



Full Length Research Article

CIRCULARLY POLARIZED LIGHT-EXCITED ALL-TRANSVERSE ORIENTATIONAL HOLE BURNING AND INDUCED ANISOTROPY IN AZO DYE DOPED POLYMER FILMS

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ARTICLE INFO

Article History:

Received 13th August, 2016
Received in revised form
24th September, 2016
Accepted 19th October, 2016
Published online 30th November, 2016

Key Words:

Polarimetric experimental setup,
PMMA, Azo dye doped polymer,
Circular polarized light,
Photoinduced anisotropy,
All transverse directions

ABSTRACT

An original polarimetric experimental setup is used to pump and probe photosensitive films. Photo-induced behavior of Azobenzene Disperse one (AZD1) doped Poly(Methyl MethAcrylate) (PMMA) using both linear and circular polarized light is studied. The anisotropy is not erased by the circular polarization light. The circular polarization light combined with relatively long lifetime of the cis state in doped polymers appears as if it activate all transverse directions of the angular hole burning through the film inducing anisotropy. Under circular polarized light, there is no preferred orientation within the film plane, trans species reorients in the propagation direction of the pump beam. The polarization state of the probe beam after propagation through the pumped film depends strongly on the angle of incidence of both pump and probe beams on the input face. In the case where circular polarized pump and probe beams are under the same angle of incidence, the probe beam "sees" anisotropic film as if it is isotropic. This work shows the possibility to reorient azobenzene-type molecules in two orthogonal directions using alternately linearly and circularly polarized beams.

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INTRODUCTION

Amorphous azo dye doped polymers are very interesting for their potential applications in optics and photonics (Zhao and Ikeda, 2009; Bandara, 2012; Sekkat and Knoll, 2002). These potentialities come from the photo-isomerization that modifies the molecular dielectric polarization and thus the refractive index as well as the absorption of the material. By using polarized light, one can induce collective molecular reorientation in a favored direction that leads to dichroism and birefringence. The optimization of these properties is important, for example for all-optical switching (Xu, 2008, 2013) and Optical Data Storage, since modulations achieved are very high. For a fixed intensity, the angular hole burning occurs when the azo dye's transition dipole moment axis has a component parallel to the oscillating electric field (E-field) vector of the pump beam (Natansohn, 1994; Buffeteau, 1998). An angular redistribution of trans molecules occurs when they relax from cis state to trans state. If azos are excited by using a linear polarized light, the molecules that are perpendicular to the E-field of pump light are no longer pumped, the

photo-isomerization process will tend to accumulate trans isomers in that direction that is the direction perpendicular to the oscillating E-field of the incoming light (Todorov, 1984). When the excitation light is turned off, usually the anisotropy decreases and reaches a residual value or vanishes. *Circular polarized light* was used to erase the anisotropy in azo containing polymers (Natansohn, 1996, 2002; Rochon, 1992; Cojocariu, 2004; Xie, 1993; Meng, 1996). This technique of erase was reported for the first time by Rochon *et al* (Rochon, 1992). Since then, no significant studies have been published for further verification (Sajti, 2001; Yavrian, 2002) but the idea has been widely used in many references (Mendonça, 2007a, b; Priimagi, 2009, 2014; Vapaavuori, 2013; Filippo, 2009; Goulet-Hanssens, 2014; Choi, 1999; Cao, 2008; Hautala, 2014; Yager, 2006) and even all-optical switching prototypes based on azo dye doped polymer using two cross-linear polarized beams for pumping and a circularly polarized beam for the "erasure" was suggested (Xu, 2013). In our previous study (Saad, 1998a, b, c), a transient out of plane rotation of the director in azo dye doped nematic liquid crystals using linearly polarized light was observed. Although, the molecular reorientation in viscous matrices such liquid crystals is completely different from that in rigid matrices such solid polymer. In viscous matrices, the reorientation can involve a collective motion of the polymeric molecules

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themselves whereas in solid matrices, the reorientation involves the azobenzene molecules only and polymeric chains will practically not move. Also, there is a big difference between azobenzene molecules *bonded* to (or in) the polymer chain and the *unbonded* one, hence the classification of these materials into two categories arises: azobenzene groups containing polymers (the copolymers) and azo dye doped polymers. Unpolarized light can push the azo molecules in viscous polymer containing azos (Wu, 1999) to orient in a direction which will be along the propagation direction of the excitation light. Dumont *et al.* are reported that using circular polarized light to pump DR1 doped PMMA induces the angular redistribution and produces photo-assisted poling of the azobenzene molecules (Dumont, 1999; Sekkat, 1992). Barrett *et al.* are demonstrated that circularly polarized light induces a reversible anisotropic dilatation in these materials (Tanchak, 2005). Recently, Ramanujam *et al.* published a series of color pictures taken by a polarization microscope revealing that both linear and circular polarized light creates anisotropy in isotropic azobenzene polymers (Ramanujam, 2013). Although, inducing the anisotropy using a linear polarized light is easy to understand owing to the reorientation of the azobenzene molecules in directions perpendicular to the oscillating E-field direction of the light. However, this fails to explain why circularly polarized light induces the anisotropy.

