

Photoinduced manipulations of photochromes in polymers: Anisotropy, modulation of the NLO properties and creation of surface gratings

Yomen Atassi, Jerome Chauvin, Jacques A. Delaire, Jean-Francois Delouis, Isabelle Fanton-Maltey and Keitaro Nakatani

PPSM, URA 1906 of CNRS, Ecole Normale Supérieure de Cachan, 61, avenue du Prdt Wilson 94235 Cachan Cedex, France

Abstract: Photochromes in solid matrices such as polymers or sol-gels are interesting because of their potential applications as optical filters or optical memories. Besides their reversible color change which is used in these applications, they have also raised a new interest because other optical or physicochemical properties can be changed under light control. We review here the optical properties induced by irradiation with polarized light. First, it has been known for more than two decades that birefringence and UV-visible dichroism can be induced in azo polymers. More recently, such phenomena have also been found with spiropyrans. Secondly, when thin polymer films are irradiated with an interference pattern, it is possible to create both refractive index and thickness gratings.

Other optical properties arise from the coupling between photochromism and nonlinear optical (NLO) properties. First, when the polarized excitation beam is superimposed with a DC electric field directed perpendicular to it, a non centrosymmetric arrangement of dipoles can be created in a polymeric medium, and second order NLO susceptibilities can be measured. Secondly, it is possible to photoswitch the NLO response of previously oriented photochromic and NLO active polymers (photoswitching) by irradiating alternatively each form of the photochrome. Thirdly, when two coherent beams at frequencies ω and 2ω are superimposed on the same NLO sample, it is also possible to induce non centrosymmetry. This method, called "all-optical poling" is very promising to create NLO devices such as electro-optical modulators or frequency converters.

Keywords: photochromes, birefringence, photoassisted poling, photoswitching of NLO properties, surface gratings, azobenzene, spiropyrans, fulgides, diarylethenes, anils.

INTRODUCTION

Photochromism has been widely studied in polymers as well as in solutions (ref.1,2). It is usually defined as the reversible photoinduced transformation between two molecular states whose absorption spectra are significantly different. Photochromic molecules have received an increasing interest over the last ten years: new photochromic systems have been found, with increased photochemical stability, and new applications have been developed (ref.3). Photochromic polymers offer advantages because they are easier to use in practical applications, as in photochromic sunglasses or optical memories. Our work deals with optical applications of photochromic polymers other than color change, but connected with it, namely dichroism and birefringence, photoinduced surface gratings, photoassisted orientation and disorientation and photoswitching of the nonlinear optical (NLO) response. We will develop below the different optical (and structural) phenomena which can be induced by irradiation with polarized light of thin polymer films containing photochromic molecules. Among these molecules, azo dyes play a dominant role probably due to some specific features of the trans \rightarrow cis isomerization reaction which occurs in a good yield in solid state matrices ($\Phi_{\text{trans} \rightarrow \text{cis}} = 0.11$ and $\Phi_{\text{cis} \rightarrow \text{trans}} = 0.70$ for Disperse Red One in PMMA matrix at room temperature) and to the very fast back thermal cis \rightarrow trans reaction ($k = 0.2 \text{ s}^{-1}$ for DR1 in PMMA at room temperature).

*Lecture presented at the 17th IUPAC Symposium on Photochemistry, Sitges, Barcelona, Spain, 19–24 July 1998.
Other presentations are published in this issue, pp. 2147–2232.

PHOTOINDUCED BIREFRINGENCE AND DICHROISM

It has been known since the sixties that viscous solutions of azo dyes become dichroic and birefringent when illuminated with polarized light (Weigert effect) as a consequence of the cis-trans photoisomerisation reaction. More recently, photoinduced anisotropy of azo dyes has also been studied in various thin polymer films for integrated optics (ref. 4,5,6): most often, for these applications, azo dye chromophores are chemically linked to the polymer chain in order to increase the stability of the photoinduced birefringence or dichroism.

