

Photoinduced variation of the Stokes parameters of light passing through thin films of azopolymer-based hybrid organic/inorganic materials

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Abstract. Hybrid materials synthesized by combining polymers and inorganic nanoparticles (NPs) have received considerable attention recently due to their advantageous electrical, optical, or mechanical properties. Here we present a polarimetric study of thin films prepared from photoanisotropic hybrid materials: azopolymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]) doped with different concentrations of ZnO NPs with sizes below 50 nm. To obtain full information about the polarization response of these thin films, we determined the kinetics of the Stokes parameters of light passing through the films on illumination by linearly polarized light within the absorption band of the material, namely 473 nm. Using the Stokes parameters, the birefringence values were calculated as a function of time and compared for the films with different NP concentrations.

1. Introduction

The research on azobenzenes during the last decades revealed their remarkable potential for a broad spectrum of applications: polarization holography [1,2], optical data storage [3-6], formation of surface relief gratings [7,8] etc. Using polarization holography makes it theoretically possible to achieve 100 % diffraction efficiency even in thin films of photoanisotropic media [2]. Being able to record the polarization state of light, azobenzenes also enable one to apply polarization multiplexing and increase the density of recording [9].

The most important characteristic of any photoanisotropic media, including all azopolymer based materials, is the maximal value of the photoinduced birefringence Δn_{\max} . Different methods have been exploited to determine this parameter for a given material. One of the most informative and reliable is to measure the Stokes parameters of light passing through the spot on the sample illuminated by the recording beam [5,10]. Therefore, this method was applied in our present study.

Recent reports have indicated that doping nanoparticles in azopolymers can increase the value of the photoinduced birefringence Δn_{\max} [11-14]. Thus, we synthesized hybrid organic/inorganic materials based on an amorphous azopolymer (PAZO) doped with different concentrations of ZnO

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nanoparticles. We calculated the kinetics of birefringence by measuring the photoinduced variation of the Stokes parameters of light passing through thin films of our composite materials.

2. Experimental procedures

2.1. Azopolymer matrix and preparation of the thin films

The azopolymer used as organic host in our hybrid samples was poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] or shortly PAZO. The azopolymer is commercially available from Sigma Aldrich. Its chemical structure is shown in figure 1a. Water solubility is an important advantage of this polymer. The nanoparticles from ZnO (Sigma Aldrich) have an average diameter <50 nm (figure 1b).

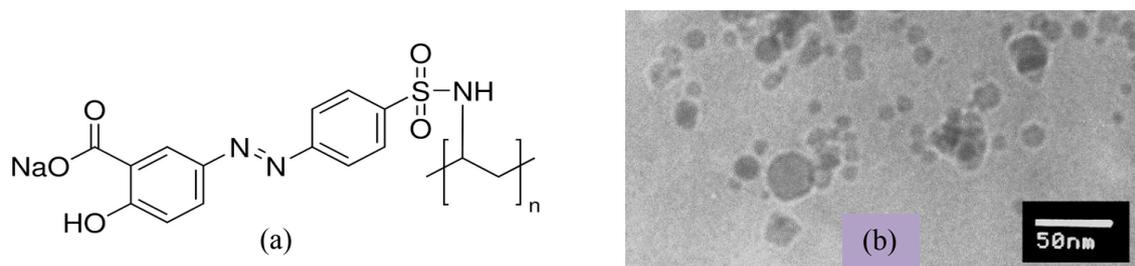


Figure 1. (a) Chemical structure of the azopolymer matrix. (b) TEM image showing the NPs size.

For this study, thin film samples were produced with different concentrations of the ZnO NPs in the azopolymer. Initially the azopolymer was dissolved in water and the nanoparticles were separately dispersed in water by sonication. The polymer solutions and the nanoparticles dispersions were then combined to achieve the desired concentration (C) of the ZnO nanoparticles in the azopolymer, namely $C = 0\%$ (or non-doped azopolymer), 0.5, 1, 2, 5 and 10%. The resulting dispersions were deposited on glass substrates and spin coated for 30 seconds at 1500 rpm. The substrates had been cleaned and polished in advance.

2.2. Thickness measurement

The precise value of the samples thickness, denoted as d , is a crucial parameter for accurate determination of the thin films optical properties, namely, the absorbance spectra and the birefringence. The thickness was measured by a high-precision Talystep profilometer with 10 nm accuracy. A groove was made on the surface of each sample, inside which the nanocomposite film was removed, with the distance between the “plateau” and the bottom of the groove corresponding to the layer’s thickness, as shown in figure 2. In order to ensure that the glass substrate was not affected, we used a tip with hardness lower than the hardness of glass.