Nevertheless, if the light is circularly polarized, in principle, it's obvious that the E-field plane-of-vibration which rotates at the frequency of the light ($\nu \sim 5 \times 10^{14}$ Hz) will be prohibited from being occupied by the trans molecules. Hence, it must be emphasized, however, that there is another favored direction during photo-isomerization which will be along the propagation axis of a circular polarization of the incident excitation light. It is unavoidable that azoic molecules will efficiently buildup aligned along the propagation axis of the circular polarized light but this is often ignored in the literature, or interpreted as a photo-bleaching of the sample (Rochon, 1992). Nunzi *et al.* was reported that circular polarized light not erase birefringence, in contrary it induces it (Bagherzadeh, 2014). But the authors have considered this as a phase transition in the studied liquid crystal polymer. Farther linearly and circularly pump beams were used to increase the switching modulation depth based on azobenzene containing polymer films (Yager, 2006; Luo, 2005; Shi, 2006). Chuang *et al.* (Chuang, 2013) are thereafter reported that azo-dye molecules can be further aligned by recovering in films two incoherent pump beams of the light with crossed linear polarization states; this increases the number of ordered molecules and enhances the birefringence.

In order to generalize the selective angular redistribution to the whole of a given sample, one possible way is trying to irradiate simultaneously several rectilinearly polarization directions. Since E-fields of nonpolarized light exists at each instant in all transverse directions, unpolarized light such power white light sources or unpolarized lasers can push the azo dyes to orient towards the propagation direction (Yager, 2006; Natansohn, 2002; Han, 2001), even the sunshine is suitable (Yin, 2009; Ichimura, 2000). In our best acknowledgement, no work has been published on azo dye doped polymer films using circularly polarized light irradiance. Her, we study photo-induced behavior of an azo dye doped polymer by using both linearly and circularly polarized light irradiance. Not only a circular polarized light not erase the anisotropy but induces it in azo doped polymers.

Materials and experimental set-up

- Fabrication of azo dye doped polymer films

The azobenzene molecule used in this work is an azo dye called AZD1 (Pham, 1997, 1995). The polymer is the poly(methyl methacrylate) abridged as PMMA (average Mw : $\sim 120,000$ by GPC powder, $T_g = 105^\circ\text{C}$). Products are from Sigma-Aldrich. AZD1 doped in PMMA samples are obtained from the mixture of two separately prepared solutions (Pham, 1995). The first is the solution of the AZD1 in tetrahydrofuran (THF) solvent. The second one is the PMMA powder dissolved in the same solvent on a magnetic stirrer for 48 hours which was used to ensure the homogeneity of solutions and prevent the formation of eventual aggregates. The gravity deposition technique was used for depositing the solution on the microscope slides (Fisher Scientific Co.) previously cleaned and dried. Next, samples was left for 24 h in the closed, small Plexiglas box to get a regulated solvent evaporation rate allowing the mixture of azo dye and polymer solution to dry slowly on a leveled glass substrates under normal laboratory conditions (20°C , RH=35-45%) during one week in darkness. Films were then heated for 1 h at 100°C in an oven to remove any remaining solvent (Buffeteau, 1998). Their average thickness measured with a Sloan's Dektak IIA profilometer is $40\ \mu\text{m}$. Weakly doped films (0,05wt%) are analyzed with a Varian Cary 100 UV-Vis spectrophotometer, a typical spectrum is depicted in Fig. 1.

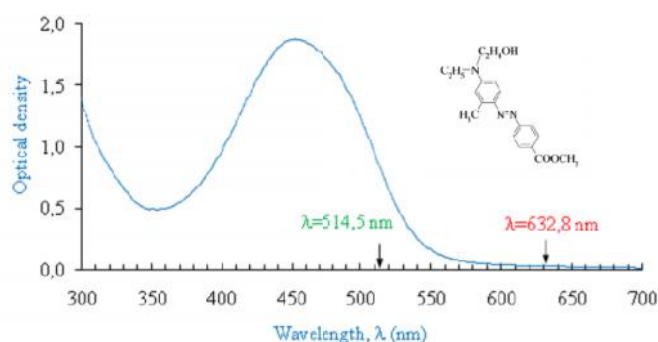


Figure 1. UV-Vis absorption spectra of AZD1 doped PMMA film (0,05wt%). Inset trans form of AZD1 molecular structure.

