Photochromic Cyan Dyes of Fulgide Derivatives in Polymer Film

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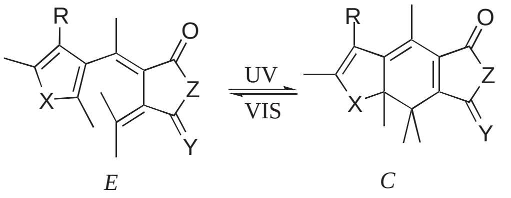
(Received December 28, 2004; CL-041621)

Photochromic polymer films doped with 3–4 wt % fulgide derivatives exhibit high thermal and photochemical fatigue resistances as well as good color property to serve as cyan dyes for rewritable color display and printing materials.

Thermally irreversible photochromic compounds,[1] such as diarylethenes[2–5] and fulgide derivatives,[6–8] have received considerable attention because of their potential application to photon-mode erasable optical switches, memories, and displays. Recently, some fulgide derivatives suitable for a photon-mode rewritable full-color display have been examined,[9] where each of the three primary colors (yellow, magenta, cyan) has to exhibit high quality of color and excellent fatigue resistances. While photochromic oxazolylfulgides as yellow dyes feature fairly good fatigue resistances,[10] pyrrolylfulgides as photochromic cyan dyes tend to suffer from extensive thermal and photochemical degradations owing to the low oxidation potential of the pyrrole ring. Though the indolylfulgides do feature excellent fatgue resistances, their color properties have some difficulties, e.g., the erased forms exhibit strong orange color.[11] This paper is concerned with exploration for photochromic cyan materials of fulgide derivatives with better color purity and fatigue resistances.



Substrate	X	Y	Z	R
1	N-Ph	O	O	H
2	N-Ph	O	O	Me
3	N-Ph	O	NH	H
4	S	$C(CN)_2$	O	H

Scheme 1. Structures and abbreviations for fulgide derivatives.

The pyrrolylfulgides **1** and **2** were prepared, according to the literatures,[6,11] from *N*-phenyl-3-acetyl-2,5-dimethylpyrrole and *N*-phenyl-3-acetyl-2,4,5-trimethylpyrrole (obtained from 1-phenyl-2,3,5-trimethylpyrrole by refluxing in acetic anhydride), respectively, by Stobbe condensation with diethyl isopropylidenesuccinate, followed by hydrolysis and dehydration. Fulgimide **3** was derived from fulgide **1**, according to the literature,[12] by treating with saturated ammonia in THF solution, followed by methylation with trimethylsilyldiazomethane in methanol solution, then treated with sodium hydride in THF. The dicyanomethylene derivative **4** was prepared from the thienylfulgide by reaction with malononitrile in the presence of diethylamine, according to the literature.[13] The ^{1}H NMR spectra of all these derivatives were satisfactory. Spin-coated polymer films doped with fulgide derivatives in 3–4 wt % were prepared from cyclohexanone or toluene solution. In order to protect from oxidative degradations, the surface of the film was overcoated with aqueous polyvinyl alcohol (PVA) to keep air-tight,[14] though all processes including spin-coating, drying, and PVA sealing, were carried out under the atmospheric air.

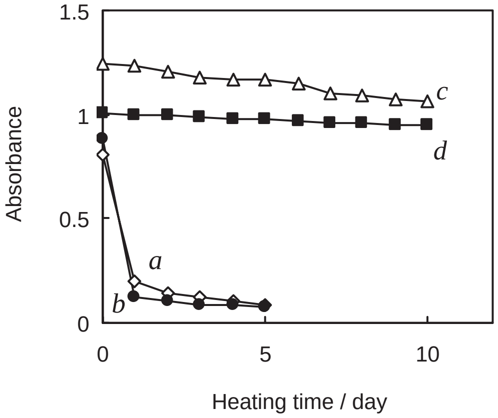


Figure 1. Thermostability of the colored forms doped in spin-coated PMMA film toward heating at 80 °C. (a) **1C** in unsealed PMMA, (b) **3C** in unsealed PMMA, (c) **1C** in PVA-sealed PMMA, (d) **3C** in PVA-sealed PMMA.

