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The Photoorientation Movement of a Diarylethene-Type Chromophore

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Abstract: We quantified coupled photoisomerization and photoorientation of a diarylethene-type chromophore in films of poly(methyl methacrylate). We found that the chromophore retains partial memory of its orientation during the A → B UV-induced isomerization and that the chromophore movement is thermalized after the A←B green light induced isomerization. The isomerization quantum yields are $\phi_{AB}^{365} = 1.1$, $\phi_{AB}^{405} = 0.32$, and $\phi_{BA}^{532} = 0.16$, and the transitions at 365 (405) and 532 nm of the B isomer are oriented at an angle of 74.3 (61.3)° to each other. This relative orientation of the transition dipoles is rationalized by MOPAC molecular orbital calculations.

Introduction

In the past decade, the phenomena of light-induced orientation of photochromic molecules in polymers have attracted much attention due to requirements in the areas of optoelectronics, photonics, and linear and nonlinear optics.[1−5] Light can orient the chromophores by photoisomerization via purely polarized transitions and induces anisotropy and quadratic and cubic optical nonlinearities. Inasmuch as optical ordering of photoisomerizable molecules is being intensively studied, its quantification is needed to bridge independent studies in photochemistry and nonlinear optics.

Photoorientation by or without photoisomerization has been known for a long time,[6,7] and photoisomerization was studied from a pure photochemical point of view.[8−10] However, tools to quantify photoisomerization-induced molecular orientation were yet to be developed. Recently, we developed the analytical theory that allows for the quantification of coupled photoisomerization and photoorientation in A ↔ B photoisomerizable systems where B is unknown, and we have used it to study quantitatively both the photoisomerization and photoorientation of photochromic spectrally distinguishable spiropyrans in films of poly(methyl methacrylate) (PMMA).[11] In this paper, we will discuss photoorientation by photoisomerization of a diarylethene-type chromophore and how this chromophore moves upon isomerization in films of PMMA. Diarylethenes are contrasted to spiropyrans by the thermal stability of the B isomer, a feature that brings about interesting photoorientation effects in spectrally distinguishable photoisomers (vide infra). The order parameter is independent of the irradiation light intensity at the photostationary state. The photochromism of diarylethenes has also been extensively studied,[2,12] and recently, we observed that when such chromophores are isomerized by polarized light, the apparent photoorientation is opposite for the UV versus the visible absorption band of the chromophores,[13] and we found that the 365- and 633-nm transitions of the B isomer of a spiropyran chromophore are nearly perpendicular.[11] We will show that quantified photoorientation of diarylethenes reveals that the closed form of such chromophores also exhibits perpendicular UV and visible transition dipole moments.

Experimental Section

The structural formula of the diarylethene chromophore, e.g., 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (Tokyo Kasei: B1536), which we have studied and which is referred to in the text as DE, and its photochemical isomer are shown in Figure 1, together with the UV−visible spectra prior to and after UV light irradiation to the photostationary state. DE-type molecules have two photochemical isomers, A and B, both of which are thermally stable at room temperature, and UV and visible light irradiations produce photoreaction in both the A → B and A ← B and the A ← B directions, respectively.

We investigated the dynamics of photoorientation of DE in films of PMMA ($T_g = 110$ °C, and molecular weight, $M_\omega = 50\,000$) by real-time dichroism. Guest−host polymer films were prepared by spin-casting from a 2-butanone solution on cleaned glass substrates. The weight ratio of the chromophore relative to the polymer was 10%; a loading ratio at which chromophore aggregation does not occur for DE in PMMA. Differential scanning calorimetry measurements (not