- Polarimetric experimental set-up

In the popularly experimental setup used for creating and probing anisotropy (Xu, 2008, 2013; Mendonça, 2007a, b; Filippo, 2009; Goulet, 2014; Choi, 1999; Bagherzadeh, 2014; Mohajerani, 2007; Luo, 2005; Chuang, 2010; Qi, 2004; Dall'Agnol, 2014; Yang, 2004), pump and probe beams are usually linearly polarized and the polarization direction of the probe beam is oriented at an angle of 45° with respect with that of the pump beam. Also, the film was set between a pair of crossed polarizer analyzer in the optical path of the probe beam. In general, the incidence angles of pump and probe beam are 0° and 45° respectively (or vice versa). However, this experimental setup is limited for several reasons. The most important are the followings. Firstly, the use a rectilinear polarization beam limit the angular hole burning exclusively to one direction; and only a certain percentage of azo molecules are activated. Secondly and importantly, only one transmittance component of the linearly polarized probe beam is detected after the analyzer. This approach leads to loss so much of data on what is happening in the sample. So change in the anisotropy was often interpreted as "randomization" and

“erasure” if the transmittance of the probe beam decreases (Xu, 2013; Luo, 2005) and as “photo-bleaching” (Mendonça, 2007a; Natansohn, 2001) if it increases whereas in reality, as our results will show, there is neither erasure nor photo-bleaching of the sample, these various behaviors are simply the manifestation of reversible anisotropy changes introducing phase shift between vertical and horizontal components of the oscillating E-field of the probe beam leading to the change in its polarization state. Thirdly is that this experimental setup does not allow the probe beam to “see” the created anisotropy at different angles of incidence especially at normal incidence. Our experimental set-up is shown in Fig. 2. The surface of the film is in Oxy plane. A CW Ar⁺ laser ($\lambda=514,5$ nm, $\phi_e\sim 100$ mW) was used as excitation source, and low power He-Ne laser ($\lambda=632,8$ nm, $\phi_e\sim 1$ mW) being a probe. The two wavelengths are placed on absorption spectrum (Fig. 1). The pump beam was fixed permanently at normal incidence on the input surface of photosensitive thin layer, i.e. parallel to Oz axis as shown in Fig. 2.

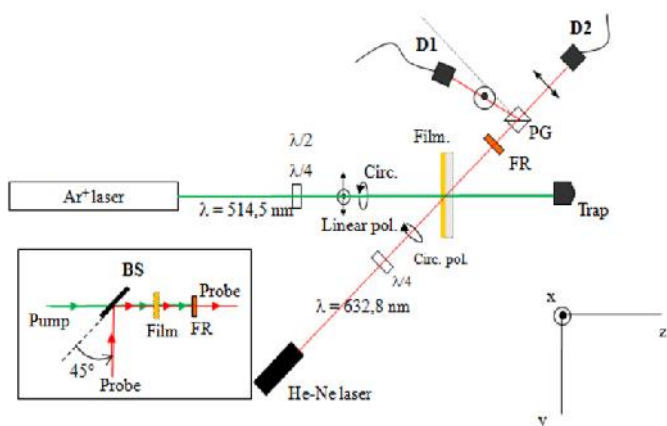


Figure 2. Polarimetric Experimental setup. The pump is a linear polarized continuous wave argon ion laser beam emitting at $\lambda=514,5$ nm. The probe beam is a linear He-Ne laser at $\lambda=632,8$ nm. Optical components $\lambda/2$ and $\lambda/4$ are half-wave and quarter-wave plates respectively. The PG component is the Glan-Taylor prism. Optoelectronic devices D1 and D2 are detectors of the light. The optical component FR is an interferential filter at $\lambda=633$ nm. Inset the coaxially pump and probe beam at incidence normal on the film