Figure 1 illustrates the thermal stabilities of the colored forms doped in PMMA film toward heating at 80 °C, demonstrating remarkable improvements in the PVA-sealed film (c, d), as compared with unsealed films (a, b) which substantially degrade within a day. The thermal stabilities (TS) for both *C* and *E* forms are listed in Table 1. The *E* forms are fairly resistant toward thermal oxidative degradations without the aid of PVA sealing, owing to their lower HOMO levels. The HOMO (Ψ_{64}) levels of the erased form **1E** (HOF $= -59.7$ kcal/mol) and the colored form **1C** (HOF $= -57.7$ kcal/mol), calculated with the MOPAC-PM5,[15] were -8.69 and -8.41 eV, respectively. Thus, the HOMO level of the erased form is significantly lower (by ca. 6.4 kcal/mol) than that of the colored form, and hence more apart from the LUMO level of oxidant species suppressing the HOMO–LUMO interactions between **1E** and oxidants (e.g., calculated LUMO level of the dioxygen Ψ_7: -2.87 eV). On the other hand, dicyanomethylene derivative **4** (both in *C* and *E* forms) exhibits high thermostability, particularly in polystyrene film without the aid of PVA sealing, owing to the strong electron-attracting dicyanomethylene group which substantially lowers the HOMO (Ψ_{58}) levels (-9.40 eV for **4E** and -8.75 eV for **4C**) far below the LUMO levels of oxidant species to effectively resist oxidative degradations.

Table 1. Photochemical reversibility (PR) and thermal stability (TS) in PVA-sealed and unsealed films

Sub-strate	Medium	PR	TS A_{10}/A_0[b]	
		A_{20}/A_0[a]	*E* form	*C* form
1	PMMA	0.51	0.90	0.09
	PMMA-PVA	0.80	1.01	0.87
2	PMMA	0.81	0.67	0.01
	PMMA-PVA	1.00	0.99	0.20
3	PMMA	0.54	(0.87)[c]	(0.08)[c]
	PMMA-PVA	0.86	0.99	0.94
4	PMMA	0.78	0.77	0.60
	PS	0.91	0.91	0.93

[a]Retainment of absorbance for the colored forms after 20 cycles (A_{20}) of repeated coloration–decoloration reaction relative to the initial value (A_0). [b]Retainment of absorbance after heating at 80 °C for 10 days. [c]After heating for 5 days.

Table 2. Absorption spectral and photochemical response times

Sub-strate	Medium	λ_{max}/nm		RTMH/s[a]	
		E form	*C* form	τ_{EC}	τ_{CE}
1	PMMA	376	635	65	11
	PS	379	620	41	8
2	PMMA	380	673	62	34
	PS	382	651	37	12
3	PMMA	355	604	86	13
4	PMMA	330	648	63	173
	PS	332	655	62	76

[a]τ_{EC} refers to RTMH for coloration on irraditation with 313–405 nm while τ_{CE} refers to RTMH for decoloration on irradiation with 546–578 nm, from a 400-W mercury lamp.

Table 1 also shows that the photochemical reversibility (PR) is significantly improved by the PVA sealing. Thus, they may be suitable for display or printing materials rewritable over a hundred times.

Absorption spectral properties and photochromic response times—required times for half maximum (RTMH)—are summarized in Table 2. In polymer films doped with only 3 to 4 wt %, the *C* forms exhibit deep and highly pure cyan color with single absorption bands in the visible region, as illustrated in Figure 2. The molar absorption coefficients of **1C**, **2C**, and **4C**, measured in toluene and ethyl acetate solutions, were in the range of 0.7, 1.0, and 1.2×10^4 mol^{-1} dm^3 cm^{-1}, respectively. Fulgimide **3**, both in *C* and *E* forms, results in significant blue shift as compared with the corresponding fulgide **1**. Also, the absorption bands shift significantly with the medium conditions such as polarity. These shifting effects should be useful for fine color tuning.

The response rates for coloration (Table 2) are less variant with the substrate structure as well as with the medium polarity. Contrary, the response rate of **4C** for decoloration is low in PMMA film, while those of **1C**–**3C** are relatively high in PS film. No such large solvent effects were found in dilute solutions: the RTMH values for decoloration of **1C** were 15, 15, and 20 s in toluene, ethyl acetate, and acetonitrile, respectively. The medium effects remain to be examined further.

In summary, the photochromic polymer films doped with the fulgide derivatives exhibit high fatigue resistances and good color property to serve as cyan dyes for rewritable color display and printing materials.

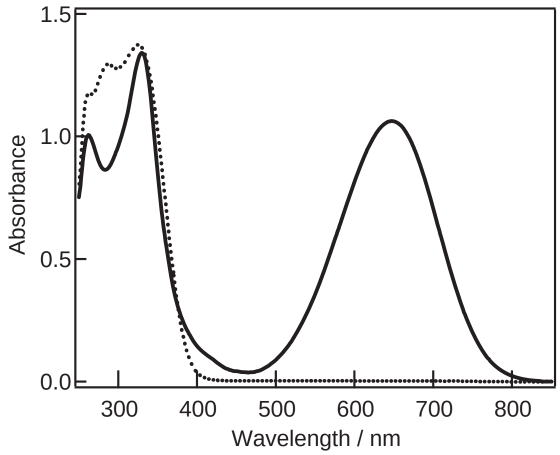


Figure 2. Absorption spectra of **4C** (solid line) and **4E** (broken line) in spin-coated PMMA film.

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Published on the web (Advance View) March 19, 2005; DOI 10.1246/cl.2005.574