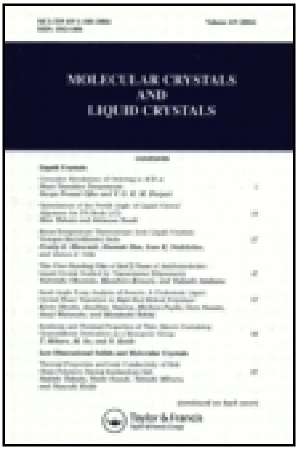

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Dynamical Studies of Optically Induced Orientation Processes in Photochromic Isomers : Experiment and Theory

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Dynamical Studies of Optically Induced Orientation Processes in Photochromic Isomers : Experiment and Theory

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Photo-orientation by photoisomerization is quantified for individualizable photoisomers of diarylethene and spiropyran-type chromophores introduced into poly-methyl-methacrylate films. We have measured isomers optical transitions relative orientations, and photochemical quantum yields in these photo-anisotropic films.

Keywords: Photo-orientation; Photoisomerization; Anisotropy

The field of organic nonlinear optics emerged since Davydov et al [1] established the correlation between enhanced nonlinear activity and charge transfer character in conjugated molecules, and recently, effects induced by photo-orientation of photoisomerizable nonlinear optical (NLO) chromophores in polymers have attracted much attention [2]. Optical poling techniques, e.g. induced molecular polar orientation, which result in second order NLO effects have been reported only recently, and optically induced nonpolar orientation which results in optical anisotropy has been known for a long time. Inasmuch as optical ordering of photoisomerizable molecules is being intensively studied, the quantification of coupled photoisomerization and photo-orientation is needed so as to bridge independent studies in the areas of optics and photochemistry.

Light can manipulate the chromophores orientation by photoisomerization via polarized transitions so as centrosymmetry and isotropy are alleviated and anisotropy and quadratic and cubic optical nonlinearities are induced. Zimmerman et al. [3], and Fisher [4], and Rau et al. [5] developed an optical pumping population change based theoretical background for photoisomerization within a pure photochemical framework; e.g. that framework in which photo-orientation effects can be disregarded. This feature can be true in low viscosity solutions where photo-induced molecular orientation can be overcome by molecular rotational diffusion. In polymeric environments, especially in thin solid film configurations, spontaneous molecular mobility can, however, be strongly hindered and photo-orientation effects are appreciable. Michl et al. [6] performed intensive research on infra-red vibrations and UV-vis electronic transitions of molecules which are already oriented either by introduction into stretched polymer films or after photo-orientation.

The theory that coupled photoisomerization, and photo-orientation processes was developed by us few years ago [7]. Yet, further theoretical developments are needed to quantify coupled photoisomerization and photo-orientation processes, and the most important concept that needed to be clearly addressed, within the framework of photo-orientation, is the polarization nature of the optical transition itself. Recently, we developed a model which is based on purely polarized optical transitions, and the related rigorous solutions of the general equations of the theory of molecular optical orientation for the full quantification of the coupled isomerization and optical ordering processes [8]. The model assumes that A↔B photo-conversion occurs upon excitation of purely polarized transition with light linearly polarized. For each of the isomers A and B, any polarized transition can be represented in the isomer's fixed molecular coordinates by an inclination angle, say ω, with respect to a reference transition that is rigidly fixed to the molecular coordinates, say that transition which corresponds to the irradiation wavelength.

In this paper, we will quantify the coupled photoisomisomerization and photo-orientation of the isomers of a spiropyran-type chromophore in films of poly-methyl-methacrylate (PMMA). The photochromism of SP derivatives has been studied extensively for a long time, and recently we have demonstrated that such chromophores exhibit interesting orientational features when isomerized by polarized light [9-11]. The apparent optically induced orientation is inverted, e.g. changes sign, for the UV versus the visible transition band of the chromophores, and suggests that the UV and visible transitions are perpendicular. Similar observation were made for a diarylethene-type chromophore primarily because both of these chromophores isomerize by induced ring opening and closing; a feature which is in clear contrast to the photo-orientation of azobenzene-type chromophores which are known to isomerize either by rotation or inversion mechanisms.