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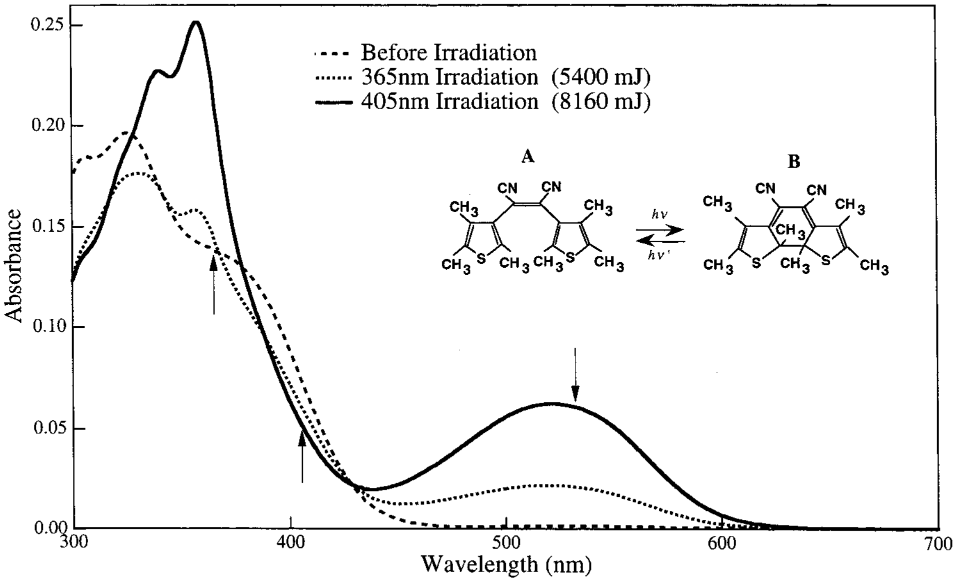

Figure 1. Absorption spectra of diarylethene before after UV irradiation to the photostationary state. The inset shows the chemical structure and ring closing/opening isomerization of diarylethene. The 365- and 405-nm irradiation and 532-nm analysis wavelengths are indicated by arrows.

shown) that we have performed on both PMMA and the 10% DE/PMMA, demonstrate that the T_g of PMMA decreases appreciably from 110 to 72 °C with the added DE solute. The DE dopants swell significantly the polymer chains for a larger volume and, consequently, are not closely packed by the PMMA matrix. Furthermore, if aggregation is present, it strongly distorts molecular absorption spectra due to intermolecular interaction, and the spectrum of a 1×10^{-4} M CCl_4 solution of DE is identical to that in the PMMA films both prior to and after irradiation even though the chromophore concentration is much smaller in this solution than in the DE/PMMA samples.[12] Residual solvent was removed from the films by heating for 1 h at 110 °C near the polymer T_g, a temperature at which polymer segmental motion is large enough to free possibly trapped solvent molecules. The films were removed from the oven and allowed to slowly cool to room temperature. The film thickness was measured by atomic force microscopy and was typically ~0.77 μm. The films were irradiated by linearly polarized UV light (365 ± 15 and 405 ± 5 nm; glass and interference filters from Irie and Sigma Co., respectively) from a high-pressure mercury lamp (Nikon Co.) and polarized green light (532 nm) from a diode-pumped frequency-doubled Nd:YVO_4 laser (Uniphase) to induce the A $\leftrightarrow$ B and A $\leftarrow$ B photoreactions, respectively. In consideration of the chromophore density (e.g., 2.37×10^{20} and 0.43×10^{20} molecules·cm^{-3} for the A and B isomers prior to UV and green photoorientation, respectively), the UV and green irradiation intensity range imposes about 4×10^{-3}−32×10^{-3} (for 365 nm) and 1.2×10^{-2}−8.5×10^{-2} (for 405 nm), and 0.55−8.2 incident photons per isomer per second, respectively. The samples were irradiated with linearly polarized light while in situ transmittance measurements were performed with a probe light polarized either parallel or perpendicular to the initial irradiating light polarization. The probe beam was propagating perpendicular to the plane of the sample and linearly polarized at 45° with respect to the plane of incidence of the irradiating beam. The transmitted parallel and perpendicular components were separated by a Wollaston prism and detected separately. The probe beam was the green laser light (incident power ~1.2 μW, and ~1-mm-diameter spot), and photoorientation processes of the isomer B are probed independently from those of isomer A. Dark conditions were employed to avoid the influence of the room light on the isomerization reaction.