Photoinduced anisotropy of trans DR1 molecules in polymer films leads to an increase of both UV absorption and refractive index in a direction perpendicular to the direction of polarization of the pump light and a correlative decrease in a parallel direction. This phenomenon has been correctly described by a model (ref. 6) which takes into account first angular photoselection (or angular hole burning) of the excited molecules during excitation by polarized light: trans molecules with transition dipole moment parallel with the electric field of the pump light are preferentially excited and convert to the cis state, and secondly angular redistribution: molecules rotate isotropically away from the initial direction of excitation during and/or after excitation and conversion to the cis state, and/or during the back cis \rightarrow trans reaction (see Fig.1). If the "hole burning" process occurs alone, then, anisotropy must disappear after the disappearance of the cis state. As this is not the case, especially for PMMA-DR1 copolymers, it means that DR1 molecules rotate during the photo-isomerization process (angular redistribution). This rotation can occur during one of the three steps of the process:

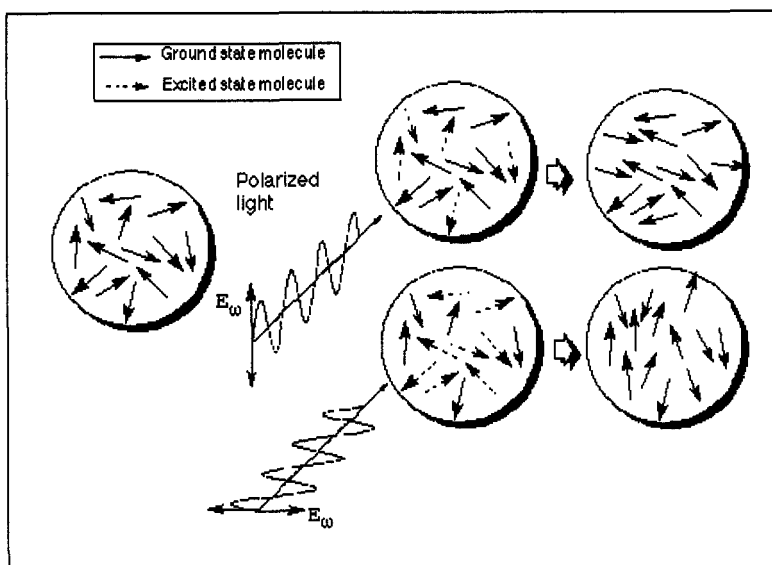


Fig. 1. Optical generation of anisotropy. The molecules excited with polarized light tend to align in a direction perpendicular to the polarization.

- during the trans \rightarrow cis photochemical reaction,
- during the lifetime of the cis molecule, as the rotational diffusion coefficient of the cis molecule may be lower, this molecule being more spherical,
- during the photochemical and/or thermal back process from the cis to the trans state.

With PMMA-DR1 copolymers, a memory effect has been put into evidence: the anisotropy remains a long time after the end of pumping (Fig.2). This memory effect can be used to register stable polarization gratings (ref.6). Pumping with light polarised in a direction perpendicular to the previous one leads to disorientation.

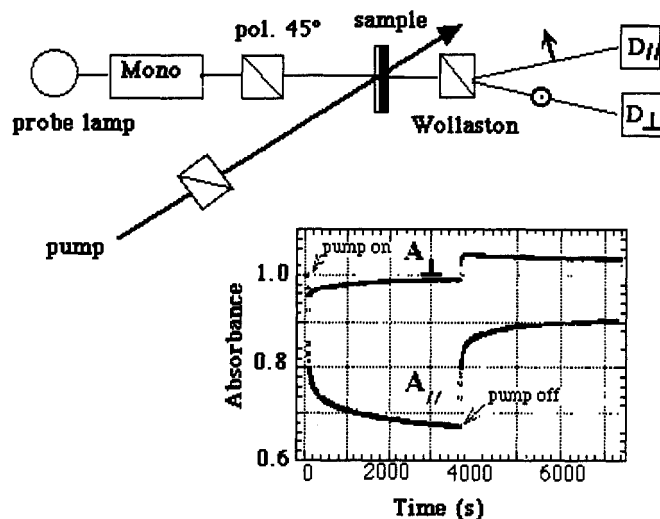


Fig. 2. Photoinduced dichroism in polymer films. Upper part: experimental arrangement. Lower part: Time evolutions of perpendicular and parallel absorbances during exposure ($I = 10 \text{ mW. cm}^{-2}$) to a linearly polarized pump beam, for a 5% DR1/PMMA sample ($e = 1 \mu\text{m}$)

