Photoinduced birefringence in azopolymer doped with Au nanoparticles

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Abstract. A study of the photoinduced birefringence in nanocomposite thin films of the azopolymer PAZO (poly[1-{4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido}-1,2-ethanediyl, sodium salt]) doped with gold (Au) nanoparticles (NPs) is presented. The NPs are with a spherical shape and mean size 10 nm. Transmission electron microscopy (TEM) and Dynamic Light Scattering (DLS) analyses of the particles have also been made. Samples were prepared with five different concentrations of the NPs in the azopolymer films varying from 0 (non-doped azopolymer film) to 4 a.u. (1 a.u. = 0.015 wt %). Birefringence was induced by a He-Cd laser with a wavelength 442 nm and measured with probe Diode Pumped Solid State (DPSS) laser at 635 nm. An increase of the photoinduced birefringence in doped azopolymer nanocomposite films compared to samples of undoped azopolymers was observed. The maximal enhancement was achieved for films with 2 a.u. of Au NPs.

1. Introduction

Due to important applications in optical storage, all-optical switching, diffractive optical elements and optical communications, and ability to record the polarization state of light, the azobenzene materials have provoked considerable attention [1–5]. The anisotropic photo response of an azobenzene material is usually characterized by the value of the photoinduced birefringence (Δn). This parameter determines also the diffraction efficiency when holographic grating is recorded in the film. There are various methods to obtain optical materials with large photoinduced birefringence. One of these approaches is to use nanocomposite materials, where different nanoparticles (NPs) are incorporated in the azopolymer matrix. These nanocomposites exhibit enhanced morphological, chemical and physical properties in comparison with the undoped azopolymer. The first azopolymer-inorganic material hybrid system, in which the photoinduced anisotropy has been studied, was reported by Reshetnyak et al. [6]. Different composite materials were fabricated in the past few years by combining azobenzene derivatives with inorganics, and these composites showed novel properties [7-15]. In our previous studies, we have observed that inclusion of inorganic non-metallic nanoparticles in azopolymer layers leads to considerable photo response improvement expressed as increase of the maximal birefringence value and reduction of the recording time in comparison to the non-doped samples [16, 17]. It has also been shown that the optical properties of organic molecules can be tuned using noble-metal
nanoparticles doped azo-based systems [18-22]. For example, Zhang et al [23] studied anisotropic properties of methylorange/Au NPs composites and observed increase of birefringence. In this work we focus on organic/inorganic nanocomposite materials prepared by incorporating Au NPs in the azopolymer poly[1-{4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], or shortly PAZO, as a typical water-soluble azobenzene polymer and particularly on the comparison of the birefringence in these hybrid materials and the non-doped azopolymer. The characteristics of recording and relaxation of Δn in samples of non-doped azopolymer PAZO and PAZO with different concentrations of gold NPs were investigated.

2. Materials and methods

2.1. Nanocomposite samples preparation
The azopolymer PAZO used as organic host in our hybrid samples is an amorphous substance, commercially available from Sigma-Aldrich with chemical structure shown in Fig. 1. The polymer is water-soluble, which is an important advantage for the nanocomposite preparation.

![Figure 1. Chemical structure of the azopolymer PAZO](image)

The Au nanoparticles are also commercially available from Sigma-Aldrich. The following procedure is used to prepare the nanocomposite thin films: Initially the azopolymer is dissolved in water. Precise quantities of the polymer solution and the NPs suspension are mixed to achieve the desired concentration of the Au NPs in the azopolymer. Samples are prepared with five different concentrations of the NPs in the azopolymer varying from 0 (undoped azopolymer film) to 4 a.u. (1 a.u. = 0.015 wt %). The resulting dispersions are deposited on preliminary cleaned and polished glass substrates and spin coated for 30 seconds at 1500 rpm.

2.2. Thickness measurement
The precise value of the sample thickness (d) is a very important parameter, especially for accurate determination of the thin film’s birefringence. The thickness is measured by high-precision Talystep profilometer (Taylor Hobson) with 1 nm vertical and 0.1 μm horizontal resolution. A groove is made on the surface of each sample, inside which the nanocomposite film is removed and the distance between the “plateau” and the bottom of the groove corresponds to the layer’s thickness.

2.3. Absorbance measurement
The transmittance T(λ) of each layer is measured by a UV-Vis-NIR Cary 5E spectrophotometer (Varian). The absorbance α is then determined using the Beer-Lambert law i.e. \( \alpha = -(1/d) \log(T) \).

2.4. Morphology and size distribution characterization of the Au NPs and nanocomposites
The morphology of the Au NPs and nanocomposite layers before and after laser irradiation is investigated by Transmission Electron Microscopy (TEM) using the microscope JEOL JEM 2100 (JEOL Ltd, Japan) at accelerating voltage 200 kV. For TEM observation, a drop of Au NPs suspension was fixed on standard Cu-grid covered with amorphous carbon membrane and dried at ambient conditions. The nanocomposite layers were exposed to hydrofluoric acid (HF) vapors, removed from
the glass substrate in distilled water and transferred onto standard Cu-grid. The size of NPs is determined by Dynamic Light Scattering (DLS-Zeta Sizer Nano-ZS, Malvern, UK).

