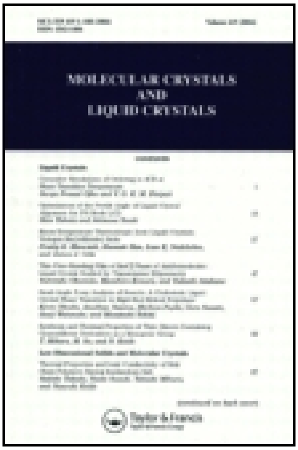

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Orientation of Azo-Dye Molecules in Polymer Films, via Photoisomerization: Dichroism Measurements and Second Harmonic Generation

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Version of record first published: 31 Aug 2006

To cite this article: Ngan Nguyen Thi Kim, Michel Dumont, Jacques A. Delaire & Keitaro Nakatani (2005): Orientation of Azo-Dye Molecules in Polymer Films, via Photoisomerization: Dichroism Measurements and Second Harmonic Generation, Molecular Crystals and Liquid Crystals, 430:1, 249-256

To link to this article: http://dx.doi.org/10.1080/15421400590946460

Mol. Cryst. Liq. Cryst., Vol. 430, pp. 249–256, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946460

Orientation of Azo-Dye Molecules in Polymer Films, *via* Photoisomerization: Dichroism Measurements and Second Harmonic Generation

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Photoinduced Anisotropy and All-Optical Poling are the result of two mechanisms, the angularly selective excitation of molecules (Angular Hole Burning) and the rotation of molecules during the excitation–relaxation cycle (Angular redistribution). In this paper we recall some previous results and we present two new experiments. The first one demonstrates the prime importance of reversible photoisomerization for angular redistribution: we compare dichroism and second harmonic generation, with photoisomerizable molecules and non photoisomerizable ones. The second experiment shows an example of the behavior of photoinduced anisotropy, in a liquid crystal azo-polymers: a 3D characterization of anisotropy is necessary.

Keywords: all-optical poling; azo-dye; photoinduced anisotropy; photoisomerization; polymer films

Photoinduced anisotropy (PIA), is known for a longtime as the Weigert effect. It is particularly efficient with azo-dye molecules in glassy materials, like polymers, in which the resonant excitation by linearly polarized light produces birefringence and dichroism. In the sixties PIA was studied in azobenzene derivatives and the role of cis–trans photoisomerization was clearly understood in a series of publications by Russian authors [1]. The first step is the angularly selective photoisomerization of trans molecules, with a probability of excitation proportional to

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$\cos^2\theta$ (θ is the angle between the transition dipole moment of the molecule and the polarization of light), which produces an *angular hole burning* (AHB) in the trans angular distribution. As molecules come back from the cis state to the stable trans state, their orientation is randomly modified. The average rotation depends on the host environment, but after many Trans–Cis–Trans cycles, *this angular redistribution* (AR) yields to the accumulation of molecules perpendicularly to the polarization of light. The reversibility of photoisomerization is necessary to ensure a great number of cycles, but the Cis–Trans back isomerization can be a spontaneous relaxation or a reverse photoisomerization process.

In the eighties a new interest arose for this mechanism because of its possible applications for processing organic materials for optoelectronics and particularly for waveguide devices [2]. Many azo-dye functionalized polymers have been studied and the disperse red 1 (DR1) and some other neighbor molecules appear to be the most efficient. Other photoisomerization processes, such as Spiropyran-photomerocyanine isomerization, lead to PIA, but generally these molecules are less stable than azo-dyes. In the same time, photo-assisted electrical poling (PAEP) was developed [3,4]: in this technique, a DC electric field is applied during the illumination of the sample, so that AR is no more an isotropic process, but is dominated by the torque exercised on the permanent dipole moment of molecules. Thus, the material is poled, at room temperature, and it acquires $\chi^{(2)}$ non-linear properties (Second Harmonic Generation – SHG – and electrooptic properties). Both PIA and PAEP have been theoretically modelized [5,6].