The probe beam axis located in the Oyz incidence plane was under an angle of incidence of 45° relative to normal incidence on the film. A quarter-wave plate ($\lambda/4$ -Plate) at $\lambda\sim 632,8$ nm are used to turn E-field plane-of-vibration of the probe light into circularly polarized light. The E-field of circular polarization state rotates at the frequency of the light ($\sim 4,74\times 10^{14}$ Hz) scanning all-orthogonal directions to its propagation axis in the film. A Glan-Taylor prism (Thorlabs Inc., Coating: 350 - 700 nm, extinction ratio: 100,000:1) was used to splits the circularly polarized probe beam into two equal rectilinear polarized components: the S-polarization component oscillates in the direction of the Ox axis and detected by the detector D1 and the horizontal component, i.e. the P-polarization oscillates in the incidence plane Oyz and detected by the detector D2. This latter make an azimuth angle ϕ with the Oy axis which equal to $+45^\circ$. Detectors are connected to a computer equipped with LabVIEW software. A beam Trap has been placed behind the sample to absorb the transmitted pump beam. The waists of the pump and probe beam at the plane of thin layer are approximately $2,94\times 10^{-3}$ m

and $0,52\times 10^{-3}$ m respectively. Since the probe beam was centered in the illuminated spot area in the film's volume.

RESULTS AND DISCUSSION

Linear polarized light build-up anisotropy

A fresh isotropic film (concentration $\sim 2,7$ wt%, thicknesses ~ 40 μm) were pumped by using P-polarized beam for enough time to reach saturation then switched off. The irradiance is $3,61$ kW/m^2 for the pump and $\sim 1,18\times 10^{-3}$ kW/m^2 for the probe. To compare, the sunlight irradiance external to the Earth's atmosphere is $1,36$ kW/m^2 . Temporal behaviors of S- and P-components of the probe are detected simultaneously. Figure 3 shows two consecutive photo-induced/relaxation anisotropy cycles.

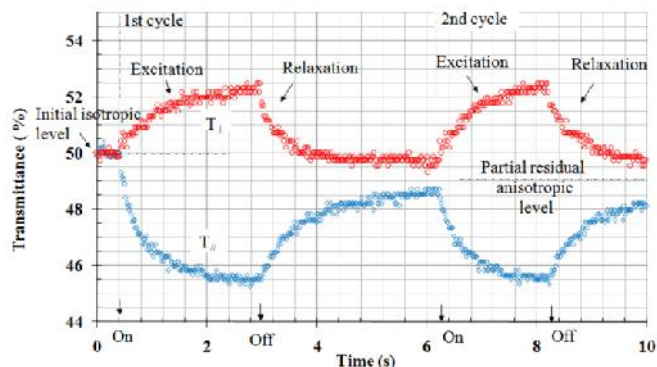


Figure 3. Two complete cycles of photo-buildup/self-randomization anisotropy in AZD1 doped in PMMA polymer film (C•2,8wt%, d•40 μm) pumped by using CW Ar⁺ laser ($\phi_e=100$ mW)

Between $t=0$ and $t=0,4$ s, fresh sample is not yet pumped. The T_{\perp} and T_{\parallel} transmittances corresponding respectively to S- and P-polarization components of the circular polarized probe beam are equal ($T_{\perp}=T_{\parallel}=50\%$), indicating the random orientation of the azo molecules (Mendonça, 2007b). At instant $t=0,4$ s, the pump light is turned on, thereafter T_{\perp} component of the probe increases while T_{\parallel} decrease, and the resulting anisotropy increases. The photo-isomerization will continue until all the azo molecules which can participate in this mechanism lie in the perpendicular position, then the anisotropy process is saturated (Todorov, 1984). Hence, the film is transformed into a negative uniaxial medium (Chuang, 2013). The evaluated birefringence by using $I=I_0\sin^2(\Delta\phi/2)$ where $\Delta\phi=2\pi\Delta n d/\lambda$ (Todorov, 1984; Zhao, 2015) is $\Delta n=(n_o-n_e)\sim 1,21\times 10^{-3}$ where n is the refractive index. As one can see, the time required to achieve saturation takes only few seconds. Because the AZD1 doped in PMMA film is transparent for the probe (Fig. 1), the famous Poynting's theorem can therefore be applied. Thus, simultaneously increase of T_{\perp} and decrease of T_{\parallel} are not due neither to the optical absorption nor to the diffusion, but to the photo-buildup anisotropy. Note that the transmittance is higher for P-polarization component of the probe than for its S-polarization one. At instant $t=3$ s, pump light is turned off, because of the spontaneous relaxation of oriented cis molecules, back to trans (Dumont, 1999; Sekkat, 1992). There is no need to change the polarization of the pump beam to being circular polarization to randomize the oriented molecules, simply cut-off the light and the randomization starts, similar behaviors was published in some references (Todorov, 1984; Mendonça, 2007a, b; Bagherzadeh-Khajeh

