

Coupling between Photochromism and Second-Harmonic Generation in Spiropyran- and Spirooxazine-Doped Polymer Films

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The photochemical ring opening of spiropyrans in polymethylmethacrylate (PMMA) host films in the presence of a high-voltage electric field (2–5 MV/cm) leads to a photo-orientation of photomerocyanines. Since photomerocyanines have rather high first-order hyperpolarizabilities, this photo-orientation leads to second-harmonic generation (SHG). The second-order susceptibility d_{33} of PMMA films doped with 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (25% w/w) has been measured at 10 pm/V. If a PMMA film doped with spiropyran and preoriented by corona poling at 90 °C is irradiated in the UV, an SHG signal of photomerocyanine is also observed as a result of a memory effect of the orientation of spiropyran molecules. The photoswitching of this nonlinear optical property can be inverted by visible light irradiation. Only partially reversible switching is observed because of a gradual light-induced disorientation of photomerocyanine dipoles. Photochemical quantum yields of the spiropyran \rightleftharpoons photomerocyanine reaction have also been determined in PMMA for one system. Dipole moments and hyperpolarizabilities of closed and open forms have been calculated by semiempirical and finite field methods for an analogous system.

Introduction

One of the main advantages of organic polymers in the manufacture of organic devices for integrated optics is their flexibility in accommodating very different chromophores (either in guest–host matrices or in covalently linked copolymers) so that their properties can be tuned very precisely.^{1–3} Another advantage, which is of great interest to us, is the possibility of combining two different properties in the same matrix. In this respect, photorefractive polymers provide a good example, as they combine photoconducting and second-order nonlinear optical (NLO) properties.⁴ We present herein a new class of materials exhibiting two distinct properties: photochromism and second-order NLO properties. We have already demonstrated new features created by the combination of these two properties on one such system based on Disperse Red One dye^{4,5} (DR1 or *N*-ethyl-*N*-(hydroxyethyl)((4-nitrophenyl)azo)aniline), a push–pull azobenzene derivative. In polymers doped with this molecule or in poly(methylmethacrylate-*co*-DR1) copolymer films, a photoassisted poling takes place at room temperature if the film is irradiated under an applied electric field of a few megavolts per centimeter;^{6–9} this is due to the thermally reversible trans–cis photoisomerization, which leads to a preferential orientation of the molecules along the applied electric field. The system studied in this work is based on the well-known photochromic couples spiropyran/photomerocyanine and spirooxazine/photomerocyanine dissolved in polymer matrices (mainly polymethylmethacrylate, PMMA). The photochromism of these compounds has been studied for many years^{10–14} and is still being thoroughly investigated because of their potential applications in photochromic glasses or lenses, in optical memories and optical switching applications. The photochromic reaction is depicted in Figure 1.

Recently, experimental values of dipole moments and first-order hyperpolarizabilities β were reported for stable merocyanines with an indoline heterocycle as a donor and different

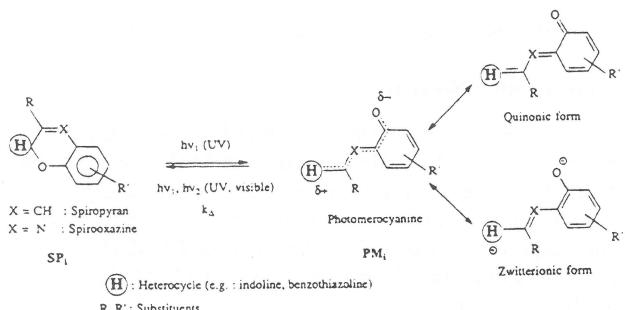
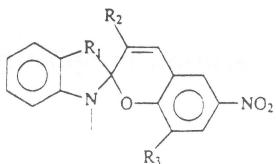


Figure 1. Photochromic reaction between spiropyran, spirooxazine, and photomerocyanine.

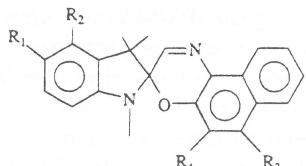
acceptor groups. For 1,3-diethylthiobarbituric acid as acceptor, the authors found a negative β value ($\beta = -46 \times 10^{-30}$ esu) and a dipole moment of 7.4×10^{-18} esu.¹⁵ This negative value has been attributed to the zwitterionic ground state of the merocyanine. It has already been pointed out previously for classic merocyanine dyes.¹⁶ In addition, second-harmonic generation (SHG) of poled films (thermally assisted poling) of liquid-crystal polymers doped with photomerocyanines has already been measured.^{14,17,18}

The main objective of this work is to demonstrate how one can combine photochromism and second-order NLO effects in such systems. This combination leads to two distinct phenomena: the first is a photoassisted poling (PAP) of the photomerocyanines in polymer films in the presence of an external electric field at room temperature, which is similar to the orientation of DR1 in PMMA that we already observed; the second is the “photoswitching” of the NLO properties of a polymer film doped with spiropyran and previously poled under an external electric field. A preliminary report on PAP has been given in the case of one specific spiropyran;¹⁹ the work is extended herein to different spiropyrans as well as to some spirooxazines whose structures are similar to those of spiropyrans but whose photochemical stability is reputed to be better.

