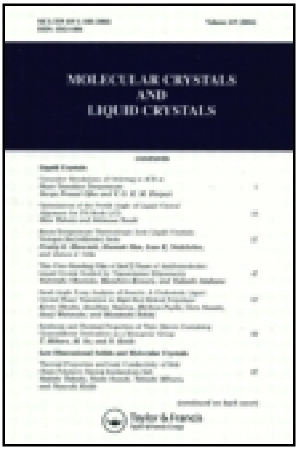

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Photoassisted Poling of Photochromic and Optically Nonlinear Molecules in Polymer thin Films

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PHOTOASSISTED POLING OF PHOTOCHROMIC AND OPTICALLY NONLINEAR MOLECULES IN POLYMER THIN FILMS

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Abstract Disperse Red One-doped or -functionalized polymethylmethacrylate, polystyrene and polyimide thin films exhibiting second order optical nonlinearity are obtained by simultaneous application of an electric field and a laser beam.

INTRODUCTION

Organic dye-doped or -functionalized polymers are widely used for their various optical properties. Our current study focuses on materials exhibiting both photochromism and nonlinear optical (NLO) properties. In a previous paper,[1] we demonstrated that photochemical reactions may be a driving force to pole molecules in a polymer matrix. This so-called photoassisted poling is very useful in the design of second order NLO materials, since they need to be non centrosymmetric. We took advantage of this method to obtain NLO active Disperse Red One (DR1)-doped and -functionalized polymethylmethacrylate (PMMA). The aim of the present paper is to summarize the principles of this phenomenon and to report on NLO materials we recently obtained by this method on other polymer matrix.

I. PRINCIPLES

Let us remind that photoassisted poling experiments were first performed on PMMA thin films (≈1 μm thick) doped (5 % w/w DR1 relative to PMMA) or functionalized with DR1 (Figure 1), and deposited on a glass substrate. The sample configuration described on Figure 2 allows us to apply both a suitable pump beam to induce photoisomerization and a DC electric field (E_p, Corona poling). The whole poling process is monitored by second harmonic generation (SHG) measurements to evidence second order NLO properties.

PMMA systems have successfully been poled, since after removal of both pump beam and electric field, SHG signal ($I_{2\omega}$) does not fall down to zero. These results have already been previously commented.[1] The following mechanism is proposed (Figure 3) : the absorption probability of a photon by a molecule scales like $\cos^2 \theta$, θ being the angle between the polarization direction of the pump beam and the transition moment of the molecule, so it is at the strongest when both directions are parallel. The latter direction is almost along the electron donor-acceptor axis, denoted by an arrow. Therefore, a circularly polarized normal incidence pump beam on the isotropic material tends to align DR1 units perpendicularly to the surface of the film (direction-dependent hole-burning),[2] making DR1 units undergo trans→cis→trans cycles. However, though the material is no more isotropic, its centrosymmetry is not broken. Application of E_p is necessary to allow DR1 molecules to align in a non centrosymmetric configuration with all "heads" on the same side.

Classical poling method requires the polymer to be heated above its glass transition temperature (T_g) while applying E_p,[3] whereas new poling method can be performed at room temperature since photoisomerization occurs even below T_g (for PMMA, $T_g \approx 120°C$).

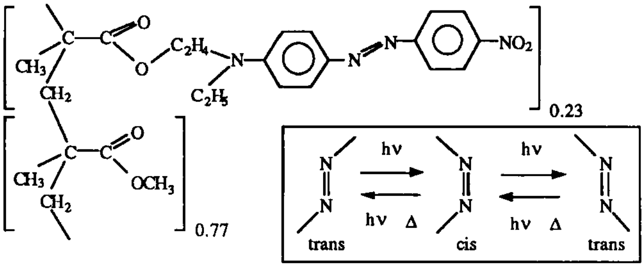

FIGURE 1 DR1-functionalized PMMA and trans-cis isomerization scheme

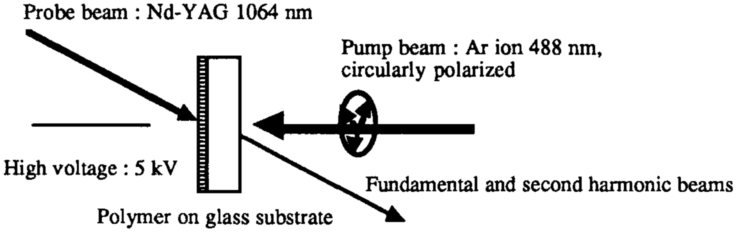

FIGURE 2 Sample configuration for photoassisted poling experiments followed by SHG