$\mathrm{Abs}_{\parallel}^{B}$ and $\mathrm{Abs}_{\perp}^{B}$ were calculated from the amount of absorbed parallel and perpendicular light, respectively, and the isotropic absorbance $\overline{A_B} = (\mathrm{Abs}_{\parallel}{}^{B} + 2\mathrm{Abs}_{\perp}^{B})/3$, the anisotropy $\Delta A_B = \mathrm{Abs}_{\parallel}^{B} - \mathrm{Abs}_{\perp}^{B}$, and the order parameter $S_B = \Delta A_B/3\overline{A_B}$ of the B isomer's orientational distribution were deduced. S_B was calculated at the steady-state of photoorientation. For all of the notations of the paper, the sub- or superscript B if any stands for the B isomer, and the primed and unprimed quantities refer to the irradiation and analysis wavelengths, respectively.

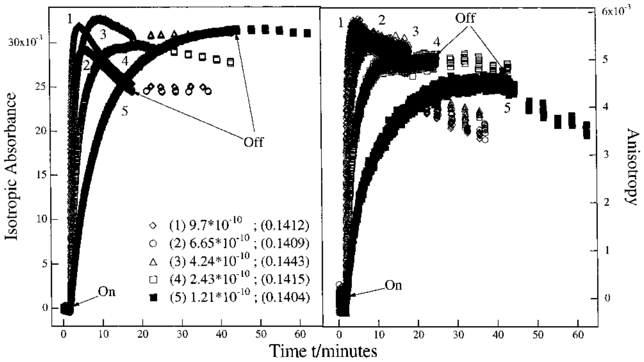

Figure 2. Real-time evolution of the isotropic absorbance (left) and the anisotropy (right) of DE in PMMA upon linearly polarized UV irradiation for several irradiation intensities. Only the 365-nm UV photoorientation is shown; 405-nm photoorientation showed similar dynamical behavior. The numbers from 1 to 5 indicate the value of the irradiation intensity in units of einstein·s^{-1}·cm^{-2} with the corresponding sample absorbance A_0', value between parentheses, at the irradiation wavelength, e.g., 365 nm. The moments of turning the irradiation light on and off are indicated. Note that, after irradiation, the isotropic absorbance is stable because the B isomer is thermally stable, and the anisotropy relaxes due to molecular rotational diffusion.

Results and Discussion

Figure 2 shows the time evolution of $\overline{A_B}$ and ΔA_B of DE/PMMA during and after linearly polarized UV irradiation for different irradiation power values. The occurrence of anisotropy is indicative of photoorientation of the chromophores. The green light-induced orientation of the chromophores shows a dynamical behavior that reverses for long irradiation times (see Figure 3). In this experiment, the DE/PMMA samples were irradiated by unpolarized UV light to the photostationary state, and linearly polarized green irradiation followed. Even though diarylethenes are robust chromophores, the reversal of the mean absorbance observed at high UV irradiation intensities is due to the isomer's degradation. In fact, the colored intensity of DE decreases to 80% after 10 UV−visible irradiation cycles.[12] To avoid possible

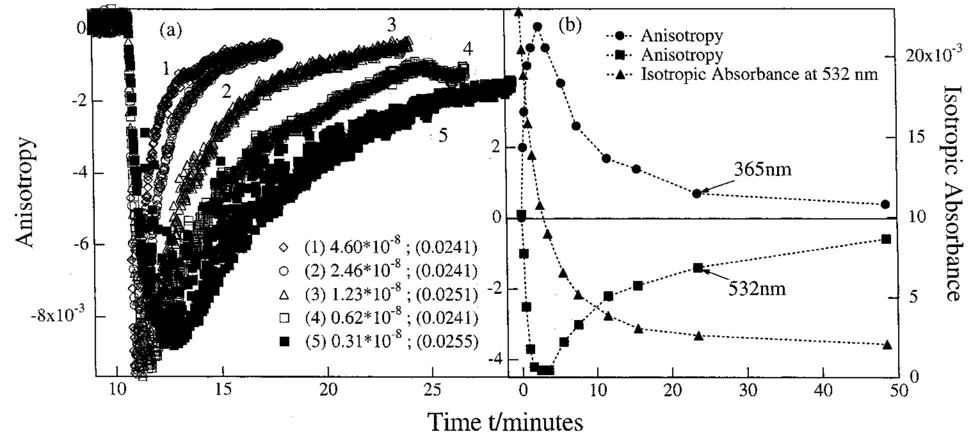

Figure 3. (a) Same as Figure 2, but for 532-nm analysis and irradiation. (b) Anisotropy observed by a UV−visible spectrophotometer after 546-nm irradiation (~1 mW/cm^2). In (b), the time refers to the irradiation duration.

