Photoinduced chirality in azopolymer-based nanocomposites with different TiO$_2$ nanoparticles concentrations

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Abstract. After its discovery, photoinduced chirality in azopolymer materials has been studied with growing interest because of its potential applications. According to our previous investigations, it is possible to induce chirality in an amorphous azopolymer with a high linear photoanisotropy by illumination with elliptically polarized light. In the present work, we studied the photoinduced chirality in thin nanocomposite films based on the azopolymer poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt], shortly PAZO, doped with TiO$_2$ nanoparticles with a size of about 20 nm. The thickness of the prepared films was approximately 550 nm and the concentration of the nanoparticles varied from 0 to 3 wt. %. A He-Cd laser beam ($\lambda = 442$ nm) was used, with the input ellipticity varying from $-1$ (left circularly polarized) to $+1$ (right circularly polarized). The ellipticity was set using a quarter-wave and a half-wave plates. We studied the dependences of the output ellipticity and the angle of self-rotation of the polarization azimuth on the input ellipticity. Based on the experimental data obtained, we could analyze the dependence of the self-rotation of the polarization azimuth on the concentration of the nanoparticles. The results show that small concentrations of nanoparticles lead to an enhancement of the self-rotation, hence, the chirality.

1. Introduction
The polarization sensitive materials have been one of the important fields of investigations in optics in the last decades [1-5]. Because of the trans-cis-trans isomerization and subsequent reorientation of the chromophores, azopolymers have significant linear photoinduced birefringence caused by linearly polarized light. Later, it was found that light circular birefringence is also induced in azopolymers on illumination with elliptically polarized [6]. As known from theory, the circular birefringence is proportional to the rotation of the azimuth $\Delta \theta$ of the light passing through an optically active media [7]. This effect is especially intriguing in the case of amorphous azopolymers because they do not have chiral groups in their chemical structure. In order to explain this phenomenon, Nikolova et al. investigated the self-induced rotation of polarized light passing through azopolymer thin films depending on the input ellipticity [8]. It was shown that supramolecular chiral structures are formed upon illumination with elliptically polarized light causing rotation of the input azimuth at an angle $\Delta \theta$. The azimuth rotation strongly depends on the ellipticity of the input light.
The photoinduced chirality can be used for many applications, as photo-switches [9-13], in many different areas – optical information storage, telecommunications, etc. Thus, the main subject of this work is studying and improving the properties of the photoinduced chirality. We prepared thin films of the PAZO azopolymer, which has a high photoinduced linear birefringence when doped with different amounts of spherical nanoparticles of TiO$_2$, and investigated the dependence of the properties of the photoinduced chirality on the concentration of the nanoparticles.

2. Experimental

The chemical structure of the polymer we used – poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt], PAZO in short, is shown in figure 1. The polymer contains azobenzene chromophore, which is responsible for the trans-cis-trans photoisomerization processes in the polymer.

We also used nanoparticles of TiO$_2$ with a size of 21 nm and a spherical shape. As shown by us earlier [14], small concentrations of these nanoparticles can increase the linear birefringence of PAZO. We prepared thin-film samples with four different concentrations of nanoparticles (0, 1, 2 and 3 wt. %) by spin-coating on a glass substrate (BK7) at 1500 rpm a suspension containing 10 mg of PAZO dissolved in 200 µl methanol and different amounts of the nanoparticles for every sample in order to obtain the desired concentrations relative to the azopolymer. The suspensions were sonicated before the spin-coating procedure in order to ensure the homogeneous distribution of the nanoparticles in the suspension.

Further, we measured the absorbance spectra of our samples on a CARY 05 spectrophotometer (Varian) and determined their thickness by an F20 Optical Thin-Film Analyzer (Filmetrics). In the left-hand side of figure 2 we show the absorbance spectrum of the sample with 2 wt. % of NPs. Bearing in mind these spectra, we chose to use a He-Cd laser as a pump laser, as its wavelength (442 nm) is well absorbed by the thin films. As known, the magnitude of azimuth rotation is proportional to the thickness of the sample [8]:

\[ \Delta \theta = \frac{2\pi \Delta n}{\lambda} \frac{e_{in}}{1-e_{in}} \, d, \]

where \(\Delta n\) is the linear birefringence, \(\lambda\) is the wavelength of the exciting light, \(e_{in}\) is the input ellipticity and \(d\) is the sample thickness. For this reason, special care was taken to measure the film thickness exactly in the spots that were later used in the photoinduced chirality experiments.
Figure 2. Left-hand panel – the absorbance spectrum of the sample with 2 wt. % NPs. Right-hand panel – the experimental optical setup for photoinduced chirality measurement.

The main experimental setup is shown in figure 2 in the right-hand side. The polarization of the laser beam was controlled via quarter- and half-wave plates, so that any desired ellipticity and initial azimuth could be achieved. For each of the samples with different concentrations of TiO$_2$ nanoparticles, the measurements were performed with input ellipticity starting from $e_{in} = 0$ to $e_{in} = 0.9$ with a step 0.1. The polarization state of the output light was determined by a PAX5710 polarimeter (Thorlabs), which allowed us to measure in real time the Stokes parameters, and hence, the ellipticity and the azimuth of the passing light. The light intensity incident on the sample was approximately 450 mW/cm$^2$, which was too low to cause any degradation of the material. Every sample was exposed for approximately 150 s, a period of time sufficient to reach saturation of the photoinduced effects. As a result, the changes of the ellipticity and the azimuth were obtained for all concentrations and for input ellipticity between 0 and 0.9. Examples of the kinetics of the azimuth rotation and the ellipticity variation during the experiment are given in figure 3.

