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The still unknown azobenzene - Wavelength dependent photoanisotropy in amorphous azobenzene polymers

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Abstract: We demonstrate a new type of anisotropy in thin films of amorphous azobenzene polymers induced between 570 and 633 nm, where the absorbance in the film is on the order of 0.05. The anisotropy has a pronounced radial contribution. This observation points to an additional mechanism for the alignment of azobenzene molecules.

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1. Introduction

Azobenzene containing polymers have provided the basis for several remarkable phenomena in light-matter interactions, such as photoinduced anisotropy [1], polarization holography [2], light initiated mass transport [3,4], polarization dependent chiral structures [5] etc.,. It is commonly assumed that when an azobenzene containing polymer is irradiated with linearly polarized light between 450 and 530 nm, the azobenzene chromophores orient perpendicular to the polarization through several *trans-cis-trans* isomerization cycles. It is necessary at the outset to emphasize that the polymer backbone plays an important role in many of the observations. For example, in the case of light initiated mass transport, polymers with crystalline or liquid crystalline domains behave in a different way than glassy amorphous polymers, even though the chromophore interacting with light is identical [6]. Similarly, in the case of photoinduced chiral structures, the response of the polymers is different depending on the polymer structure for the same chromophore [7]. Most of these phenomena thus indicate strong inter/intra molecular interaction, in addition to the interaction of light with matter. Other examples of new remarkable phenomena in azobenzene polymers are photofluidity [8], and spiral mass transport [9].

One of the interesting phenomena that was observed early was a response to red light, after irradiation to UV, blue or green light depending on the polymer structure. One of the current authors found a novel biphotonic effect in an adipate polymer containing cyanoazobenzene [10]. This process entailed irradiation at 488 nm, followed by irradiation at 633 nm. A polarization holographic grating induced by two oppositely circularly polarized light seemed to disappear, only to be revived by the red laser even several minutes after the initial irradiation. It was shown in this case that the chromophores were oriented parallel to the polarization of the red light [11]. Since then, this process has been observed by others in other systems [12]. In this article, we demonstrate that a new type of anisotropy is induced in amorphous azobenzene polymers between 570 and 670 nm, which is fundamentally different from that induced between 400 and 530 nm. While the latter aligns the molecules perpendicular to the linear polarization, the former seems to result in a predominantly radial alignment.

2. Experimental methods

Most of the experiments were performed on the copolyester, E1aP(0.25)12(0.75), whose synthesis has been described in detail earlier [13]. The copolyester E1aP(0.25)12(0.75) was synthesized via base-catalyzed (K_2CO_3), in vacuo, melt-trans-esterification of 3-[4-((4-cyanophenyl)azo)-phenoxy]-1,2-propanediol with the appropriate diphenyl diester. About 5 mg of the polyester was dissolved in 200 μ l of tetrahydrofuran and cast on clean glass plates 40 mm square. After the solvent had evaporated, the film was dried at 80° C in an oven. The thickness of the films is estimated to be approximately 3 μ m.

Most of the experiments have been performed with a continuous wave 593 nm laser. The 593 nm laser in used in these experiments is similar to the system described by Janousek et al. [14]. It is based on singly-resonant sum-frequency mixing between a 1342 nm Nd:YVO₄ laser and a 1064 nm Nd:YVO₄ laser. Both of the solid-state lasers are pumped by a broad area 808 nm laser diode. A Brewster's cut periodically poled KTP crystal is inserted in the 1342 nm resonator, where mixing with the single-pass 1064 nm laser takes place. For the experiments described here, a power of 20 mW was used, distributed in a 3 mm diameter spot.

