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Comparison of the photochromic properties of fulgides and fulgimides

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Abstract

Photochromic properties of some arylfulgimides such as furyl-, thienyl-, and thiazolylfulgimides were compared with corresponding fulgides in detail. Photochemical reversibility and thermal stability as well as the photochromic response of fulgimides were substantially comparable with those of the fulgides, both in solution and in solid polymer film. Fulgimides revealed high resistance to solvolytic degradation in hydroxylic media while corresponding fulgides underwent rapid degradations. Thus, *N*-(4-carboxyphenyl)fulgimide, being soluble in aqueous media, revealed moderate photochromic performance in aqueous ethanol solution without extensive solvolytic degradation, as well as in ionic polymer film of allylamine hydrochloride. © 1997 Elsevier Science S.A.

Keywords: Photochromism; Fulgimides; Fulgides; Solvolytic resistance

1. Introduction

Since the development of fatigue-free and thermostable fulgides [1], organic photochromic compounds have been considered as promising candidates for use in rewritable photon-mode optical memory media [2–4]. Among many criteria for practical applications the most challenging problem, nondestructive readout capability, has been basically solved in many systems, e.g., in azo-benzenes [5], diarylethenes [6,7], fulgides [8], and naphthopyrans [9]. Applications of photochromic compounds are not limited to optical memory systems: thus, applications to other functional systems include photoswitchable ion transport in bilayer membrane [10,11], photomechanical switching in polymer gel [12], photoregulated "on–off" biomaterials [13,14], switching of energy transfer [15] etc. Such applications as to photoswitchable systems would not require nondestructive readout stability but high reversibility.

Although arylfulgides exhibit excellent photochromic properties, solvolytic degradations may occur in the presence of moisture or in hydroxylic media owing to the anhydride moiety of fulgides [16,17]. High solvolytic resistance should be required for use as biomaterials in hydroxylic media and holographic recording in gelatin film. The imide derivatives of fulgides, "fulgimides" [1,13–15,18–22], are expected to resist solvolytic degradations and substantially retain the photochromic properties of fulgides. However, systematic and direct comparison of the photochromic properties of fulgides and fulgimides seems to be relatively few [1,19].

This paper is concerned with comparison of the photochromic properties of some arylfulgides and arylfulgimides (Scheme 1) in some detail, in solid polymer film and hydroxylic media.

2. Experimental details

2.1. Materials

Arylfulgides were prepared by the Stobbe reaction of diethyl isopropylidenesuccinate with aryl methyl ketones according to the reported method [23–25]. Arylfulgimides were prepared from arylfulgides by reaction with amines, followed by treatment with acetyl chloride.

2.1.1. 2-[1-(5-Methyl-2-phenyl-4-thiazolyl)ethylidene]-3-isopropylidenesuccinimide (7Z)

A mixture solution of thiazolylfulgide (**3Z**) 1.3 mmol and aniline 4.2 mmol in benzene was heated at 80 °C for 2 h. On evaporation of the solvent the residue (oil) was treated by column chromatography on silica-gel with hexane and ethyl acetate to isolate amide acid. The amide acid was dissolved in acetyl chloride and heated at 40 °C for 40 min under nitrogen atmosphere. The reaction mixture was neutralized, extracted with ether, and dried over magnesium sulfate. Crystallization from a mixture of toluene and petroleum ether gave

