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Time stability of photoinduced birefringence in amorphous and liquid-crystalline azopolymers

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One of the most important parameters for every optical data storage media is the stability of the recorded information in time. When polarization holography is used for data recording, the information is encoded via the photoinduced anisotropy (most often birefringence) in the media.

In this article we present a study on the stability of the photoinduced birefringence (Δn) in amorphous (P_1) and liquid-crystalline (LC) azobenzene polymer (P_2) with similar structures of the backbone and the chromophore unit, but different spacers between them. As our experiments indicate, 72 % of the photoinduced birefringence is retained in the polymer P_1, and 104 % in the polymer P_2 one hour after the end of the recording process i.e. the stability of the birefringence in the LC polymer is considerably higher than in the amorphous.

Keywords: birefringence, time stability, optical data storage, azopolymer

INTRODUCTION

Azobenzene materials have attracted considerable attention since 1984 when Todorov *et al.* established the possibility to record high-efficient polarization diffraction gratings in layers of azo dye methyl-orange in polyvinyl alcohol (PVA) matrix [1]. The observed high values of reversible photoinduced anisotropy (birefringence and dichroism) on irradiation with linearly polarized light are obtained by two main processes: selective *trans-cis* isomerization followed by reorientation of the *trans*-azobenzenes. The *trans-cis-trans* process for reorientation of the molecules is illustrated in Fig. 1. As the *trans* isomer is the stable form of the azo molecule, the *trans-cis* isomerization is always photoinduced (*hv*), but the *cis-trans* isomerization can be either photoinduced (*hv*'), or can result from spontaneous thermal relaxation (*kT*).

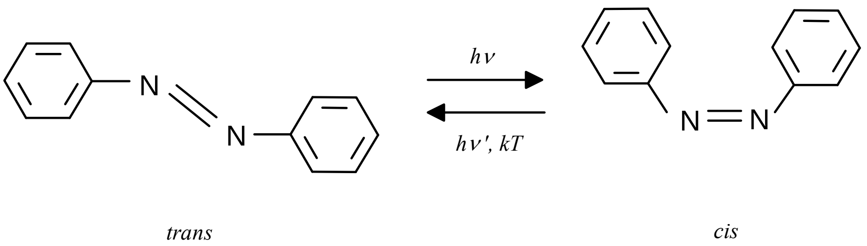

Fig. 1. *Trans–cis–trans* isomerization of azobenzenes.

The process continues until most of the azo molecules lie in direction perpendicular to the polarization of the writing beam. In such position they cease to absorb light [1, 2].

Azopolymers have found numerous applications related with polarization recording and in particular polarization holography [2] – optical elements with unique polarization properties can be inscribed in them [3, 4], as well as surface relief gratings [5, 6] and chiral structures [7, 8]. They are also good candidates for reversible holographic storage [9–13] allowing also polarization holographic multiplexing [14].

Recording in azopolymers is highly reversible, as it has been shown by Ramanujam and co-

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workers: more than 10 000 cycles of optical recording and erasure have been realized without apparent fatigue of the media [15]. This is a certain advantage, but on the other hand raises the question about the stability of the recorded information in time.

In order to optimize the performance, many different types of azobenzene materials have been studied – azo dye solutions, azo dyes in polymer or gelatin matrix [1, 16], azo dyes chemically attached to the polymer backbone (called azopolymers) [6–15], even hybrid materials based on azopolymers doped with inorganic nanoparticles [17–19].

Here we present a study on the stability of the photoinduced birefringence (Δn) in two azopolymers with similar structure of the backbone and the chromophore unit, but different spacers between them. As a result, one of them is amorphous (P_1) and the other is liquid-crystalline (P_2).