Although all the samples contained the same amount of azopolymer, their thicknesses varied slightly and were in the range 410 – 450 nm.

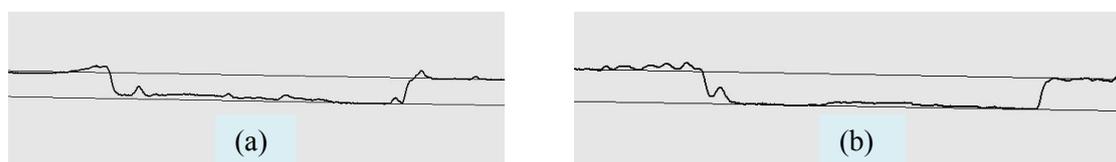


Figure 2. Typical thickness profiles: (a) $C = 2\%$, $d = 410$ nm, (b) $C = 10\%$, $d = 440$ nm.

2.3. Spectra of the absorption coefficient

The absorbance spectra were determined by a UV-Vis-NIR Cary 5E spectro-photometer (Varian). The normalized spectra of the transmittance $T_{norm}(\lambda)$ were directly measured and then the absorption coefficient spectra $\alpha(\lambda)$ were calculated using the Beer-Lambert law i.e. $\alpha = -(1/d)\log(T_{norm})$ (figure 3). The reflections from the front and back side of the samples were compensated by placing

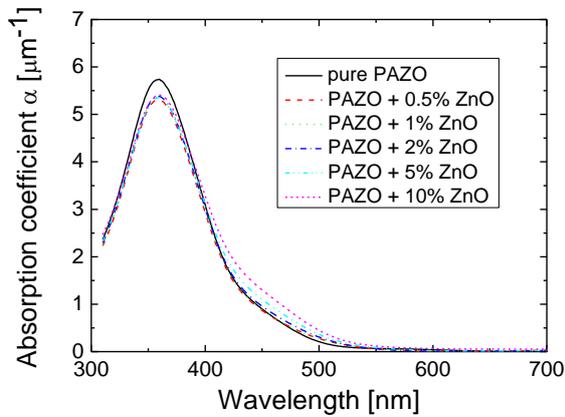


Figure 3. Absorption coefficient spectra for all samples with $C = 0, 0.5, 1, 2, 5$ and 10% .

a glass substrate in the reference arm of the spectrophotometer. Thus, the absorption coefficient spectra characterized the properties of the material and were not influenced by the film thickness, as was the absorbance A .

Doping the azopolymer with ZnO NPs did not shift the peak of the spectra which was at 359 nm for all samples. On the other hand, there was some increase of the absorbance with the increase of the concentration in the 400-500 nm wavelength range. It can be related to an interaction between the NPs and the azopolymer matrix. Still, the scattering was low even for the sample with the highest

NPs concentration (10%), which was confirmed by the low absorbance in the range 600-700 nm.

The spectra also showed that the pump laser wavelength (473 nm) was absorbed by the samples, but at the same time, being far from the absorbance peak, the laser light could penetrate and influence the entire film. In contrast, the light at the probe beam wavelength (633 nm) was virtually not absorbed by the samples.

2.4. Kinetics of the Stokes parameters

The Stokes parameters contain all the information about the polarization state of light. Knowing the state of polarization of the incident light and measuring the Stokes parameters of the beam after the sample, we can determine its photoinduced birefringence [2]:

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

where λ is the wavelength of the probe laser, d is the film thickness, and S_2 and S_3 are components of the Stokes vector (S_0, S_1, S_2, S_3).

Birefringence was induced in the sample by a vertically polarized beam from a diode-pumped solid-state (DPSS) laser ($\lambda_{rec} = 473$ nm, intensity 400 mW/cm²). The probe beam from a He-Ne laser ($\lambda_{probe} = 633$ nm) was linearly polarized at 45°. It passed through the spot on the sample illuminated by the pump laser; the Stokes parameters of the output beam were measured by a PAX5710 Polarization Analyzing System (Thorlabs). A screenshot illustrating the device interface is given in figure 4a, while the kinetics of the Stokes parameters for the sample with $C = 10\%$ is presented in figure 4b.