A home-made pulsed dye laser was used for irradiation at 570 nm; this was used only to check whether an anisotropy can be induced at this wavelength. We did not measure the

power or the duration of the laser pulse. A continuous wave 670 nm laser was used for irradiation at longer wavelengths. The 670 nm laser was an external cavity tapered diode laser operated in the Littrow configuration with an external diffraction grating for tuning [15]. The laser was operated at relatively low power and the output was spatially filtered through a pinhole to obtain a pure TEM₀₀ output beam. After the spatial filtering, approximately 35 mW was available for the experiments. For the experiments described here, the power of the laser was 20 mW concentrated in a 2 mm diameter spot. A continuous wave HeNe laser at 633 nm capable of emitting 20 mW was also used for irradiation. Again the size of the laser spot on the film was 3 mm diameter. These results were compared to the results of irradiation at 532 nm from a frequency doubled YAG laser, with a power output of 20 mW in a 3 mm diameter spot. As a source of longer wavelength, a continuous wave diode laser operating at 800 nm was also used. The laser power in this case could be adjusted from 20 mW up to 100 mW, by varying the current. This laser was employed to check whether anisotropy could be induced at this wavelength. All the lasers were linearly polarized horizontally.

A Leica microscope equipped with crossed polarizers and a $\lambda/4$ plate (but not a quartz wedge) and a CCD camera was utilized to study irradiated areas. A Unicam UV4 double monochromator was used to record the absorption spectra.

3. Results and discussion

Absorption spectrum

The absorption spectrum of a film E1aP(0.25)12(0.75) before and after irradiation at 593 nm, between 550 nm and 750 nm is shown in Fig. 1. The absorbance beyond 590 nm is less than 0.05. A tiny absorption peak at 593 nm in the spectra must arise from azobenzene, as this absorption peak is also seen in other amorphous azobenzene polyesters. After irradiation at 593 nm (power density of 5 mW/cm², irradiation time 150 min), a slight increase in absorption over the range 550 nm - 670 nm can be seen.

Anisotropy measurements

The azobenzene polyester, E1aP(0.25)12(0.75) was irradiated for 300 s with a horizontally polarized beam from a frequency doubled YAG laser at 532 nm. Before irradiation, the film is macroscopically isotropic. The absorbance of the film at this wavelength is approximately 0.1. After irradiation, the film exhibited the well known uniaxial symmetry, with the polarization direction of the incident beam being the optic axis. Figure 2 shows a polarization microscope picture of the film between crossed polarizers, with the film at 45° to the irradiation direction. As the film is rotated, it exhibits four positions of total extinction. This is due to an in-plane orientation of the azobenzene chromophores perpendicular to the polarization of the incident light.

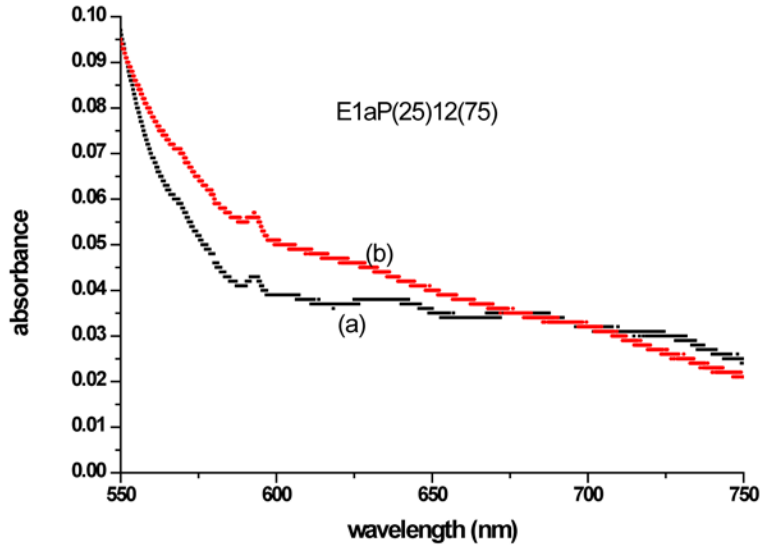


Fig. 1. Absorption spectra of the azobenzene polyester E1aP(0.25)12(0.75) before and after irradiation at 593 nm. The film thickness was approximately 2.5 μm . (a) Spectrum of the unirradiated film and (b) spectrum of film irradiated at 593 nm for 150 min., at a power density of approximately 5 mW/cm^2 .