2.5. **Birefringence kinetics measurement**

Birefringence is induced in the samples by a vertically polarized beam from He-Cd laser ($\lambda_{\text{rec}} = 442$ nm). The probe beam from a diode-pumped solid-state (DPSS) laser ($\lambda_{\text{probe}} = 635$ nm) is linearly polarized at 45°. It passes through the illuminated by the pump laser spot on the sample and the parameters of Stokes of the output beam are measured by a PAX5710 Polarization Analyzing System (Thorlabs). 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 [3]:

$$\Delta n = \frac{\lambda}{2nd} \arctan \left( \frac{S_3}{S_2} \right)$$

where $\lambda$ is the wavelength of the probe laser, $d$ is the film thickness, and $S_2$ and $S_3$ are two of the four components of the Stokes vector.

3. **Results and discussion**

TEM analysis revealing the morphology of Au NPs is presented in Fig 2a, as well as the morphology of nanocomposite layers before and after recording with polarized light – in Figure 2c and d, respectively. As seen, the Au NPs have spherical shape and average diameter about 10 nm as demonstrated in Fig. 2b by DLS analysis. It is also seen that the NPs have narrow size distribution.

**Figure 2.** a) TEM image of morphology of Au NPs at magnification 100 000x, b) DLS data for the size distribution of Au NPs, c) TEM images of the nanocomposite before exposure and d) after exposure with linearly polarized light at magnification 40 000x
The TEM study of the nanocomposite material with concentration of 2 a.u. of the gold NPs in the azopolymer PAZO revealed that the Au NPs are homogeniously distributed in the polymer matrix as visualized in Fig. 2c. After irradiation with linearly polarized light, the Au NPs remain still homogeniously distributed (Fig. 2d). Moreover, additional honeycomb-like domains appeared as a result of the polymer irradiation. This is probably due to trans-cis-trans isomerisation and reorientation of the azobenzene molecules.

In Figure 3 the spectra of absorbance are presented for samples with different concentration of Au NPs in the polymer. The peak of absorption is at 358 nm for all samples. Hence, doping the azopolymer with Au NPs does not shift the absorbance peak. On the other hand, there is an increase of absorbance for the hybrid materials in the 320-500 nm wavelength region.

**Figure 3.** Spectra of absorbance for samples with 0, 1, 2, 3 and 4 a.u. concentration of Au NPs

The spectra also show that the pump laser wavelength (442 nm, left arrow) is absorbed by the samples, but at the same time, being far from the absorbance peak, it allows laser light to penetrate and influence the entire film. In contrast, the light at the probe beam wavelength (635 nm, right arrow) is not absorbed by the samples.

Using Eq. (1), we can obtain the kinetics of birefringence shown in Fig. 4 a).

**Figure 4.** a) Birefringence kinetics for samples with Au NPs with 0, 1, 2, 3 and 4 a.u. concentration; b) dependence of $\Delta n_{\text{max}}$ on the concentration of Au NPs
It could be seen that the \( \Delta n_{\text{max}} \) value increases for the nanocomposite films compared to the non-doped sample and has the highest value at Au concentration of 2 a.u., which is more clearly seen in Fig. 4 b). This result correlates with our previous studies of azopolymers doped with ZnO and SiO\(_2\) NPs [16,17], where we have also observed an enhancement of \( \Delta n_{\text{max}} \) for the doped samples. The optimal concentration of the NPs depends on their chemical structure, size and shape. The exact mechanism leading to the increase of the birefringence is still to be clarified.

4. Conclusion

We present a polarimetric study of thin films of photoanisotropic hybrid materials based on azopolymer matrix doped with Au NPs with different concentrations. For all nanocomposite films, the value of \( \Delta n_{\text{max}} \) is higher than for the non-doped sample. The highest value of \( \Delta n_{\text{max}} \) is obtained at 2 a.u. concentration of the gold nanoparticles in the azopolymer PAZO.

Acknowledgements

This work is financially supported by contract ДН 18/5 with the National Science Fund of Bulgaria.

