

Improvements in the fatigue resistances of photochromic compounds

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Abstract

Whereas the majority of heterocyclic fulgides undergo extensive photooxidative degradations when used in naked spin-coated polymer films under the air, the degradations can be substantially depressed by a simple treatment: putting together a pair of the films on face-to-face and sealing with an adhesive to keep air-tight. By similar treatment, photodegradations of fulgimides in silica sol–gel matrices can also be substantially depressed, though fulgides undergo extensive hydrolysis. The method was less effective with some derivatives such as sulfur-containing fulgides, and little or nil effective with some spiropyrans, implying that some other degradation modes are dominant. The method provides a measure for the contribution of oxidative degradations by molecular oxygens, or else when the method is little effective it may imply some other degradation modes. The sealing treatment may also improve the thermal stabilities a little. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochromism; Fatigue resistance; Photooxidations; Polymer films; Silica sol–gel matrices; Fulgides; Fulgimides; Spiropyrans

1. Introduction

Extremely high photochemical fatigue resistances and thermal stabilities are required for photochromic compounds to be used in reversible photon-mode switching devices [1–12] as well as rewritable memory, and recently a great deal of improvements have been achieved in the photochromic properties of organic photochromic systems such as diarylethenes [1,2,5–13], fulgides [3,4,14–26], azobenzene [27], and spiropyrans [28–33]. Though heterocyclic fulgides are one of the good candidates, the majority of fulgides undergo extensive photochemical fatigues upon repeated coloration–decoloration cycles in spin-coated polymer films, when used in a naked film under the air. Molecular modifications [20] as well as addition of stabilizers such as antioxidants [22] are effective to improve fatigue resistances. Recently we proposed a simple and yet quite effective method to improve photochemical fatigue resistances of fulgides **1** and **5** (Scheme 1) in thin films of polystyrene (PS) or poly(methyl methacrylate) (PMMA) without addition of stabilizers nor with any changes in the molecular structures [34,35].

In the present work, further investigations have been made to expand the method and/or to find its limitations, by using some more different fulgides shown in Scheme 1, together

with the commercial spiropyrans as a different photochromic system. The method will also provide a useful information on the degradation modes and/or a measure for the contribution of oxidative degradations by molecular oxygens.