PHOTOINDUCED SURFACE GRATINGS

Recently, it has been discovered that it is possible to inscribe surface gratings on the surface of a thin azo polymer film on exposure of the film by an interference pattern of polarized light at a wavelength near the absorption maximum of the dye (ref. 7,8)(see Fig. 3). The thickness modulation, which can reach several hundreds of nanometers, occurs at a rate which depends on the T_g of the polymer. This modulation can be explained by translational diffusion of azo molecules from the clear fringes to the dark fringes in a direction perpendicular to the fringes, this diffusion being initiated by the photoisomerisation reaction.

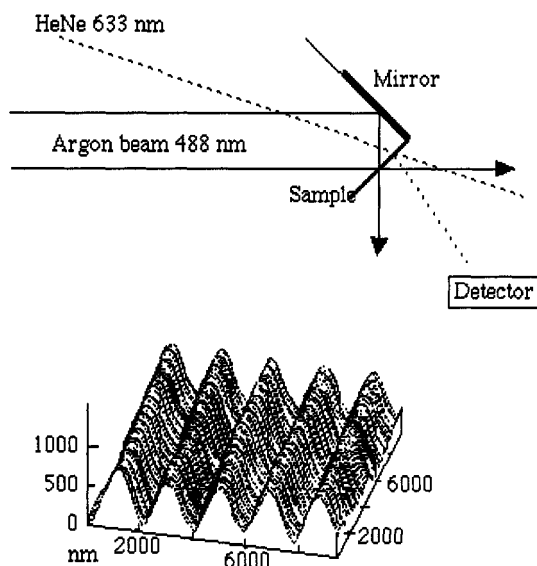
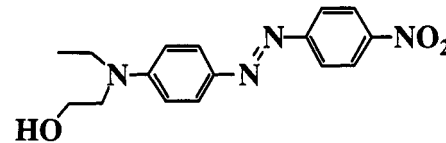
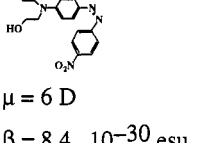
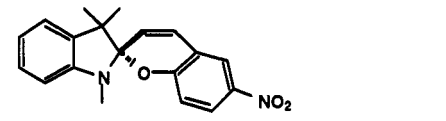
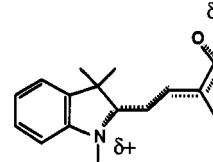
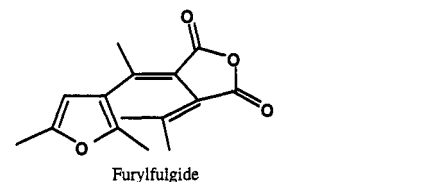
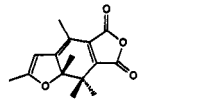
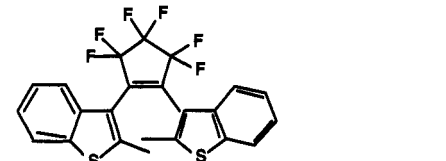
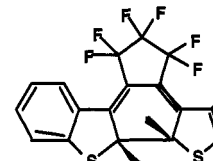
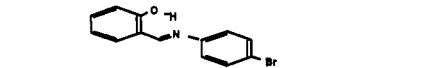
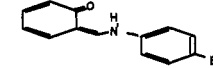


Fig. 3. Optically inscribed diffraction gratings in azo polymer films. Upper part: experimental set-up for grating inscription; lower part: Atomic force microscope surface profile of an optically inscribed copolymer PMMA-co-DR1 grating.