EXPERIMENTAL

Azopolymer samples preparation and characterization

The polymers used in our experiments are side-chain cyanoazobenzene polymers. Their chemical structures are shown in Fig. 2. They were synthesized by radical-type polymerization, as described elsewhere [20]. The azopolymer denoted as P_1 is amorphous and the polymer P_2 is liquid-crystalline (LC). As seen in Fig. 2, the structures of their backbone and chromophore units are the same, but they differ in the spacer between the backbone and the azochromophore. The amorphous character of P_1 is determined by the short and rigid spacer, and the LC properties of P_2 – by the flexible methylene chain, that allows the chromophore units to form LC domains.

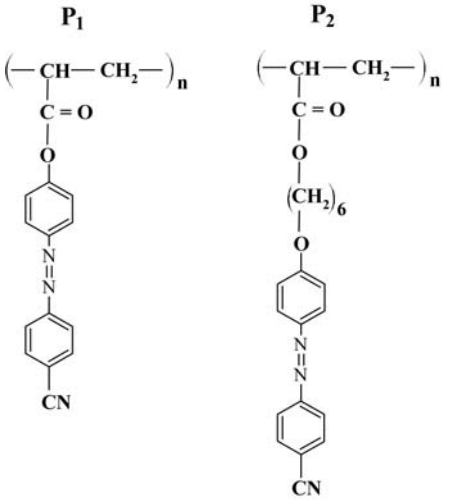

Fig. 2. Structures of the azopolymers P_1 and P_2 used in the present study.

The glass transition temperatures T_g and molecular weights M_w of the two polymers were measured by differential scanning calorimetry (DSC) and gel-permeation chromatography (GPC), respectively and the following data were obtained – P_1 ($M_w = 1.46\times10^4$ g/mol, $T_g = 106$ °C) and P_2 ($M_w = 2.05\times10^3$ g/mol, $T_g = 35$ °C).

Thin films from the two polymers dissolved in 1,2-dichloroethane were prepared by spin coating onto glass substrates. The samples based on the LC polymer P_2 were heated above 80 °C and then rapidly cooled to room temperature; the other samples were not thermally processed. The thickness of the films was measured by high-precision Talystep profilometer and is 0.73 μm for the P_1 film and 0.80 μm for the P_2 film.

Polarimetric setup for photoinduced birefringence measurement

The kinetics of the photoinduced birefringence Δn is measured by a classical polarimetric scheme [1, 9–11]. Vertically polarized recording beam at 473 nm with intensity 400 mW/cm^2 is used to induce birefringence. The sample is placed between crossed polarizers oriented at ±45° with respect to the vertical. The intensity I of a probe beam from He-Ne laser ($\lambda_{probe} = 633$ nm) passing through the system is measured by a digital optical power meter (Thorlabs PM100). From this intensity, the value of the photoinduced birefringence can be easily determined using the following equation [1]:

$$\Delta n(t) = \frac{\lambda_{probe}}{\pi d}\arcsin\sqrt{\frac{I(t)}{I_0}} \qquad (1)$$

where d is the thickness of the film, I_0 is the intensity of the probe beam before the start of the recording and at parallel polarizers.

RESULTS AND DISCUSSION

Data for the time stability of the photoinduced birefringence can be found already in the first articles on azobenzenes. For instance, this issue is addressed by Todorov *et al.* and there is a comment that the decay of the birefringence may be slowed down substantially by preliminary thermal treatment of the samples [1]. Indeed, after such treatment more than 50 % of the photoinduced birefringence (and about 30 % of the diffraction efficiency) is retained for a long time after the acting light is stopped.

Later, Natansohn and co-workers [11] proposed a model for the birefringence relaxation. They obtained a good fit of the experimental data with a biexponential function of the type $y = C\exp(-k_C t) + D\exp(-k_D t) + E$, where one of the exponential terms corresponds to a "fast" decay process, the other – to a "slow" decay process and the constant value E, normalized to $E_n = E/(C + D + E)$ represents the fraction of the induced birefringence retained permanently in the polymer film. For the investigated azopolymers the value of E_n was 84 %, calculated however on the base of relatively short (25 seconds) measurement of the birefringence decay.