2. Experimental

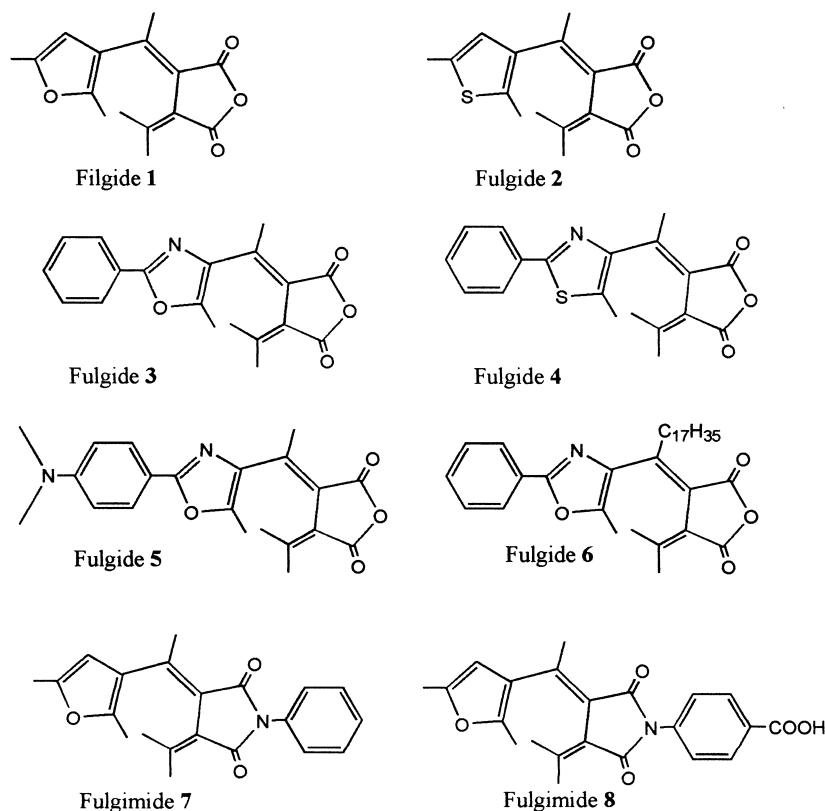
2.1. Materials

Fulgides **1–4** [23], **5** [25], **6** [24], and fulgimides **7** and **8** [26] were prepared by the Stobbe condensation reactions of diethyl isopropylidenesuccinate with 3-acetyl derivatives of heteroaromatic compounds, according to the literatures [14–16]. Spiropyrans were commercially available (Nihon Chemicals) and used as received. Solvents were of purest grade (Wako Chemicals) and freshly used without further purification. Commercial polymers were used as received: polystyrene (Wako Chemicals), poly(methyl methacrylate) (Nakarai Chemicals). For screen printing, a mesium ink (EG-000 MFG, Teikoku-Process), solvent (H-003 MFG, Teikoku-Process), and a super fine paper (Epson SO41104, HJA4SP1) were commercially obtained.

2.2. Apparatus and procedures

Electronic absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. For the measurements of

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photochromic fatigue resistances, the UV (365–366 nm) and Vis (436–545 nm) beams were irradiated from a 100 W high-pressure mercury lamp (Riko Kagaku), through suitable combinations of glass filters (Hitachi). For the estimation of photochemical quantum yields, monochromatic light beams were isolated from a 120 W mercury lamp through a diffraction grating of a Hitachi 204 fluorescence spectrophotometer, and the reaction vessel of a standard 10 mm-depth square cell was placed in the sample chamber of the spectrometer. Reactions in solution were carried out without deaeration.

Solid polymer films were spin-coated on a $22 \times 22 \text{ mm}^2$ silica glass plate by means of a photoresist spinner (Kyowa Riken) from a solution of a fulgide (ca. 15 mg) and polymer (ca. 1.5 g) dissolved in cyclohexanone (ca. 8–10 g). The spin-coated films were then subject to the sealing treatment as illustrated in Fig. 1. Thus, a “sealed film” was prepared by putting together a pair of spin-coated films on

face-to-face, after dry for 12 h under the air. Then, the peripheral four sides were spread with an adhesive agent of epoxy resins (High Super-5, Semedain) to keep air-tight. The sealed films thus prepared were compared with “naked” single films (spin-coated films neither sticking nor sealing). Alternatively, an “unsealed” film, the peripherals of a pair of spin-coated films were only partially spread with the adhesive just to tie together but not sealed, was also prepared for more close comparison. Silica sol–gel matrices were prepared from a neutral mixture of 0.5 mol tetraethoxysilane (TEOS) and 0.5 mol methyltrimethoxysilane (MTMOS) in 1:1 aqueous 2-propanol solution containing a fulgide or fulgimide in 1.4–2.3 wt.%. After leaving at room temperature for 4 days, the mixture sol was pasted on a silica glass and dried for 2 days at room temperature. Then, a pair of dried silica gels were put together on face-to-face and the peripheral four sides were spread with an epoxy adhesive to keep air-tight (“sealed gel”).

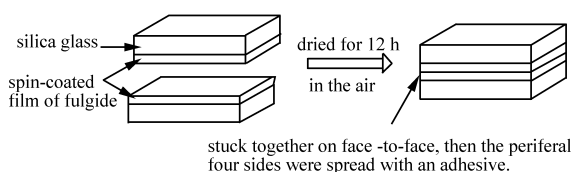


Fig. 1. Preparation for a “sealed film”.

3. Results and discussion

3.1. Photochemical fatigue resistances of fulgides in polymer thin films

Fig. 2a demonstrates a substantial improvement in the fatigue resistance of fulgide **1** in sealed polystyrene (PS)

