Rapid Communications

Photoassisted Poling of Azo Dye Doped Polymeric Films at Room Temperature

Z. Sekkat and M. Dumont

Institut d'Optique Théorique et Appliquée, Bât 503, B.P.147, F-91403 Orsay Cédex, France
(FAX: +33-1/6941-3192)

Abstract. The reversible cis-trans photoisomerization of disperse red 1 (DR1) in PMMA thin films has been demonstrated to be strongly polarization sensitive [1]. In this communication two mechanisms are identified: the angular hole burning and the angular redistribution of molecules. It is shown that, in the presence of a DC electric field, the redistribution is not centrosymmetric and produces a poling of the film. The evolution of the second-order nonlinear susceptibility, $\chi^{(2)}$, is monitored by measuring the electro-optic effect by attenuated total reflection and by second-harmonic generation.

Azobenzene derivatives constitute a family of dye molecules well-known for their photochromatic properties which are due to the reversible cis-trans photoisomerization with respect to the N = N double bond. In this family, the disperse red 1 (DR1) has been widely used as a dopant (or as a bonded radical) in polymeric thin films for its large optical nonlinearities and for its electro-optic properties. In recent publications [2,3] we have shown the reversible change of the absorption spectra of DR1 doped PMMA films exposed to a pump beam (inside the blue-green absorption band) and the associated variations of the index of refraction have been measured by Attenuated Total Reflection (ATR). In [1] we found that photisomerization of DR1 is very sensitive to the polarization of the pumping light which induces birefringence in the film. Similar results have been obtained by different researchers with other dye molecules (Shi et al. [4], Malouin et al. [5]). In this paper we will demonstrate the existence of two mechanisms and the possibility of poling the film by applying a DC electric film in combination with optical pumping.

Films are prepared by dissolving purified DR1 in a commercially available solution of PMMA (molecular weight 496K) in chlorobenzene and by spin coating the solution onto a glass slide. The remaining solvent is evaporated by a soft baking (a few min at $\simeq 100°$ C). With pump beam intensities less than 100 mW/cm^2, no photodecomposition has been observed.

The polarization sensitivity of photisomerization is due to the one-dimensional shape of these molecules. It is a good approximation to consider that their polarizability tensor and their second- and third-order hyperpolarizability tensors have only one component along the molecular z-axis: α_z, β_z, γ_z, respectively. μ, the permanent dipole of the molecule, is also parallel to the z axis. The probability for a molecule to be pumped from the trans shape to the cis shape is proportional to $\alpha_z \cos^2 \theta_p$, where θ_p is the angle between the pumping light electric field and the molecular axis. Therefore, molecules parallel to the pump polarization are pumped more efficiently than the others and a hole is burned in the angular distribution of the trans molecules. As the cis-shape has a smaller polarizability and a blue shifted absorption spectrum, the photoinduced anisotropy (and dichroism) can be explained by the anisotropic depletion of the trans-state by this angular hole burning. This simple model predicts [1] that a weak pump beam induces an index variation (or an optical density variation) three times larger for a probe beam polarized along the polarization of the pump beam than for a probe beam polarized perpendicularly ($\Delta n_{\parallel} = 3\Delta n_{\perp}$). For large pump intensities, saturation reduces this ratio which tends towards 1, since all molecules tend to be pumped, even with θ_p near $\pi/2$.

Experimental results [1] show that $\Delta n_{\perp}$ is much smaller than $\Delta n_{\parallel}/3$. This can be explained by a second mechanism which has been widely developed to explain the Wegert effect [6] in viscous solutions [7] and in polyvinyl alcohol films for holography [8]: during the photoisomerization and relaxation cycle, the molecular orien-
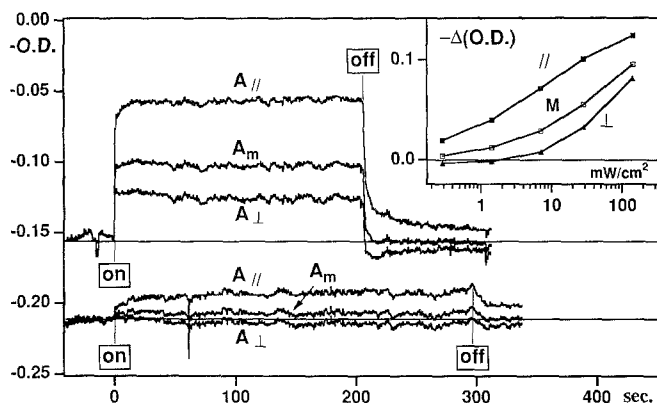
Fig.2. ATR experimental arrangement. The probe laser is a diode emitting at $\lambda = 830$ nm. The reflectivity of the sample and its modulation at frequency Ω are recorded as a function of the incidence angle. Experimental curves are shown in the inset of Fig.3

