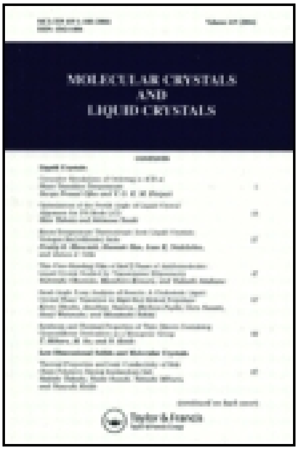

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Remarkable Improvements in the Photochromic Reversibilities of Fulgides in Solid Films

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Remarkable Improvements in the Photochromic Reversibilities of Fulgides in Solid Films

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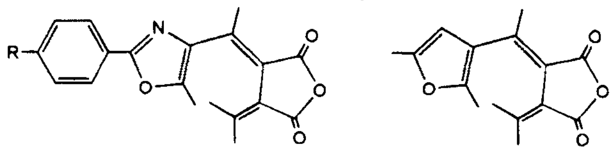
Oxazolyl fulgide with *p*-dimethylaniline group (fulgide **1**) revealed favorable absorption spectra, high photochromic responses and high thermostabilities in a polystyrene or a poly(methyl methacrylate) film spin-coated on a silica glass, but it suffered from extensive photochemical fatigues while phenyl-substituted oxazolyl fulgide (fulgide **2**) revealed much less fatigues. The photochemical fatigues of fulgide **1** could be substantially suppressed by a simple treatment of the spin-coated films to keep air-tight. Similar improvement in the photochemical fatigue resistance was obtained with films of the well-known furylfulgide. Further, thermal stabilities were significantly improved towards heating at 80 °C. These effects are ascribable to the effective shielding of the air (molecular oxygen).

Keywords: photochromic fulgides; photochemical fatigue resistance; sealed air-tight film; dimethylaniline group

INTRODUCTION

Photochromic compounds are promising candidates for use in photon-mode rewritable memory and rapid photoswitching devices [1,2], if sufficient photochemical fatigue resistance and thermal stability are fulfilled. Molecular modifications [3-5] as well as addition of stabilizers such as antioxidants [3,5] are effective to substantially depress the photochemical degradations. We here report a simple and yet effective method to improve photochemical fatigue resistance in solid films without addition of stabilizers nor with any changes in the molecular structures, by using oxazolylfulgides with a strong electron-donating *p*-dimethylaniline group (fulgide **1**), with phenyl group (fulgide **2**), and the well-known furylfulgide [6] (fulgide **3**).



Fulgide 1: R=N(CH_3)$_2$ **Fulgide 2**: R=H **Fulgide 3**

RESULTS AND DISCUSSION

Absorption Spectra and Quantum Yields

Figure 1 illustrates the spectral changes of fulgide **1** (2.5 wt%) in a spin-coated polystylene (PS) film on irradiation with 365-366 nm light. The absorption maxima of the colored and erased forms are strong and well separated (190 nm) from each other. Table 1 compares the absorption spectra and photochemical quantum yields of fulgides **1**-**3** measured in dilute toluene solution. Reflecting the strong electron-donating group, the erased form of fulgide **1** exhibits an increased absorption coefficient (3.5 times of fulgide **2** and 6 times of fulgide **3**) while the colored form about 2 times of fulgides **2** and **3**. The quantum yield for coloration is significantly increased though the decoloration quantum yield is decreased.

TABLE 1. Absorption spectra and quantum yields in toluene [a)]

Substrate	Erased Form			Colored form		
	λ_{max}/nm	ε_{max}	ϕ_{EC}	λ_{max}/nm	ε_{max}	ϕ_{CE}
Fulgide **1**	324	36,300	0.28	511	19,700	0.011
Fulgide **2**	337	10,100	0.18	465	11,000	0.054
Fulgide **3**	345	6,100	0.19	495	9,200	0.048

a) ε_{max} refers to the molar absorption coefficient / $M^{-1}cm^{-1}$ at λ_{max}, ϕ_{EC} and ϕ_{CE} refer to the quantum yields for coloration with 365 nm light and decoloration with 470-510 nm light, respectively.