Marjan, 2014; Mohajerani, 2007). As one can see, the T_{\perp} component of the probe beam decreases while the $T_{//}$ component increases “exponentially” and the resulting anisotropy decreases. This is due to the thermal reorientation of some azobenzene molecules which tends to restore the thermodynamically randomized state (Natansohn, 1994; Rochon, 1992). At long-term; T_{\perp} and $T_{//}$ components tends towards another enduring steady state level which is quite different from the initial isotropic level; we have called it “partial residual anisotropic level” (Fig. 3). This behavior is a common characteristic of azo dye containing polymers films. Nevertheless, the thermal relaxation of molecules back to randomize trans state is incomplete: the anisotropy does not recover its initial isotropic value, either because of an incomplete cis–trans relaxation or because of some deformations of the doped polymer (Blanche, 1999). When the laser is turned off, a substantial number of cis azobenzene isomers remain “trapped” in their new orientation (Natansohn, 1994; Rochon, 1992) and long-term macroscopic anisotropy has been optically induced.

At instant $t=6,3$ s in Fig. 3, the P-polarized pump is turned on again on the same region (not in its amorphous state). As one can see, its effect is to produce the same amount of anisotropy in the same time interval like for the first cycle. The only difference compared to the first cycle is that the T_{\perp} and $T_{//}$ transmittances are now symmetrical with respect to the horizontal line that indicates “persistent partial anisotropic level”. This is because the excited region is already partially ordered after the first irradiation and is not yet randomized completely. Indeed, at microscopic scale (Natansohn, 2001), buildup anisotropy again on the same irradiated region involves moving the azo dyes from a thermodynamically stable state with partially anisotropy to another oriented state identical to the previous one (Natansohn, 1994). Even the initial isotropic level is never restored by pumping with the same beam whatever its polarization state, the reversible optically induced anisotropy, which was attributed to the molecular reorientation induced by the photo-isomerization of the azobenzene molecules, once no irreversible processes that could indicate sample’s photo-bleaching were observed, in accord with the literature (Mendonça, 2007a). Nevertheless, complete randomization can be achieved by heating samples below the glass transition temperature of the PMMA (Sigma-Aldrich, $T_g \sim 105$ °C), in accordance with the literature (Natansohn, 1994; Mohajerani, 2007; Heydari, 2011).

Linear compared to circular polarized light

S-polarized light like P-polarized one build anisotropy in azo dye doped polymer. Here, three principal polarimetric experimental configurations of interaction are studied. Results are presented in Fig. 4. First, the oscillating E-field of pump beam is in the incidence plane (P-polarization which is in the Oyz plane). Curves number 1 corresponds to this mode of excitation. Second, the E-field of pump beam is oriented orthogonally to the incidence plane. Curves number 2 corresponds to this mode of excitation. Third, the pump beam is circularly polarized. Curves number 3 corresponds to this mode of excitation. First and second photo-inducing/relaxation anisotropy cycles of curves labeled 1(sp) and 1(pp) are similar to those in Fig. 3. Thus, for the instance, a curve 2(ps) corresponds to the P-polarization of the probe and S-polarization of the pump beams, and so on. The probing time interval for the 1st and 2nd cycles are $\Delta t=2,6$ s and $\Delta t=2$ s

respectively. Curves 2 and 3 consist each of an only one photo-building/relaxation cycle. For the latter, the pumping time interval ($\Delta t=4$ s) is nearly two times longer than those of curves 1. Saturation levels under pumping are almost accomplished. As one can see, the most important conclusion is that the greatest anisotropy was obtained when azo dye-doped polymer was pumped by circularly polarized pump beam, i.e. the circularly polarized light can create a certain order in azo dye doped polymer samples.