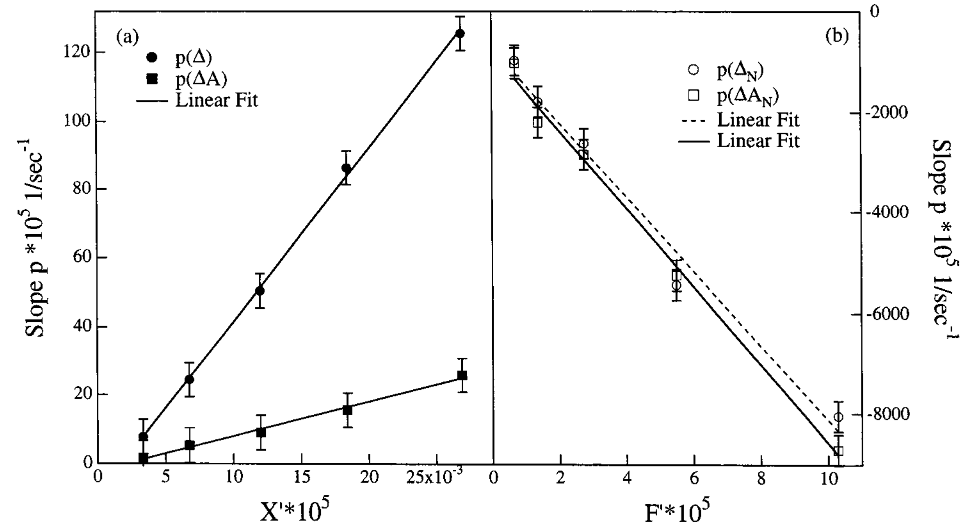

Figure 4. Slopes, (a) p(Δ) and p(Δ*A*), and (b) p(Δ$_N$) and p(Δ*A*$_N$), of the observed change of the early time evolution of the isotropic absorbance and the anisotropy, respectively, on the irradiation intensity (UV for (a) and green for (b)). The full lines are linear fits. $F' = 10^3(1 - 10^{-A'_0})I'_0/A'_0$; and $X' = F'A'_0$.

photodegradation complications after successive irradiation cycles, each photoorientation experiment has been done on a different previously nonirradiated sample, and for data analysis, only the slopes and the maximum absorbances at high irradiation intensities were considered.

The fitted slopes, $p(\Delta)$ and $p(\Delta A)$, of the early time evolution of $\overline{A}_B$ and ΔA_B, respectively, showed a linear dependence on the irradiation light intensity for both UV- (Figure 4a) and green (Figure 4b) light-induced orientation. The solid lines in Figure 4a are linear theoretical fits by[11]

$$p(\Delta) = 1000I'_0(1 - 10^{-A'_0})\phi'_{AB}\epsilon_B \tag{1}$$

$$p(\Delta A) = \frac{6}{5}1000I'_0(1 - 10^{-A'_0})\phi'_{AB}P_2(\cos\omega)P_2^{AB}\epsilon_B \tag{2}$$

where I'_0 is the incident flux of photons per centimeter squared, A'_0 is the sample absorbance prior to irradiation, ϕ'_{AB} is the UV-induced A → B photochemical quantum yield, P_2^{AB} is a parameter that characterizes the memory of the orientation of the UV transition of the chromophore during the A → B photoisomerization, $P_2(\cos\omega)$ is the second-order Legendre polynomial of cos ω, and ω is the angle between the B isomer's irradiation, e.g., UV, and analysis, e.g., visible, transition moments. For a system without A ← B themal isomerization, $P_2(\cos\omega)$ is given at the photostationnary state by[11]

$$S_B = -\frac{2}{13}P_2(\cos\omega) \tag{3}$$

Table 1. Order Parameter S_B at the Photostationary State of UV Irradiation, and the Irradiation Intensity Expressed in Units of einstein·s^{-1}·cm^{-2}