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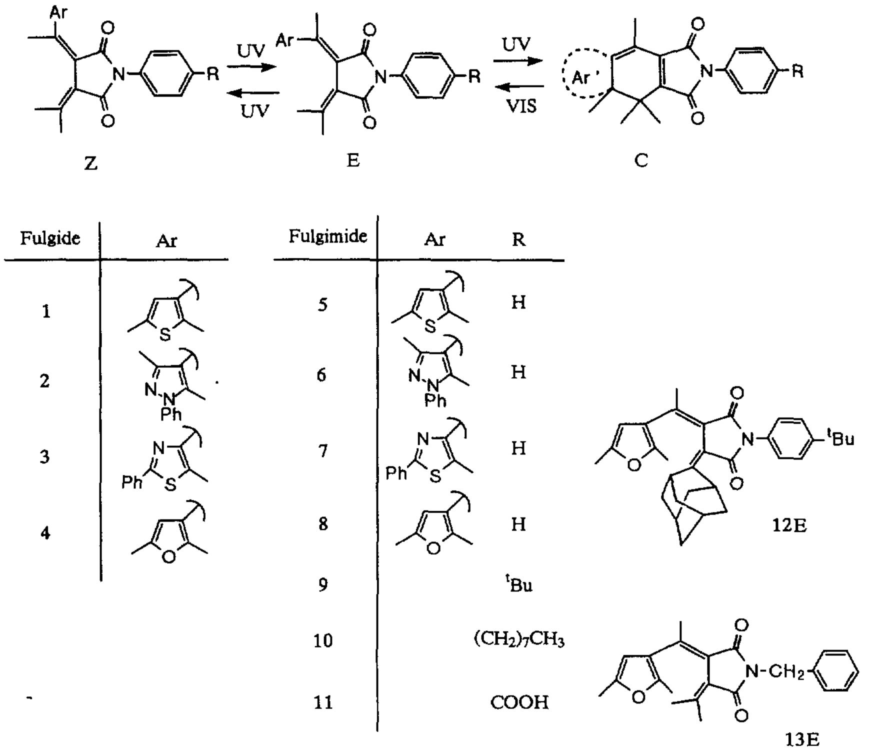

Scheme 1. Structures and abbreviations. Fulgimides **8–11** refer to furylfulgimides with substituent R at the *para* position of the *N*-phenyl ring.

pure yellow needles of **7Z**, mp 190–191 °C. The purity was checked by TLC on silica-gel (with hexane–ethyl acetate) which gave single spot. ^{1}H NMR and elemental analysis data, shown in Table 1 and footnote respectively, were satisfactory. Fulgimides **5Z** and **6Z** were prepared by the similar method.

2.1.2. N-(4-Carboxyphenyl)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidenesuccinimide (11Z and 11E)

A mixture solution of furylfulgide (**4Z**) 7.7 mmol and 4-aminobenzoic acid 21 mmol in pyridine was heated at 80 °C for 48 h. After workup, crystallization from a mixture of ether and petroleum ether gave pure yellow granules of **11Z**. By the similar method starting with fulgide **4E**, fulgimide **11E** was obtained as yellow crystals. ^{1}H NMR and elemental analysis data, shown in Table 1 and footnote respectively, were satisfactory.

2.2. Apparatus and procedure

Melting points were measured with a micro-melting point apparatus (Yanaco MP-S3, Yanagimoto). Electronic absorption spectra were recorded on a Hitachi 200-10 spectrophotometer, and ^{1}H NMR spectra were obtained on a Hitachi

Table 1
Physical constants of fulgimides

Fulgimide	Melting point/°C	^{1}H NMR (CDCl$_3$) δ/ppm
5Z	155–156	2.22 (3H, s), 2.30 (3H, s), 2.55 (3H, s), 2.60 (3H, s), 2.68 (3H, s), 6.80 (1H, s), 7.60 (5H, s)
6Z	188–189	1.73 (3H, s), 1.85 (3H, s), 1.90 (3H, s), 1.98 (3H, s), 2.16 (3H, s), 7.10 (5H, s), 7.17 (5H, s)
7Z[a]	190–191	2.10 (3H, s), 2.38 (3H, s), 2.50 (3H, s), 2.53 (3H, s), 7.20–8.06 (10H, m)
8Z	149–150	1.35 (3H, s), 2.02 (3H, s), 2.20 (3H, s), 2.31 (3H, s), 2.58 (3H, s), 5.92 (1H, s), 7.38 (5H, m)
9Z	179–181	1.37 (9H, s), 2.03 (3H, s), 2.22 (3H, s), 2.32 (3H, s), 2.60 (3H, s), 5.92 (1H, s), 7.32 (4H, m)
10Z	80–82	0.83 (3H, t, J=5 Hz), 1.05–1.65 (14H, m), 2.00 (3H, s), 2.20 (3H, s), 2.29 (3H, s), 2.55 (3H, s), 2.58 (3H, s), 5.92 (1H, s), 7.23 (4H, s)
11Z[b]	>200[d]	1.97 (3H, s), 2.08 (3H, s), 2.21 (3H, s), 2.23 (3H, s), 2.44 (3H, s), 5.97 (1H, s), 7.50 (2H, d, J=9 Hz), 8.16 (2H, d, J=9 Hz), 10.16 (1H, br.s)
11E[c]	>200[d]	1.33 (3H, s), 2.00 (3H, s), 2.19 (3H, s), 2.29 (3H, s), 2.56 (3H, s), 5.90 (1H, s), 7.54 (2H, d, J=9 Hz), 8.17 (2H, d, J=9 Hz), 8.80 (1H, br.s)
12Z	192–193	1.27 (9H, s), 1.28–1.94 (14H, br), 2.03 (3H, s), 2.19 (3H, s), 2.45 (3H, s), 5.88 (1H, s), 7.35 (4H, m)