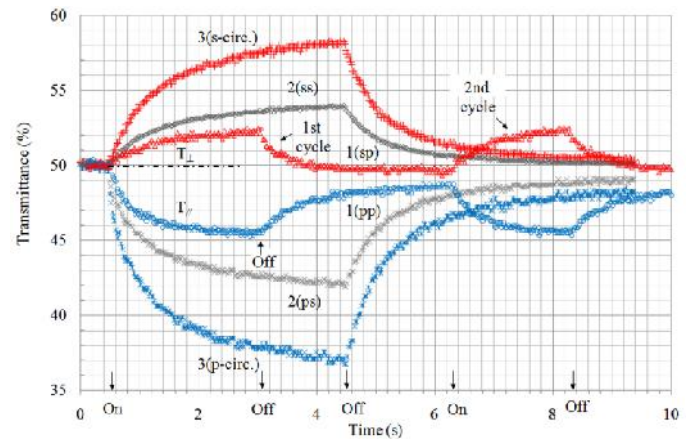


Figure 4. Circularly compared to linearly polarized pump beam: the photo-induced anisotropy of AZD1 doped PMMA polymer dependence on the polarization state. The first letter after the curve number represents the probe beam’s polarization state, and the second letter represents the excitation beam’s polarization. Thus, for example, curve 1 corresponds to the vertically (s) rectilinear polarized probe and horizontally (P) polarized excited beams with respect to the incidence plane. For each excited polarization, the excitation starts at $t=0,4$ s. T_{\perp} and $T_{//}$ are perpendicular and parallel transmittances corresponding to S- and P-probe beams respectively

Thus, pumping with S-polarized light compared to the P-polarized one does not enhance photo-induced anisotropy in azo dye doped polymer because for each of the two polarization states, only one direction of the angular hole burning are excited in the doped film. The amount of created anisotropy in doped samples will be the same for S- and P-polarized pump beam; this is because the two cases are quite symmetric. The amplitude difference that appears between 1(sp) and 2(ss) curves, for example, is due to the orientation of the index ellipsoid in the 3D space (Chuang, 2013) as seeing by the rectilinear polarization of the probe beam combined to the effective thickness of the sample. In fact, the induced index ellipsoid by pumping with P-polarization state is the same as that induced by pumping with S- polarization of the excitation beam. In two cases, only one direction of angular hole burning are activated, i.e. the two cases are equivalent. The only difference is the optical axis orientation in space 3D. In all cases, the extraordinary axis of the created oblate ellipsoid of refractive indices will be oriented in rectilinear polarization direction of the excitation beam.

Alternately linear and circularly polarized pump light

Doped film has been pumped alternately by using successively P- and circular polarized beam. The laser beam is circularly polarized with a quarter-wave plate in order to selectively pump molecules parallel to the plane of the sample and to accumulate them in the perpendicular direction (Sekkat, 1992; Tanchak, 2005). Results are shown in Fig. 5.

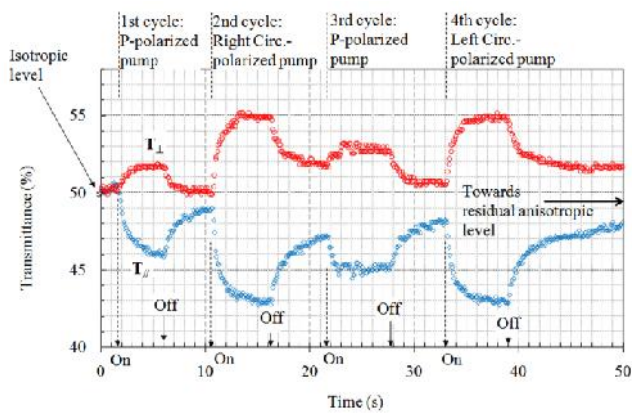


Figure 5. Four photo-induced/relaxation cycles in an AZD1 doped PMMA film cyclically pumped with On/Off successively P-linearly and circularly polarized beam

Between $t=0$ s and $t=1,5$ s, the sample is isotropic. The 1st cycle is the same as the first one shown in Fig. 3. The T_{\parallel} component of the probe decreases while the T_{\perp} increases. The 2nd cycle was induced by using right-circular polarized beam, the 3rd cycle by using the P-polarized beam and the 4th cycle by left-circular polarized light. In general, switching off the pump beam leads to a considerable decrease of the resulting anisotropy. Moreover, no significant changes were observed by using right- or left-circular polarized beam (see Fig. 6). Note that under the same experimental conditions, the induced anisotropy by using P-polarized beam during the 3rd cycle is higher than that induced during the 2nd cycle of the Fig. 3. This is because the 3rd cycle was created after illuminating the film by circular polarized beam while the 2nd cycle in Fig 3 was after the illumination by P-polarized beam. As one can see, pumping by using a circularly polarized light before pumping with linearly polarized one appears as if it contributes to the increase of the anisotropy. Moreover, the induced anisotropy by circular polarization state (2nd and 4th cycles, Fig. 5) appears as if it is much greater than that induced by linearly polarized one.