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SP1 -R₁ = -S-, -R₂ = -CH₃, -R₃ = -OCH₃; 8-methoxy-3-methyl-6-nitro-3'-methylspiro[2H-1-benzopyran-2,2'-benzothiazoline]
SP2 -R₁ = -S-, -R₂ = -OC₂H₅, -R₃ = -OCH₃; 3-ethoxy-8-methoxy-6-nitro-3'-methylspiro[2H-1-benzopyran-2,2'-benzothiazoline]
SP3 -R₁ = -C(CH₃)₂-, -R₂ = -H, -R₃ = -H; 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline]
SP4 -R₁ = -C(CH₃)₂-, -R₂ = -H, -R₃ = -CH₂SC₂H₅; 8-(ethylthio)methyl-6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline]



SP5 -R₁ = -H, -R₂ = -H, -R₃ = -piperidinyl, -R₄ = -H; 1,3,3-trimethyl-6-piperidinylspiro[indoline-2,3'-[3H]naphthoxazine] or "Red PNO"
SP6 -R₁ = H, -R₂ = -H, -R₃ = -H, -R₄ = -H; 1,3,3-trimethylspiro[indoline-2,3'-[3H]naphthoxazine] or "Blue A"
SP7 -R₁ = -CH₃, -R₂ = -CH₃, -R₃ = -H, -R₄ = -H; 1,3,3,4,5-pentamethylspiro[indoline-2,3'-[3H]naphthoxazine] or "Blue D"
SP8 -R₁ = -Cl, -R₂ = -H, -R₃ = -H, -R₄ = -H; 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphthoxazine]
SP9 -R₁ = -H, -R₂ = -H, -R₃-R₄ = -CH=CH-CH=CH-; 1,3,3-trimethylspiro[indoline-2,3'-[3H]phenanthroxazine]

Figure 2. Spiropyran and spirooxazine molecules used in this study.

Experimental Section

1. *Polymer Films.* Doped polymer films of spiropyrans and spirooxazines (SP1 to SP9, Figure 2) in PMMA were prepared by spin coating on an ITO (indium tin oxide) glass plate from a chloroform solution containing PMMA (6% w/w) and chromophore (10% or 25% w/w relative to PMMA). The films (thickness of around 1 μm) were dried at 110 °C for 2 mn and at 80 °C for 2 h.

SP3, SP8, and SP9 were purchased from Aldrich Co.; SP5, SP6, and SP7 were provided by EniChem Co.; and SP1, SP2, and SP4 were provided by Professor Guglielmetti (Université d'Aix-Marseille II). The PMMA used was Elvacite 2041 from DuPont, and the chloroform was purchased from Prolabo (spectrophotometric grade). All chemicals were used without further purification.

2. *Poling Process.* Two types of poling were performed depending on the aim of each experiment. (i) Classical corona poling at high temperatures (thermally assisted poling): Under a voltage of 5 kV applied to a gold-plated stainless steel needle located 1 cm from the surface of the film, the polymer film was heated up to 90 °C (near T_g , the glass transition temperature of PMMA) and slowly cooled down to room temperature. (ii) PAP at room temperature: Since SHG measurements were performed in situ during poling, this process will be described in detail in paragraph 4 of this experimental section.

3. *Kinetic Measurements.* Photochemical reaction quantum yields, as well as thermal back reaction rate constants, were measured on a continuous pump-probe irradiation setup,²⁰ with one beam perpendicular to the other and both having an incidence angle of 45°. The pump beam was generated by a Xe-Hg arc lamp (450 W), and the probe beam by a Xe arc lamp (150 W). In order to select the appropriate wavelength, interference filters were put on the pump path and monochromators on the probe path. The photon flux of the pump beam was measured by using Aberchrome 540, an actinometer

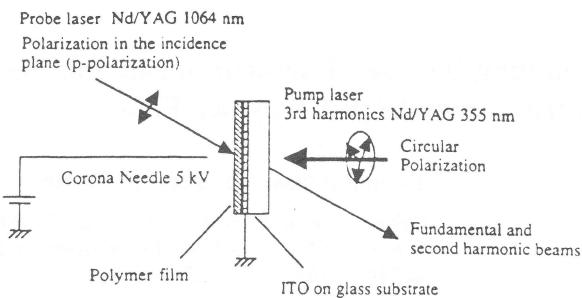


Figure 3. Experimental setup for in situ measurements of SHG (configuration around the sample).

purchased from Aberchromics Ltd. The intensity of the probe beam was negligible compared to that of the pump beam.

4. *Second-Harmonic Generation (SHG).* SHG measurements were carried out using as the probe beam the fundamental (1064 nm) of a Q-switched, mode-locked picosecond Nd-YAG laser (30 ps pulse width, 10 Hz repetition rate). The polymer film sample was mounted on a rotating plate. For all experiments described in this paper, the incidence angle was set at 30°, and polarization was fixed in the incidence plane (so-called p-polarization). For each laser pulse, the SHG signal arising from the sample was integrated and compared to the SHG signal arising from a urea powder reference, in order to eliminate laser fluctuation. The integrated signal was monitored by a Keithley 199 multimeter connected to a PC compatible computer.

Absolute values of the quadratic susceptibility d_{33} were determined by comparison with the second-harmonic signal generated by a reference quartz crystal ($d_{11} = 0.5 \text{ pm/V}$).