More recently all-optical poling (AOP) has been demonstrated in the same kind of materials [7,8]. In AOP, the coherent excitation by strong laser pulses (ω and by weak resonant harmonic pulses (2ω) produces non centrosymmetric AHB and the AR leads to a large $\chi^{(2)}$. AOP allows the orientation of non-centrosymmetric molecules without permanent dipole moment, for which orientation by an electric field is impossible (octupolar molecules [9,10]). The symmetry of the resulting angular distribution is determined by the common elements of symmetry of molecules and of the optical excitation. The general model for the three processes is given by two coupled equations, representing the angular distributions in Trans and in Cis (here, for simplicity, we ignore the reverse photoisomerization from Cis to Trans):

$$\frac{\mathrm{dn_T}(\Omega)}{\mathrm{dt}} = -\mathrm{Pr}(\Omega)\mathrm{n_T}(\Omega) + \frac{1}{\tau_c}\int \mathrm{R_{CT}}(\Omega' \to \Omega)\mathrm{n_C}(\Omega')\mathrm{d}\Omega' + \left(\frac{\mathrm{dn_T}(\Omega)}{\mathrm{dt}}\right)_{\mathrm{Diffusion}}$$

$$\frac{\mathrm{dn_C}(\Omega)}{\mathrm{dt}} = \int \mathrm{R_{TC}}(\Omega' \to \Omega)\mathrm{Pr_T}(\Omega')\mathrm{n_T}(\Omega')\mathrm{d}\Omega' - \frac{1}{\tau_c}\mathrm{n_C}(\Omega) + \left(\frac{\mathrm{dn_C}(\Omega)}{\mathrm{dt}}\right)_{\mathrm{Diffusion}}$$

$\mathrm{Pr}(\Omega)$ is the probability of excitation of a molecule of orientation $\Omega = \{\varphi, \theta, \psi\}$. $\mathrm{R_{CT}}$ and $\mathrm{R_{TC}}$ are the probabilities of rotation from Ω' to Ω in the photoisomerization processes. Except in the case of PAEP, they depend only on the angle between Ω' and Ω. In the case of AOP, $\mathrm{Pr}(\Omega)$ is given by:

$$\begin{aligned}\mathrm{Pr}(\Omega) \propto\, & 2\alpha''_{\Omega}(-2\omega;2\omega) \bullet \Re\mathrm{e}(\vec{\boldsymbol{E}}^{*}_{2\omega} \otimes \vec{\boldsymbol{E}}_{2\omega}) + (2\beta''_{\Omega}(-2\omega;\omega,\omega) \\ & + \beta''^{*}_{\Omega}(-\omega;-\omega,2\omega)) \bullet \Re\mathrm{e}(\vec{\boldsymbol{E}}^{*}_{2\omega} \otimes \vec{\boldsymbol{E}}_{\omega} \otimes \vec{\boldsymbol{E}}_{\omega}) \\ & + \gamma'_{\Omega}(-\omega;-\omega,\omega,\omega) \bullet \Re\mathrm{e}(\vec{\boldsymbol{E}}^{*}_{\omega} \otimes \vec{\boldsymbol{E}}^{*}_{\omega} \otimes \vec{\boldsymbol{E}}_{\omega} \otimes \vec{\boldsymbol{E}}_{\omega})\end{aligned}$$

$\vec{\boldsymbol{E}}_{\omega}$ and $\vec{\boldsymbol{E}}_{2\omega}$ are the electric fields of ω and 2ω pump beams. α''_{Ω}, β''_{Ω} and γ''_{Ω} are the imaginary part of the linear and non-linear polarizability tensors of a molecule of orientation Ω, in the laboratory frame. The first term (α) is the one-photon absorption, the third (γ) is the two-photon absorption: both are centrosymmetric. The second term (β) represent the non-centrosymmetric interference responsible for AOP. These three terms are the resonant contributions to the excitation, when 2ω is near the molecular transition (here the $\pi{-}\pi^{*}$ band of azo-dyes). The transient solution of the above equations has been calculated in the case of PIA, for which only the first term exists [5,6]. For AOP, the general form is too complicated to be solved, but the asymptotic solution is very simple ($\mathrm{n_T}(\Omega, \mathrm{t} = \infty) \propto 1/\mathrm{Pr}(\Omega)$) [11,12].