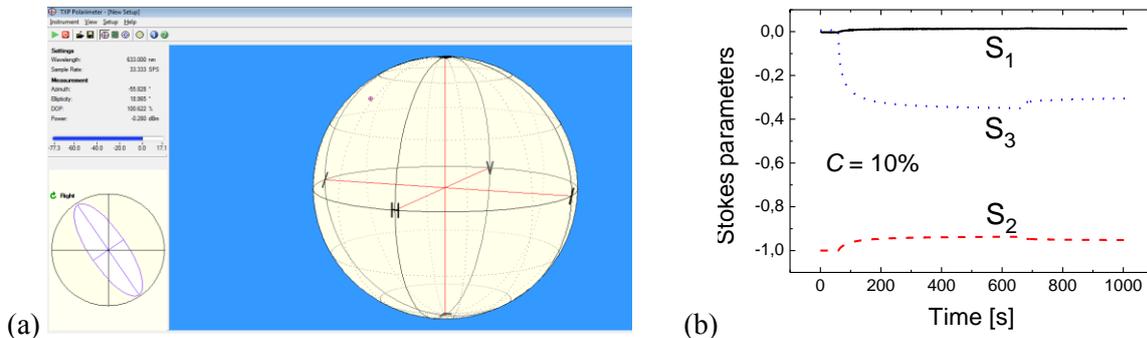


Figure 4. (a) Polarimeter interface. (b) Example of the Stokes parameters kinetics.

3. Results and discussion

Using equation (1), we can obtain the kinetics of birefringence shown in figure 5a.

As seen in figure 5b, doping the azopolymer with ZnO nanoparticles led to an increase of the maximal value of the photoinduced birefringence. In order to quantify this increase or enhancement, we can use the “Increase Ratio” parameter, defined as follows [14]:

$$IR(C) = \frac{\Delta n_{\max}(C) - \Delta n_{\max}(0)}{\Delta n_{\max}(0)} \cdot 100\% , \quad (2)$$

where $\Delta n_{\max}(C)$ is the maximal saturated value of the photoinduced birefringence for nanocomposite film with concentration of the NPs relative to the azopolymer C , and $\Delta n_{\max}(0)$ is the maximal saturated value of the photoinduced birefringence for the non-doped (or “pure”) film.

In the present study, the maximal $IR = 34\%$ was obtained for the sample with 10% concentration of the ZnO NPs in the PAZO polymer. It is interesting to compare this with our earlier results for nanocomposites of P₁ azopolymer and ZnO NPs [12]. Then, we observed a peak at 0.5% followed by a decrease of the birefringence at higher dopant concentrations. The reason for the continued increase of the birefringence in the PAZO + ZnO NPs even at high concentrations of the dopant is probably the better refractive index matching between the PAZO polymer used here and the nanoparticles, leading to lower scattering of the hybrid samples.

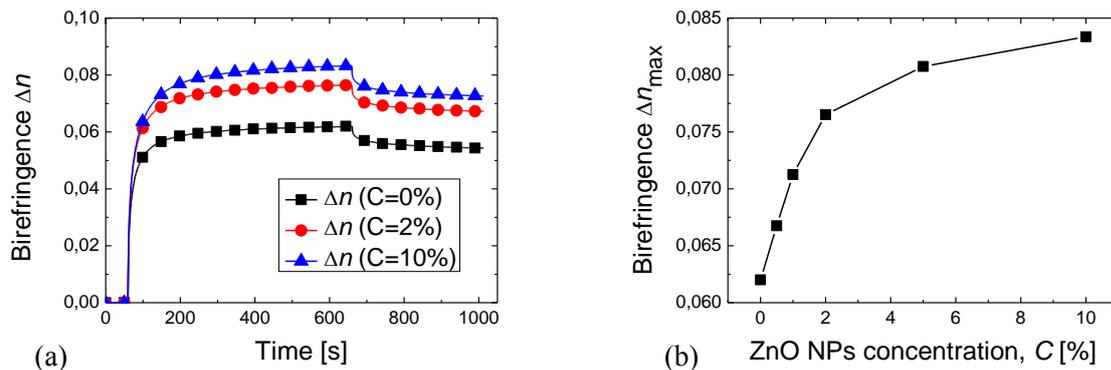


Figure 5. (a) Birefringence kinetics for samples with ZnO NP concentrations $C = 0, 2$ and 10% . (b) Dependence of the maximal value of the birefringence on the concentration for all samples.

4. Conclusions

In this article we presented a polarimetric study of thin films prepared from photoanisotropic hybrid materials: an azopolymer denoted as PAZO doped with different concentrations of ZnO NPs: $C = 0\%$ (or non-doped azopolymer), 0.5, 1, 2, 5 and 10%. Measuring the photoinduced variation of the Stokes parameters of light, we calculated the kinetics of birefringence and its maximal value for each NPs concentration. The highest increase ratio of 34% was obtained at 10% concentration of the ZnO nanoparticles.

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