Fig.1. Photoinduced dichroism in a DR1 doped PMMA film (2.5% of DR1; thickness $\simeq 1.5\mu m$). The experimental curves represent the decimal logarithm of the transmission (i.e., minus the optical density) of a probe beam ($\lambda = 514$nm) polarized in a direction parallel ($A_{\parallel}$ or perpendicular ($A_{\perp}$) to the linear polarization of the pump beam ($\lambda = 488$nm). The pump beam intensity is 0.28 mW/cm^2 for the lower curves and 28 mW/cm^2 for the upper curves (which have been translated upward by 0.05). $A_m = (A_{\parallel}+2A_{\perp})/3$ represents the isotropic absorption, its variations are proportional to the number of molecules transferred to the cis form. The inset gives the optical density variations as a function of the pump beam intensity (measured 3 min after the pump switched off). At low pump intensity, the cis population is small and $A_{\perp}$ is negative as a consequence of the angular redistribution. At high pump intensity, saturation of the hole burning process tends to equalize $A_{\perp}$ to $A_{\parallel}$

tation is redistributed. If the pump intensity is low and if the thermal relaxation from cis to trans is fast (i.e., if saturation is very low), the cis population is negligible. Then, missing molecules near the parallel orientation are necessarily found near the perpendicular orientation. More precisely, one finds $\Delta n_{\perp} = -\Delta n_{\parallel}/2$ (or $\Delta A_{\perp} = -\Delta A_{\parallel}/2$ for absorption). Todorov's experiments [8] illustrate this angular redistribution. In the case of DR1 in PMMA, hole burning and redistribution are in competition and $\Delta n_{\perp}$ or $\Delta A_{\perp}$ may be positive or negative according to pump intensity. This is illustrated by Fig.1 which gives some results from transient photoinduced dichroism. These experiments and a complete model will be discussed with more details in another publication. After the switching off of the pump beam, the cis population completely disappears in a few seconds but the anistropy survives several minutes (may be hours). The relaxation is not exponential: this could be due to differences of mobility of dye molecules in different sites within the polymer.

With both mechanisms the source of the anisotropy is the selective optical pumping proportional to $\alpha_z \cos^2\theta_p$. The symmetry of this process produces alignment of molecules but not orientation. The angular distribution of molecules is anisotropic but the average dipole moment of the distribution remains zero (equal number of molecules with angles θ_p and $\pi-\theta_p$). Similarly, the second-order nonlinear susceptibility $\chi^{(2)}$ is zero, since the distribution remains centrosymmetric. The angular redistribution is a kind of thermalization and, therefore, it was worth performing the optical pumping in the pres-
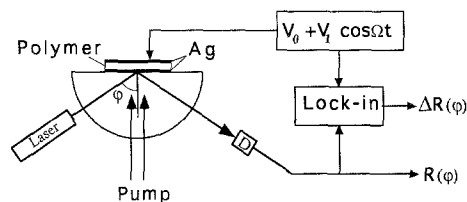
ence of an electric field in order to orient this redistribution process. For probing the photoinduced $\chi^{(2)}$ we used the ATR method which gives a measurement of the Pockels effect [3,9] and Second-Harmonic Generation (SHG).