The sample's environment, described in Figure 3, allowed us to pump and/or pole the molecules, while probing the sample with the fundamental beam, and to follow PAP.

Pumping was performed with the third harmonics of the same laser (355 nm) with a beam flux of approximately 10 mW/cm². The polarization was made circular by means of a $\lambda/4$ plate, and the incidence was normal to the sample's surface.

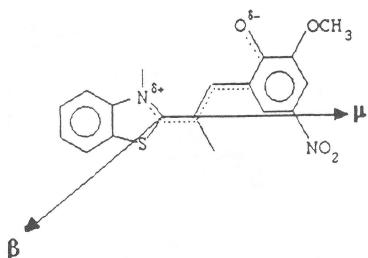
Poling at room temperature could also be performed on this setup. A high voltage of 5 kV was applied on the corona needle located at around 1 cm off the film surface. ITO served as ground electrode. A few of the poling experiments mentioned in this paper were performed by contact poling. For this purpose, a thin layer of gold was deposited on films prepared in conformance with the process described in paragraph 1 of this experimental section. This technique enables avoiding the use of the corona needle, and the actual voltage across the film can be measured by a casual multimeter.

Results

1. *Calculation of Molecular First-Order Hyperpolarizability by a Finite Field Method.* Calculation of the molecular first-order hyperpolarizability of the studied molecules has been performed by the finite field technique in combination with the MNDO molecular orbital method.²¹ The MNDO Hartree-Fock matrix elements were computed using the MOPAC molecular orbital program. It is generally admitted that the polarizability of a molecule with respect to an electric field is described by the creation of an induced dipole moment. One can use a power series expansion of the dipole moment to describe its interaction with the electric field as follows:

$$\mu_i(E) = \mu_i^0 + \sum_j \alpha_{ij} E_j + \sum_{j,k} \beta_{ijk} E_j E_k + \sum_{j,k,l} \gamma_{ijkl} E_j E_k E_l + \dots \quad (1)$$

where μ_i^0 is the permanent dipole moment, α_{ij} the elements of the polarizability tensor, and β_{ijk} and γ_{ijkl} the elements of the

Figure 4. Calculated μ and vectorial β for compound PM1.

first and second hyperpolarizability tensors, respectively. The first-order hyperpolarizability is given as the second derivative of the dipole moment with respect to the applied field. In the finite field method, this derivative is calculated by fitting the dipole moment into a polynomial of the applied field E . According to the Hellman–Feynman theorem,²¹

$$\beta_{ijk} = \frac{1}{2} \left(\frac{\partial^2 \mu_i}{\partial E_j \partial E_k} \right)_{E=0} \quad (2)$$

In practice, this is numerically performed by computing

$$\beta_{ijk} = [\mu_i(2E, 0, 0) + \mu_i(-2E, 0, 0) - 2\mu_i(0, 0, 0)]/8E^2 \quad (3)$$

The values of the electric field components used in our calculations were equal to 0.001 au.

Finally, we give, as usual, the projection of vectorial β on the ground state dipole moment, which was defined as follows:

$$\beta = \bar{\beta} \cdot \bar{\mu} / ||\bar{\mu}|| \quad (4)$$

where $\bar{\beta} \cdot \bar{\mu} = \beta_x \mu_x + \beta_y \mu_y + \beta_z \mu_z$ and $\beta_i = \beta_{iii} + \beta_{ijj} + \beta_{ikk}$.

Structural data of SP1 and PM1 are not available. However, we managed to provide a potential structure of these compounds based on crystallographic data of analogous molecules.^{22,23} The most stable conformation of PM1 was deduced from published results (Figure 4).^{24,25}

Values of β are 1.9×10^{-30} and -43.0×10^{-30} esu for SP1 and PM1, respectively. The dipole moment increases from 7.5 D for SP1 to 13.6 D for PM1. In PM1, both vectors make an angle of 142° . These calculations confirm the expected increase of the absolute value of β , in going from the closed to the open form of the molecule.

Negative β values for photomerocyanines have already been found theoretically and experimentally (by electric-field-induced second-harmonic generation) for stable merocyanines.^{15,16} This negative sign was recently interpreted as a consequence of the zwitterionic characteristic of merocyanine's ground state (Figure 1), which leads to an electronic polarization opposite to the charge transfer in the ground state. The presence of the nitro group on the benzene ring of compounds SP1 to SP4 enhances the electron-attracting power and yields its high absolute β value relative to that of the related photomerocyanine. Detailed calculations will be provided elsewhere.²⁶

2. Kinetics Measurements. Rate Constants of the Thermal Back Reaction. After the photostationary equilibrium was reached by irradiating a spiropyran film at 320 nm, the back reaction was allowed to proceed in the dark at room temperature. Optical density (OD) measurements at the absorption maximum of the photomerocyanine (λ_{\max} , see Table 1) were carried out over a few hours (Figure 5). The kinetics is quite well fitted to a biexponential function (Table 1).