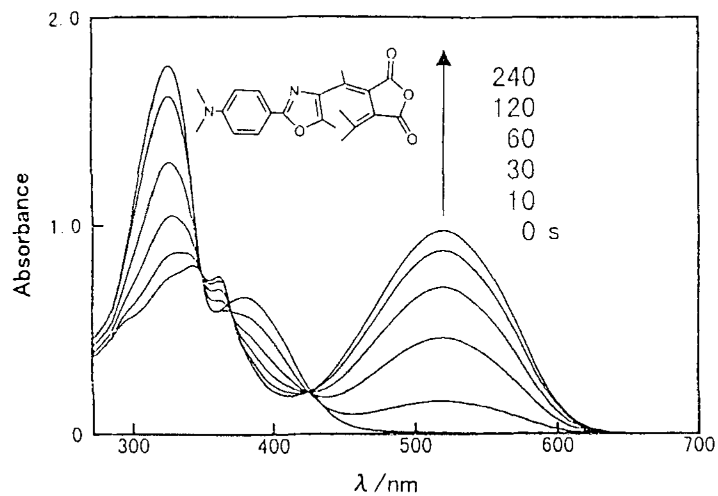


FIGURE 1. Spectral changes of fulgides **1** (2.5 wt%) in a spin-coated PS film on irradiation with 365-366 nm light.

Photochemical Fatigue Resistances

In a solid thin film of polystyrene (PS) or poly(methyl methacrylate) (PMMA), spin-coated on a silica glass under the air, fulgide **1** underwent extensive photochemical fatigues upon repeated coloration-decoloration cycles as illustrated in Figure 2(a), while fulgide **2** revealed much less fatigues. The photochemical fatigues of fulgide **1** could be substantially suppressed by a simple treatment. Thus, a "sealed film pair" was prepared by joining a pair of spin-coated films with each other on face-to-face, after drying in the air (Figure 3). Then, the periferal four sides were spread with an adhesive agent of epoxy resins to keep air-tight. Figure 2(b) demonstrates a remarkable improvement in the fatigue resistance of a sealed film pair as compared with a naked single film (a): the sealed film pair retained 73 % of the initial absorbance upon 100 cycles of repeated coloration-decoloration reaction whereas the naked single film (or a unsealed film pair) retained only 12 % upon 23 cycles of repetition. Table 2 numerically compares the photochemical fatigues of fulgides in sealed and unsealed films. A "unsealed film pair", which was prepared by joining a pair of spin-coated films on face-to-face but not sealed air-tight, revealed extensive fatigues similar to those of the naked single film, implying a dominant role of the atmospheric oxygen in the photo-