References

[1] Todorov T, Nikolova L and Tomova N 1984 Polarization Holography 1. A new high-efficiency organic material with reversible photoinduced birefringence Appl. Opt. 23 pp 4309–12.
[2] Natansohn A and Rochon P 2002 Photoinduced motions in azo-containing polymers Chem. Rev. 102, pp 4139-75
[3] Nikolova L and Ramanujam P S 2009 Polarization Holography (Cambridge University Press, Cambridge)
[4] Ikeda T and Tsutsumi O 1995 Optical switching and image storage by means of azobenzene liquid-crystal films Science 268 pp 1873–5
[5] Lausten R, Rochon P, Ivanov M, Cheben P, Janz S, Desjardins P, Ripmeester J, Siebert T and Stolow A 2005 Optically reconfigurable azobenzene polymer-based fiber Bragg filter Appl. Opt. 44 pp 7039–42
[6] Reshetnyak V, Shanskii L, Yaroshchuk O, Tereshchenko A, Lindau J, Pelzl G, Janovski F and Otto K 1999 Photoorientation of polymer fragments in a system azopolymer-microporous glass Mol. Cryst. Liq. Cryst. 329 pp 447-456
[7] Suda M, Nakagawa M, Iyoda T and Einaga Y 2007 Reversible photoswitching of ferromagnetic FePt nanoparticles at room temperature J. Am. Chem. Soc. 129 pp 5538–43
[8] Li X, Chon J W M, Evans R A and Gu M 2008 Two photon energy transfer enhanced three-dimensional optical memory in quantum-dot and azo-dye doped polymers Appl. Phys. Lett. 92, 063309
[9] Nishizawa K, Nagano S and Seki T 2009 Novel liquid crystalline organic-inorganic hybrid for highly sensitive photoinscriptions Chem. Mater. 21 pp 2624–31
[10] Hubert C, Rumyantseva A, Lerondel G, Grand J, Kostcheev S, Billot L, Vial A, Bachelot R, Royer P, Chang S-H, Gray S K, Wiederrecht G P and Schatz G C 2005 Near-field photochemical imaging of noble metal nanostructures Nano Lett. 5 pp 615–19
[11] Zhou J, Yang J, Sun Y, Zhang D, Shen J, Zhang Q and Wang K 2007 Effect of silver nanoparticles on photoinduced reorientation of azo groups in polymer films Thin Solid Films 515 pp 7242–46
[12] Ahonen P, Schiffrin D J, Papro’ny J and Kontturi K 2007 Optical switching of coupled plasmons of Ag-nanoparticles by photoisomerisation of an azobenzene ligand Phys. Chem. Chem. Phys. 9 pp 651–658
[13] Sidhaye D S, Kashyap S, Sastry M, Hotha S and Prasad B L V 2005 Gold nanoparticle networks with photoresponsive interparticle spacings Langmuir 21 pp 7979–84
[14] Manna A, Chen P-L, Akiyama H, Wei T, Tamada K and Knoll W 2003 Optimized photoisomerization on gold nanoparticles capped by unsymmetrical azobenzene disulfides Chem. Mater. 15 pp 20–28
[15] Wu S, Shen J, Huang J, Wu Y, Zhang Z, Hub Y, Wu W, Huang W, Wang K and Zhang Q 2010 Ag nanoparticle/azopolymer nanocomposites: In situ synthesis, microstructure, rewritable optically induced birefringence and optical recording Polymer 51 pp 1395–1403
[16] Nedelchev L, Nazarova D, Dragostinova V and Karashanova D 2012 Increase of photoinduced birefringence in a new type of anisotropic nanocomposite: azopolymer doped with ZnO nanoparticles Opt. Lett. 37 pp 2676–78
[17] Nazarova D, Nedelchev L, Sharlandjiev P and Dragostinova V 2013 Anisotropic hybrid organic/inorganic (azopolymer/SiO₂ NPs) materials with enhanced photoinduced birefringence Appl. Opt. 52 pp E28–E33
[18] Nealon G L, Greget R, Dominguez C, Nagy Z T, Guillon D, Gallani J L and Donnio B 2012 Liquid-crystalline nanoparticles: Hybrid design and mesophase structures Beilstein J Org. Chem. 8 pp 349–370
[19] Rahman Md L, Biswas T K, Sarkar S M, Yusoff M M, Yuvaraj A R and Kumar S 2016 Synthesis of new liquid crystals embedded gold nanoparticles for photoswitching properties J Colloid Interf Sci 478 pp 384–393
[20] Sidhaye D S, Kashyap S, Sastry M, Hotha S and Prasad B L V 2005 Gold nanoparticle networks with photoresponsive interparticle spacings Langmuir 21 pp 7979–84
[21] Duan J, Wang M, Bian H, Zhou Y, Ma J and Liu C 2014 Azobenzene mesogen-passivated gold nanoparticles: Controlled preparation, self-organized superstructures, thermal behavior and photoisomerization Mater. Chem. Phys. 148 pp 1013–21
[22] Karpinski P and Miniewicz A 2009 Investigation of enhancement of photoinduced reorientation of liquid-crystal molecules in the presence of azo-dye and gold nanoparticles EPL 88 56003
[23] Zhang J, He T, Wang C, Zhang X and Zeng Y 2011 Enhancement of two-photon absorption and photoinduced birefringence in methyl orange by Au nanoparticles Opt. Laser Technol. 43 pp 974–977