The rate constants obtained compare well with those already reported in the literature.^{27–30} They are generally lower than in nonpolar solvents and have about the same order of magnitude as in polar solvents: 2.5 s^{-1} in toluene and $7.7 \times 10^{-4} \text{ s}^{-1}$ in

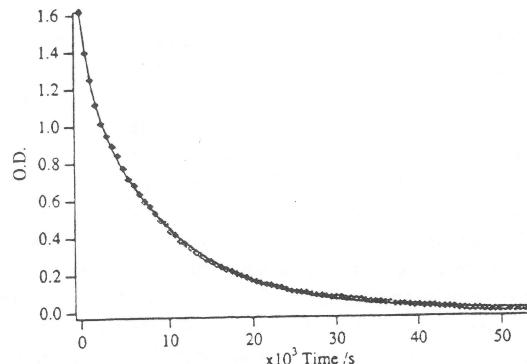


Figure 5. Kinetic study of the thermal back reaction for the SP3–PM3 system followed at 584 nm. Since only PM3 absorbs at this wavelength, OD is directly proportional to the concentration of PM3. The kinetics were fitted to a biexponential.

TABLE 1: Rate Constants for the Thermal Back Reaction

compound	λ_{\max}	k_1/s^{-1}	k_2/s^{-1}
SP3	584	7×10^{-4}	1×10^{-4}
SP5	625	1×10^{-2}	6×10^{-4}
SP6	580	4×10^{-2}	4×10^{-3}
SP7	562	2×10^{-2}	2×10^{-3}
SP9	589	2×10^{-2}	1×10^{-3}

TABLE 2: Experimental Data Concerning the Photochemical Reaction with Pump Beams at 320 and 372 nm

wavelength/nm	320	372	588
$\epsilon_{\text{SP3}}/\text{L mol}^{-1} \text{ cm}^{-1}$	11.7×10^3	6.6×10^3	0
$\epsilon_{\text{PM3}}/\text{L mol}^{-1} \text{ cm}^{-1}$	11.7×10^3	10.3×10^3	13.2×10^3
pump wavelength/nm	320	372	
beam flux/einstein $\text{s}^{-1} \text{ dm}^{-2}$	6.8×10^{-8}	2.1×10^{-7}	
$\alpha/\%$	84	77	
$\Phi_{\text{SP-PM}}$	0.102	0.135	
$\Phi_{\text{PM-SP}}$	0.019	0.023	

ethanol for compound SP1.^{31,32} The biexponential behavior is usually attributed to the presence of different conformations of photomerocyanine. However, it can also be due to the presence of different locations in the polymeric matrix, though this phenomenon is usually better described by a stretched exponential.

Quantum Yields. Although irradiation in the UV region is usually utilized for the ring-opening reaction, both spiropyran and photomerocyanine absorb in this region, and photochemical reaction may occur both ways. The quantum yields $\Phi_{\text{SP-PM}}$ and $\Phi_{\text{PM-SP}}$ were determined for SP3/PM3 in the UV region, as this system provides the most efficient conditions for this experiment: first, it has a very good colorability, enabling us to conduct accurate measurements of OD change, and, second, its thermal back reaction is the slowest among the available compounds, thereby allowing us to neglect this process.

Since we cannot measure ϵ_{PM} , the extinction coefficient of PM3, directly, we have to combine two methods described in the literature for quantum yield determination: Fischer's method³³ determines the extinction coefficient of PM3 at the desired wavelength, and Rau's method³⁴ ultimately enables us to reach $\Phi_{\text{SP-PM}}$ and $\Phi_{\text{PM-SP}}$. Fischer's method needs to use pump–probe experiments at different wavelengths mentioned in the results given in Table 2. From this method, we get the ϵ_{PM} values at the three wavelengths utilized in the experiments. From these data, we deduce α , the reaction extent at two pump wavelengths, and then $\Phi_{\text{SP-PM}}$ and $\Phi_{\text{PM-SP}}$. The colorability (product of $\Phi_{\text{SP-PM}}$ and ϵ_{PM}), which describes the ability of this spiropyran to evolve color, is 2.4×10^3 at 588 nm when ϵ is expressed in $\text{L mol}^{-1} \text{ cm}^{-1}$.

The values obtained are rather high for photoisomerization processes in polymer matrices and are close to those reported

in the literature.^{27,35} In these determinations, all side reactions have been neglected. In particular, due to the slow rate constants given in Table 1 and to the short time scale of steady-state irradiation for all these measurements (a few minutes), it is justified to neglect the thermal back reaction.

3. Photoassisted Poling of Photomerocyanines Demonstrated by SHG. PMMA films of thicknesses of approximately 1 μm doped with spiropyrans or spirooxazines (10% w/w) were studied with the experimental setup described above for SHG measurement at an incidence of 30° with in situ UV irradiation and electric field poling (Figure 3). As expected, depending on the β values calculated above, spiropyrans are not good candidates for SHG. However, the photomerocyanines display a much better efficiency. Furthermore, their high dipole moment (in the ground state) may lead to orientation under an applied external electric field. Two kinds of experiments have been conducted, in accordance with the sequence of external perturbations applied to the samples: either the electric field and the UV irradiation are both acting at the same time (experiment I) or the UV irradiation is being performed first and then the electric field is being switched on (experiment II). In both experiments, the times involved are the same. A third kind of experiment will be described in the next section. In the case where polarization of the fundamental laser beam is within the incidence plane, the intensity of the second-harmonic signal, $I_{2\omega}$, is³⁶