[a] Pure crystals of yellow needles, 12% yield from fulgide **3Z**. Calcd. for $C_{25}H_{22}N_2O_2S$: C, 72.46; H, 5.32; N, 6.76%. Found: C, 72.39; H, 5.30; N, 6.66%.
[b] Pure crystals of yellow granules, 18% yield from fulgide **4Z**. Calcd. for $C_{22}H_{21}NO_5$: C, 69.67; H, 5.54; N, 3.69%. found: C, 69.15; H, 5.59; N, 3.67%.
[c] Pure crystals, 15% yield from fulgide **4E**.
[d] Decomposed.

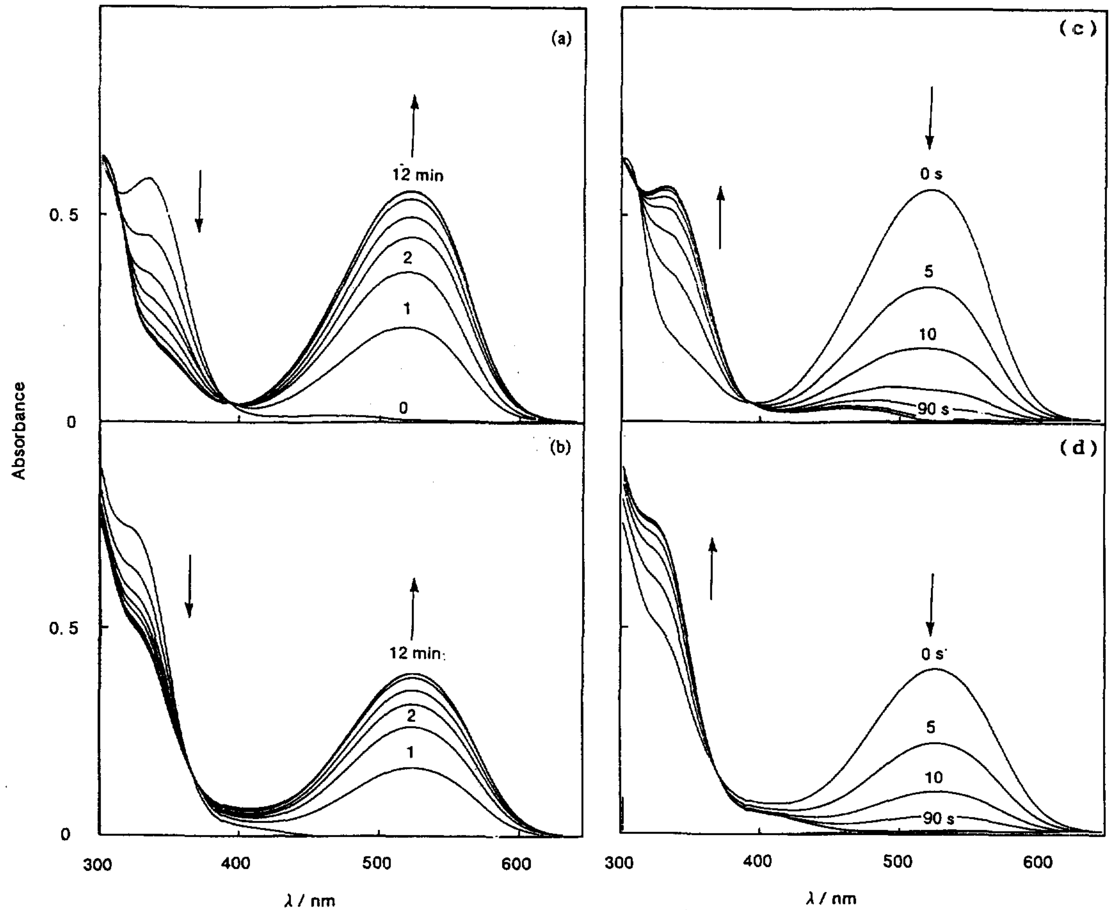

Fig. 1. Photochemical coloration of fulgide **1E** (a) and fulgimide **5E** (b) with 365–366 nm light, and decoloration of the colored solutions **1C** (c) and **5C** (d) with visible light (436 and 545 nm), in 0.1 mM in toluene.

R-24 spectrometer. Quantum yields were estimated by the method of total absorption of incident light [26] using a toluene solution of furylfulgide actinometer [23] by parallel irradiation in a merry-go-round irradiation apparatus.

Solvents were distilled before use. Photochemical and thermal reactions were carried out under the air without elimination of the dissolved oxygen. Usually, the E- and C-forms of fulgides and fulgimides were photochemically obtained in solution starting with Z-forms upon repeated UV and visible light irradiation until stationary states were attained.

3. Results and discussion