A close correlation has been established between a short-term (30 min) and long-term (1 week) stability of the photoinduced birefringence in a family of amorphous azobenzene polyesters [12]. The polyester with highest short-term stability of 89 % demonstrated also highest long-term stability of 83 % one week after the recording.

The amorphous polymers are usually preferred for storage applications because of the lower scattering in them compared to the LC ones. On the other hand, as our experiments indicate, the stability of the birefringence in the LC polymer is considerably higher than in the amorphous. The results are shown in Table 1 and Fig. 3. The coefficients r_t are defined as $r_t = \Delta n(t)/\Delta n_{max}$, where in this case t is the time expired after the end of the recording process and Δn_{max} is the maximal value of the birefringence reached during the recording.

Table 1. Summary of the time stability data for azopolymers P_1 and P_2.

Azopolymer	Δn_{max}	r_{10min}	r_{30min}	r_{1hour}
P_1	0,030	85 %	75 %	72 %
P_2	0,066	102 %	102 %	104 %

As seen, after 1 hour 72 % of the photoinduced birefringence is retained in the polymer P_1, and 104 % in the LC polymer P_2. The fact that the value of Δn is even slightly increasing in the LC polymer after the end of the recording is attributed to the relaxation from *cis* to *trans* state of some of the chromophores, which tend to orient in direction parallel to the already optically oriented majority of the azomolecules. The data for Δn_{max} and r_{10min} are in good agreement with our earlier measurements on the 10 min birefringence stability in polymers P_1 and P_2 [19]. The extended one hour measurement of the time stability in the present experiment is sufficient for the "fast" decay process to complete. Therefore we can use the linear relation between the short-term (30 min) and long-term stability established in [12] for amorphous azopolymers and estimate the long-term stability of the recording in the polymer P_1 to about 65 %.

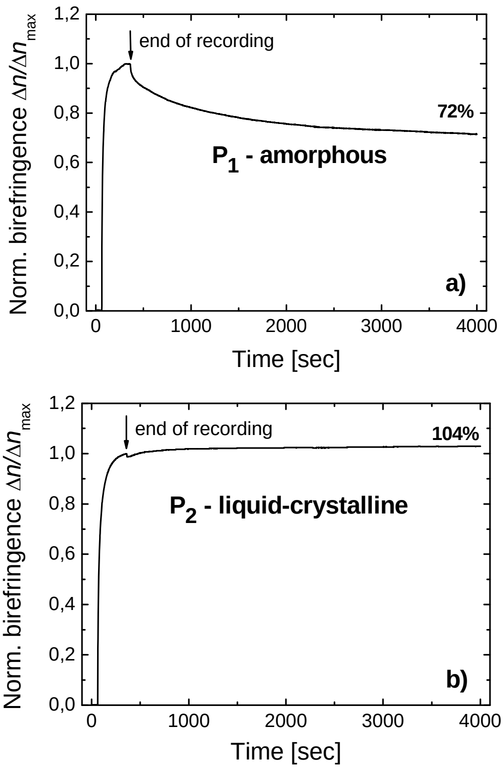

Fig. 3. Time dependence of the normalized birefringence during the recording and in the following 1 hour for the amorphous azopolymer P_1 (a), and for the LC polymer P_2 (b).

CONCLUSIONS

Based on the experimental measurement of the photoinduced birefringence for one hour after the end of the recording, we have found the value of the anisotropy retained – 72 % in the amorphous azopolymer P_1 and 104 % in the LC polymer P_2. The long-term stability in P_1 was estimated as 65 % using data from the literature.

This results also suggest that a co-polymer of the amorphous P_1 and the LC polymer P_2 may possess an optimal combination of properties – amorphous state and in the same time relatively high time-stability of the photoinduced anisotropy.