For ATR measurements, the DR1 doped PMMA film (5% by weight) is spin coated onto a glass slide previously covered with a thin semitransparent silver layer (30 to 50nm). Then a silver electrode is deposited onto the polymer film by vacuum evaporation. The glass slide is put in optical contact with a half sphere through which an infrared laser beam ($\lambda = 830$nm) is reflected on the sample (Fig.2). The reflectivity $R(\rho)$, measured as a function of the incidence angle, exhibits a set of dips corresponding to the excitation, through the thin silver layer, of the successive guided modes inside the film. TM (Transverse Magnetic) and TE (Transverse Electric) polarizations produce two different sets of modes, permitting a very sensitive measurement of n_o and n_e, the indices of refraction in the plane of the film and perpendicularly to it, respectively (the optical axis is assumed to be perpendicular to the plane of the film). The electro-optic effect is observed by applying a modulated voltage ($\simeq 2$kHz) on the top electrode and by monitoring the reflectivity modulation $\Delta R(\rho)$ induced by the modulation of the indices (inset in Fig.3). By measuring the modulation of all the TE and TM modes we obtain the variations Δn_e, Δn_o and Δh (the piezoelectric variation of thickness) [9]. In this letter, we shall only discuss the results obtained from the modulation of the TM mode with the largest incidence angle: this mode directly gives Δn_e with a good precision.

In a first experiment a large DC voltage ($V_0 \simeq 100$V) is applied to a sample (1.8μm thick) which is illuminated through the thin silver layer with a 488 nm argon-laser beam. The laser beam is circularly polarized in order to selectively pump molecules parallel to the plane of the sample and to accumulate them in the perpendicular direction. The pump beam is switched off after 15 min and the DC voltage a few minutes later. A significant Pockels effect is observed during the following hours; it strongly decreases after a few days but never completely vanishes. Similarly, a sample without electrodes, submitted during 15 min to a corona discharge (5000V on a sharp needle at 1cm from the sample), produces, after two hours, a significantly large SHG signal (with a pulsed Nd:YAG laser) from the

region which had been illuminated by a circularly polarized 488 nm laser beam during the corona discharge application.

A more precise ATR experiment has been performed in which the linear electro-optic signal is monitored continuously during the poling cycle and the relaxation. An AC voltage ($V_1 \cos\Omega t$) is added to the DC voltage ($V_0 = 125V$) and the incidence angle of the probe beam is fixed at the top of the modulation signal (inset in Fig.3). This angle has to be manually adjusted after the switching on (or off) of the DC voltage and of the pump beam in order to correct the dip shifts induced by molecule reorientation.

In Fig.3 the dotted curve shows the amplitude of the modulation signal, at frequency Ω, when the DC voltage is applied without pumping beam. The sample has been baked at $120°$ C and its $\chi^{(2)}$ signal is zero before the experiment. The simultaneous application of the DC field E_0 and of the AC field E_1 produces a strong modulation of Δn_e which contains the contribution of linear and quadratic electro-optic effects. Axis 3 being the optical axis normal to the film, the variation of $n_e^2 = 1 + \chi_{33}(E_0, E_1)$ is:

$$2n_e \Delta n_e = \chi_{333}^{(2)} (E_0 + E_1 \cos\Omega t) + \chi_{3333}^{(3)} (E_0 + E_1 \cos\Omega t)^2$$

$$= (\chi_{333}^{(2)} + 2\chi_{3333}^{(3)} E_0) E_1 \cos\Omega t + \frac{1}{2}\chi_{3333}^{(3)} E_1^2 \cos 2\Omega t$$

$$+ \text{ unmodulated terms.}$$

$\chi^{(2)}$ and $\chi^{(3)}$ can be expressed as functions of the density of trans molecules (N) and of the projections of the angular distribution $G(\cos\theta)$ on the Legendre polynomials [10]:

$$A_p = \int_0^\pi G(\cos\theta) P_p(\cos\theta) \sin\theta \, d\theta ,$$

$$\chi_{333}^{(2)} = N\beta_z \left(\frac{3}{5}A_1 + \frac{2}{5}A_3\right),$$

$$\chi_{3333}^{(3)} = N\gamma_z \left(\frac{1}{5} + \frac{4}{7}A_2 + \frac{8}{35}A_4\right) + \chi^{(3)} \text{ (PMMA)} .$$