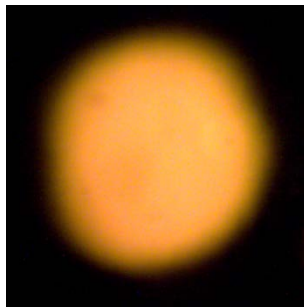


Fig. 2. Polarization microscope picture of E1aP(0.25)12(0.75) irradiated at 532 nm with horizontal polarization. The film was rotated by 45° to obtain the above image.

When the film was irradiated with horizontally polarized light at 593 nm (20 mW, 3 mm diameter, 300 s exposure), the film showed the structure shown in Fig. 3, in the polarization microscope between crossed polarizers. The colors in the figure are due to a $\lambda/4$ plate inserted as a compensator. The axis of the quarter wave plate was slightly turned away from the normal extinction position of the analyzer, resulting in the orange-green color of the lobes.

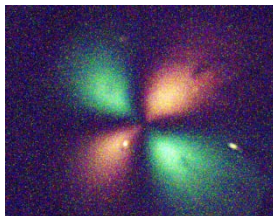


Fig. 3. Polarization microscope picture of E1aP(0.25)12(0.75) irradiated at 593 nm with horizontal polarization. The polarization direction of irradiation coincides with the linear polarization direction of the microscope. The axis of the $\lambda/4$ plate does not coincide with axis of the polarizer, resulting in the orange-green color of the lobes.

The image was recorded in a normal orthoscopic configuration. Remarkably, irradiation with circularly polarized light results in a similar pattern. In the case of linearly polarized light, a large number of measurements with different intensities and exposure times showed that at low photon doses (approximately 10^{17} - 10^{18} photons), a normal uniaxial behavior results, suggesting that the molecules align initially perpendicular to the polarization of the light.

A close up of the central region (Fig. 4) shows brush like formation radiating from the centre, implying a radial component to the alignment of the indicatrix.

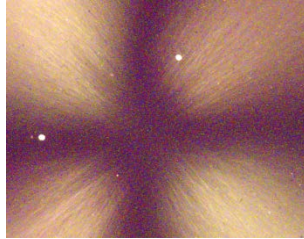


Fig. 4. A close up (200 x) view of the central area of Fig. 3. The white dots are dust on the film.

However, when the film is rotated between crossed polarizers in the microscope, the cross pattern shows some asymmetry as shown in Fig. 5. A series of experiments was done to estimate the effect of intensity of the laser beam. The laser intensity was varied between 350 W/m^2 to 3500 W/m^2 and the exposure time was adjusted to give a constant total incident photon dose of approximately 4.5×10^{19} photons. The results in all cases were similar, all resulting in a cross pattern. These results may seem to indicate that the Gaussian profile of the laser beam can be of importance providing a gradient force. To estimate this effect, the laser beam was first expanded to 20 mm diameter, and the film was exposed through a 2 mm aperture. This corresponds to an intensity gradient of 1% - the results were the same. Even expanding the laser beam to 6 cm diameter, and exposing the film through the 2 mm aperture in the centre of the beam produced a cross pattern. In this case, the intensity gradient was less than 0.5%. The exposure time in the last two cases were 4 hours and 6 hours respectively, giving approximately the same photon dose.

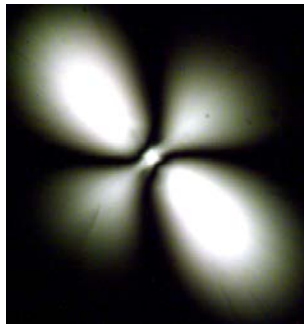


Fig. 5. Same film as in Fig. 3 but rotated through $+45^\circ$ with the axis of the quarter wave plate exactly at the extinction axis of the analyzer.