Table I Dipole moments and first order hyperpolarisabilities of photochromes

Trans Disperse Red One	Cis Disperse Red One
	
$\mu = 9 \text{ D}$ $\beta = 44.6 \cdot 10^{-30} \text{ esu}$	$\mu = 6 \text{ D}$ $\beta = 8.4 \cdot 10^{-30} \text{ esu}$
spiropyran	photomerocyanine
	
$\mu = 7.5 \text{ D}$ $\beta = 1 \cdot 10^{-30} \text{ esu}$	$\mu = 13.6 \text{ D}$ $\beta = -40 \cdot 10^{-30} \text{ esu}$
 <p style="text-align: center;">Furylfulgide</p>	 <p style="text-align: center;">Dihydrobenzofuran derivative</p>
$\mu = 7.2 \text{ D}$ $\beta\mu = 6.6 \cdot 10^{-48} \text{ esu}$	$\mu = 6.6 \text{ D}$ $\beta\mu = 91 \cdot 10^{-48} \text{ esu}$
Diarylethene (open form)	Diarylethene (closed form)
	
$\beta\mu = 13 \cdot 10^{-48} \text{ esu}$	$\beta\mu = 55 \cdot 10^{-48} \text{ esu}$
N-salicylidene-4-bromoaniline (yellow, stable)	(red, unstable)
	
$\beta = 2.3 \cdot 10^{-30} \text{ esu}$	$\beta = 1.3 \cdot 10^{-30} \text{ esu}$

Such an optomechanical effect, which is very easily processed, opens the door to applications in real time holography, holographic interferometry and optical memories.

NONLINEAR OPTICAL PROPERTIES OF PHOTOCROMES

The different photochromic systems studied in this work are presented on Table I. Disperse Red One (DR1) is probably the most studied photochrome due to its very interesting NLO properties in polymers

(ref. 4,5) as we will describe below. The spirocyan / photomerocyanine group has also been investigated in detail in polymers and in solutions as well, and the NLO properties have already been described (ref. 9,10). More recently, we have shown that it was possible to observe NLO response with the furylfulgide system (ref. 11), and Lehn and coworkers (ref. 12) have shown that some diarylethene compounds can switch photochemically between a low and a high level of NLO response. The first two systems are thermally reversible (on a second timescale for *cis* DR1 in PMMA and on a day timescale for photomerocyanine in PMMA). On the contrary, the last two systems are thermally stable, but their closed form can be reversed to the open one by visible light irradiation. At first sight, these last two systems seem more suitable for stable optical recording but the first one, through photoinduced birefringence, dichroism or inscription of surface gratings, can also be used for the same purpose.

Dipole moments μ and first order hyperpolarisabilities β (or product $\mu\beta$) are given in Table I. They have been calculated by semi-empirical MNDO or AM1 molecular orbital methods in the MOPAC package (ref. 13), together with a finite field algorithm to determine β . The products $\mu\beta$ of furylfulgide and diarylethene in their open and closed forms have been determined experimentally by the EFISH technique. The main conclusion of these data is the large increase of β in going from a colorless to a colored form of a photochrom: this is true for spirocyan/photomerocyanine, but also for fulgides and diarylethenes. *Trans* DR1 has a larger β and a larger μ than *cis* DR1, the same holds for photomerocyanine compared to spirocyan, but furylfulgides (and probably diarylethenes) show no significant change in μ upon irradiation.

PHOTOASSISTED POLING AND PHOTOSWITCHING OF THE NLO RESPONSE OF PHOTOCHROMES IN POLYMERS

We have shown that illumination of azobenzene derivatives in polymer films lead to anisotropy. We will now study the influence of a DC electric field during this reorientation process.

Photoassisted poling

Thermally assisted poling is the usual way used to break the natural isotropy of chromophors in polymers for second-order NLO. This now classical technique consists in applying a DC electric field on a polymer film while heating it close to its glass transition temperature (T_g) and cooling it down to room temperature. Five years ago, we proposed an alternative method, photoassisted poling (ref. 14)(see Fig. 4); it requires illumination of the polymer film in the absorption band of the chromophore and simultaneous application of an electric field either by contact electrodes or by a corona discharge.

