



Temperature Dependence of Photoinduced Birefringence in Thin Azopolymer Films

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Abstract. In this work we study the dependence of the photoinduced birefringence on the initial temperature of the layer, as well as the possibility of recording and thermal erasure in thin azopolymer films. To determine the temperature dependence, the sample is placed on a hot stage, which can maintain or vary the temperature of the sample with a high precision. Birefringence is induced with a linearly polarized light from a laser at 442 nm, and its value is determined by measuring the Stokes parameters of a probe laser beam after the sample. The birefringence is erased by placing the sample on a hot stage.

Keywords: azopolymer, birefringence, laser, Stokes parameters, anisotropy.

1. INTRODUCTION

Azopolymers are one of the most widely studied materials for polarization holographic recording (Nikolova and Ramanujam, 2009; Wang, 2017) because of the possibility to induce birefringence in them that reaches high values. There is also a wide variety of azopolymer structures (Natansohn and Rochon, 2002). Research on azomaterials can be traced back to 1984 when the group of T. Todorov found that they are suitable for recording high efficiency diffraction gratings (Todorov et al, 1984). Azopolymers find application in all-optical switching, optical communications, optical storage and diffractive optical elements (Natansohn et al, 1992; Nedelchev et al, 2003; Hvilsted et al, 1995; Ryabchun et al, 2014).

The recording of the polarization state of light is due to trans-cis-trans photoisomerization and reorientation of azo-chromophore under the action of linearly polarized light. Thus, optical anisotropy is induced. The azopolymers can recover their initial isotropic form by heating or by irradiating with circularly polarized light.

Temperature has the greatest impact on the physical properties of the polymers when it is close to the corresponding glass-transition temperature. Most often, the birefringence is erased by heating the polymer to T_g , but there are also known cases when it is necessary to heat up much above glass-transition temperature (Ferreira et al, 2012; Ivanov et al, 2005; Nedelchev et al, 2016; Nazarova et al, 2016; Wu et al, 1998; Zebger et al, 2002).

In this paper, we study the dependence of the photoinduced birefringence on the initial temperature of the layer, as well as the possibility of multiple cycles of recording and thermal erasure in thin azopolymer film.

2. MATERIALS AND METHODS

The amorphous azocopolymer P_{1-2} that we study, is synthesized in the Institute of Optical Materials and Technologies and its synthesis has been described earlier (Martinez-Ponce et al, 2004). Chemical structure of P_{1-2} is presented in Fig. 1 a). To prepare the experimental sample, the polymer is dissolved in 1,2-dichloroethane, then dropped onto glass substrates

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and spin-coated at 1500 rpm. Absorption spectra were measured with a spectrophotometer Cary 5E-UV-VIS (Fig. 1a). The thickness was measured with a Talystep profilometer Taylor Hobson (Fig. 1b) and is $d = 700$ nm.

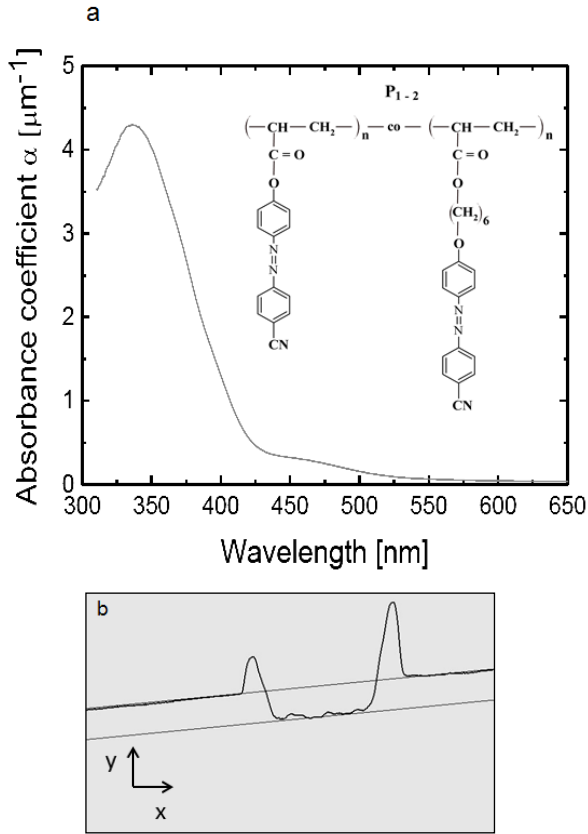


Fig. 1 (a) Chemical structure of azocopolymer P_{1-2} , (b) thickness measurement profile.