All the A_p are functions of the DC field and of time, as a consequence of the driving torque (potential energy $-\mu E_0 \cos\theta$) and of the viscosity of the polymer. At thermal equilibrium for those molecules which are free to rotate, $G(\cos\theta)$ is the Langevin function. The main term of its development [11] is A_1 which characterizes the molecular orientation and which begins as a linear function of $\mu E_0/kT$, for small values of μE_0. In first approximation, the stationary value of $\chi^{(2)}$ is proportional to $\mu\beta_z E_0/kT$. A_2 characterizes the molecular alignment and varies quadratically with E_0: it is easily observed from the variation of the anisotropy $[\chi_{33}^{(1)} \propto \alpha_z(1+2A_2); \chi_{11}^{(1)} \propto \alpha_z(1-A_2)]$. Nevertheless, A_2 is a small correction in the expression of $\chi^{(3)}$. Therefore, we can estimate the contribution of $\chi^{(3)}$ from the 2Ω modulation of the ATR
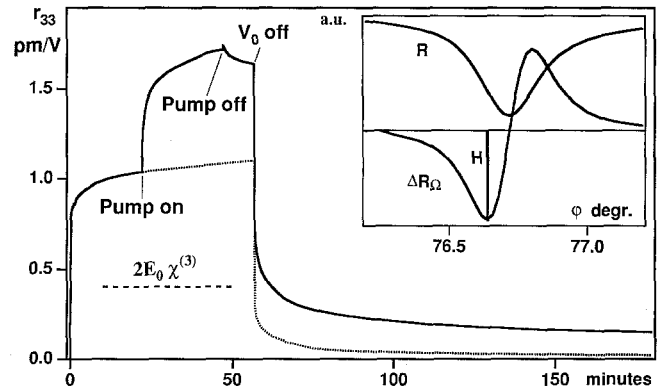

Fig.3. Evolution of the amplitude H of the modulation signal at frequency Ω of a DR1-PMMA film (thickness $1.8\mu m$). The inset shows an ATR reflectivity dip $R(\rho)$, its modulation $\Delta R\Omega(\rho)$, and the definition of the amplitude which is proportional to Δn_e. H has been directly expressed in the useful form of the Pockels coefficient, $r_{33} = 2E_1^{-1}n_e^{-3}\Delta n_e$. The DC voltage $V_0 = 125$ V is applied from t = 0 to t $\simeq$ 1h. The dotted curve represents the signal without optical pumping and the full line the signal obtained with a circularly polarized pump beam applied during 25 min ($\lambda = 488$nm). Approximately 10% of the 82 mW/cm^2 incident beam is transmitted through the silver layer. Each experiment begins with a completely isotropic sample. The dashed horizontal line gives the estimated value of the $\chi^{(3)}$ contribution during the presence of the DC voltage: the signal above this line is due to the $\chi^{(2)}$ arising from molecule's orientation

signal for $V_0 = 0$ (because of the high viscosity, molecules are not able to rotate at frequencies as high as 2kHz and there is no contribution of $\mu\beta_z E_1^2$ at 2Ω).

In Fig.3, the estimated contribution of $2\chi^{(3)} E_0$ has been indicated. One can see the importance of the pure $\chi^{(2)}$ term which indicates that many molecules are free to rotate even at room temperature. When the DC field is switched off (without any optical pumping) the $\chi^{(2)}$ signal falls rapidly but a small part of it needs hours to vanish completely. This indicates that the majority of the oriented molecules relax in less than one second but some of them are in a much more viscous environment. The contribution of some of these slow molecules is also evident from the slope of the plateau during the build-up of orientation.

At the moment the circularly polarized pump beam is switched on, a large increase of the $\chi^{(2)}$ signal appears. This is shown in Fig.3 for the case of a light flux of 83 mW/cm^2 (approximately 10% of this light is transmitted through the silver layer). This indicates that a part of the molecules which are tightened to the polymer, strongly enough to be unable to rotate under the sole action of the electric field, may be oriented after undergoing a photoisomerization and relaxation cycle. The optical pumping increases A_2 (as proved by the anisotropy), but its conjunction with the DC field increases A_1 (and possibly A_3).

When the pumping beam is switched off, the $\chi^{(2)}$ signal changes only a little until the removal of the DC field. Then it drops fast but the remaining signal is much larger than in the absence of optical pumping.

Several days later, a small electro-optic effect is always present (in the case of Fig.3 we have r_{33} = 0.4 pm/V after 5 min, 0.14 pm/V after 4 hours, 0.06 pm/V after 2 days, and 0.03 pm/V after 18 days). If a reverse DC field is applied, without optical pumping, a reverse $\chi^{(2)}$ is observed, but after a rest time of the order of one hour the previous value of $\chi^{(2)}$ is restored. The small quantity of hardly tightened molecules which have been oriented with the help of optical pumping are not affected by a further application of the electric field.