Figure 3. Left-hand panel – azimuth rotation curve in real time accounting for the sample thickness. This is the highest value of $\Delta \theta / d$ for all measurements. The sample has 2 wt. % of NPs and $e_{in} = 0.9$. Right-hand panel – ellipticity change curve of the sample with 1 wt. % NPs and $e_{in} = 0.5$. Again, the thickness is accounted for.

3. Results and discussion

Figure 4 and 5 show the dependencies of the azimuth rotation and the difference between the output and the input ellipticity for different samples. All data points correspond to the saturated values at the end of the exposure and are normalized to the thickness of the sample.
Figure 4. Dependence of the azimuth rotation $\Delta \theta$ on the initial ellipticity for three different samples; left – undoped sample, center – sample with 2 wt. % of NPs, right – 3 wt. % NPs.

Figure 5. Dependence of the difference between the output and the input ellipticity for three different samples. From left to right: 0 wt. % NPs, 1 wt. % NPs and 2 wt. % NPs.

As seen from the graphs, the change of the ellipticity is $0 \, \mu\text{m}^{-1}$ for $e_{in} = 0$ and so is the azimuth rotation. This is an expected result, because $e_{in} = 0$ means linear polarization. We do not expect any chirality because linearly polarized light cannot cause the formation of circular birefringence in azopolymers. The direction of azimuth rotation corresponds to the sign of the incident light’s ellipticity. If we change the sign of the input ellipticity, the direction of rotation will change too; therefore, at the point where the input ellipticity changes its sign ($e_{in}=0$) there must not be any chirality. The maximal change of the ellipticity is reached at $e_{in} = 0.4-0.5$; after that $\Delta e$ decreases with the increase of the input ellipticity. For circular input polarization, we do not expect any change of the ellipticity.

The behavior of the curves in figure 4 illustrating the dependence of $\Delta \theta$ is similar. The highest value is reached at $e_{in} = 0.9$. The highest value for $\Delta \theta/d$ of $38^\circ/\mu\text{m}$ is obtained for the sample with 2 wt. % of NPs. In comparison, for the undoped sample this value is $37^\circ/\mu\text{m}$, so we have enhancement of $\Delta \theta$ as a result of the presence of the nanoparticles. For the sample with 3 wt. % NPs, however, $\Delta \theta/d$ decreases at $e_{in} = 0.9$.

4. Conclusions

We prepared samples with five different concentrations of TiO$_2$ nanoparticles in the azopolymer varying from 0 to 3 wt. %. For each NPs concentration, the changes were determined in the parameters of the elliptically polarized input light. The largest rotation of the azimuth was reached when the input ellipticity was 0.9, and the highest change in the ellipticity was obtained at $e_{in} = 0.4-0.5$. The azimuth rotation of the sample with 2 wt. % NPs was larger ($\Delta \theta/d = 38^\circ/\mu\text{m}$) than that of the undoped sample ($\Delta \theta/d = 37^\circ/\mu\text{m}$). We should also point out that the azimuth rotation is directly related to the circular birefringence as mentioned in the beginning, so the experimental set up presented can be used for direct measurement of the circular birefringence. For higher concentrations of TiO$_2$ nanoparticles, the optical quality of the sample deteriorates and the maximal birefringence decreases.
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References
[1] Todorov T, Nikolova L, and Tomova N 1984 Appl. Opt. 23 4309-4312
[2] Natansohn A and Rochon P 2002 Polymers Chem. Rev. 102 4139-4176
[3] Emoto A, Uchida E and Fukuda T 2012 Polymers 4 150-186
[4] Wang X 2017 Azo Polymers: Synthesis, Functions and Applications (Springer-Verlag, Berlin, Heidelberg)
[5] Nedelchev L, Mateev G, Otsetova A, Nazarova D and Stoykova E 2018 Int. J. Inform. Theor. Appl. 25 245-254
[6] Nikolova L, Todorov T, Ivanov M, Andruzzi F, Hvilsted S and Ramanujam P S 1997 Opt. Mater. 8 255-258
[7] Azzam R M A and Bashara N M 1977 Ellipsometry and Polarized Light (North-Holland, Amsterdam)
[8] Nikolova L, Nedelchev L, Todorov T, Petrova T, Tomova N, Dragostinova V, Ramanujam P S and Hvilsted S 2000 Appl. Phys. Lett. 77 657–659
[9] Wu Y L, Natansohn A and Rochon P 2004 Macromolecules 37 6801–6805
[10] Iftime G, Labarthet F L, Natansohn A and Rochon P 2000 J. Am. Chem. Soc. 122 12646–12650
[11] del Barrio J, Tejedor R M and Oriol L 2012 Eur. Polym. J. 48 384–390
[12] Shibaev V, Bobrovsky A and Boiko N 2003 Prog. Polym. Sci. 28 729–836
[13] Yager K G and Barrett C J 2006 J. Photochem. Photobiol. A 182 250–261
[14] Mateev G, Nedelchev L, Georgiev A and Nazarova D 2019 Open Mat. Sci. 5 19-23