REFERENCES

1. T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.*, **23**, 4309 (1984).

2. L. Nikolova, P. S. Ramanujam, Polarization Holography, Cambridge Univ. Press, Cambridge, 2009.
3. T. Todorov, L. Nikolova, *Opt. Lett.*, **17**, 358 (1992).
4. G. Martinez-Ponce, T. Petrova, N. Tomova, V. Dragostinova, T. Todorov, L. Nikolova, *Opt. Lett.*, **29**, 1001 (2004).
5. D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar, J. Kumar, S. K. Tripathy, *Macromolecules*, **28**, 8835 (1995).
6. I. Naydenova, L. Nikolova, T. Todorov, N. C. R. Holme, P. S. Ramanujam, S. Hvilsted, *J. Opt. Soc. Am. B*, **15**, 1257 (1998).
7. L. Nedelchev, L. Nikolova, T. Todorov, T. Petrova, N. Tomova, V. Dragostinova, P. S. Ramanujam, S. Hvilsted, *J. Opt. A: Pure Appl. Opt.*, **3**, 304 (2001).
8. J. del Barrio, R. M. Tejedor, L. Oriol, *Eur. Polym. J.*, **48**, 384 (2012).
9. A. Natansohn, P. Rochon, J. Gosselin, S. Xie, *Macromolecules*, **25**, 2268 (1992).
10. S. Hvilsted, F. Andruzzi, C. Kulinna, H. W. Siesler, P. S. Ramanujam, *Macromolecules*, **28**, 2172 (1995).
11. M. S. Ho, A. Natansohn, P. Rochon, *Macromolecules*, **28**, 6124 (1995).
12. L. Nedelchev, A. S. Matharu, S. Hvilsted, P. S. Ramanujam, *Appl. Opt.*, **42**, 5918 (2003).
13. A. S. Matharu, S. Jeeva, P. S. Ramanujam, *Chem. Soc. Rev.*, **36**, 1868 (2007).
14. D. Ilieva, L. Nedelchev, T. Petrova, N. Tomova, V. Dragostinova, L. Nikolova, *J. Opt. A: Pure Appl. Opt.*, **7**, 35 (2005).
15. N. C. R. Holme, P. S. Ramanujam, S. Hvilsted, *Opt. Lett.*, **21**, 902 (1996).
16. T. D. Ebralidze, A. N. Mumaladze, *Appl. Opt.*, **29**, 446 (1990).
17. J. Zhou, J. Yang, Y. Sun, D. Zhang, J. Shen, Q. Zhang, K. Wang, *Thin Solid Films*, **515**, 7242 (2007).
18. L. Nedelchev, D. Nazarova, V. Dragostinova, D. Karashanova, *Opt. Lett.*, **37**, 2676 (2012).
19. L. Nedelchev, D. Nazarova, V. Dragostinova, *J. Photoch. Photobio. A*, **261**, 26 (2013).
20. G. Martinez-Ponce, Ts. Petrova, N. Tomova, V. Dragostinova, T. Todorov, L. Nikolova, *J. Opt. A: Pure Appl. Opt.*, **6**, 324 (2004).

ВРЕМЕВА СТАБИЛНОСТНА ФОТОИНДУЦИРАНОТО ДВУЛЪЧЕПРЕЧУПВАНЕ В АМОРФЕН И ТЕЧНОКРИСТАЛЕН АЗОПОЛИМЕР

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(Резюме)

Един от най-важните параметри на всяка среда за оптичен запис на информация е стабилността на записаната информация във времето. Когато записа се извършва чрез поляризационна холография, информацията се кодира чрез фотоиндуцираната в средата анизотропия (най-често двулъчепречупване).

В настоящата статия е представено изследване на фотоиндуцираното двулъчепречупване (Δn) в два азополимера – аморфен P_1 и течнокристален P_2 с еднакви структури на главната верига и хромофора, но различни дължини на страничните вериги. Както показват експерименталните данни, един час след прекратяването на записа в полимер P_1 се запазват 72 % от фотоиндуцираното двулъчепречупване, а в полимер P_2 – 104 % т.е. стабилността на двулъчепречупването в течнокристалния полимер е значително по-висока отколкото в аморфния.