In fact, we intuitively assumed that AOP differs from PIA, only by the pumping probability and that the AR mechanism is the same. Nevertheless, up to recently, this assumption had not be verified experimentally: one of our goal is to show that in AOP there is a rotation of molecules, like in PIA. Similarly, the non-centrosymmetric term in $\mathrm{Pr}(\Omega)$ has been widely studied (particularly the symmetry properties [10]) but the competition with the two centrosymmetric terms (one- and two-photon absorption) is generally ignored. For that purpose we have designed an experimental setup, which records simultaneously the growing of SHG and of the dichroism, for different wavelenghts. We built a 2D setup, with pump and probe beams almost normal to the film and a 3D setup (Fig. 1), with two orthogonal directions of pumping and three directions for probing. In the 2D experiment, we measure the absorption for two orthogonal directions of polarization, in the plane of the sample: this configuration, used in most experimental works up to now, is sufficient when one can assume that the third direction, perpendicular to the film, is equivalent to one which is probed in the plane. This configuration is limited to isotropic materials excited by a linearly polarized pump beam.

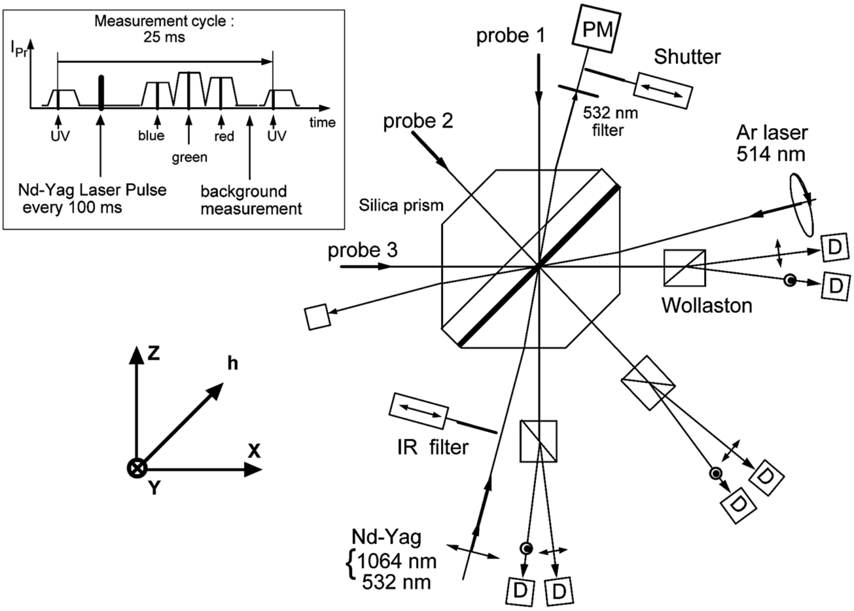

FIGURE 1 The 3D experimental setup, with all the possible pump and probe directions. The sample, spin coated on a glass slide, is put in optical contact with the two prisms, with the help of an index matching oil. In AOP experiments, the film is pumped simultaneously by 1064 and 532 nm pulses. One second every 30 seconds, the IR filter cuts the 532 nm pump, while the shutter in front of the photomultiplier is opened, for measuring the SHG from the sample. The configuration presented here has been used in Ref. [13] for 3D pumping: the Nd-Yag laser beams are linearly polarized in the X direction, while an Ar laser beam, propagating along X, is circularly polarized in order to pump molecules in the (Y, Z) plane. Because of the refractive index of the sample, the two laser beams cross each other at right angle, while the probe beams are not exactly orthogonal, but this small angle is taken into account for the precise interpretation of measurements. The three probe beams are made of a periodic succession of 2 ms pulses of different wavelenghts, produced by a multi-slit monochromator and a rotating slit-wheel [12]. The Nd-Yag laser is synchronized with the probe pulses cycle.

A series of experiments, with DR1 in PMMA (doped polymer or copolymer), has clearly demonstrated the anisotropy induced by two-photon absorption and the simultaneous growing of anisotropy and of SHG, in AOP [13]. With the 3D setup, it has been verified that linearly polarized pumping beams induce an axial symmetry of the molecular distribution, which validates the numerous 2D experiments performed previously (PMMA is intrinsically an isotropic medium).

With the experimental arrangement, as shown in Figure 1, we tried to improve $\chi^{(2)}$ (SHG) by a 3D pumping. Indeed the quadrupolar centrosymmetric pumping terms (one- and two-photon absorption) accumulate molecules in the plane perpendicular to the polarization of the pumps (plane Y, Z, in Fig. 1): this reduces $\chi^{(2)}$, since the non-centrosymmetry is created in X direction, only. We hoped to improve $\chi^{(2)}$ by pumping these lost molecules with a CW laser beam, circularly polarized, propagating along the X direction. In fact, we observed a decrease of SHG, which we theoretically interpreted as a too large decrease of trans population [13]. The calculation shows that an improvement could appear, only with very week pumps, which would correspond to extremely slow poling. Nevertheless, after a period of CW pumping, the speed of poling by AOP was faster, probably because of the increase of mobility of molecules.