3.1. Photochemical responses and absorption spectra

Fig. 1 compares the photochemical coloration and decoloration reactions of thienylfulgides **1** and thienylfulgimides **5** in dilute toluene solution upon irradiation with UV and visible light, showing slight differences in the response rates and spectra. The colored form of the fulgimide **5C** is slightly red-shifted and its color intensity (Ac value) at the photostationary state (PSS) is lower, as compared with those of

Table 2

Absorption spectral data of fulgides and fulgimides [a]

Compound No.	C-form		E-form	
	λ_{max}/nm	A_C	λ_{max}/nm	A_E
1	520	0.55	333	0.56
2	550	0.23	335	1.83
3	488	0.66	297	1.66
4	494	0.89	345	0.64
5	525	0.39	323	0.76
6	540	0.15	335	1.97
7	497	0.59	308	1.76
8	505	0.54	332	0.65
9	505	0.51	331	0.63
10	508	0.45	328	0.60
11 [b]	510	0.66	332	0.81
12	520	0.21	330	0.57

[a] Each in 0.1 mM in toluene solution. A_C, absorbance of the colored solution at photostationary state attained on prolonged UV irradiation; A_E, absorbance of the decolored solution on prolonged irradiation with visible light.

[b] Molar absorption coefficients were estimated from the ^1H NMR signal intensities of isomeric mixture solution: $\epsilon_{max}/M^{-1}\,cm^{-1} = 7000$ (**11E**), 8300 (**11Z**), 6500 (**11C**).

