Research Article

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Improvement of the photoinduced birefringence in azopolymer PAZO doped with TiO_2 nanoparticles via thermal treatment

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Abstract: We present a study of the photoinduced birefringence in nanocomposite films of the azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]) doped with TiO_2 nanoparticles (NP) with different concentrations before and after thermal annealing. The NP represent nanopowder with primary particle size 21 nm. The concentration of the NP was varied from 0% (non-doped azopolymer film) to 5 wt%. The thermal process, applied to the nanocomposite films, includes 1 h heating at 200°C. Previous studies of PAZO show that the polymer is stable up to 270°C. We study the dependence of the maximal birefringence induced with He-Cd laser (λ = 442 nm) on the concentration of the TiO_2 NP in the azopolymer thin films as well as thermal effect on the absorbance spectra of the thin films. As indicated by our results, the birefringence is higher for the thermally annealed samples. An increase of the photoinduced birefringence is also observed for the nanocomposite layers with 1% NP for the non-annealed films, and with 2% NP for the annealed films.

Keywords: nanocomposite, azopolymer, birefringence, thermal annealing

1 Introduction

Azopolymers are known as one of the most efficient media for polarization recording [1–3]. Because of the *trans-cis-trans* isomerization and reorientation of the molecules on illumination with polarized light, a significant photoinduced birefringence (Δn) can be achieved. Many researchers have studied this effect and its applications [4–6]. For example, Martinez-Ponce suggested a mathematical model, based on the Mueller matrices to investigate the properties of polarization holographic gratings [5]. The mechanism of the photoinduced motions in azopolymers was viewed by Natansohn and Rochon who suggested three kinds of motions – molecular, nano- and macro- motions [6]. Obtaining high values of the photoinduced birefringence in those materials would allow further development of polarization holography and creation of unique polarization optical devices.

One of the recent approaches is to produce nanocomposite films, containing azopolymer doped with different nanoparticles (NP) [7–9]. Our recent investigations on similar nanocomposites with ZnO, Goethite and silica NP have shown an increase of the Δn [10–12]. Although there is no yet established model to explain this effect, a possible mechanism is suggested. It assumes that the light scattered from the NP is able to address the "off-plane" azochromophores, to reorient them, and thus to contribute to the birefringence increase [10]. The scattering of light by small particles has been discussed in [13, 14].

This encourages us to continue with investigations of similar nanocomposites. The azopolymer used in the present study is PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzene-sulfonamido]-1,2-ethanediyl, sodium salt) and is already investigated by our group [15, 16]. For doping NP, we chose nanoparticles of TiO_2 (21 nm size) because of the large difference between the refractive indices of PAZO and TiO_2. Our goal is to produce samples with various concentrations of TiO_2 NP in PAZO in order to find the optimal concentration of the NP that leads to highest increase of Δn. Literature survey shows

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that there are other researchers that have studied TiO_2 NP, including the effect on the photoinduced Δn in azopolymer. For example, Fernandez *et al.* [7] investigated the influence of the TiO_2 NP on the optical and electrical properties of thin films of PAZO prepared by sol-gel method. Our method of thin film preparation is different. We use spin-coating technology and investigate concentrations of the TiO_2 NP between 0 and 5 wt%. The present results are compared with similar azopolymer-based nanocomposites in our previous work [10, 12].

2 Thin films preparation

In the present study, commercially available azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt) was used (Sigma Aldrich, #346411). The TiO_2 NP were also purchased (Sigma Aldrich, #718467) and they represent nanopowder with 21 nm primary particle size (TEM), as indicated in the product specifications. As no specific shape is mentioned, we consider them to be nanospheres.

To prepare the nanocomposite thin films, for each desired NP concentration the following procedure was used. Initially, 40 mg PAZO were dissolved in 300 µL distilled water under stirring for 1 hour at 40°C and 1700 rpm using magnetic stirrer IKA® RET B 8000. At the same time, a dispersion of the TiO_2 NP in distilled water was prepared by sonication (Elmasonic P 60 H, frequency 37 kHz at room temperature for 1 hour). 100 µL of the NP dispersion was then added to the azopolymer solution and the resulting suspension was sonicated under the same conditions for 1 hour. The concentration of the PAZO in water is chosen according to our previous research [15], so we expect the thickness of the films to be approximately 400-500 nm.