On the other hand, it was reported that if DR1 azo dye doped PMMA polymer is pumped with circularly polarized light, the anisotropy will be erased (Priimagi, 2009, 2014; Vapaavuori, 2013; Filippo, 2009; Luo, 2005). Our results show however that circular polarized light not erase anisotropy but induces an anisotropy which appears if it is greater than that induced by linearly polarized one (see Fig. 5). Natansohn and Rochon (Natansohn, 2002) are pointed out that if the light is circularly polarized, there will be no preferred orientation within the film plane, but about the same amount of dichroic molecules will probably align in the homeotropic direction. The progressively decrease of the circular dichroism as a function of number of photo-induced chirality/switching cycles in some azobenzene mesogens in their smectic phase has been attributed by the same authors (Heydari, 2011) to the tendency of the circular polarized light to align the chromophores perpendicularly to its polarization, i.e., in the direction of propagation of light. Chun-I Chuang *et al.* are used two different beams from two identical laser diodes at 532 nm to irradiate the Disperse Red 19 (DR19) doped in PMMA polymer (Chuang, 2013). Their results show that the photo-induced anisotropy by superposing two beams with crossed linearly polarization states on a doped film is much higher than that obtained by using only a single beam. Those authors have stated that azo-dye molecules can be further aligned by the extra polarized pump light, thus

increase the number of ordered molecules and enhance the induced birefringence. Nevertheless, our results show that during the irradiation with circularly polarized light, the trans molecules tends to orient in a direction perpendicular with the plane of the film which may induce some out-of-plane orientation, whereas in-plane orientation would be minimal since the incoming beam is circularly polarized (Tanchak, 2005). We have modified slightly the experimental setup shown in Fig. 2 to see is there some chirality induced or not. We have inserted a beam splitter ($R=T=50\%$) in the optical path of the pump beam between the $\lambda/4$ -plate and the film.

This beam splitter (the BS component inset Fig. 2) was mounted so that the pump and probe beams are at an incidence of 45° (not the same) on the input face of the film. The results show that $T_{\perp} \approx T_{\parallel} \approx 50\%$. There is no significant change in the polarization state of the probe beam. Thus, no chirality was induced (Blanche, 1999; Kalachyova, 2015), this is because trans species reorients towards the propagation direction of the pump beam: the film was transformed into a positive uniaxial medium (Chuang, 2013) whose optical axis is parallel to O_z axis. The experimental setup, shown in Fig. 2, is especially a powerful tool to study the angular redistribution behavior of azo dye doped polymers. Using circular polarized light allows us to pump and probe much better the samples for the following reasons. On the one hand, the E-field of circularly polarized light rotates at the angular frequency (ω) of the light. For the Ar^+ lasers emitting at $\lambda=514,5$ nm, $\omega \sim 5,83 \times 10^{14}$ cycles/s. Here, one cycle signifies 2π . If we trace the trajectory of the rotating E-field vector, we find it traces out a helix in the propagation direction in the medium with a pitch of just one wavelength, as shown in Fig. 6. The corresponding temporal frequency is $\nu \sim 5,83 \times 10^{14}$ Hz and the oscillating E-field rotates around its propagation axis while traversing a spatial period in the medium during the time period $T=1,71 \times 10^{-15}$ s.

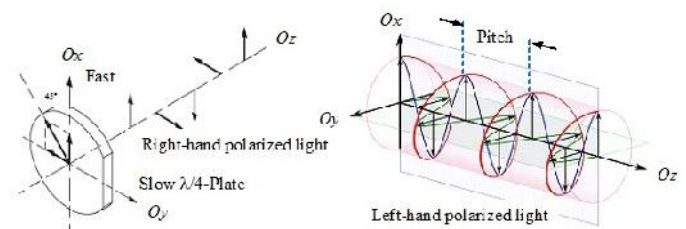


Figure 6. Circular polarization states. At left, right-circular polarization state is shown. Action of the $\lambda/4$ -plate on the E-field of the linearly polarized light is to rotate it at the frequency of the light. At right, the helix wraps in the opposite sense for left-circular polarized light

Even if the E-field of circularly polarized light that oscillates perpendicularly to the propagation direction cannot exist at the same instant in all perpendicular directions for a given transverse plane (for example, the Oxy plane in Fig. 2), the E-field which rotates at the frequency of the light scans a spiral like a “disk” volume in the film, as shown in Fig. 6. Further, the rotationally E-field of circularly polarized pump beam scans continuously a certain number N of periods through the doped film thickness. Indeed, the refractive index of isotropic azo dye-doped PMMA is approximately $n \sim 1,49$ (this is a Sigma-Aldrich manufacturing value) and the excitation wavelength in the doped film is $\lambda \sim 345,30$ nm this is because $\lambda = \lambda_0/n$ where $\lambda_0=514,5$ nm in vacuum. Then, for the typical value $40 \mu\text{m}$ of thickness, $N=L/\lambda=40 \mu\text{m}/0,3453 \mu\text{m} \sim 116$.