Birefringence is induced in the sample by a vertically polarized beam from pump laser with wavelength $\lambda_{\text{pump}} = 442$ nm as shown in Fig. 2. The probe laser beam with $\lambda_{\text{probe}} = 635$ nm passes through a polarizer oriented at 45° and through the sample in the area irradiated by the pump laser. The value of birefringence is determined by measuring the Stokes parameters S_2 and S_3 of the probe laser beam by a polarimeter PAX5710 Polarization Analyzing System, Thorlabs (Berberova et al, 2016):

$$\Delta n = \frac{\lambda_{\text{probe}}}{2\pi d} \arctan\left(\frac{S_3}{S_2}\right) \quad (1)$$

To investigate the thermal erasure of the birefringence in the azopolymer, the sample is placed on a THMS 600 (Linkam Scientific), which can accurately maintain or vary the sample temperature at a set heating or cooling rate.

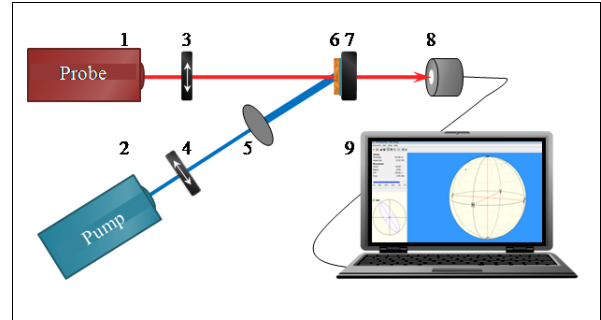


Fig. 2 Optical setup: 1 – DPSS probe laser (635 nm, $P < 2\text{mW}$), 2 – He-Cd pump laser (442 nm, $P = 105$ mW), 3 – polarizer oriented at 45° , 4 – vertical polarizer, 5 – beam expander, 6 – azopolymer sample, 7 – hot stage, 8 – Thorlabs polarimeter, 9 – computer.

3. RESULTS AND DISCUSSION

The important parameters of each photoanisotropic media are the maximum value of the photoinduced birefringence Δn_{max} , the response time τ needed to reach 80% of Δn_{max} , as well as parameter r , which reflects the optical storage properties of the material and defined as ratio of the birefringence Δn_{rel} retained after the relaxation to the maximal value of the photoinduced birefringence Δn_{max} (Nedelchev et al, 2003).

The birefringence recording/reading/ erasure experiment consists of the following stages (Fig. 3):

First, the temperature of the sample is elevated to the desired value. Then, background is measured for 60 seconds to reduce the experimental error, after which the pump laser is turned on and birefringence is induced. At this stage, Δn_{max} and τ can be determined. Upon reaching saturation, the pump radiation is turned off and a relaxation process is observed, with the parameter r being determined from the



curve obtained. Finally, the residual birefringence is erased by heating at rate $5^{\circ}\text{C}/\text{min}$ from the starting temperature. The probe laser radiation is on throughout the entire experiment.

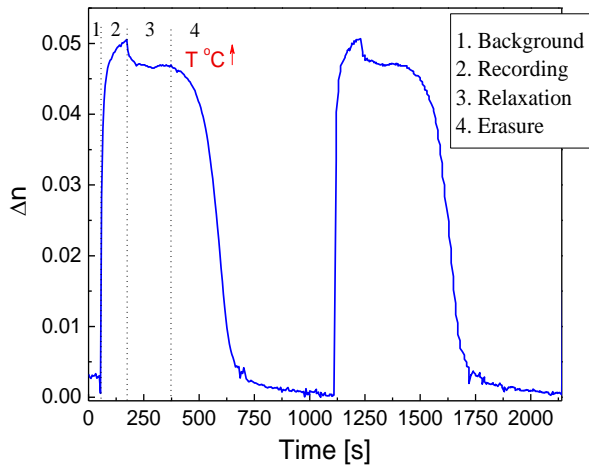


Fig. 3 Experimental steps and two cycles of recording and thermal erasure of birefringence for the P_{1-2} azocopolymer.