This increase of the molecular orientation is not due to a thermal effect: we proved this by illuminating the sample on the opposite side after blackening the thick silver electrode. The energy deposition is larger than in the previous experiment since there is no reflection. Index and thickness variations have been measured. They correspond to an increase of a few degrees of the temperature, but the $\chi^{(2)}$ signal remains unchanged.

Finally, a second-harmonic generation experiment has been used for monitoring the building up of $\chi^{(2)}$. A DR1-PMMA film, prepared on an ITO coated glass plate, is illuminated by a pulsed Nd:YAG laser (λ = 1.06 μm, incidence angle 50°) and the SHG signal is measured with a photomultiplier. The sample is exposed to a corona discharge (+5000 V) produced by a sharp point at a distance of 1 cm. A small SHG signal appears when the corona discharge is switched on (EFISH signal) but its amplitude is multiplied by more than a factor 2 by a perpendicular illumination with a circularly polarized laser beam ($\simeq$100 mW/cm^2 at λ = 488 nm).

Similar results have been obtained with DMANAB (4-dimethylamino-4'nitroazobenzene). They demonstrate that the polarization selective optical pumping of azobenzene derivatives produces an angular redistribution of molecules which can be oriented by a strong electric field. This provides a method for poling azo dye doped films at room temperature for producing second-order nonlinearities. The electro-optic r_{33} coefficient is rather small in DR1 doped PMMA and this method appears to be less efficient than high temperature poling by a factor of 3 to 5. Nevertheless, we must notice that experiments have been done with a very low dye concentration (5% by weight) and that in these samples a large part of dye molecules is free to rotate and relaxes very fast. A lot of materials are presented in literature, in which the azo dye molecules are linked to the polymer chain [4]. They

permit a large increase of the dye concentration (by at least a factor 10) with a reduced mobility of molecules. These materials have given stable $\chi^{(2)}$ properties by poling at high temperature. Even less efficient, their poling at room temperature by optical pumping would be useful as it would permit the precise drawing of patterns of oriented molecules.

References

1. Z. Sekkat, M. Dumont: Appl. Phys. B **53**, 121 (1991)
2. Z. Sekkat, M. Dumont, R. Loucif-Saibi, J. Delaire: J. Appl. Phys. **71**, 1543 (1992)
3. M. Dumont, D. Morichère, Z. Sekkat, Y. Levy: In *Photopolymer Device Physics, Chemistry, and Applications II*, ed. by R. Lessard. SPIE Proc. **1559**, 127 (1991)
4. Yongqiang Shi, W.H. Steier, Lupin Yu, Mai Chen, L.R. Dalton: Appl. Phys. Lett. **58**, 1131 (1991); ibid **59**, 2935 (1991)
5. C. Malouin, P. Galarneau, R.A. Lessard: In *Organic Molecules for Nonlinear Optics and Photonics* ed. by J. Messier, F. Kajzar, P. Prasad, NATO ASI Series E, Vol. 194 (Kluwer, Dordrecht 1991) p.513
6. F. Weigert: Verh. Phys. Ges. **21**, 485 (1919)
7. B.S. Neporent, O.V. Stolbova: Opt. Spektrosk **10**, 287 (1961) [Opt. Spectrosc. **10**, 146 (1961)]; Opt. Spektrosk **14**, 624 (1963) [Opt. Spectrosc. **14**, 331 (1963)]; O.V. Stolbova: Opt. Spektrosk **16**, 532 (1964) [Opt. Spectrosc. **16**, 288 (1964)]; A.M. Makushenko, B.S. Neporent, O.V. Stolbova: Opt. Spektrosk **31**, 557 (1971) [Opt. Spectrosc. **31**, 295 (1971)]; Opt. Spektrosk **31**, 741 (1971) [Opt. Spectrosc. **31**, 397 (1971)]
8. T. Todorov, L. Nikolova, N. Tomova: Applied Optics **23**, 4309 (1984)
9. M. Dumont, Y. Lévy, D. Morichère: In *Organic Molecules for Nonlinear Optics and Photonics* ed. by J. Messier, F, Kajzar, P. Prasad, NATO ASI Series E, Vol.194 (Kluwer, Dordrecht 1991) p.461
10. M.G. Kuzyk, J.E. Sohn, C.W. Dirk: J. Opt. Soc. Am. B **7**, 842 (1990)
11. J.W. Wu: J. Opt. Soc. Am. B **8**, 142 (1991)