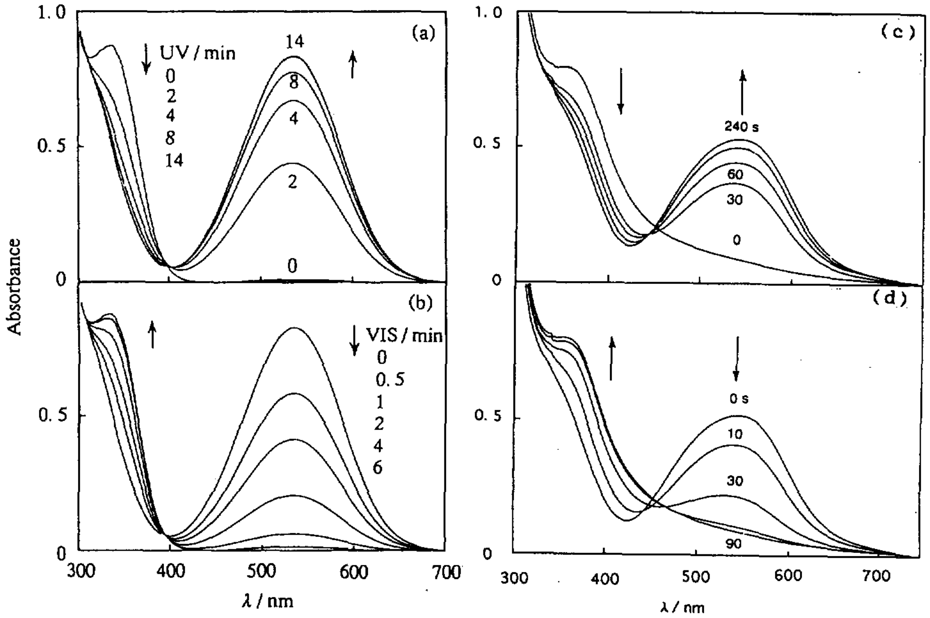

Fig. 2. Photochemical coloration (a) and decoloration (b) of fulgimide **11** in 0.1 mM in 1:1 aqueous ethanol, and in 20 wt.% in solid PAAH film of 1 μm thickness (c, d). With 365–366 nm light (a, c), and 436 + 545 nm light (b, d).

fulgide **1C**. Similar tendency was found in the Ac values of other fulgimides **6–8** vs. fulgides **2–4**, as listed in Table 2.

The lower apparent rate and Ac value of fulgimide **5** may be attributable, at least partially, to the spectral features. Thus, in the case of fulgide **1** (Fig. 1(a)), relatively large fraction of the incident light of 366 nm is absorbed by **1E** and small fraction by **1C**, thus allowing selective excitation of **1E** and smooth forward reaction. With fulgimide **5** (Fig. 1(b)), on the other hand, selective excitation of **5E** is less effective at 366 nm where significant fraction of the incident light is absorbed by the colored form **5C** as the reaction proceeds, thus causing to lower the apparent coloration rate. The apparent rate may not be exactly consistent with the quantum yield (ϕ_{EC}), since ϕ_{EC} is determined in the initial stages of the reaction where light absorption by the colored form is least significant. At the pss, only half the incident light quanta are absorbed by **5E** whereas the other half are absorbed by **5C** and cause the reverse reaction.

Fig. 2(a) and (b) illustrates photochromic reactions of the carboxylated fulgimide **11** in a hydroxylic solvent, and Fig. 2(c) and (d) in the ionic film of poly(allylamine hydrochloride) (PAAH) spin-coated on a silica-glass plate. The absorption maximum of **11C** was shifted from 510 nm in toluene to 532 nm in aqueous ethanol and 545 nm in PAAH. The slipping of the isosbestic point around 450 nm (c), (d) suggests a thermal equilibrium of some conformational changes after photochemical reactions, though not yet examined in detail. In PAAH film the photochemical responses seem to be rather low. The quantum yields of fulgimide **11** for coloration (ϕ_{EC}) and decoloration (ϕ_{EC}) were similar to those of fulgide **4** [27], both in toluene solution and in polymer film. Thus, ϕ_{EC} of **11E** was 0.19 at 366 nm while ϕ_{EC} of **11C** at 545 nm was 1.1 times of that with **4C** in toluene solution.

3.2. Thermal stability

As listed in Table 3, many of the fulgides and fulgimides were relatively thermostable in dilute toluene solution at 50 °C, except for pyrazolylfulgide **2C** and pyrazolylfulgimide **6C** which underwent rapid bleaching. In solid polymer film at 80 °C, on the other hand, many of the C-forms (**1C**, **4C**, **5C**, **6C**, **11C**) underwent irreversible thermal degradations while the E-forms were relatively stable. This tendency was not accounted for by the heat of formation (as a measure for the relative stability of the C- and E-form) calculated by the MOPAC-PM3 program [28]. The C-forms would be more susceptible to the compression effects from the polymer matrix than the E-forms since the former are planar while the latter are non-planar and flexible, thus possibly leading to the relative instability of the C-forms in the polymer [29]. In the case of thiazolylfulgide **3**, however, the E-form was unstable while C-form was stable in the polymer film (Fig. 3(a)). The reversion of the thermal stabilities of **3C** vs. **3E** is not explainable yet. Anyway, fulgimide **7** reveals a high thermostability in PMMA film as compared with the corresponding fulgide **3** (Fig. 3(b)).