$$I_{2\omega} \propto (\chi_{\text{eff}}^{(2)})^2 I_\omega^2 \sin^2\left(\frac{\pi}{2} \frac{l}{l_c}\right) \quad (5)$$

where l_c is the coherence length of the polymer at frequency ω , I_ω the intensity of the fundamental beam, l the film thickness, and $\chi_{\text{eff}}^{(2)}$ an effective second-order susceptibility, which is a linear combination of $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$. The susceptibility tensor components can be written as (indices in uppercase refer to the bulk coordinates, and those in lowercase, to the individual molecules)¹

$$\chi_{ijk}^{(2)}(-2\omega; \omega, \omega) = N f_i(2\omega) f_j(\omega) f_k(\omega) \langle \beta_{ijk}(-2\omega; \omega, \omega) \rangle_{ijk} \quad (6)$$

in which N is the density number of NLO chromophores, f_i , f_j , and f_k are the local field factors, and the term in brackets is a weighted sum of the values of the different β_{ijk} 's, an average over all orientations of the dipolar chromophore in the polymer.

According to the low value of β for spiropyran, we may only consider the contribution of photomerocyanine molecules. So, $I_{2\omega}$ is proportional to N^2 (N being the density number of photomerocyanine molecules) and to the square of β , averaged over all the orientations of the molecules.

In Figure 6, the $I_{2\omega}$ signal for compound SP3 is plotted versus time during the two different experiments described above. In these experiments, contact poling was performed with an applied voltage of 200 V between the gold coating and the ITO. The same film was used in two different spots for both experiments. The main feature is the large increase of the SHG signal, which starts in experiment I when UV light is switched on and in experiment II when the electric field is switched on (with the ring opening reaction having been carried out before). The plateau value reached in experiment I was 10 pm/V after a few minutes of irradiation. The second feature is the difference between the maximum intensities reached in both experiments; i.e., the maximum intensity reached in experiment I is approximately twice the amount in experiment II. This enhancement factor has been obtained on many samples oriented either by contact poling or by corona poling. The latter method yields higher potential³⁷ but is sensitive to UV and visible light illumination and charge injection phenomena.⁸ Although the

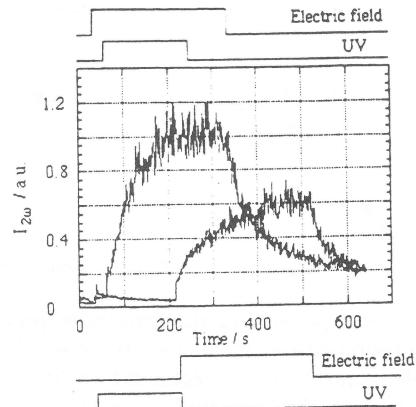


Figure 6. Photoassisted poling at room temperature monitored in situ on the SP3 (spiropyran)-PM3 system (in PMMA, 25% w/w): comparison between experiment I (simultaneous poling and pumping) and experiment II (poling after pumping). Note the higher SHG intensity reached in experiment I for the same pumping and poling field conditions. Contact poling was chosen for better control of the poling field.

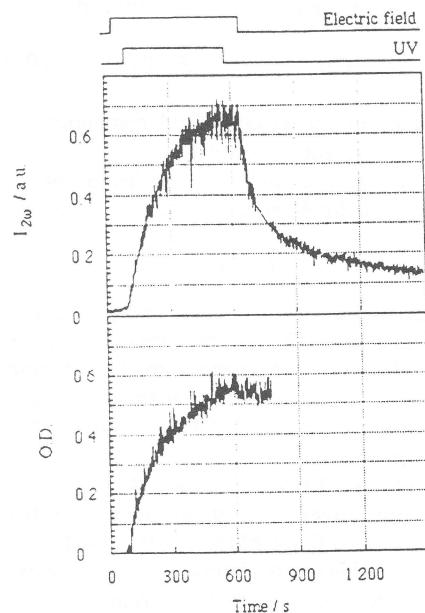


Figure 7. Photoassisted poling at room temperature monitored in situ on the SP3-PM3 system (in PMMA, 10% w/w) and OD followed at 532 nm. Since only PM3 absorbs at this wavelength, OD is directly proportional to the concentration of PM3.

exact ratio fluctuated between 1.5 and 3, it was always larger than 1. Since irradiation conditions were exactly the same in both experiments, the number of photomerocyanine molecules formed during both experiments was the same, and the difference in intensity was only due to a difference in the efficiency of orientation (see Discussion).