Figure 2, presents new experiments made with two octupolar molecules (i.e. optically non-linear molecules, without permanent dipole moment). On the left side, the molecule familiarly named “octopus”, is the first octupolar azo-dye molecule synthesized in Torino University (G. Viscardi). The three arms of this molecule can perform trans–cis photoisomerization. Nevertheless spectra in liquid solutions and in PMMA films show a strong photochromism with a well defined isobestic point, indicating a single photoisomer. The 2D experiment, presented here, shows the simultaneous growing of anisotropy and of SHG, like with DR1, and a clear evidence of rotation of molecules (angular redistribution). Indeed, after a fast decrease, due to the depopulation of trans state (AHB), the optical density at 457 nm, for the polarization perpendicular to that of the pump beams, progressively increases and exceeds the initial optical density when the pump is switched off (relaxation of the photoisomer).

On the right side of Figure 2, results obtained in similar conditions with ethylviolet are presented. This molecule is the first octupolar molecule which have been oriented by the AOP technique [9], but the mechanism was not understood, since this molecule is not photoisomerizable. Figure 2 shows that the SHG signal and the photoinduced anisotropy are much smaller than with octopus. The observed anisotropy indicates that there is no rotation of molecules, but only an angularly selective photodegradation. When the pump is switched off the irreversibility of AHB is evident. The comparison of these molecules clearly demonstrates the prime importance of reversible photoisomerization, for the photo-orientation processes of dye molecules in polymer matrices.

The 3D setup is of great interest for materials which are not intrinsically isotropic, like liquid crystal polymers (or small molecules