Regarding to the solvolytic behavior in hydroxylic solvent, fulgimide **7** revealed a high resistance to solvolytic degradation as compared with fulgide **3** whose C-form was extensively degraded, as shown in Fig. 3(c) and (d). Also, Fig. 3 (broken lines denoted with VIS and UV) demonstrates that the photochromic properties of fulgimide **7** are substantially retained upon heating for several days in the polymer film or standing at room temperature in hydroxylic solvent. The (unexpected) stability of fulgide **3E** in hydroxylic solvent is attributable to small exothermic heat (-2.6 kcal mol^{-1}) for the alcoholysis reaction as compared to a larger exothermicity with **3C** (-12.8 kcal mol^{-1}), calculated for the methano-

Table 3
Thermal stability and photochemical reversibility in solution and polymer film [a]

Compound No.	Medium	Thermal stability A/A_0 [b]		Photochemical reversibility	
		E-form	C-form	Cycle	A/A_0 [c]
1	toluene	1.0	0.99	10	0.67
	PMMA	0.80	0.44	30	0.22
2	toluene	1.0	0.45	10	0.75
	PMMA	0.91	0.74	30	0.90
3	toluene	0.97	0.97	40	0.87
	ethyl acetate	0.96	0.92		
	PMMA	0.43	0.97	10	0.97
	SMA	0.64	0.91		
4	toluene	1.0	0.90	10	0.93
	PMMA	0.29	0.09		
5	toluene	0.94	0.89	10	0.58
	PMMA	0.93	0.26	30	0.19
6	toluene	1.0	0.45	10	0.47
	PMMA	0.90	0.52	30	0.93
7	toluene	0.98	0.97	10	0.76
	ethyl acetate	0.97	0.96		
	PMMA	0.89	0.88	10	0.98
	SMA	0.90	1.0		
11	toluene	1.0	0.83	10	0.81
	aqueous ethanol			10	0.85
	PMMA	0.63	0.11		
	PAAH	0.85	0.80	10	0.95

[a] Each in 0.1 mM in solution, and 20 wt% in polymer film. PMMA: poly(methyl methacrylate), SMA: copolymer of styrene with maleic anhydride, PAAH: poly (allylamine hydrochloride).

[b] Stability of the absorbance (relative to the initial value) on heating for 10 days at 50 °C for solution, or on heating at 80 °C for polymer film.

[c] Stability of the absorbance of the colored form (relative to the initial value) upon denoted number of coloration–decoloration cycle.

lysis (instead of ethanolysis) reactions with the MOPAC-PM3 program.

The carboxylated fulgimide **11**, which was significantly soluble in an aqueous solution, revealed good thermostability in aqueous ethanol solution at room temperature as well as in the ionic PAAH film at 80 °C (Fig. 4), though not stable (comparable with that of the corresponding fulgide **4**) in the PMMA film (Table 3). Owing to the ionic carbonyl group