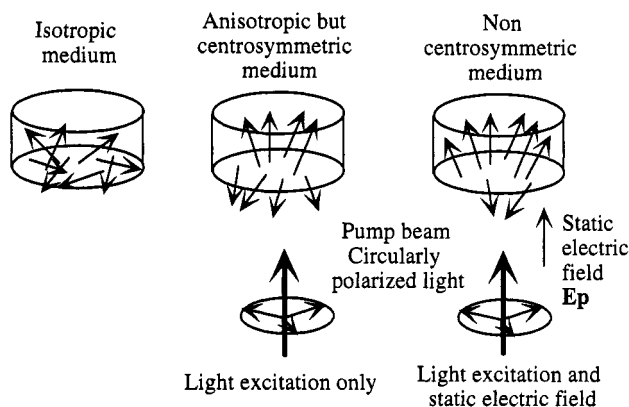


Fig. 4. Photoassisted poling. The starting polymer film is centrosymmetric (left). Under excitation with circularly polarized light, the dipoles tend to lie in a direction perpendicular with the plane of the film (middle). In presence of a static electric field (1 MV cm^{-1}), the molecules tend to line up in the direction of the field (right).

The best arrangement consists in illuminating the polymer film under normal incidence with a circular polarization. It has also been demonstrated that this method of poling takes advantage of a photochemical reaction occurring in a polymeric medium. Photochromic reactions seem necessary in order to induce this process. This new poling technique is interesting as it can be used for the drawing of optical waveguides for polymeric electro-optic modulators or frequency doublers. Room temperature photoassisted poling of photochromes in polymer films was initially demonstrated for DR1 or similar azo compounds in guest-host polymers or in copolymers. As shown previously, pumping with circularly polarized light will induce a preferential orientation in a direction perpendicular to the plane of the film, and parallel to the DC electric field, a majority of dipoles being aligned with the field. By comparison with thermally assisted poling, it has been shown that both methods lead to similar values of nonlinear susceptibilities, although photoassisted poling leads to less stable orientation. Recently, we have shown that photoassisted poling of DR1 works in polyimides covalently linked with DR1 (ref. 15), although these polyimides are very rigid at room temperature. As shown on Fig. 5, the second harmonic intensity generated (SHG) from the fundamental of a Nd/YAG laser increases during visible light irradiation (488 nm from an argon ion laser). Photoassisted poling can be thermally activated, as shown on the same figure where the SHG signals generated at room temperature and at 90 °C are compared. Due to the high T_g value of this polymer, no thermally assisted orientation takes place at this last temperature. One advantage of this method applied to polyimide films is to avoid thermal degradation of DR1 during thermally assisted poling at temperature higher than 200°C. The main interest in the use of polyimide films for NLO is the very good long term stability of orientation.

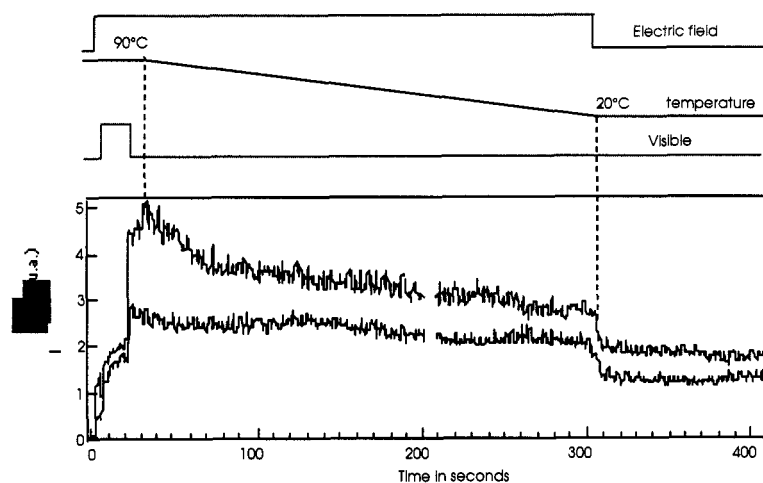


Fig. 5. Photoassisted orientation at room temperature (lower curve) and at 90°C (upper curve) in a soluble copolymer polyimide-co-DR1.