I (× 10^{10})	365 nm	1.21	2.43	4.24	6.65	9.70
	405nm	3.72	6.76	13.2	17.3	26.0
S_B	365 nm	0.055	0.060	0.058	0.064	0.062
	405 nm	0.027	0.026	0.024	0.021	0.021

For DE in PMMA, the values of S_B obtained at the photostationnary state of UV irradiation are given in Table 1. From these values, it noteworthy that for different irradiation intensities and wavelengths, the value of S_B is fairly constant, e.g., ~0.060 and ~0.024 for 365- and 405-nm irradiation, respectively; a feature that is theoretically rationalized by eq 3. *The factor of −2/13 is the constant of photoorientation by photoisomerization* and refers to the maximum orientation, e.g., the orientation observed at the irradiation wavelength for systems either without A ← B thermal isomerization such as diarylethenes or where the irradiation intensity is extrapolated to infinity, such as azobenzenes and spiropyrans.

For the evaluation of the parameters above, ϵ_B should be known. We have determined ϵ_B by the method of Fisher,[9] which

Table 2. Data of Coupled Photoisomerization and Photoorientation of DE[a]

λ/nm	ϵ_A	ϵ_B	ϕ_{AB}	ϕ_{BA}	$P_2(\cos \omega_{532}^{UV})$	ω_{532}^{UV}	$P_2{}^{A_{UV} \rightarrow B_{UV}}$
365	4436	8332	1.10		−0.39	74.3	−0.43
405	2402	423	0.32		−0.015	61.3	−1.04
532	0	4574		0.16			

[a] The extinction coefficients are expressed in units of $L \cdot mol^{-1} \cdot cm^{-1}$.

holds not only for isotropic but also for anisotropic samples when the isotropic absorbance is considered. For this determination, two different locations, which have exactly the same absorbance value in the UV region of an all-cis DE/PMMA sample, were irradiated by linearly polarized 365- and 405-nm UV lights to the photostationnary state, respectively, and the parallel and perpendicular spectra were measured on the entire UV−visible spectrum by a spectrophotometer (model UV-1600, Shimadzu) with two custom-built polarizers for the sample and the reference. The obtained extinction coefficients are summarized in Table 2 together with the photochemical quantum yields and the parameters obtained from the photoorientation experiments. The fitted slope of the isotropic absorbance of Figure 4b of the green photoorientation experiments yielded ϕ_{BA}^{532}. It is noteworthy that for systems without $A \leftarrow B$ thermal isomerization, and if analysis is performed at the irradiation wavelength, $A \leftarrow B$ photoorientation predictions suggest a slope ratio $p(\Delta A)/p(\Delta)$ equal to 1.2,[11] and the slopes, calculated from Figure 4b, of the green photoorientation of DE give a ratio of $p(\Delta A)/p(\Delta)$ of ∼1.1.

To our knowledge, the quantum yields of coloring and bleaching of DE have not yet been measured, but those of other diarylethene derivatives have been determined. The values that we found in PMMA by irradiation at 532 and 405 nm, e.g., $\phi_{BA}^{532} \sim 0.16$ and $\phi_{AB}^{405} \sim 0.32$, respectively, are close to those, e.g., $\phi_{BA}^{546} \sim 0.14$ and $\phi_{AB}^{334} \sim 0.27-0.33$, found in CCl_4 and benzene solutions for other diarylethene derivatives that are structurally related to DE.[12] Even though little free volume change is needed for DE ring opening and closing, the PMMA matrix does not seem to hinder the isomerization movement of the chromophore. Perhaps the large swelling of the polymer chains, which is mirrored by the decrease of T_g with the added DE solutes (vide infra), provides enough free volume for the photoinduced movement of the chromophores. It is noteworthy that polymer thin films present a distribution of free volumes to solutes, and the film properties are averaged for chromophores in different sites. Quantum yields depend on the excitation wavelength, and when side reactions are present, they can be larger than 1. Indeed, a single photon may lead to the isomerization of more than one chromophore by side reaction isomerization. The value of 1.1 that we found for ϕ_{AB}^{356} at 365 nm might reflect the existence of an energy transfer between neighboring open-form molecules to induce close ring isomerization, a feature that may occur in polymer films with high chromophore concentration. Other authors have also found a quantum yield of 2 for the isomerization of another diarylethene derivative in films of poly(vinyl butyral), and they too have attributed it to an energy transfer from the open to the closed ring form.[14]