Each film is prepared by depositing 200 µL of the suspension on a glass substrate (BK7) and then spin coating at 1500 rpm for 30 seconds. In this way we obtain thin films with 5 different concentrations (0, 0.5, 1, 2, and 5 wt%) of the TiO_2 NP in PAZO. For each concentration, we have prepared two series of samples. One of the series was heated for an hour at 200°C. The birefringence measurement is performed approximately one hour after that procedure. The other series was not annealed. Thus, we can make a comparison between annealed samples (AS) and non-annealed samples (NAS) at the given concentration. From previous investigations, we know that the PAZO polymer is stable up to 270°C and therefore the thermal treatment does not affect the optical properties of the azopolymer [16, 17].

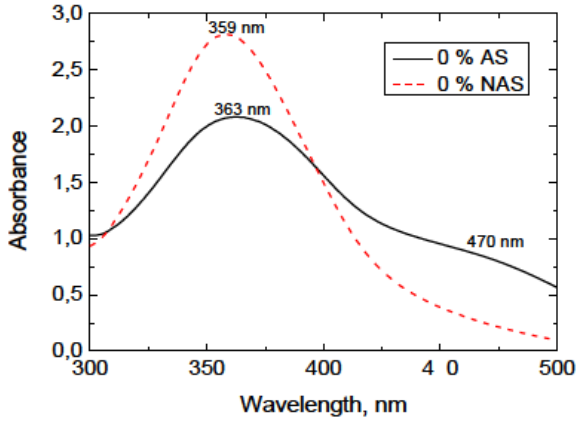
3 Characterization of the samples

The photoinduced birefringence was calculated using the following equation [1, 16]:

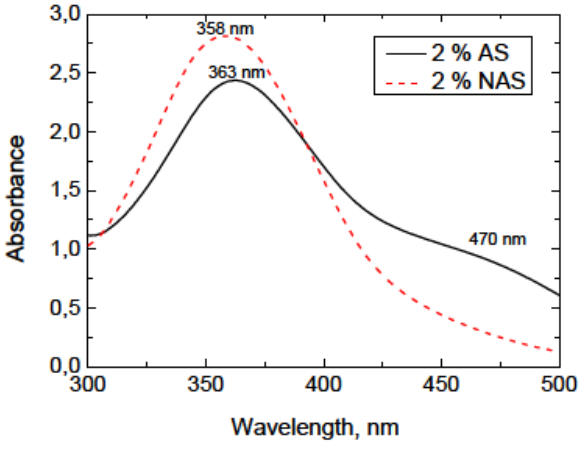
$$\Delta n = \frac{\lambda}{2\pi d} \arctan\left(\frac{S_3}{S_2}\right), \tag{1}$$

where S_2 and S_3 are the Stokes parameters, λ is the wavelength of the probe laser and d is the thickness of the sample. As can be seen, it is very important to determine precisely the thickness of the samples. All the thicknesses were measured by optical thin films analyzer "Filmetrics F20". The measured values for all samples are in the range 450 – 550 nm.

We measured the absorbance spectra (using spectrophotometer CARY05) of the studied samples. Figure 1 presents the spectra of the thermally annealed sample (AS)



(a)



(b)

Figure 1: Absorbance spectra of the samples: a) with 0 wt% TiO_2 in PAZO and b) with 2 wt% TiO_2 NP in PAZO. The red dashed lines corresponds to the non-annealed samples (NAS) and the black solid lines to the samples annealed (AS) at 200°C.

and non-annealed sample (NAS) with 2 wt% of TiO_2 NP in PAZO as well as the spectra of the annealed and non-annealed films without NP.