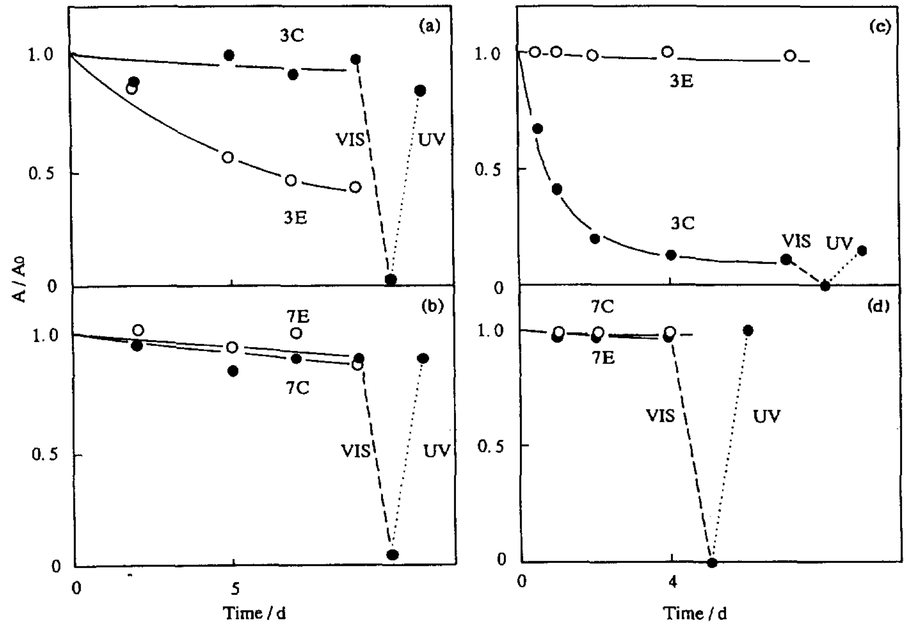

Fig. 3. Thermal stabilities of fulgide **3** and fulgimide **7** in PMMA film (20 wt.%) at 80 °C (a, b) and in 1:2 toluene–ethanol solution at room temperature (c, d). A/A_0 refers to the absorbance relative to the initial value, at the maximum wavelength for E-isomer (open circle) or C-isomer (solid circle).

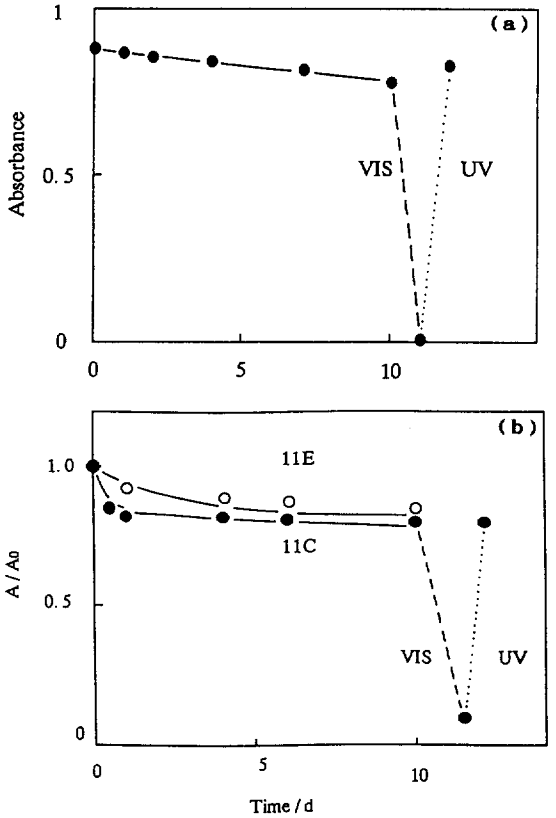

Fig. 4. Thermal stabilities of fulgimides **11E** (open circle) and **11C** (solid circle) in 0.1 mM in 1:1 aqueous ethanol at 25 °C (a), and in 20 wt.% in solid PAAH film at 80 °C (b). A/A_0 refers to the absorbance relative to the initial value, at the maximum wavelength for E-isomer (open circle) or C-isomer (solid circle).