$P_2{}^{A_{365} \rightarrow B_{365}} \sim -0.4$ and $P_2{}^{A_{405} \rightarrow B_{405}} \sim -1$ show that the orientation of the UV transition dipole of the chromophore is partially retained, e.g., not thermalized, upon isomerization from A to B after UV irradiation, a feature which suggests that the chromophore does not tumble indiscriminately before it cools off as it does when isomerized from B to A by green irradiation. Figure 3b shows that the green light-induced orientation observed at both 532 and 365 nm disappears after all B forms are isomerized to A forms; a feature which demonstrates that isomer A is not oriented by green light-induced $A \leftarrow B$ isomerization, and the observed anisotropy at both 532 and 365 nm is due to the orientation of only isomer B. If orientation occurs in A at any time by green irradiation, some anisotropy should remain at 365 nm after all B are isomerized to A. This behavior is theoretically rationalized by $P_2{}^{A_{365} \leftarrow B_{532}} \sim 0$, since the orientation of A is proportional to that of B through $P_2{}^{A_{365} \leftarrow B_{532}}$.[15] The lack of orientation in A may be due to the large amount of energy that needs to be dissipated during the photochemical process induced by the 532- or 546-nm photon; perhaps when the molecule is excited, it shakes strongly before it relaxes. $\omega_{532}^{365} = 74.3$ and $\omega_{532}^{365} = 61.3°$ demonstrate that the direction of the UV, e.g., 365 and 405 nm, and visible, e.g., 532 nm, transitions of the B isomer, e.g., the closed form, are oriented toward perpendicular directions and rationalize the result of Figure 3b. This finding is reinforced by the result of Figure 5 which shows that the calculated 365- and 532-nm transitions, with 0.960 878 and 0.398 422 respective oscillator strengths, of the closed form of DE are indeed perpendicular to each other. The UV and visible transitions of the closed form of DE have been calculated by using the CNDO/S (completely neglected differential overlap/spectroscopy) with the associated AM1 parametrization for geometry optimization which are available with the MOPAC molecular orbital software.[16]

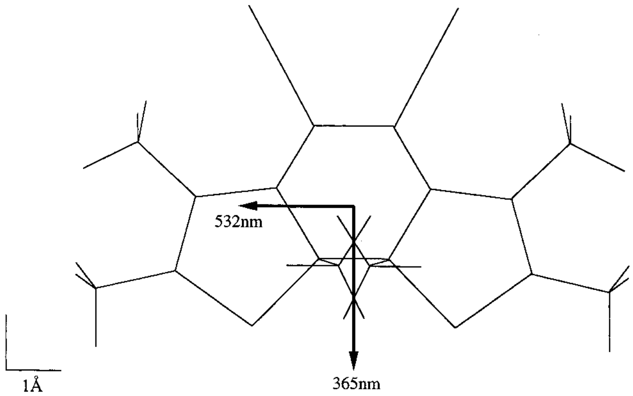

Figure 5. Drawing of the top view and transition moment vectors at 365 and 532 nm of the closed form of DE obtained by CNDO/S AM1 MOPAC molecular orbital calculations. The 532 nm is parallel to the long axis of the molecule.

Conclusions

Diarylethenes are oriented by photoisomerization via purely polarized transitions. The movement of the chromophore has been discussed for both UV- and green light-induced isomerization. The quantum yields and the orientation parameters are determined. The UV and visible transitions of the closed-form isomer are perpendicular; a finding that is rationalized by molecular orbital calculations. Quantified photoorientation reveals the symmetry nature of molecular transitions of photochromic isomers.

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