Before thermal treatment, typical bands are observed related to the azopolymers. The bands at λ_{max} = 358 (359) nm are characterized by $\pi \rightarrow \pi^*$ transition of azo groups, where the spectra clearly indicate that there are no shifts due to the addition of NP. After thermal annealing, in both causes there are shifts of $\pi \rightarrow \pi^*$ bands with 4 nm towards lower energy (bathochromic effect) as well as decrease of absorption bands (hypochromic effect). The bands of n $\rightarrow$ π transitions, which always appear above 400 nm show weak bathochromic and hyperchromic (increase of the intensity) effects. Based on the observed results for the non-doped and doped samples, the following conclusions can be drawn: (i) the NPs do not affect the polymer after thermal annealing; (ii) after thermal annealing probably sub molecular packing arranged the polymer dye as resulting strong π-π stacking is indicated by hypochromic effect of $\pi \rightarrow \pi^*$ bands (forbidden symmetry); (iii) n $\rightarrow$ π transitions are considerably increased due to the extra polarization of π electrons by non-bonding electron pair of azo nitrogens (allowed symmetry).

4 Measurement of the photoinduced birefringence

The experimental setup for measuring the photoinduced birefringence is shown in Figure 2. The pump laser used is He-Cd laser (Kimmon Koha) with λ = 442 nm (vertical polarization). The power of the pump beam on the sample is 100 mW and the irradiated area is approximately 0.1 cm^2. Diode laser with λ = 635 nm (linear polarization at 45°) was used as probe laser. The probe beam passes through the sample and its polarization state is measured by PAX5710 Polarization Analyzing System (Thorlabs), which allows us to determine the Stokes parameters in real time. The probe laser beam is exactly perpendicular to the samples.

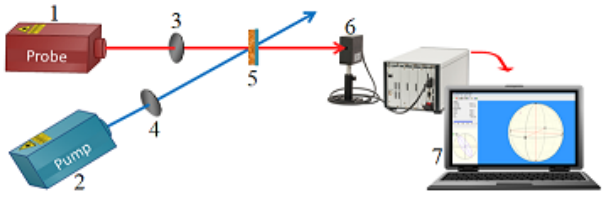
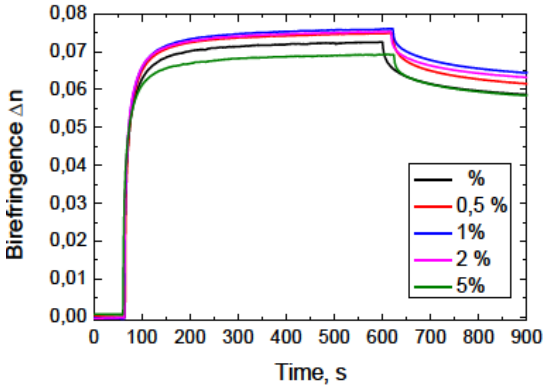


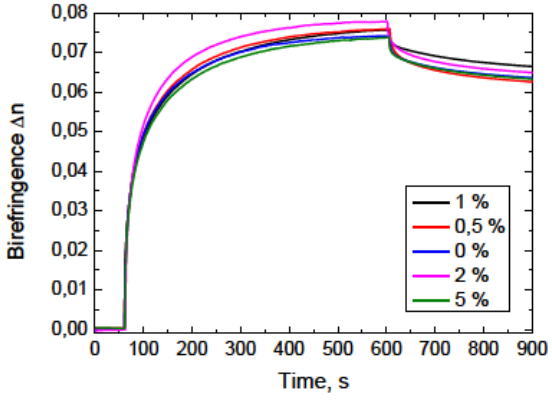
Figure 2: Experimental setup for measuring the birefringence. 1 – probe laser (635 nm), 2 – pump laser (442 nm), 3 – polarizer oriented at 45°, 4 – vertical polarizer, 5 – sample, 6 – polarimeter, 7 – computer

The experimental procedure for every sample is the following: 1-minute measurement of the background signal of the probe laser. At that time, the film has to be isotropic because all the azomolecules are oriented at random. After that, we turn on the pump laser and illuminate the sample. When the pump laser is turned on, the processes of isomerization and reorientation of the azomolecules start and because these processes are selective on the angle between the axis of the azomolecule and the polarization of the laser, the birefringence starts to increase. After 9 minutes saturation is reached and then the experiment continues with 5 minutes of relaxation when the pump laser is turned off again. Using Eq. (1), we calculate $\Delta n(t)$ and can determine the maximal photoinduced birefringence (Δn_{max}) and the response time (τ), defined as the time to reach 80% of the maximal Δn.