Subjecting P_{1-2} to recording and thermal erasure, we can establish the maximum value of the birefringence is retained after two cycles (Fig. 3). The temperature of the film is 30°C when starting a birefringence recording in each cycle, the heating rate is $10^{\circ}\text{C}/\text{min}$, and complete erasure occurs at 90°C .

Fig. 4 and Fig. 5 show the dependence of Δn_{max} , τ and r on the starting temperature of the sample P_{1-2} . The highest value of the birefringence is achieved when the sample is at room temperature – 25°C , but birefringence may still be induced at 100°C .

The media is also most stable at 25°C , but on the other hand, the response is faster at higher temperatures. These results make it possible to select the most suitable parameters of the azomaterial based on its application.

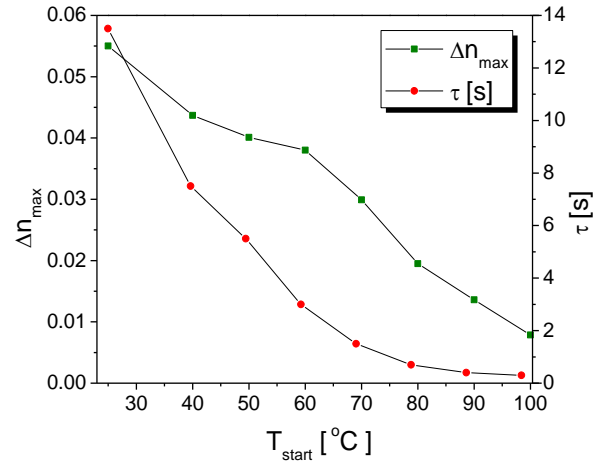


Fig. 4 Dependence of the maximal value of the birefringence Δn_{max} and response time τ for the P_{1-2} on the starting temperature.

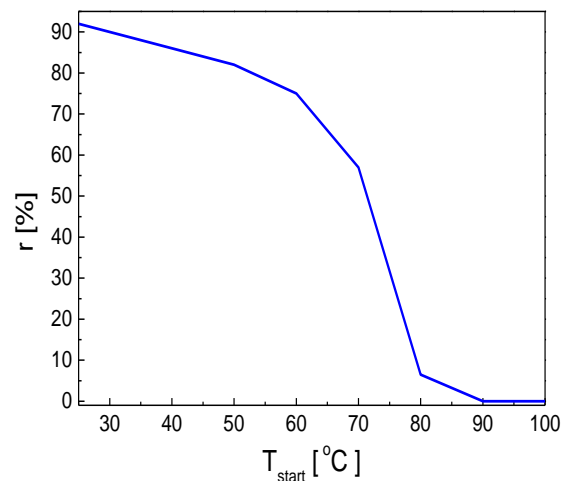


Fig. 5 Dependence of the parameter r for the P_{1-2} on the starting temperature.

4. CONCLUSIONS

In this work, we studied the dependencies of the maximal photoinduced birefringence Δn_{max} , response time τ and the stability parameter r of the thin azopolymer film from the different starting temperatures of the sample, as well as the possibility of thermal erasure of the birefringence.

Our results show that the different starting temperatures influence the parameters of the sample in a different way: for example, at 60°C

Δn_{\max} is 70 % of Δn_{\max} at 25 °C, but the τ decreases four times.

In addition, anisotropy in a sample can easily be erased thermally, after which the polymer can be successfully used for several recording and erasure cycles.

ACKNOWLEDGMENTS

This work is financially supported by contract ДН 08/10 with the National Science Fund of Bulgaria. Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-155/28.08.2018 with Bulgarian Ministry of Education and Science is used in the present investigations.

