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Reversible photoinduced modifications of polymers doped with photochromes : anisotropy, photo-assisted poling and surface gratings.

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In this paper, different optical methods which lead to orientation or translation of several photochromes in polymer matrices are discussed. These methods lead to dichroic or birefringent, or nonlinear optically active materials or to stable surface gratings. They have mainly been demonstrated for azobenzene-type photochromes, but some of these effects also occur for other kinds of photochromes like spiropyrans, fulgides or diarylethenes.

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

INTRODUCTION

Photochromism has been widely studied in polymers as in solutions^{[1][2]}. It is usually defined as the reversible photoinduced transformation between two

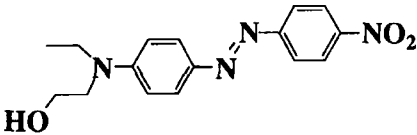
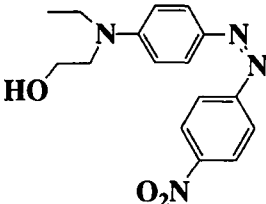
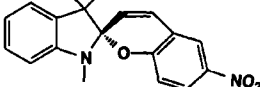
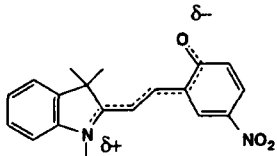
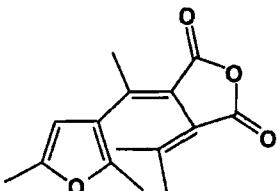
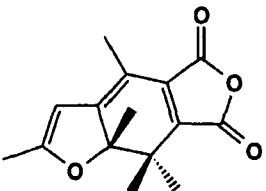

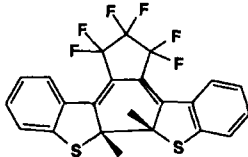
molecular states whose absorption spectra are significantly different. Photochromic molecules have received an increasing interest over the last ten years : new photochromic systems have been found, with increased photochemical stability, and new applications have been developed[3]. Photochromic polymers 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, photoassisted orientation and disorientation and photoinduced surface gratings. We will mainly develop here the second order nonlinear optical (NLO) properties of our samples .

NONLINEAR OPTICAL PROPERTIES OF PHOTOCHROMES

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 optical properties in polymers[4][5] as we will describe below. Spiropyran / photomerocyanine group has also been investigated in detail in polymers and in solutions as well, and the NLO properties have already been described[6][7]. More recently, we have shown that it was possible to observe NLO response with the furylfulgide system[8], and Lehn and coworkers[9] 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 in 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[10], 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

TABLE I Dipole moments and first order hyperpolarisabilities of photochromes

<p>Trans Disperse Red One</p>  <p>$\mu = 9 \text{ D}$ $\beta = 44.6 \cdot 10^{-30} \text{ esu}$</p>	<p>Cis Disperse Red One</p>  <p>$\mu = 6 \text{ D}$ $\beta = 8.4 \cdot 10^{-30} \text{ esu}$</p>
<p>spiropyran</p>  <p>$\mu = 7.5 \text{ D}$ $\beta = 1 \cdot 10^{-30} \text{ esu}$</p>	<p>photomerocyanine</p>  <p>$\mu = 13.6 \text{ D}$ $\beta = -40 \cdot 10^{-30} \text{ esu}$</p>
 <p>Furylfulgide</p> <p>$\mu = 7.2 \text{ D}$ $\beta\mu = 6.6 \cdot 10^{-48} \text{ esu}$</p>	 <p>Dihydrobenzofurane derivative</p> <p>$\mu = 6.6 \text{ D}$ $\beta\mu = 91 \cdot 10^{-48} \text{ esu}$</p>
<p>Diarylethene (open form)</p>  <p>$\beta\mu = 13 \cdot 10^{-48} \text{ esu}$</p>	<p>Diarylethene (closed form)</p>  <p>$\beta\mu = 55 \cdot 10^{-48} \text{ esu}$</p>

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 spiropyran/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 spiropyran, but furylfulgides (and probably diarylethenes) show no significant change in μ upon irradiation.