II. PHOTOASSISTED POLING OF DR1-POLYSTYRENE AND -POLYIMIDE

One of the drawbacks of polymeric materials for second order NLO is the lack of ability to keep the poled orientation. However, according to some reports, it seems that, first, polystyrene (PS) has a stronger capacity to hold this orientation [4] and, second, high-T_g polymers like polyimides (PI) are suitable for this purpose.[5] We performed photoassisted poling on DR1-doped PS and PI (both 5 % w/w DR1 relative to polymer). The general features of $I_{2\omega}$ variation shape of these two materials is similar to those of PMMA systems,[1] i.e. an electric field dependent SHG signal when only E_p is on, a slow $I_{2\omega}$ increase when both E_p and the pump beam are on (as the poling takes place), and finally a remnant $I_{2\omega}$ even after everything has been switched off (Figure 4).

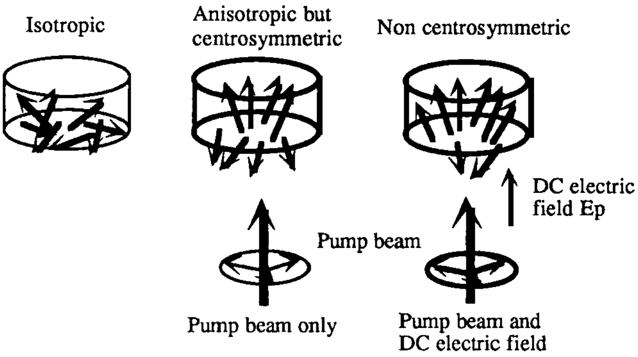

FIGURE 3 Proposed mechanism for photoassisted poling

In the present paper, we would like to focus on $I_{2\omega}$'s drop when the pump beam is switched on, that occurs in DR1-functionalized PMMA and in PI but not in DR1-doped PMMA and in PS. This phenomenon had been previously attributed to trans→cis isomerization.[1] However, since it seems to occur faster than isomerization does [6] and deeper compared to trans→cis conversion extent, we found more relevant to attribute this fact to a drop of voltage across the film in presence of the pump beam, making impossible to maintain a constant electric field on the sample. At the moment when the drop occurs, no noticeable orientation has taken place yet, so $I_{2\omega}$ depends mainly on the electric field. This statement has been checked by two series of measurements : on the one hand, xerographic discharge measurements showed a faster voltage decay on the PI sample in presence of light compared to darkness and, on the other hand, the same SHG experiment on DR1-doped polyvinylcarbazole (5 % w/w), known to have a strong electric conductivity in presence of light (photoconductivity), yields a $I_{2\omega}$ drop down to almost zero. The electric field drops to such a weak value that even photoassisted poling cannot take place in this matrix.

DR1-doped PI exhibits a second order susceptibility of about $\chi^{(2)}{}_{33} = 24$ pm/V, 30 mn after switching E_p off. After one week, the remnant SHG signal is only 5 % relative to the initial one. This value is slightly higher than for PMMA (4 %). PS matrix keeps about 20 % of its SHG signal after the same period of time.

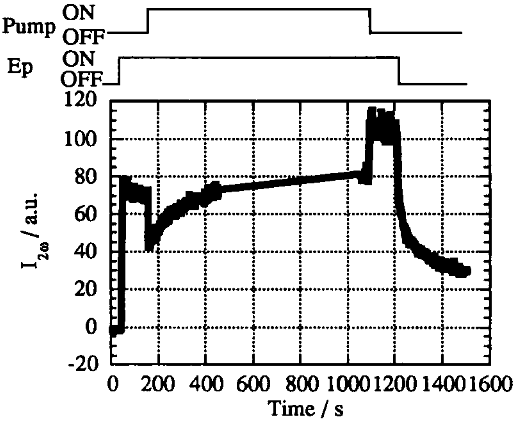

FIGURE 4 Photoassisted poling of a DR1-PI film monitored by SHG

CONCLUSION

Studying various polymeric matrix lead us to a better understanding of the phenomena occurring during photoassisted poling. Using other photochromic species and seeking for a better stabilization of the orientation may be two interesting paths to investigate.

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