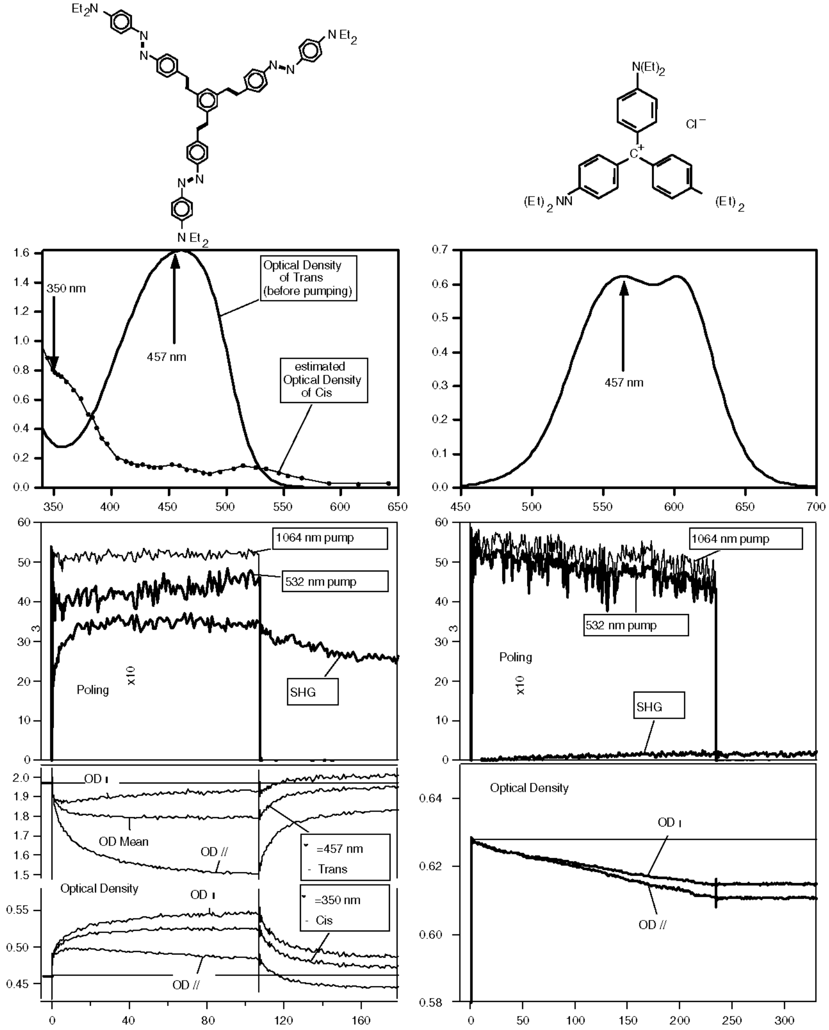

FIGURE 2 Comparison of AOP with two octupolar molecules. On the left "octopus" is photoisomerizable, as shown by the spectra obtained in solution. The spectrum of the photoisomer has been determined by the Fischer-Rau method. In this 2D experiment, the pump beams are linearly polarized and the optical densities are measured with polarizations parallel ($OD_{\|}$) and perpendicular ($OD_{\perp}$) to that of the pumps. $OD_{\mathrm{mean}} = (OD_{\|} + sOD_{\perp})/3$ is sensitive only to the populations of trans and cis. At $\lambda = 457\,\mathrm{nm}$, OD_{mean} decreases like trans population and at $\lambda = 350\,\mathrm{nm}$, it increases like cis population. The increasing difference between $OD_{\perp}$ and $OD_{\|}$ is characteristic of angular redistribution. On the right, the non photoisomerizable octupolar molecule, ethylviolet, is much less efficient for SHG and PIA. This behavior is characteristic of photodegradation without rotation of molecules.

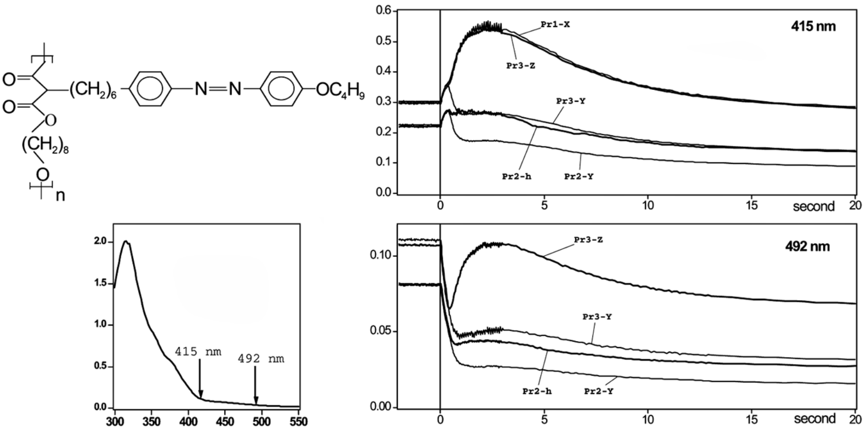

FIGURE 3 PIA of a liquid crystal polymer [15]. The sample has been previously illuminated by unpolarized UV light, which make the material isotropic. At time t = 0 the film is pumped with a CW 488 nm, Y polarized, laser beam. Before the 488 nm irradiation, the optical density from probes 1 and 3 is higher than that of probe 2, because of the 45° incidence (see Fig. 1). After 0.4 s the liquid crystal properties appear. The symmetric increase of absorption for X and Z polarizations prove that molecules are oriented perpendicularly to the film.

studied in another paper in this issue [14]). We give an example in Figure 3. The polymer used in this experiment is one of those studied in reference [15], by other experimental methods based on birefringence measurements. The material is first illuminated with unpolarized UV light, which produces the almost stable cis form (an absorption band appears in 450–500 nm region). Then, the material is isotropic, since the Cis form is not mesogenic: this is evident from the measurement of optical densities. The two graphs on the right of Figure 3 show the evolution of the optical density for two wavelenghts and for the different directions of polarization, when the film is pumped by a CW laser beam, linearly polarized in the Y direction. During the first half second, all 415 nm signals increase and all 492 nm signals decrease, which can be interpreted as the cis to trans photoisomerization. But suddenly, absorption increases abruptly for Z and X polarization, decreases for Y and is stationary for the horizontal in plane polarization. At this point, a strong anisotropy appears, with molecules oriented perpendicularly to the plane of the film: the liquid crystal properties of the trans shape appear, with an homeotropic orientation. The behavior of this material and of different homologues, is quite complicated. The detailed description of PIA experiments in these polymers is out of the scope of this paper and will be published else where. We have presented this experiment to show that photoisomerization leads to surprising results, when the material exhibits self-organization tendencies: a careful 3D study of PIA is necessary.

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