The structure formula of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyrane-2,2'-indoline], referred to in the text as SP, which we have studied and its photochemical isomer can be found in Ref. 8. We have studied the steady-state and dynamics of photo-orientation of SP and DE chromophores dispersed in films of PMMA (guest-host films) by real time dichroism. Details about the films preparation and experimental arrangement can be found in Ref. 8. The irradiation light was linearly polarized, UV (365 ± 15 nm) and green (546 ± 5 nm), from a high pressure mercury lamp and induced the A↔B and A←B photoreactions, respectively. Consideration of the chromophores density (e.g.,

1.19×10^{20} and 0.87×10^{20} molecules.cm^{-3} for the A and B isomers prior to UV and green photo-orientation, respectively), the UV and green irradiation intensity range imposes about 0.14 to 1.42 and 0.26 to 1.79 incident photons per isomer per second, respectively. The probe was the red light (λ = 633 nm) of a He-Ne laser (power ~ 2.4 mW, and ~ 1 mm-diameter spot), so as photo-orientation processes of the isomer B are probed independently from those of the isomer A. Dark conditions were employed to avoid the influence of the room light on the isomerization reaction.

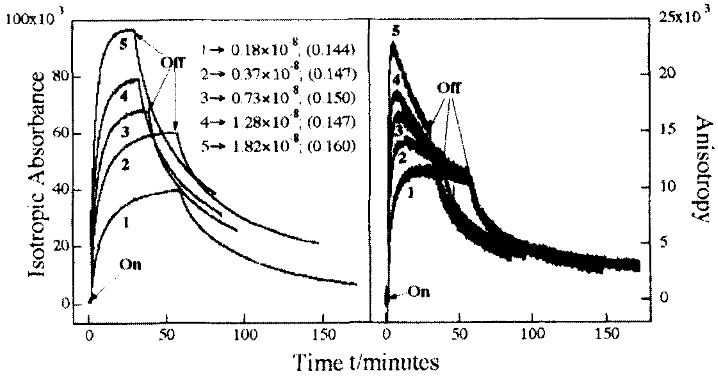

FIGURE 1 Real time evolution of the isotropic absorbance (left) and the anisotropy (right) of SP in PMMA upon linearly polarized UV irradiation for several irradiation intensities. The numbers from 1 to 5 indicate the value of the irradiation intensity in units of Einstein.s^{-1}.cm^{-2} with the corresponding sample absorbance at the irradiation wavelength, e.g. 365 nm (value between brackets). The moments of turning the irradiation light on and off are indicated.

Absorbance of light polarized parallel and perpendicular to the irradiating light polarization was measured and the isotropic absorbance, the anisotropy, and the order parameter were deduced. The latter was calculated at the steady-state of photo-orientation. Fig. 1 shows the time evolution of the anisotropy for a SP/PMMA during and after linearly polarized UV irradiation for different irradiation power values. The occurrence of anisotropy is indicative of photo-orientation of the chromophores. The green light induced orientation of the chromophores showed a dynamical behavior (not shown) similar to that of Fig. 1. In this experiment, the SP/PMMA samples were irradiated by unpolarized UV light to the photo-stationary state, and linearly polarized green irradiation followed. The spiropyran molecules degrade after successive irradiation cycles, and each photo-orientation experiment has been done on a different previously non irradiated sample so as to avoid degradation complications. The samples had similar absorbance values prior to UV irradiation, and the samples absorbances were accounted for.

The fitted slopes of the early time evolution of the isotropic absorbance and the anisotropy showed a linear dependence on the irradiation light intensity for both the UV and green light-induced orientation as predicted by the theory, and the reciprocal of the order parameter obtained at the steady-state of the UV light induced A↔B photo-orientation showed a linear dependence on the reciprocal of the irradiation light intensity also as predicted by the theory. The theoretical fits yielded $\phi_{AB}^{365} = 0.053$, $\phi_{BA}^{365} = 0.030$, $\phi_{BA}^{546} = 0.003$, and $\omega_{633}^{365} = 71.25$ and $\omega_{633}^{546} = 29.24$ degrees for the angles between the B isomer's transition moments at 365 and 633, and 546 and 633 nm, respectively. $\varepsilon_B^{546} = 11380$, $\varepsilon_B^{365} = 11100$ and $\varepsilon_B^{633} = 3460$ L mol^{-1}cm^{-1} were adapted from the literature [12], and the fastest component (k = 0.00125 s^{-1}) of the thermal isomerization rate of SP in PMMA [9] was used for the determination of ϕ_{BA}^{546}. The above values of ε_B have been adapted from those determined in assumed isotropic SP/PMMA samples, and the method of Fischer for the determination of ε_B holds even for anisotropic samples provided that the isotropic absorbance is considered and is properly measured. The quantum yields are reasonably small for photoisomerization processes in polymeric environments whereby molecular movement can be hindered far below the polymer Tg, and are in agreement with those reported in the literature. The orientation of the chromophore is partially retained, e.g. not thermalized, after the UV light induced A→B photoisomerization, and $\omega_{633}^{365} = 71.25$ degrees demonstrates that the direction of the 365 and 633 nm transitions of the B isomer are nearly perpendicular.

Acknowledgments

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