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Photoinduced birefringence in thin azopolymer films recorded at different temperatures

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In this work we investigate the dependence of characteristics of polarization recording and erasure in thin azopolymer films on the starting temperatures of the sample. Polarized light from DPSS laser with wavelength 444 nm is used for recording of photoinduced birefringence. For erasing the records, thermal method is applied. Birefringence is successfully recorded at different starting temperatures from 25 to 100°C. 3D graphics for visualization of the experimental data are presented. Photoinduced birefringence is calculated from real time monitored Stocks parameters during the entire experiment. This investigation allows us to determine the optimal conditions of recording at elevated temperatures in order to achieve shortest response time or maximal birefringence.

Keywords: Azopolymers; Temperature dependence of photoinduced birefringence; Polarization recording.

INTRODUCTION

In the last few decades material science has a huge development, and increasingly expanding borders. Extensive applications and increased demands for different materials are some of the reasons for this development. Some of the most investigated materials for polarization holographic recording are azobenzene containing polymers [1-3]. The main feature that defines the widespread use of these materials is photo-induced optical anisotropy in them. Investigation of the anisotropy in azopolymers is of interest to applications in photonics and optical data storage [4-6], as well as for fundamental research [7, 8]. Many researchers [9-15] observed that the physical properties of azopolymers depend significantly on temperature, especially near the glass-transition temperature (T_g), where the mobility of polymer chains increases. In some cases birefringence is relatively stable below the azopolymer T_g [9] and is erasable by heating the polymer to this temperature. However some studies report that maximum birefringence can be obtained at temperatures above the T_g [11, 13].

This paper presents experimental data obtained from real time monitoring of recording and thermal erasure of birefringence with different starting temperatures of the thin film samples. Dependence of the maximal photoinduced birefringence, response time and relaxation decrease on the recording temperature are presented.

EXPERIMENTAL

Materials

The polymer used is side-chain amorphous azocopolymer, denoted as $P_{1\text{-}2}$, synthesized in the Institute of Optical Materials and Technologies, as described by Martinez-Ponce *et al* [16].

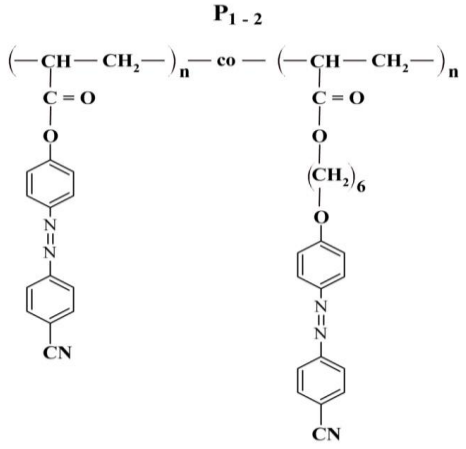

Fig. 1. Chemical structure of azocopolymer $P_{1\text{-}2}$.

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Its chemical structure is presented in Fig.1. The molecular weight of P_{1-2} is M_w = 3600 g/mol and its glass transition temperature T_g is 102°C.

Methods of characterization

In this work we use thin films of the azocopolymer P_{1-2}. It was dissolved in 1,2-dichloroethane and the solution was spin coated at 1500 rpm on glass substrates making thin homogeneous film. As the thickness of the film is important for the determination of photoinduced birefringence [see Eq. (1)], we used a Talystep profilometer (Taylor Hobson) in order to measure it. The thickness for our samples was 700 nm. The birefringence is determined by recording the Stokes parameters of probe laser beam (λ_{probe} = 635 nm, power <2 mW) passing through the samples. The measurement is performed by PAX5710 Polarization Analyzing System (Thorlabs) and the birefringence is calculated from the following expression [3,17]:

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

where d is the film thickness, and S_2 and S_3 are two of the four Stokes parameters. Vertically polarized light from DPSS laser with λ_{rec} = 444 nm and power 43 mW was used for recording.

