Photochromism of an Indolylfulgide Trapped in a Hybrid Sol-Gel Matrix

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An indolylfulgide has been trapped in a hybrid organic-inorganic matrix prepared by the sol-gel process using methyltriethoxysilane. Photochromic properties of doped films have been studied.

Photochromic properties of materials have been of continuing interest to chemists[1] as well as materials scientists in the past several decades because of their potential for various applications. From this viewpoint, organic and hybrid organic-inorganic polymers doped with organic photochromes are the suitable candidates.[2] For this reason, many papers have been devoted to photochromic reactions in polymers to clarify the relationship between the kinetics of photochromic reactions and the structures of the polymeric hosts.[3]

Fulgides have been known as the thermally irreversible photochromic compounds.[1] Indolylfulgides such as **1** (Figure 1) are thermally durable and fatigue resistive.[4] Although the electronic[5-8] and steric effects[7] of substituents of the indolylfulgides on their photochromic and spectroscopic properties have been well studied, the medium effects on the properties of indolylfulgides have not been reported.[9] The hybrid organic-inorganic materials prepared from the sol-gel process combine a more or less rigid amorphous matrix with optically responsive systems trapped inside the polymeric network.[10] In this paper, we report our study on photochromic properties of the indolylfulgide **1** trapped in a sol-gel medium.

Doped sol-gel matrices were prepared by hydrolysis-condensation of an organically modified silicon alkoxide (methyltriethoxysilane=MTEOS) in conformity with the published procedure.[3c] Photochromic coatings were elaborated by spreading the doped sol (photochrome content = 1.76×10^{-2} mol dm^{-3}) on flat glass plates, using the spin-coating technique. Films thus obtained were dried at 70 °C and maintained at this temperature for 29 h.

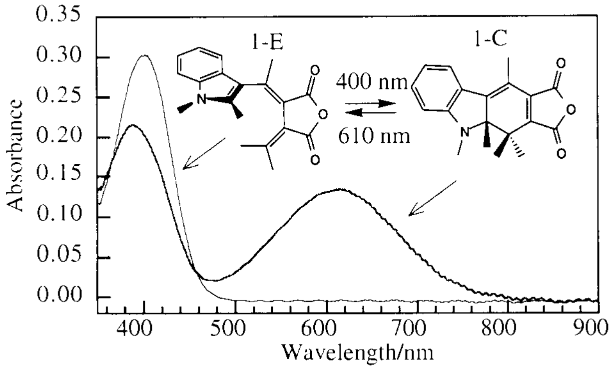

Figure 1. Absorption spectra of an indolylfulgide doped hybrid film. Thickness of the film: 4.70 μm.

Table 1. Absorption maxima of the two forms in various media

Medium	λ_{max}/nm	
	E form	C form
toluene	385	584
dimethylformamide (DMF)	/	585
acetonitrile	/	586
tetrahydrofuran (THF)	386	578
THF/water pH=7 [a]	395	597
THF/water pH=1 [a]	395	597
sol-gel matrix	400	≈ 610

[a]The THF/water volume ratio was 65/35.

The absorption spectra of the indolylfulgide in sol-gel derived host medium before and after UV irradiation are shown in Figure 1. Additional spectral data concerning the indolylfulgide **1** dissolved in various media are listed in Table 1.[5] An important red shift is observed in the MTEOS matrix compared to usual organic solvents (27 nm for **1C**, relative to the toluene). Such a shift could be explained by the polarity of the matrix, the potential acidity of the medium and, as shown for other photochromes,[3b,c,e,11] hydrogen bond type interactions of carbonyl groups with residual silanols. In fact, the increase of polarity from toluene to DMF or acetonitrile solutions did not induce a red shift of λ_{max}. Moreover, in THF/water mixtures the band remained unchanged while increasing the acidity of the medium. Consequently, the red shift observed in the MTEOS matrix can be mainly attributed to hydrogen bonds between silanols and carbonyl groups of the fulgide, as shown by the

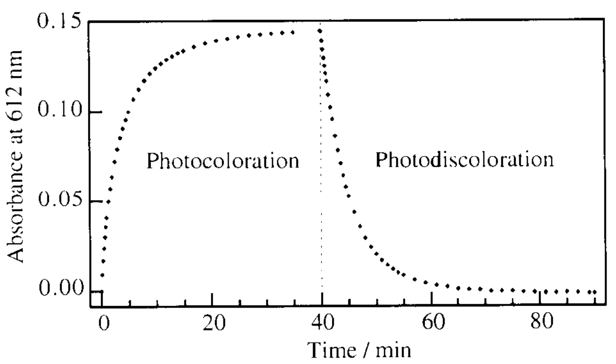

Figure 2. Cycle of photocoloration-photodiscoloration of a film recorded at 40 °C. Photocoloration: 5.5 W/m^2 at 400 nm (half height width: 50 nm) ; photodiscoloration: 14 W/m^2 at 600 nm (half height width: 50 nm).