Conversely, illumination of a poled azo polymer film with a light beam at an incidence angle different from zero and with polarization either parallel or perpendicular to the incidence plane leads to a disorientation of chromophores. The observed decay of SHG intensity during pumping cannot be explained by trans-cis isomerization only, as this decay is totally irreversible for the copolymer and partially irreversible for the doped polymer. So, it is due to light induced disorientation of dipoles.

Photoassisted poling of DR1 in polymers is strongly efficient because of the many trans \rightarrow cis \rightarrow trans cycles that chromophores can undergo under pumping. We have shown that photoassisted poling was also possible for other photochromes like spiropyrans (ref. 10) and furylfulgides (ref. 16). Due to the very slow thermal back reaction of photomerocyanine in PMMA (almost one day) and to the stability of the closed form of furylfulgide, we can exclude in these two cases the possibility of multiple excitations. However, as shown on Figure 6 in the case of the spiropyran described in Table 1 (Nitro-Bips), photoassisted poling is feasible.

As shown on this figure, the application of a DC field is immediately followed by the rise of a SHG signal. The plateau value obtained after some time is higher (two to three times) when the electric field is

applied during pumping by UV light (the third harmonics of a Nd/YAG laser) than when it is applied after pumping, which is evidence of assisted poling (ref. 10) This synergistic effect can be interpreted as follows: ring opening of spiropyrans and formation of an extended conformation of photomerocyanine induces a conformational change in the surroundings which creates a cavity necessary for rotation of molecules in the field. After the end of pumping, the polymer backbone finds again a relaxed conformation around the photochrome which makes the rotation more difficult. Such a local "heating effect" of the polymer is much less during the ring closure reaction of the furylfulgide, as this reaction is not accompanied by a large change in geometry.

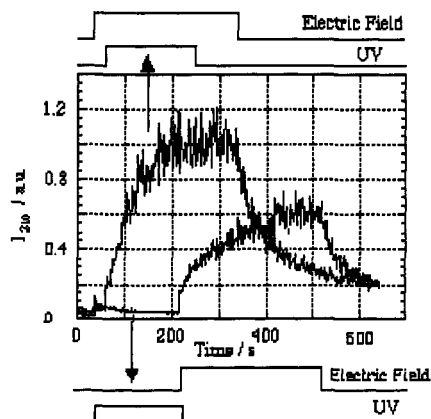


Fig. 6. Photoassisted poling of Spiropyran (10 % w/w in PMMA) . Upper curve: DC electric field applied during pumping; Lower curve: electric field applied after pumping.

Photoswitching of SHG

We mentioned in Table 1 the large increase in the first order hyperpolarisability coefficient in going from the colorless to the colored form of a photochrome. So by choosing an appropriate wavelength, it is possible to favor one or the other form and then to modulate or switch the SHG signal by means of light.

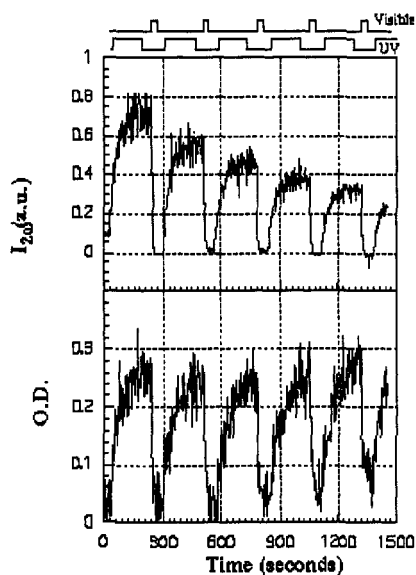


Fig. 7. Photoswitching of Furylfulgide-Dihydrobenzofuran dissolved in a PMMA film.