Film between crossed polarizers

In order to follow the temporal development of the anisotropy, the film was irradiated with horizontally polarized 593 nm laser with 20 mW power. A polarizer with its transmission direction vertical was placed after the film. A screen was placed after the analyzer to observe the display. Initially, only a weak beam is transmitted. We show below a series of images, as a function of time, the series taking about 4 minutes for completion (Fig. 6). When the

analyzer is set to complete extinction, the four lobes appear simultaneously in transmitted light. The formation of isogyres shows that the film is gradually becoming biaxial. An appended movie shows the temporal development of the anisotropy (Fig. 7, [Media 1](#)). Since, at the extinction the transmitted light is too weak for recording, the analyzer was misaligned approximately 2^0 to let some light through. In this case, two of the lobes seem to appear first. (If the analyzer is misaligned to the other side, the other two lobes appear first). After prolonged irradiation, the isogyres merge and the system appears 'uniaxial', with the optic axis perpendicular to the plane of the film. When the film is examined in a polarized microscope with crossed polarizers, the image shown in Fig. 8 results. This is not conoscopic imaging – the beam incident on the film can be convergent, parallel or divergent. However, there is some asymmetry when viewed through crossed polarizers in a polarization microscope when the film is rotated about an axis perpendicular to it, as in Fig. 5.

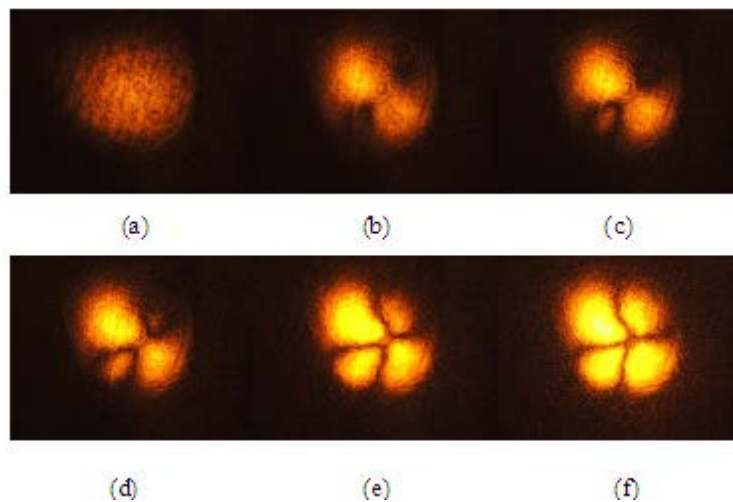


Fig. 6. A time series of the development of anisotropy in E1aP(0.25)12(0.75) as a function of time (top row followed by bottom row). The entire series takes approximately 4 mins.

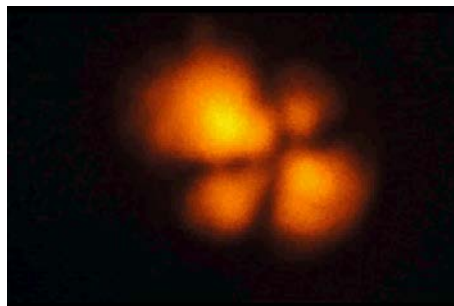


Fig. 7. A representative frame from the appended movie showing the temporal development of the anisotropy. [\[Media 1\]](#)

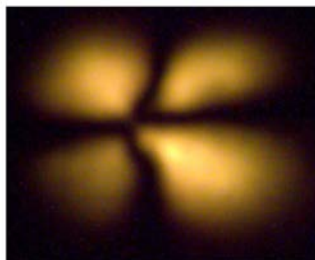


Fig. 8. Polarized microscope image after the completion of the irradiation.

The anisotropy induced is very stable in time, and can survive at 120°C for several days, and even white light irradiation for more than 36 hrs. Irradiation with horizontally and circularly polarized light at 633 nm results in similar patterns [Fig. 9]. In this case, the power in the laser beam was 20 mW and the irradiated spot is 3 mm in diameter. The irradiation time was approximately 120 minutes.