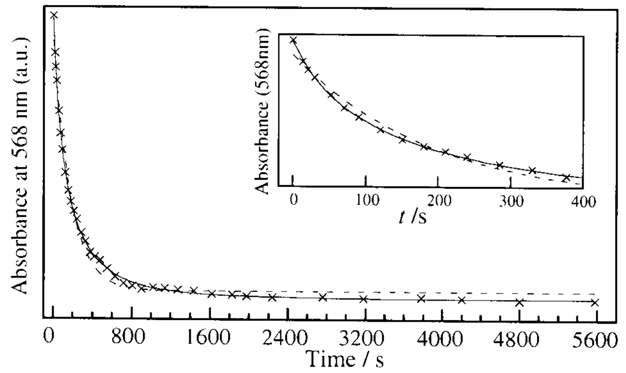

Figure 3. Photodiscoloration kinetics of 568-nm light irradiation. The dashed line is the best fit of the expression[14] corresponding to a single photodiscoloration process: $\log(10^{A(t)} - 1) = \log(10^{A(0)} - 1) - kt$. The solid line is the best fit of the expression based on a gaussian distribution of photodiscoloration energies.

20 nm red shift measured after addition of water to tetrahydrofuran. However, in comparison with an aqueous solvent, the red shift is enhanced in the gel matrix. This can be explained by the lower mobility of the photochrome, in agreement with the 8 nm red shift observed for a furylfulgide from a solvent to the structurally corresponding polymer.[9]

A typical cycle of photocoloration/photodiscoloration is depicted in Figure 2. The photodiscoloration process of **1C** was studied in detail. The samples were colored by a Xenon lamp monochromated at 400 nm. Two discoloration experiments were carried out using monochromatic light from a Kr laser, at 568 nm and 676 nm (higher and lower in energy, respectively, than the absorption maximum of **1C**). Kinetic curves were obtained by measuring the absorbance at the irradiation wavelength during the discoloration (Figure 3). The two kinetics neither fitted with the model of a homogeneous photodiscoloration in a homogeneous medium (single exponential decay) nor with Tomlinson's model[12] which takes the thickness heterogeneity of discoloration into account. However the kinetic data fitted very well with a model based on a distribution of photodiscoloration energies (Figure 3).[3c,e,13] The width of the gaussian distribution represents the dispersion of the photodiscoloration energies caused by a local inhomogeneity of environment. Moreover a slight but notable shift of the absorption band maximum appeared during each photodiscoloration. The following shifts were measured between the initial absorption band (colored film) and the absorption band when the absorption height became half of the initial: a red shift of 4 nm for the photodiscoloration at 568 nm and a slight blue shift of 1.5 nm for the photodiscoloration at 676 nm. These shifts may also be explained in terms of local inhomogeneity of environment (nature of the surrounding groups: methyl or silanol) which may induce a distribution of hydrogen bonds. As discussed above, the absorption of **1C** in the visible region is sensitive to the environment. The apparent absorption band of the film is therefore the sum of a multitude of absorption bands. The photodiscoloration is obviously more effective for molecules having the absorption maximum near the irradiation wavelength. Thus for the irradiation at 568 nm the "blue" contribution of the apparent absorption band was discolored more rapidly, inducing a red shift of the absorption maximum. For the irradiation at 676 nm the "red" contribution of the apparent absorption band was discolored more rapidly, inducing a blue shift of the absorption maximum. These kinetics and spectral results revealed the local inhomogeneity of environments for the indolylfulgides in this sol-gel matrix.

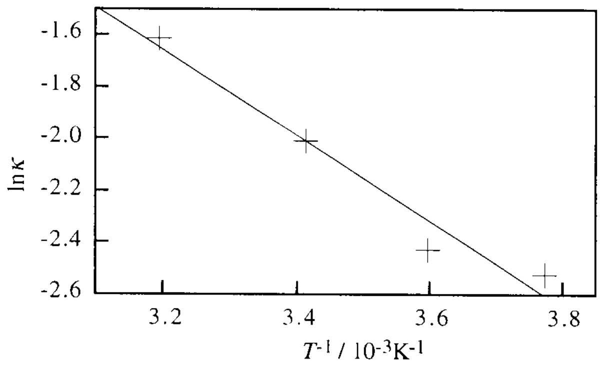

Figure 4. Arrhenius plot for the determination of the photodiscoloration activation energy (from 265 to 313 K).

To obtain the order of magnitude of the activation energy of photodiscoloration of **1C** in the MTEOS matrix, decrease of absorption was monitored when irradiated with the light of 600 nm (polychromatic source centered on 600 nm, half height width of 50 nm) at various temperatures as the function of irradiation time. The photochemical rate constants κ[14] were calculated, and the activation energy was obtained by plotting lnκ versus T^{-1} (Figure 4). The calculated average activation energy of the photodiscoloration for **1C**-doped hybrid film is 14+/-3 kJ/mol.

References and Notes

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