Photomodulation of SHG signal has been demonstrated for spiropyran / photomerocyanine case (ref. 10), but this system suffers from at least two drawbacks: i) the high β species (photomerocyanine) is not thermally stable and slowly goes back to spiropyran, leading to a decrease of SHG signal in the dark, ii) the recycling ability of spiropyran / photomerocyanine is rather low. Furylfulgide / dihydrobenzofuran system seems much better as there is no back thermal reaction and as the photoconversion can be repeated several times (ref. 17). The experiment shown in Fig. 7 has been done as follows: a previously oriented sample of furylfulgide in PMMA (10 % w/w) is alternatively irradiated by UV light (third harmonics of a picosecond Nd/YAG laser, 353 nm, 20 mJ) and visible light (argon ion laser 514 nm, 1mW) in absence of any external DC electric field. We measure both SHG signal ($I_{2\omega}$) generated by the fundamental of the Nd/YAG laser (1064 nm) and the optical density change (O.D.) of the sample at 532 nm (second harmonics of the same Nd/YAG laser) which is proportional to the amount of the closed form. After the first UV irradiation (see Fig.7), $I_{2\omega}$ increases as the closed form is generated from the open one. This increase is due to the higher β value of the closed form. When irradiation is stopped, $I_{2\omega}$ stabilizes. Visible light irradiation lowers $I_{2\omega}$ as the closed form opens again back to the initial form. A subsequent UV irradiation switches $I_{2\omega}$ to a high level again, and so on. Although we cannot get rid of the lowering of the plateau at each cycle, this disorientation process is slow compared with the case of spiropyran.

So, in the previous example, photoswitching of the NLO property is not completely reversible, despite the reversibility of the photochromic reaction. In the search for completely reversible systems, we recently investigated the second order NLO properties of a photochromic crystal (ref. 17). Indeed it has been known for several years that N-salicylidene-aniline ("anil") compounds exhibit photochromism in various states (solution, crystal, rigid glass and organic matrix). We prepared N-salicylidene-4-bromoaniline (see Table 1) which is photochromic in the crystalline state. Moreover, it crystallizes in a noncentrosymmetric structure. Figure 8 (upper part) shows the reversible modulation of transmission of the crystal at 500 nm (maximum absorption wavelength of the colored form) under irradiation at 365 nm and 490 nm alternatively. Figure 8 (lower part) shows the totally reversible SHG intensity change correlated to the change of the molecular species. The modulation is not a totally on/off type: the SHG intensity drop is about 64 % with the fundamental at 1064 nm and 10 % when the fundamental is 1907 nm. The drop in the second order susceptibility in going from the initial yellow form to the final red form correlates with the calculated drop in molecular coefficient β (see Table 1). The main component of β is not in the same direction in both isomers, which can explain part of the change in susceptibility. The self-absorption of the second harmonic beam at 532 nm by the red compound may contribute to the drastic drop of SHG intensity at 1064 nm. On the other hand, resonance enhancement should have an opposite effect. We do not have any clear explanation for such a different modulation intensity at both wavelengths.