REFERENCES

- Berberova N., Nazarova D., Nedelchev L., Blagoeva B., Kostadinova D., Marinova V. and Stoykova E., 2016. *Photoinduced variation of the Stokes parameters of light passing through thin films of azopolymer-based hybrid organic/inorganic materials*, J. of Phys.: Conference Series 700 (1), art. no. 012032.
- Ferreira Q., Ribeiro P. A., Oliveira O. N. Jr. and Raposo M., 2012. *Long-term stability at high temperatures for birefringence in PAZO/PAH layer-by-Layer films*, ACS Appl. Mater. Interfaces, 4, 1470-1477.
- Hvilsted S., Andruzzi F., Kulinna C., Siesler H. W. and Ramanujam P. S., 1995. *Novel side-chain liquidcrystalline polyester architecture for reversible optical storage*, Macromol., 28(7), 2172-2183.
- Ivanov M., Ilieva D., Minchev G., Petrova Ts., Dragostinova V., Todorov T. and Nikolova L., 2005. *Temperature-dependent light intensity controlled optical switching in azobenzene polymers*, Appl. Phys. Lett., 86 (18), 181902.
- Martinez-Ponce G., Petrova T., Tomova N., Dragostinova V., Todorov T. and Nikolova L., 2004. *Investigations on photoinduced processes in a series of azobenzene-containing side-chain polymers*, J. Opt. A: Pure Appl. Opt., 6(4), 324–329.
- Natansohn A. and Rochon P., 2002. *Photoinduced Motions in Azo-Containing Polymers*, Chem. Rev., 102 (11), 4139-75.
- Natansohn A., Rochon P., Gosselin J. and Xie S., 1992. *Azo polymers for reversible optical storage. 1. Poly[4'-[[2-(acryloyloxy)ethyl] ethylamino]-4-nitroazobenzene]*, Macromol, 25, 2268-2273.
- Nazarova D., Mateev G., Ivanov D., Blagoeva B., Kostadinova D., Stoykova E. and Nedelchev L., 2016. *Photoinduced birefringence in thin azopolymer films recorded at different temperatures*, Bul. Chem. Comm., 48, Special Issue G, 75-78.
- Nedelchev L., Matharu A. S., Hvilsted S. and Ramanujam P. S., 2003. *Photoinduced anisotropy in a family of amorphous azobenzene polyesters for optical storage*, Appl. Opt., 42(29), 5918-5927.
- Nedelchev L., Ivanov D., Mateev G., Blagoeva B., Kostadinova D., Berberova N. and Nazarova D., 2016. *Multiple cycles of recording/reading/erasing birefringence in azopolymers*, Bul. Chem. Comm., 48, Special Issue G, 33-36.
- Nikolova L. and Ramanujam P. S., 2009, *Polarization Holography*, Cambridge University Press, Cambridge.
- Rochon P., Gosselin J., Natansohn A. and Xie S., 1992. *Optically induced and erased birefringence and dichroism in azoaromatic polymers*, Appl. Phys. Lett., 60(1), 4-5.
- Ryabchun A., Sobolewska A., Bobrovsky A., Shibaev V. and Stumpe J., 2014. *Polarization holographic grating recording in the cholesteric azobenzene-containing films with the phototunable helix pitch*, J. Polymer Sci., Part B: Polym. Phys., 52, 773.
- Todorov T., Nikolova L. and Tomova, N., 1984. *Polarization holography. 1: A new high-efficiency organic material with reversible photoinduced birefringence*, Appl. Opt., 23 (23), 4309-4312.
- Wang X., 2017. *Azo Polymers: Synthesis, Functions and Applications*, Springer-Verlag, Berlin.



Wu Y., Demachi Y., Tsutsumi O., Kanazawa A., Shiono T. and Ikeda T., 1998. *Photoinduced alignment of polymer liquid crystals containing azobenzene moieties in the side chain. 1. Effect of light intensity on alignment behaviour*, *Macromolecules*, 31 (2), 349-354.

Zebger I., Rutloh M., Hoffmann U., Stumpe J., Siesler H. W. and Hvilsted S., 2002. *Photoorientation of a liquid crystalline polyester with azobenzene side groups. 1. Effects of irradiation with linearly polarized blue light*, *J. Phys. Chem. A*, 106 (14), 3454-3462.