PHOTOINDUCED BIREFRINGENCE AND DICHROISM

It has been known since the sixties that azo dye viscous solutions 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[4][5][11] : 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[11] which takes into account both angular photoselection of the excited molecules (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 angular redistribution (molecules rotate during and/or after excitation and conversion to the cis state, or during the back cis --> trans reaction). With PMMA-DR1 copolymers, a memory effect has been put into evidence : the anisotropy remains a long time after the end of pumping. This memory effect can be used to register stable polarization gratings[11]. Pumping with light polarised in a direction perpendicular to the previous one leads to disorientation.

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^[12]; it requires illumination of the polymer film in the absorption band of the chromophor and simultaneous application of an electric field either by contact electrodes or by a corona discharge. 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 light of circular polarization 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 polyimids covalently linked with DR1^[13], although these polyimids are very rigid at room temperature. As shown on Fig. 1, 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 polyimid 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 polyimid films for NLO is the very good long term stability of orientation.

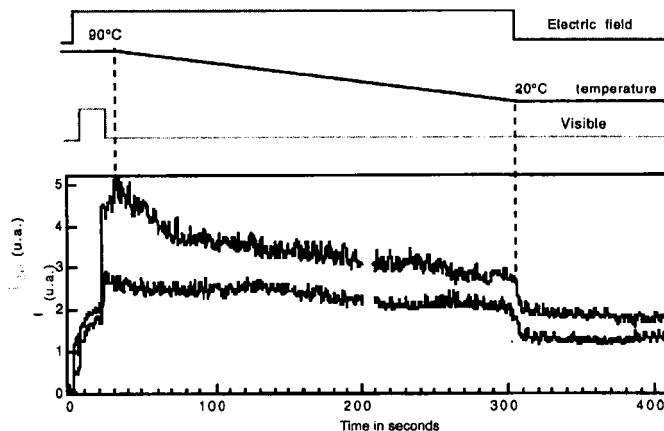


FIGURE 1 : Photoassisted orientation at room temperature (lower curve) and at 90°C (upper curve) in a soluble copolymer polyimid-co-DR1.

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. This is shown on Figure 2 for two PMMA films, first a polymer doped with DR1 (10 % w/w) and second a PMMA and DR1 copolymer (molar fraction of DR1 : 0.23)

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. In the case of the doped polymer, the partial reversibility of the SHG response can be explained as follows : a fraction of DR1 molecules engaged in large sites change irreversibly their orientation as they

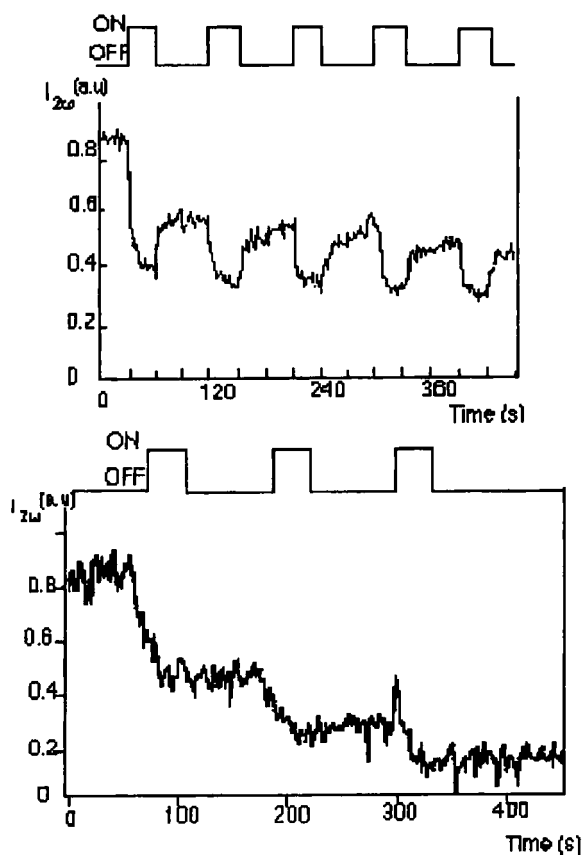


FIGURE 2 : Influence of the photoisomerisation of DR1 on second harmonic generation by a DR1-doped PMMA film (upper curve) and a DR1-functionalized PMMA copolymer film (lower curve). Pump and probe beams are both polarized normal to the incidence plane.

photoisomerize, a smaller fraction is trapped in smaller sites and have to recover their initial orientation after pumping. In the copolymer, the isomerization reaction of the chromophore induces a conformational change of the polymer backbone which renders the disorientation irreversible.