The kinetics of both signals' growth are also different (Figure 6). The increase of $I_{2\omega}$ in experiment II is characteristic of the dynamics of rotational diffusion of dipoles under an applied electric field in polymer media.³⁸ It is highly nonexponential, with a fast increase followed by a much slower one. The increase of $I_{2\omega}$ in experiment I has been compared in Figure 7 with the rate of ring opening as probed by the measurement of the increase of OD at 532 nm (second harmonics of the Nd-YAG laser being used as a probe) in the absorption band of the photomerocyanine molecule. In experiment II, we considered the influence of the time delay between the end of the UV irradiation and the beginning of corona poling: when this delay was increased from 10 to 100 s, we observed that the longer the delay, the lower the plateau value we obtained for $I_{2\omega}$. It is

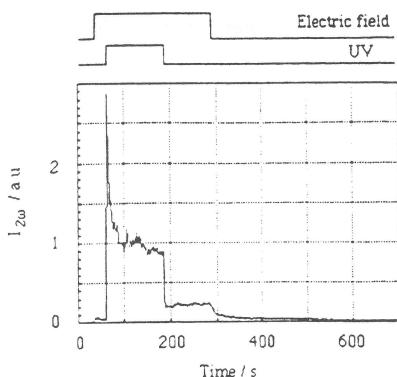


Figure 8. Photoassisted poling at room temperature monitored in situ on the SP5 (spirooxazine)-PM5 system (in PMMA, 10% w/w).

worthwhile to note that the thermal ring closure of photomerocyanines after irradiation is not significant on this time scale (Figure 5); thus, it cannot explain this decrease. One hypothesis is that the polymer slowly reorganizes around the open molecules, thus resulting in a more and more difficult orientation in the applied electric field.

In both experiments, after the end of both electric field and irradiation sequences, there was a fast decay of the $I_{2\omega}$ signal followed by a slower one. Considering once again the kinetics of the thermal back reaction in Figure 5, we cannot attribute the decay of the SHG signal to this reaction, which converts the system back to the NLO inactive spiropyran form, but rather to a fast disorientation mechanism. The decay kinetics of the signal in Figure 7 (top curve) fits a Kohlrausch-William-Watt^{39,40} stretched exponential, $I_{2\omega}(t) = I_{2\omega}(0) \exp[-(t/\tau)^\alpha]$, where $I_{2\omega}(0)$ represents the second-harmonic intensity at the start of the decay, τ a characteristic relaxation time, and α a parameter representing the width of the distribution of relaxation times. We found $\tau = 74 \pm 3$ s and $\alpha = 0.29 \pm 0.03$. For DR1 in PMMA poled by the same photoassisted technique, Blanchard and Mitchell⁷ found $\tau = 1200 \pm 400$ s and $\alpha = 0.43 \pm 0.05$.

The same kind of experiments were repeated for the other three spiropyrans listed in Figure 2 (25% w/w in PMMA). For SP1, we observed the same effects as above and again a factor of three between the maximum values of $I_{2\omega}$ in experiment I compared with experiment II. In addition, a weak fluorescence at 532 nm appeared during UV irradiation in this system. We measured the emission of the same film under excitation at 355 nm with a conventional spectrofluorimeter. Since we observed a weak fluorescence band around 500 nm that disappeared after UV irradiation, we attributed this to spiropyran.²⁷

Both of the other spiropyrans studied (SP2 and SP4) were also slightly fluorescent at 532 nm. In addition, we observed the photoassisted poling of the photomerocyanine form, but these compounds were found to be very photoreactive;⁴¹ thus, in experiment I the $I_{2\omega}$ signal decayed before reaching a plateau value. We noted that intermittent irradiations during poling were more efficient in these systems. However, because of this high level of instability, they were not investigated any further.

Spirooxazines are reputed to be more photochemically stable. For that reason, photoassisted poling was also tried with some commercial spirooxazines dissolved in PMMA (25% w/w) under the same conditions as above. Among the five compounds listed in Figure 2, only SP5 exhibited a clear SHG signal in experiment I (Figure 8). But this increase was weak compared to the spontaneous fluorescence of the material under UV irradiation. This fluorescence was attributed to the spirooxazine (closed form) as the signal decays during UV irradiation. SP5 has indeed a fluorescence spectrum with a maximum at 470 nm, which disappears in the open form. Each of the four other

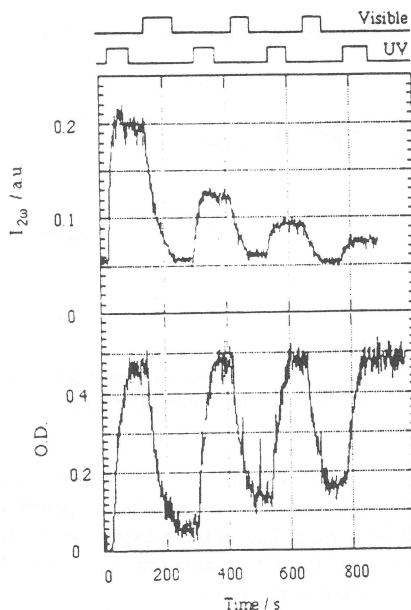


Figure 9. Photoswitching of a previously poled polymer film of SP3 (in PMMA, 25% w/w) and OD followed at 532 nm. OD change is related to the ring-opening and -closure reactions, under the influence of alternate UV and visible irradiations.

spirooxazines studied (SP6 to SP9) were fluorescent under UV irradiation but did not yield SHG.