The temperatures of recording are 25, 40, 50, 60, 70, 80, 90 and 100 °C. At first, we evaluate the background for 60 seconds. Then we turn on the recording laser for 300 s, than there are another 300 seconds for relaxation. In these three stages the temperature is constant. Then starts the heating. The control of temperature and subsequent thermal erasure was achieved by mounting the samples on stage THMS600 (Linkam Scientific), which is capable of maintaining a given speed of heating with high precision. We heated the sample with speed of 10 °C/min until reaching 100 °C. From our previous investigations, we know that the temperature for which the birefringence is reduced by 50% ($T_{50\%}$) is approximately 75 °C, and the temperature of complete erasure is 85 °C. For this reason in the last two experiments (at 90 and 100 °C) the films weren't heated because their starting temperature was high enough to erase the birefringence immediately after the end of recording. Also their recording and relaxation time were reduced to 180 and 120 seconds respectively.

RESULTS AND DISCUSSIONS

The experimental curves for starting temperatures 40, 50, 60 and 70 °C are shown on Fig. 2. In these cases the temperature of recording is below $T_{50\%}$.

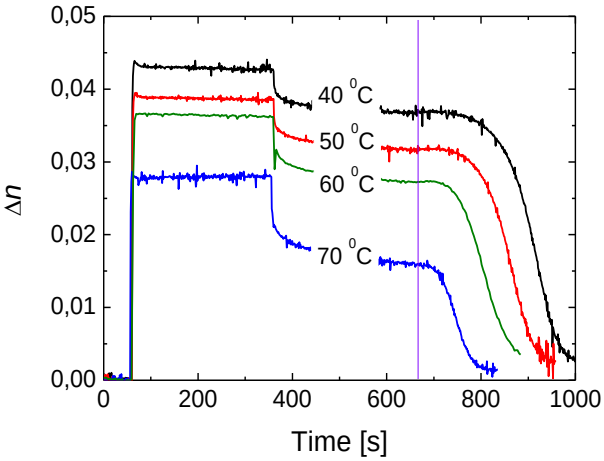

Fig. 2. Birefringence values during recording and thermal erasure. Recording temperatures are: 40°C, 50°C, 60°C, 70°C . The vertical line at 660 seconds indicates the start of temperature increase.

As seen from Fig. 2, the maximal induced birefringence is Δn = 0.045 at starting temperature 40°C and decreases with increasing the starting temperatures. However, the response time τ, as defined in Ref. 5, decreases as well, which is a desirable effect for many applications. Also we introduce a parameter R [%] as the ratio between the birefringence after 300 s of relaxation and the maximal value of the birefringence for the given recording temperature. It gives us information about the memory of the material and according to our results R decreases too. It is interesting that we observe the same value of $T_{50\%}$ – around 75 °C, though the recording temperature increases. As $T_{50\%}$ is higher than 70 °C, there is still residual anisotropy even for the sample with relaxation at 70 °C.

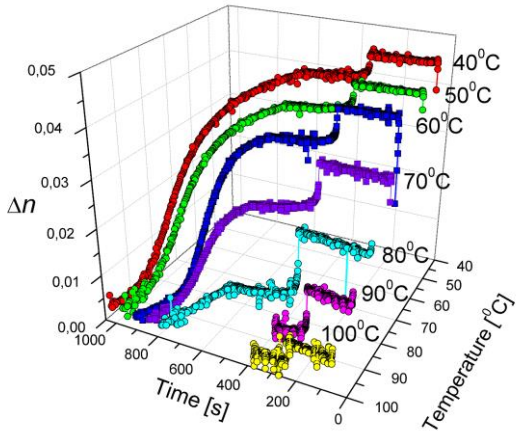

Fig. 3. 3D graph for all starting temperatures.