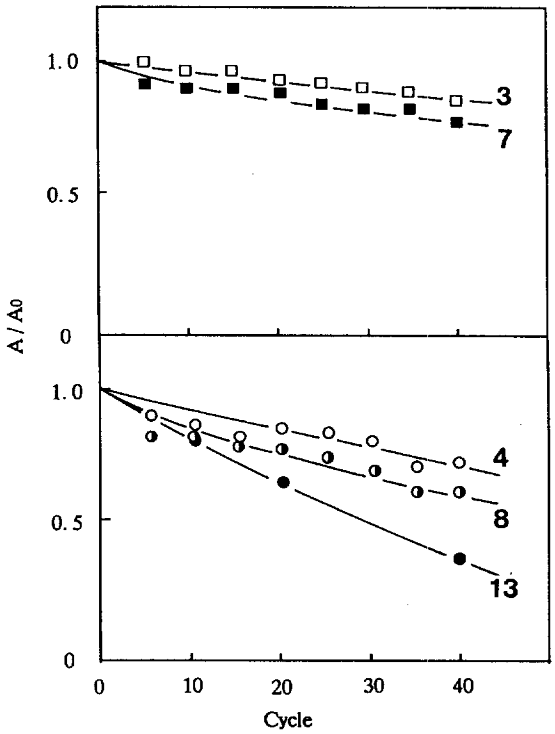

Fig. 5. Photochemical recyclizability of fulgides **3**, **4** and fulgimides **7**, **8**, **13** (each in 0.1 mM) in toluene. A/A_0 refers to the absorbance relative to the initial value.

fulgimide **11** would be uniformly dispersed and stabilized by ionic interactions in the ionic PAAH polymer, whereas in the PMMA polymer no such ionic stability is expected.

3.3. Photochemical reversibility

The reversibility for photochemical coloration–decoloration cycle has been measured in toluene solution and solid PMMA film. A conversion not less than 80% was attained for the coloration process while in decoloration process the absorbance of colored form was reduced to 0.01 or less, in each cycle. Fig. 5(a) illustrates similar photochemical reversibilities of thienylfulgide **3** and thienylfulgimide **7** in toluene. Fulgimide **13** revealed poor reversibility implying photochemical decompositions presumably of the *N*-benzyl amido group [22]. In PMMA film, the reversibilitis of fulgimides **5**, **6**, and **7** were slightly lower than those of fulgides **1**, **2**, and **3**, respectively, as shown in Table 3.

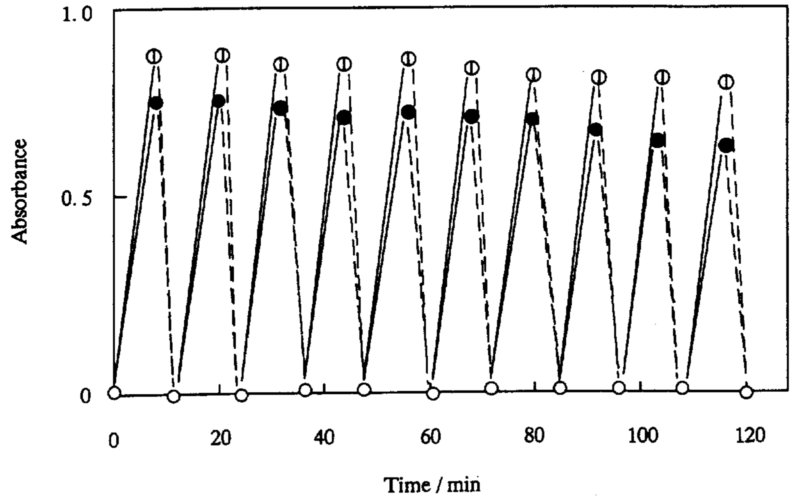

Fig. 6. Photochemical recyclizability of fulgimide **11** in 1:1 aqueous ethanol (solid circle), and that of fulgide **4** in toluene (open circle). Coloration with UV light (solid line), decoloration with visible light (broken line).

Regarding the resistance to the solvolytic degradations in hydroxylic media, photochemical reversibility of fulgimide **11** was examined. Fig. 6 (solid circle) demonstrates a moderate reversibility without substantial solvolysis in 1:1 aqueous ethanol solution. The reversibility is almost comparable with that of fulgide **4** obtained in a non-hydroxylic toluene solution (open circle). It should be noted that the photochromic performance could be achieved with the fulgimide in the highly solvolytic conditions where any fulgides (if soluble) would have rapidly degraded.

In summary, solvolytic resistance and thermal stability of fulgides could be remarkably improved by conversion into *N*-arylfulgimides, without substantial deterioration of the photochromic properties such as spectral features and photochemical responses.

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