Under the irradiance, the rotating E-field will accomplish continuously 116 helical pitches into the film at each instant. So, the rotating E-field of circular polarized light scans helically the whole volume of the irradiated spot. Also, the emit beam of the pump light having a range of frequencies. For Ar⁺ lasers, the frequency bandwidth due to the Doppler broadening $\Delta\nu_D \sim 2,7$ GHz and the broadening natural emission linewidth $\Delta\nu_N \sim 450$ MHz (Siegman, 1986; Silfvast, 2004). The coherence time $\tau=1/\Delta\nu_D \sim 3,7 \times 10^{-10}$ s. After each coherence time, new wavetrains are constantly emitted by the laser. This means that if we were to look toward the incident wave vector direction (do not try this!), we would at least for an instant “see” a superposition of the wavetrains emitted in that direction. We would “see” a resultant wave having a given polarization state. That state would only last for an interval less than the coherence time before it changes (Hecht, 2002). Changes of the polarization state after each coherence time contributes to scan efficacy the irradiated spot of the film. On the other hand, the characteristic time of the photo-induced anisotropy curves shown in figures 3 and 4 is on the order of the second, in agreement with the literature (Zhao, 2009).

Taking into account the long live time of cis state of the order of few seconds in our azo doped polymer, which is consistent with the literature (Zhao, 2009; Saad, 1999a, b, c), the E-field of circular polarized light which rotates at the frequency of the light combined with the polarization state change after each coherence time appears as if it activates the angular hole burning in all transverse directions in the film at each instant: it scans permanently the whole irradiated volume. Thus, relaxing molecules that undergoes the reverse reaction cis to trans will forced to reorient in the propagation direction of the pump beam perpendicularly to the E-field of circularly polarized light, since only the propagation direction is perpendicular to the rotating E-field vector of the light. Under our experimental conditions, the action of circularly polarized light appears as if it enhance the amount of reoriented azobenzene molecules along the propagation direction of the light. Recently, Oates and Bin have proposed a mathematical modeling based on light-induced anisotropic diffusion (Bin, 2015) in which the trans- (or cis) azo-molecule is considered to be a microscopic dipole, determined by the microstructure (molecular conformation) of the trans (or cis) azo molecule. The results of this models show that in the case of a circularly polarized Gaussian laser beam, the spatial distribution of the trans vector align in the propagation direction of the laser beam. Of course, trans molecules aligned in this direction are usually “invisible” to a probe beam under normal incidence (Natansohn, 2002; Dall’Agnol, 2004), as confirmed with our experimental setup (inset Fig. 2).

This is also the case of the experimental setup in followings references (Xu, 2008; Luo, 2005) and even many others. Photo-inducing and controlling the anisotropy is would enable the orientation/reorientation and polarimetric detection of information bits in such materials (Mislter, 2005; Pirani, 2016). An immediate possible application is thinking about the design, for example, of an all-optical switching device that would work preferentially at normal incidence using alternately linear/circular polarized beam in which the oscillating E-field orient and reorient alternatively the azobenzene molecules in two perpendicular directions, where one of them will evidently in the propagation direction of the light. Of course, the residual anisotropy should be taken into account in designing devices.

Conclusion

We have studied the behavior of AZD1 dye doped PMMA polymer by using both pump and probe circular polarized light. Our results show that circular polarized light doesn't erase anisotropy, but induces anisotropy which is much greater than that induced by linearly polarized light. The use of circular polarized light activates all perpendicular directions of the angular hole burning in polymer film intensifying the angular redistribution and enhances photo-induced anisotropy. Under circular polarized light, trans molecules align towards the propagation direction of the pump light. The reorientation of azobenzene molecules successively in two orthogonal directions using cyclically linear and circular polarizations will be useful for applications such all optical switching and Optical Data Storage. Photo-induced behavior study of other azo dye doped polymers using both rectilinearly, circularly and elliptically polarized light is natural extensions of this work. Also, it will be interesting to investigate separately the action of circular polarized light on azo dye doped and azo groups containing polymers.

Acknowledgment

This work were supported by the - Fonds de Recherche du Québec–Nature et Technologies (FQRNT) - under the grant FT073270. The measurements were performed with help of Marc-Antoine Blanchet in Center for Optics, Photonics and Lasers (COPL) at Laval University.

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