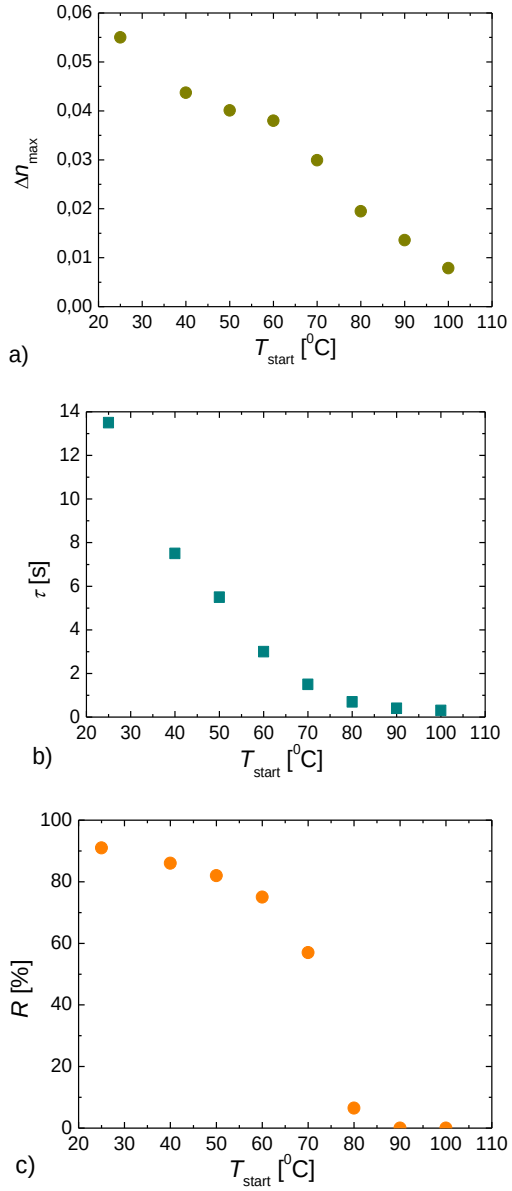

Fig. 4. Recording temperature dependences of (a) the maximal induced birefringence, (b) response time, and (c) parameter *R*.

In comparison, for higher starting temperatures (80, 90 and 100 °C) no residual birefringence after relaxation is observed. For these experiments we obtain very fast response, less than 1 second. All the results are visualized in a 3D Graph on Fig. 3 and summarized in Fig. 4.

As seen from the graphs, even at higher temperatures we are still able to induce birefringence while we illuminate the film with the recording laser.

The birefringence decrease at higher temperatures, as shown in Fig. 4(a), indicates the possibility to achieve an increase of birefringence at lower temperatures (below 20°C), which will be subject to our further studies. Fig. 4(b) shows a rapid decrease of the response time. At 60 °C the response is more than 4 times faster, than at room temperature, namely it drops from 13.5 s at 25°C to 3 s at 60 °C. We should also note on Fig. 4(c) the significant decrease at 70 °C of the parameter *R*, which reflects the memory properties of the material. It is reduced nearly ten times between 70 °C (R = 57%) and 80 °C (R = 6.5%). This temperatures are very close to the temperature of half-erasure $T_{50\%}$ = 75 °C.

CONCLUSIONS

In conclusion we can summarize that the parameters of the induced birefringence strongly depend on the temperature. The maximal birefringence and the parameter *R* decrease when increasing the temperature. On the other hand, the response time τ is reduced at higher temperatures and this gives us the opportunity to choose the optimal combination of parameters for a given application. We should also note, that the temperatures of half- and full erasure ($T_{50\%}$ and T_{erase}) remain the same for all starting temperatures.

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ФОТОИНДУЦИРАНО ДВУЛЪЧЕПРЕЧУПВАНЕ В ТЪНКИ АЗОПОЛИМЕРНИ СЛОЕВЕ ЗАПИСАНИ ПРИ РАЗЛИЧНИ ТЕМПЕРАТУРИ

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(Резюме)

В тази работа са изследвани характеристиките на поляризационен запис и изтриване в тънък азополимерен слой в зависимостт от различните стартови температури на образеца. За записа на фотоиндуцираното двулъчепречупване е използван лазер с дължина на вълната 444 nm. Изтриването на записите става чрез загряване на образеца. Успешно е реализиран запис на двулъчепречупване при различни температури от 25 до 100°C. Представена е тримерна (3D) графика за визуализация на експерименталните данни. Фотоиндуцираното двулъчепречупване е изчислено на базата на параметрите на Стокс, регистрирани в реално време през целия експеримент. Това изследване ни позволява да определим оптималните условия за запис при по-високи температури с цел да постигнем най-кратко време на отклик или максимално двулъчепречупване.