4. Photoswitching of the SHG Efficiency of a Previously Poled Spiropyran Sample. In the photoassisted poling described previously, the SHG signal only appears during the application of an electric field which orients the NLO active molecules and creates the mandatory non-centrosymmetry. In order to switch from an NLO inactive to an NLO active material, a third type of experiment was carried out with films of PMMA doped with SP3. This film was first poled by the corona technique near the T_g of the polymer (see Experimental Section); then the SHG signal was measured with the arrangement of Figure 3, under UV irradiation but without any external electric field (Figure 9). At the beginning, $I_{2\omega}$ was close to zero, as a consequence of the low value of β for spiropyrans. Under UV irradiation, spiropyran rings opened, as shown by the OD measured using the same arrangement at 532 nm (Figure 9). As the photochemical reaction proceeded, there was a fast concomitant increase of $I_{2\omega}$, which was a result of the polar order of photomerocyanines formed from oriented spiropyran molecules. The maximum $I_{2\omega}$ signal corresponds to a d_{33} value of 1 pm/V. When UV irradiation was stopped, there was a slow decay of $I_{2\omega}$ (Figure 10). This decay could be accelerated by photoinducing the ring closure of photomerocyanine by irradiation at 514 nm (argon ion laser, 1 mW cm⁻²); it was followed by a correlated decay of $I_{2\omega}$. The photochemical cycle spiropyran \rightleftharpoons photomerocyanine can be repeated several times, and as shown in Figure 9, a partial reversibility of the SHG signal was observed. In fact, although the maximum OD reached by the system was the same during at least the first four cycles, which means that the amount of photomerocyanine evolved was the same under these irradiation conditions, the $I_{2\omega}$ signal decreased regularly at every cycle, implying that irradiation irreversibly leads to disorientation.

When an oriented sample colored by UV light was kept overnight in the dark at room temperature, it became almost colorless and lost its NLO activity, as all photomerocyanine molecules closed back to spiropyran. But, a subsequent UV irradiation 14 h after the first one led again to an SHG signal whose maximum value was 45% less than the first one (Figure 10). This means that the initially oriented sample still kept in

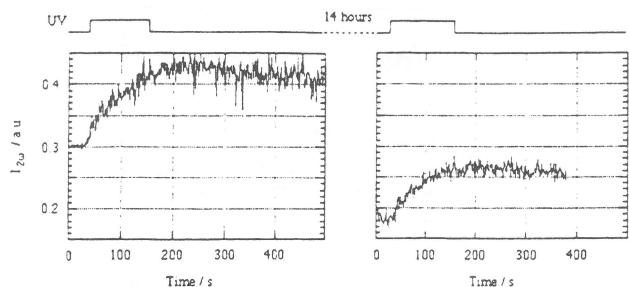


Figure 10. Memory effect in a previously poled polymer film of SP3 (in PMMA, 25% w/w). A second photoswitching was performed 14 h after the first one.

memory the initial orientation, in spite of the fact that a fraction of the molecules had been photochemically opened and closed. It is worthwhile to note that, in these experiments, the decay of $I_{2\omega}$ after the end of the UV irradiation was much slower than in the case of experiments I and II.

Discussion

1. Photoassisted Poling of Photomerocyanines in a PMMA Matrix. Photoassisted poling was demonstrated recently^{5–7} for the azo dye DR1 either doped in or covalently bound to PMMA. The process can be explained if one considers that the trans \rightleftharpoons cis photochemical reaction induced by natural light at normal incidence increases the rotational mobility of the chromophore and causes a polar order in the direction of the applied electric field. Two effects are generally considered to explain such an increase: first, *cis*-DR1 is more compact and more mobile than *trans*-DR1 and orients once it is formed; second, during the photochemical or the thermal reactions occurring between both isomers, the electric field may preferentially bias the reorientation process along the field direction. In DR1 systems, it is difficult to distinguish both mechanisms, as the lifetime of *cis*-DR1 is very short (≈ 5 s), which precludes any observation of its orientation, at least by conventional SHG techniques. Compared to DR1, the spiropyran/photomerocyanine system looks different: first, the photoproduct has a much higher β coefficient than the starting molecule; second, the thermal reaction is slow. However, as the open form absorbs at the irradiation wavelength (355 nm), a photoinduced ring-closure reaction occurs at the same time as the ring opening and leads to a photochemical equilibrium.

The maximum SHG efficiencies that we obtained in experiments I and II differ by a factor of two. This increased efficiency of the photoassisted poling when both electric field and UV light are applied simultaneously has also been observed when the electro-optical measurements were conducted by the attenuated total reflection (ATR) method.⁴² Experiment II highlights the rotational diffusion of the photomerocyanine, which has a high dipole moment, and experiment I shows that orientation occurs both during and after the ring opening. Actually, if the orientation had occurred only after ring opening, we would have observed the same efficiency in both experiments.

Let us assume that the contribution of spiropyran is negligible compared to that of photomerocyanine. If we suppose that photomerocyanine molecules orient just after ring opening, then $I_1(t)$, the second-harmonic intensity measured in experiment I, can be deduced easily by combining $I_2(t)$, the intensity measured in experiment II, with $N(t)$, the amount of photomerocyanine formed, as featured by kinetic measurements. Similar samples irradiated under the same conditions have to be considered (Figures 6 and 7). According to eqs 5 and 6, the second-harmonic intensity is proportional to N^2 , the square of the number of NLO efficient molecules. For this reason, the square