Photoassisted poling of DR1 in polymers is strongly efficient because of the many $\text{trans} \rightarrow \text{cis} \rightarrow \text{trans}$ cycles that chromophores can undergo under pumping. We have shown that photoassisted poling was also possible for other

photochromes like spiropyrans^[7] and furylfulgides^[14]. 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 3 in the case of the spiropyran described in Table 1 (Aberchrome), photoassisted poling is feasible .

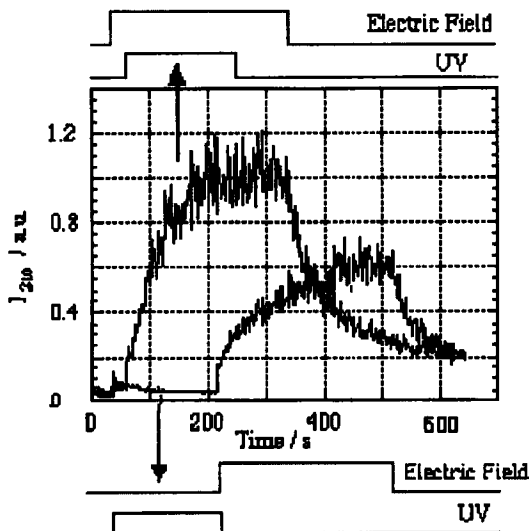


FIGURE 3 : Photoassisted poling of Spiropyran (10 % w/w in PMMA) . Upper curve : DC electric field applied during pumping; Lower curve : electric field applied after pumping.

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 an evidence of assisted poling^[7]. 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.

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.

Photomodulation of SHG signal has been demonstrated for spiropyran/photomerocyanine case^[7], 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^[14]. The experiment shown in Fig. 4 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. 4), $I_{2\omega}$ 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.

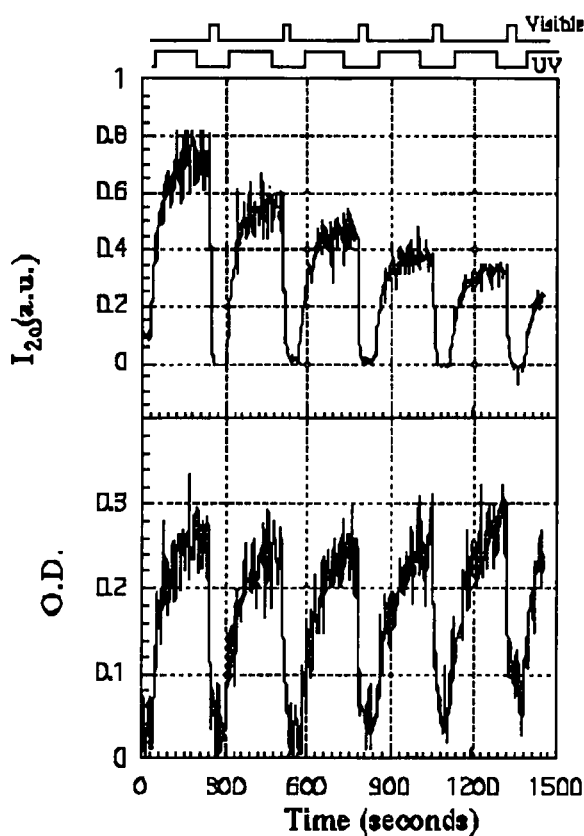


FIGURE 4 : Photoswitching of Furylfulgide-Dihydrobenzofuran

ALL-OPTICAL POLING

Photoassisted poling still requires the presence of a DC electric field. A method has been proposed four years ago^[15] which leads to an overall orientation of dipoles with the help of light only. In order to perform this orientation, it is necessary to superpose 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 ($\langle E^3 \rangle \neq 0$). 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.