The birefringence kinetics for the AS and NAS are shown in Figure 3.

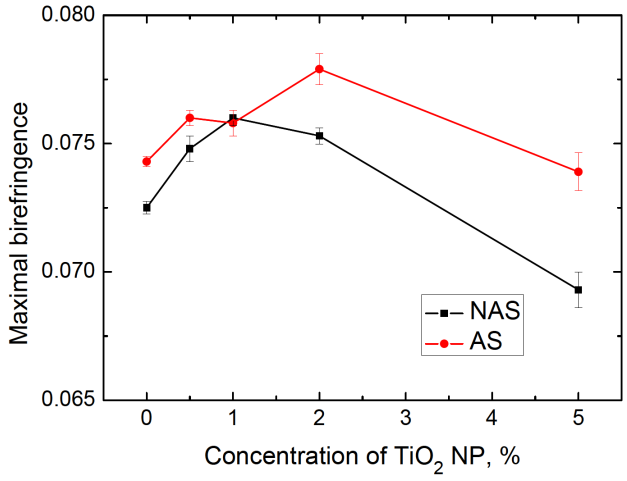


(a)

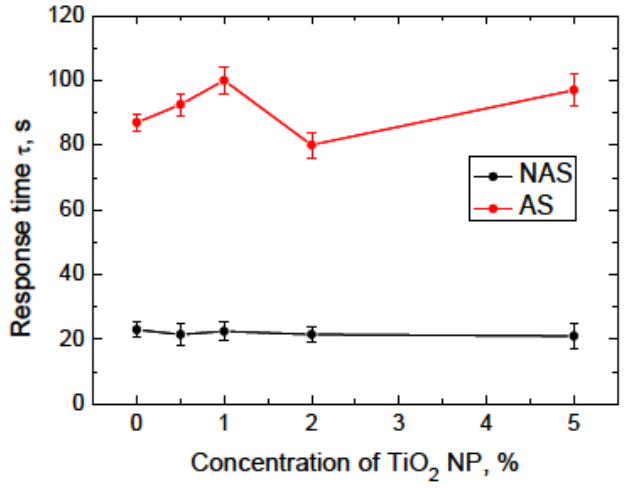


(b)

Figure 3: The dependence of Δn on time: (a) for the non-annealed samples, and (b) for the annealed samples.



(a)



(b)

Figure 4: Dependence on the NP concentration of (a) the maximal birefringence, and (b) the response time.

These experimental results are summarized in the next two graphs, where the dependences of the maximal value of the photoinduced birefringence and the response time on the NP concentration are presented.

As seen in Figure 4, we achieve maximal photoinduced birefringence for 1 wt% for the NAS and for 2 wt% for the AS. The values of the Δn for the AS are higher than for the NAS. On the other hand, the NAS have significantly lower response time.

5 Conclusion

We have prepared two series of samples – annealed and non-annealed – with five different concentrations of the TiO_2 nanoparticles in the azopolymer PAZO. The measured thicknesses of all samples were in the range 450-550 nm. The spectra of the annealed samples have higher absorption above 400 nm and lower in the range 300 – 390 nm. For the non-annealed samples, there is a peak of photoinduced Δn for 1 wt.% of TiO_2 NP and for the annealed samples the peak is at 2 wt.%. That is the difference with the investigations of Fernandez *et al.* [7], who prepared samples with 0, 10, 20, 30 etc. wt% of TiO_2 NP and showed that the sample with pure PAZO has the largest Δn and with the increase of the TiO_2 concentration Δn decreases. In addition, the annealed samples we studied had higher value of Δn for all concentrations, but non-annealed samples had lower response time.

These results about the NP influence on the photoinduced birefringence are in agreement with our earlier studies of azopolymer-based nanocomposites. In [10, 12], where ZnO and SiO_2 NP were used, a maximum of Δn for concentration in the range 0.5 – 2 wt.% was observed. As suggested in [10], a possible reason for the birefringence increase on doping the azopolymer with small concentrations of NP could be the scattering of light by the NP that allows to excite and reorient the off-plane azochromophores.

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