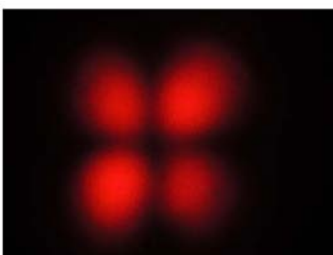


Fig. 9. Image obtained when the film was irradiated with horizontally polarized light at 633 nm. The image was obtained on a screen placed after a crossed linear polarizer.

Irradiation at 670 nm (20 mW, focused to approximately 2 mm, irradiated for 18 hours) produces the following figure (Fig. 10) in a polarization microscope. This is typical of a uniaxial alignment, with the centre of the Gaussian laser beam thermally inducing the concentric circles. Thus, the region around 670 nm seems to be a transition region. At 800 nm, no anisotropy could be induced in the film, even after 24 hours of irradiation at 100 mW in a 2 mm diameter spot.



Fig. 10. Polarization microscope picture of the area irradiated at 670 nm. The film is at 45° to the polarization direction.

The cross like structure was observed in the case of several amorphous azobenzene polymers such as E1aP, DNO [13, 16] and azobenzene dendrimers. However, no anisotropy could be induced in liquid crystalline polymers such as E1a12 or P6a12 [17]. However, in the

case of P6a4 [10], in which a biphotonic effect was first observed, irradiation at 532 nm followed by irradiation at 593 nm resulted in the familiar uniaxial symmetry.

Conclusion

The experiments described above seem to show that there are still processes involving azobenzene that we hardly know anything about. When an amorphous azobenzene polymer is irradiated between 570 and 670 nm, a different kind of molecular arrangement compared to the familiar uniaxial arrangement created at 532 nm seems to result. A low absorbance, combined with the absence of any characteristic absorption peaks in this wavelength region makes this observation remarkable. Preliminary investigations seem to show that the molecules have a pronounced radial alignment. Since this alignment is independent of the polarization of the incident light, one explanation seems to be obvious, viz., the molecules align along the gradient of the laser field, however small the gradient may be. When the film is irradiated at 532 nm, the molecules align perpendicular to the polarization of the incident light as a result of photoinduced *trans-cis-trans* isomerization. A different model based on nonradiative dissipation of photon energy associated with partial or incomplete photoactivated isomerization transition involving the same *trans* state was proposed recently by Manzo et al. [18]. In our case, there are no obvious excited states in wavelength region of interest. Our results do not seem to depend on the photon intensity, but only on the photon dose at the given wavelength. At 593 nm, this is approximately 3×10^{18} photons/cm². At 633 nm, this is an order of magnitude greater. The wavelength interval in which the radial alignment takes place is also limited to approximately 80 nm. The results suggest a new alignment mode, in which molecules in electronic ground state, but in vibrationally excited states may participate in the reorientation process. The asymmetry in anisotropy pattern as the film is rotated, suggests that initially the molecules align orthogonal to the light polarization, followed by a component orthogonal to the film surface on prolonged irradiation. As the referee of this manuscript suggested: "the two components may be associated with an internal inhomogeneity in the film (e.g. alignment orthogonal to the film might be favored in the proximity of the surface and a normal alignment in the bulk), or may be present everywhere in the film".

Other molecular arrangements to explain the observation may also exist: a biaxial torus alignment as in liquid crystals [19] or a radial-hedgehog alignment [20]. These models have been proposed for nematic liquid crystals confined in a capillary, where the walls of the capillary act as anchoring points for homeotropic alignment. The images that we observe are very similar to the biaxial torus figures; however, in this case, the glass substrate on which the film is deposited could act as the anchoring surface. Another plausible explanation for linearly polarized light is that the same wavelength orients the molecules initially perpendicular to the polarization and later parallel to the polarization, as for the biphotonic effect. However, this fails to explain why circularly polarized light induces the observed anisotropy.

An examination of the anisotropic processes in amorphous films containing azobenzene with a dye laser between 530 nm and 590 nm is under way. In order to completely rule out the possibility of the intensity gradient playing any role, experiments involving a flat top irradiation profile are envisaged.

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