PHOTOINDUCED SURFACE GRATINGS

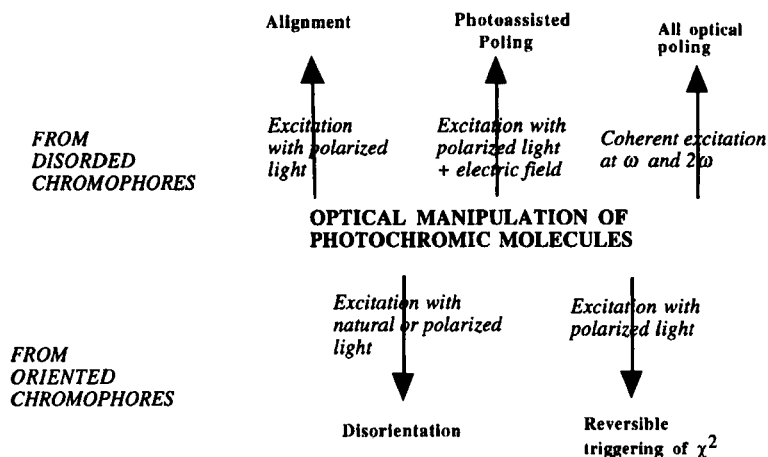
Finally, it is possible to inscribe surface gratings on the surface of azopolymers on exposure of the film by an interference pattern of polarized light at a wavelength near the absorption maximum of the dye[15][16]. The thickness modulation, which can reach several hundreds of nanometers, occurs at 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.

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

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 spiropyrans 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.

SCHEME 1 : Optical manipulation of photochromic molecules in polymer films.



References

- [1] H. Dürr and H. Bouas-Laurent, *Photochromism, Molecules and Systems* (Elsevier, Amsterdam, 1990).
- [2] C.B. McArdle, *Applied Photochromic Polymer Systems*, (Blackie, Glasgow, 1992).
- [3] M. Irie, *Supramolecular Science*, **3**, 87 (1996); *Pure & Appl. Chem.*, **68**, 1367 (1996).
- [4] S. Xie, A. Natansohn and P. Rochon, *Chem. Mater.* **5**, 403 (1993).
- [5] Z. Sekkat and W. Knoll, *Advances in Photochemistry*, (Wiley & Sons, 1997).
- [6] V. Krongauz, Ref. 2, Chapter 4, p. 121.
- [7] Y. Atassi, J.A. Delaire and K. Nakatani, *J.Phys. Chem.*, **99**, 16320 (1995).
- [8] H.G. Heller and J.R. Langan, *J.Chem. Soc. Perkin II*, 341 (1981).
- [9] S.L. Gilat, S.H. Kawai and J.-M. Lehn, *Chem. Eur. J.*, 275 (1995).
- [10] Q.C.P.E., *Publication 560*, (Department of Chemistry, Indiana University, Indiana, USA).
- [11] M. Dumont, S. Hosotte, G. Froc and Z. Sekkat, *SPIE Proceedings*, **2042** (Quebec, 1993).
- [12] Z. Sekkat, D. Morichere, M. Dumont, R. Loucif and J.A. Delaire, *J. Appl. Phys.*, **71**, 1543 (1991).
- [13] J. Chauvin, K. Nakatani, J. Delaire, C. Marestin, R. Mercier and B. Sillion, *SPIE* **2998**, 205 (1997).
- [14] J. Delaire, Y. Atassi, I. Maltey and K. Nakatani, *Pure Appl. Opt.*, **5**, 529 (1996).
- [15] J.M. Nunzi, F. Charra, C. Fiorini and J. Zyss, *Chem. Phys. Lett.* **219**, 349 (1994).
- [16] P. Rochon, E. Batalla and A. Natansohn, *Appl. Phys.Lett.* **66**, 136 (1995).
- [17] D.Y. Kim, J. Kumar and S.K. Tripathy, *Appl. Phys. Lett.* **66**, 1166 (1995).