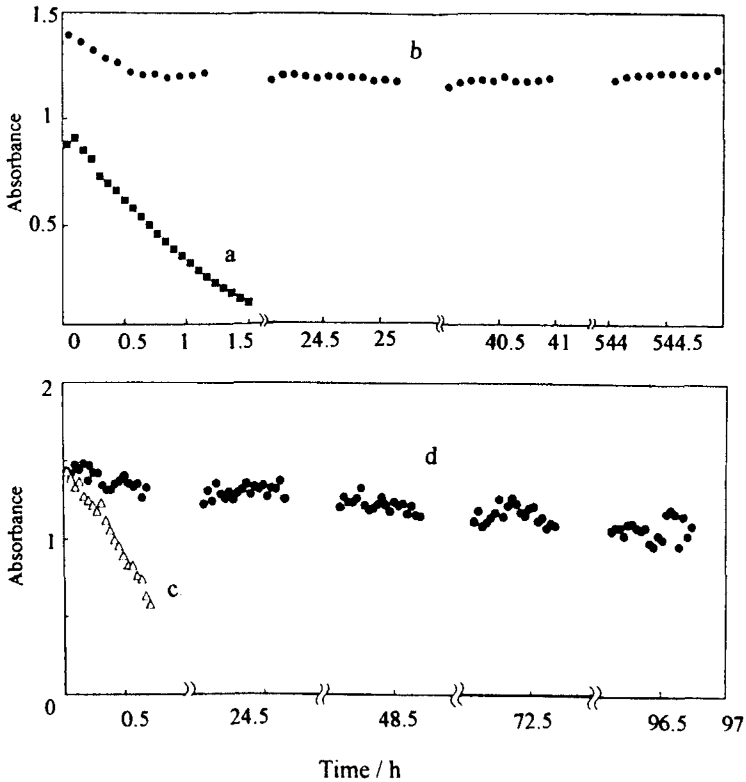


FIGURE 2. Photochemical reverrsibilities of PS films.
Upper: Fulgide **1** (2.5 wt%) in a naked single film (a) and a sealed film pair (b), on alternate irradiations with UV (3 min) and visible (3 min) light beams. Lower: Fulgide **3** (4.7 wt%) in a unsealed film pair (c) and a sealed film pair (d), on alternate irradiations with UV (90 s) and visible (40 s) light beams.

chemical fatigues. The slight degradations observed in the initial stages in Figure 2(b) are ascribable to the air saturated during the film treatments before sealing with the adhesive. Almost similar improvements in the fatigue resistance were obtained with fulgide **3** as illustrated in Figure 2 (c, d).

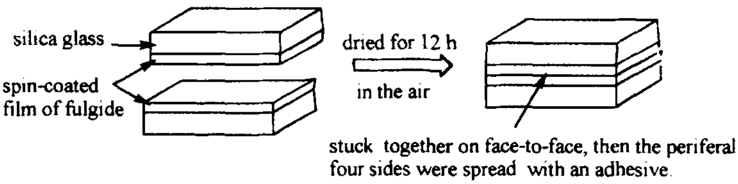


FIGURE 3. Preparation of a sealed film pair.

TABLE 2. Photochemical fatigues in sealed and unsealed films [a)]

Sample film	Cycle number	A/A_0
Fulgide **1** in unsealed PS film	23	0.12
in sealed PS film	100	0.73
Fulgide **1** in unsealed PMMA film	20	0.41
in sealed PMMA film	100	0.77
Fulgide **2** in unsealed PMMA film	20	0.73
in sealed PMMA film	100	0.77
Fulgide **3** in unsealed PS film	20	0.39
in sealed PS film	100	0.75

a) A/A_0 refers to the absorbance value after *n* cycles of repetition relative to the initial absorbance of the colored form. "Sealed film" refers to a sealed film pair, "unsealed film" refers to a naked single film or a unsealed film pair.

Thermal Stabilities

Thermal stabilities of the sealed and unsealed films were measured in the dark on heating at 80 ℃ for long periods, as listed in Table 3. The sealed film pair of fulgide **1** in PS revealed only slight improvements in the thermal stabilities of both colored and erased forms. Thus, upon heating for 4 months at 80 ℃ in the dark the absorbance values of the colored and erased forms of the sealed PS film pair were decreased to 80 % and 87 %, respectively, which are almost similar to those values obtained with the naked single film, 73 % and 80 %, respectively. A large difference was obtained with the colored form of fulgide **3** in a sealed film pair: the absorbance of the colored form in the sealed film pair was decreased to 69 % upon heating for 4 weeks whereas absorbance of the naked single film was decreased to 13 % upon heating for only a day. However, the erased form of fulgide **3** was less stable in the sealed film pair than in the naked single film upon heating for 4 weeks.

Regarding to the physical properties of adhesives such as the oxygen permeabilities and their effects should await further investigations.

TABLE 3. Thermal stabilities of fulgides in PS films at 80 ℃

	Erased form		Colored form	
Sample film	Heating / day	A/A_0	Heating / day	A/A_0
Fulgide **1** in unsealed film	120	0.80	121	0.73
in sealed film	120	0.87	120	0.84
fulgide **3** in unsealed film	28	0.74	1	0.13
in sealed film	28	0.54	28	0.69

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