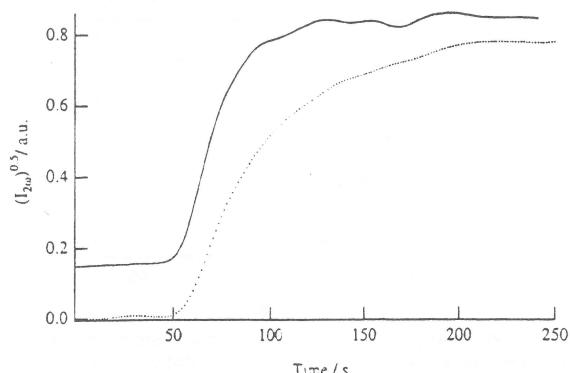


Figure 11. Convolution product of $(I_2(t))^{1/2}$ (from experiment II) with the kinetics of ring opening (dotted line) and $(I_1(t))^{1/2}$ (from experiment I, solid line).

root of $I_1(t)$ is obtained by the convolution product of the square root of $I_2(t)$ and the rate of production of photomerocyanine molecules, given by dN/dt :

$$(I_1(t))^{1/2} \propto \int_0^t \left(\frac{dN}{dt} \right)_{\tau=t} (I_2(t-\tau))^{1/2} d\tau \quad (7)$$

In Figure 11, we compare the experimental signal $(I_1(t))^{1/2}$ with the one deduced from eq 7. It appears that the rate of increase of the experimental signal is much faster than the computed one. This has been checked for two different pump intensities and agrees with the fact that, in experiment I, the orientation occurs both during and after the photochemical ring opening.

Although the spirooxazines that we studied all present photochromic properties in PMMA under our irradiation conditions, only one, SP5, presented a photoassisted poling effect. This can be due to two reasons, which may in fact coexist. First, it is known that the open form of spirooxazines has a more pronounced quinonoid character (Figure 1).⁴³ This neutral, quinonoid form has a lower dipole moment, which is not conducive to promoting rotational diffusion under an applied external electric field. Second, the spirooxazines SP6, SP7, SP8, and SP9 are not optimized for NLO; they lack an efficient electron-attracting or -donating group in their structure, as opposed to the nitrospiropyrans that we used. It is worthwhile to note that the lone spirooxazine that yielded photoassisted poling (SP5) is the one with a piperidinyl substituent, which can be considered as a donating group through the lone pair on the nitrogen. Calculations of β are in progress to assess these hypotheses.

2. Photoswitching of NLO Properties of a Photochromic Material. In the course of signal processing for telecommunications or cable TV, there may be a significant need for materials whose NLO properties can be switched on and off reversibly. This could be performed in different ways (thermal jump, electric field, etc.), but a convenient one is the simple flash of light on the material. Although not entirely reversible, the system PMMA/SP3 offers an example of such a photoswitchable material. The polar order is given to the closed form of the molecules by thermal poling, and UV irradiation switches the NLO properties on. The polar order is partly preserved during ring opening. Ring closure can be carried out by visible light irradiation; this step leads, to some extent, to disorientation, as a subsequent UV irradiation leads to a lower $I_{2\omega}$ signal. Disorientation of a poled PMMA/DR1 film by irradiation with linearly polarized light has already been observed;²⁰ it is due to a randomization of oriented molecules after the excitation by light that initiates its change of geometry. Polymer matrices or porous materials, whose cavities are such that this random-

ization is impossible, may exist in which the molecules always return to their initial orientation after a photochemical cycle.

Finally, our research has also highlighted the role of the concentration of spiropyrans on the orientation phenomenon. The decay of the $I_{2\omega}$ signal after photoassisted poling depends on the dye concentration; it is slower at 25% w/w than at 10%. Concentrated solutions of spiropyrans are known to yield photomerocyanine dimers and higher aggregates.⁴⁴ As already proposed by Krongauz et al.,¹⁸ we may consider a noncentrosymmetric arrangement of dipoles in the film leading to SHG. Such aggregates may stabilize the field-induced orientation.

Conclusion

In polymer films, the change in dipole moment accompanying the ring opening of spiropyrans allows the photomerocyanine molecules to be oriented in an external electric field. This orientation has been demonstrated by second-harmonic generation. If the photochemical reaction is carried out in the presence of the electric field, the orientation of the giant dipoles of photomerocyanines occurs during and after ring opening; i.e., among all the paths that the excited spiropyrans can take during the course of the ring opening, those leading to the orientation of dipoles in the direction of the electric field are favored. This photoassisted poling was already demonstrated for azobenzene-type derivatives; it has been shown herein that this new process of poling at room temperature can be extended to other photochromes provided that the photochemical reaction is accompanied by a change in dipole moment. Other photochromic systems, like fulgides⁴⁵ or diarylethylenes,^{46,47} may present the same effect provided that they are functionalized with electron-attracting and -donating groups, which will confer NLO properties on them. We believe that this method can be used in the manufacturing of optical waveguides active for SHG.

A new effect that we have called "photoswitching" of SHG efficiency was highlighted for previously poled spiropyran-doped PMMA films. When these films were further irradiated in the near UV at room temperature, they exhibited SHG; this SHG signal was suppressed by visible irradiation. Although complete reversibility has not been achieved, we have demonstrated that this mechanism could apply to optimized systems. Our present work is aimed at increasing both the chemical stability of the open form, by preventing thermal back reaction and degradation, and the stability of poled molecule orientation, by a judicious choice of matrix and photochrome.

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