
5. W. Si, B. Hans-Jürgen, Solar-Thermal Energy Conversion and Storage Using Photoresponsive Azobenzene-Containing Polymers, *Macromolecular Rapid Communications* **41**, 1900413 (2019)
6. A. Miniewicz, A. Sobolewska, W. Piotrowski, P. Karpinski, S. Bartkiewicz, E. Schab-Balcerzak, Thermocapillary Marangoni Flows in Azopolymers, *Materials* **13**, 2464 (2020)
7. A. Timóteo, J. Ribeiro, P. Ribeiro, M. Raposo, Dynamics of creation photoinduced birefringence on (PAH/PAZO) n layer-by-layer films: Analysis of consecutive cycles, *Optical Materials* **51**, 18-23 (2016)
8. F. Raquel, G. Junkal, E. Arantxa, T. Agnieszka, Hybrid materials based on azopolymer and sol-gel synthesized silver-containing titanium oxide nanoparticles with photoinduced birefringence, *RSC Advances* **5**, 15740-15748 (2015)
9. M. Ghoneim, A. El-Sonbati, M. Diab, A. El-Bindary, L.S. Serag, Supramolecular Assembly on Coordination of Azopolymer Complexes: A Review, *Polymer-Plastics Technology and Engineering*, **54**, 100-117 (2015)
10. M Suzuki, S. Ohara, M. Sakamoto, K. Noda, T. Sasaki, N. Kawatsuki, H. Ono, Temperature dependence of the diffraction efficiency of circular polarization gratings made by liquid crystal molecules with anisotropic absorption, *Optical Materials Express*, **14**, 1857-1864 (2024)
11. Nazarova, D, Mateev, G, Ivanov, D, Blagoeva, B, Kostadinova, D, Stoykova, E, Nedelchev, L. Photoinduced birefringence in thin azopolymer films recorded at different temperatures. *Bulgarian Chemical Communications* **48**, Special Issue G, 75-78 (2016)
12. L. Xiao, Z. Weiguang, J. Ye, H. Jianjia, C. Dongzhong, Phase Behaviors and Photoresponsive Thin Films of Syndiotactic Side-Chain Liquid Crystalline Polymers with High Densely Substituted Azobenzene Mesogens, *Chemphyschem: European Journal of Chemical Physics and Physical Chemistry*, e202400421 (2024)
13. G. Mateev, L. Nedelchev, A. Georgiev, D. Nazarova, Improvement of the photoinduced birefringence in azopolymer PAZO doped with TiO₂ nanoparticles via thermal treatment, *Open Material Sciences*, **5**, 19-23 (2019)
14. L. Nedelchev, D. Ivanov, B. Blagoeva, D. Nazarova, Optical anisotropy induced at five different wavelengths in azopolymer thin films: Kinetics and spectral dependence, *Journal of Photochemistry and Photobiology A: Chemistry*, **376**, 1-6 (2019)