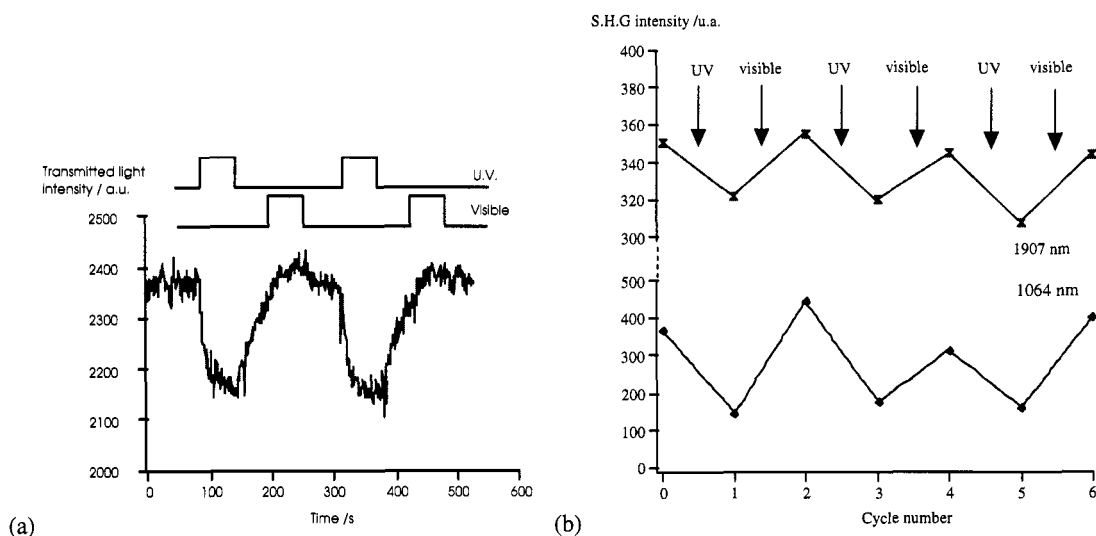


Fig. 8. Photochromism of N-salicylidene-4-bromoaniline in the crystalline state. Panel (a): transmitted light intensity at 500 nm, showing the variations during UV irradiation-thermal decay-visible irradiation cycles; panel

(b): photoswitching of SHG at 1907 nm (upper curve) and at 1064 nm (lower curve). On the x axis, odd numbers correspond to "after UV irradiation" and even numbers correspond to "after visible irradiation".

ALL-OPTICAL POLING

Photoassisted poling still requires the presence of a DC electric field. A method has been proposed four years ago (ref.18) which leads to an overall orientation of dipoles with the help of light only. In order to perform this orientation, it is necessary to superimpose two coherent beams, one at frequency ω and the other at frequency 2ω , both beams propagating in the same direction through the thin polymer film. In such conditions, it is possible to show that, although the mean electric field $\langle E \rangle = \langle E_\omega + E_{2\omega} \rangle$ is zero whatever the phase shift, the mean value of the third power of E is different from zero ($\langle E^3 \rangle \neq 0$) (see Fig. 9). The interference between these two beams results in a periodical orientation of the molecular dipoles with a period which exactly corresponds to the period necessary to have phase matching for SHG. Such all-optical poling has been efficiently realized with films of PMMA doped with DR1 or copolymerized with it. Once again, the photochemical isomerization is at the origin of the orientation which occurs at room temperature. All optical poling is a powerful method to create non centrosymmetric media able to modulate light whatever its polarization is. Furthermore, it is the only practical method which can be used to orient octupoles.

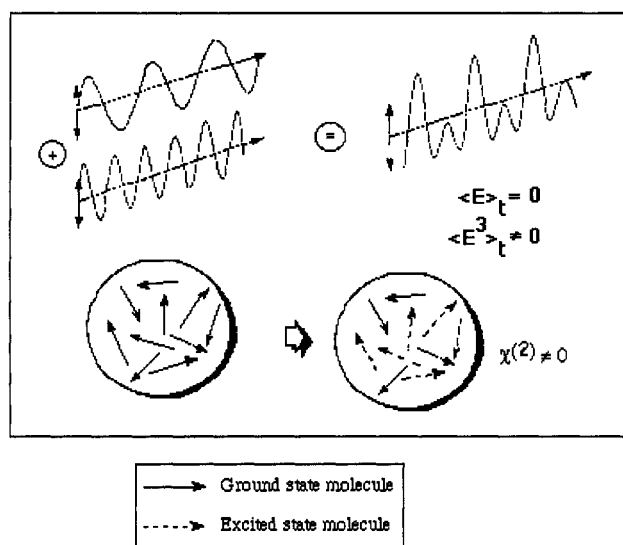


Fig. 9. All optical poling by interference between a fundamental and a second harmonic wave. It is shown that the time averaged cubic power of the resulting electric field is different from zero. A selective excitation of molecules in a given orientation may result and lead to all-optical poling.

CONCLUSION

Scheme 1 summarizes all the optically induced processes in polymer films containing photochromes. Although most of these processes have only been demonstrated for azo polymers, we have shown that some of them also work for different photochromes like spiropyran or furylfulgides. All these processes are interesting for applications in data storage and processing, in telecommunications via optical fibers and there are still a large variety of photochromes that can be studied by these different methods.

ACKNOWLEDGEMENTS

The authors acknowledge Pr. Joseph Zyss (L.P.Q.M., ENS de Cachan) and Dr. Michel Dumont (IOTA, Orsay) for many fruitful discussions.

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