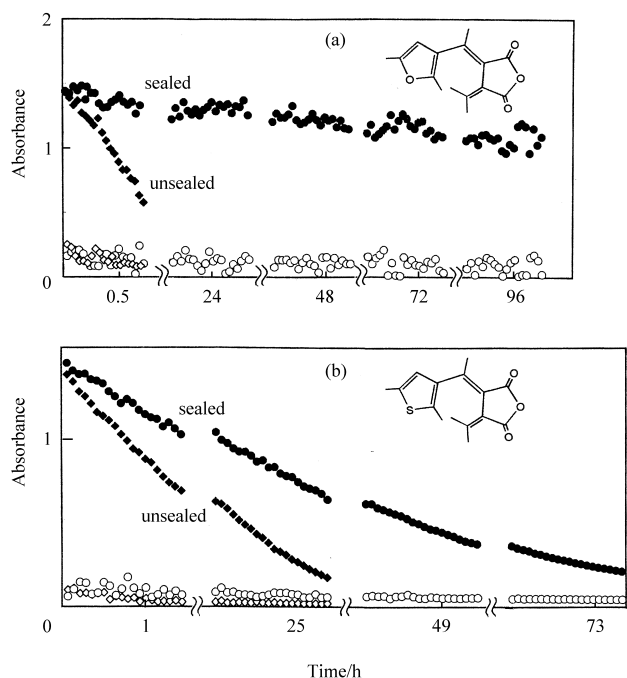


Fig. 2. Improvements in the photochemical fatigue resistances of fulgides **1** (a) and **2** (b) in sealed PS films as compared with unsealed films. (a) Absorbances at 500 nm measured on irradiation with UV for 90 s and Vis for 40 s. (b) Absorbances at 530 nm measured on irradiation with UV for 240 s and Vis for 40 s, in each cycle. The abscissa indicates the total time elapsed for the UV and Vis irradiation as well as for standing in the dark.

film, as compared with unsealed film which undergoes extensive degradations [34,35]. The results imply a dominant role of oxidative degradations by atmospheric molecular oxygen in the photochemical fatigues, which could be substantially depressed by the sealing treatment. On the other hand, sulfur-containing analog (fulgide **2**) reveals a significant but less extensive improvement by the sealing treatment as shown in Fig. 2b, implying that the contribution of oxidative degradations is less than half and other important degradation modes should be involved. Fig. 3 illustrates similar improvements in the fatigue resistances of oxazolyl and thiazolyl fulgides in sealed films as compared with those in naked single films. Here again, it is notable that the sulfur-containing analog (fulgide **4**) reveals rather less improvement in the sealed film (Fig. 3b), while oxazolyl fulgide **3** reveals excellent improvement (Fig. 3a). The substitution of sulfur atom for the heterocyclic oxygen atom may substantially alter the excited state properties and reactivities so as to change the major degradation modes. Introduction of a strong electron-donating group (fulgide **5**) led to the most extensive degradations in the unsealed film, though the absorption coefficients were remarkably increased [34,35]. By the sealing treatment, however, the photochemical degradations could be substantially suppressed as shown in Fig. 4a. More excellent fatigue resistance was achieved in the sealed film of fulgide **6** possessing a large alkyl chain as shown in Fig. 4b, presumably because of the higher quantum yields

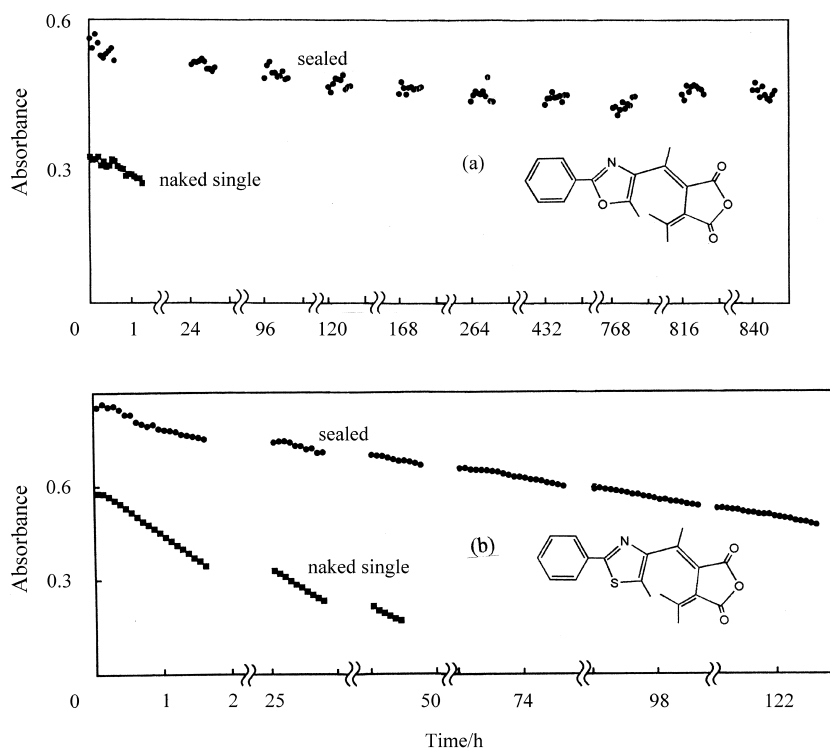


Fig. 3. Improvements in the photochemical fatigue resistances of fulgides **3** (a) and **4** (b), in sealed PS films as compared with naked single films. (a) Absorbances at 460 nm measured on irradiation with UV for 60 s and Vis for 180 s. (b) Absorbances at 490 nm measured on irradiation with UV for 180 s and Vis for 120 s, in each cycle.

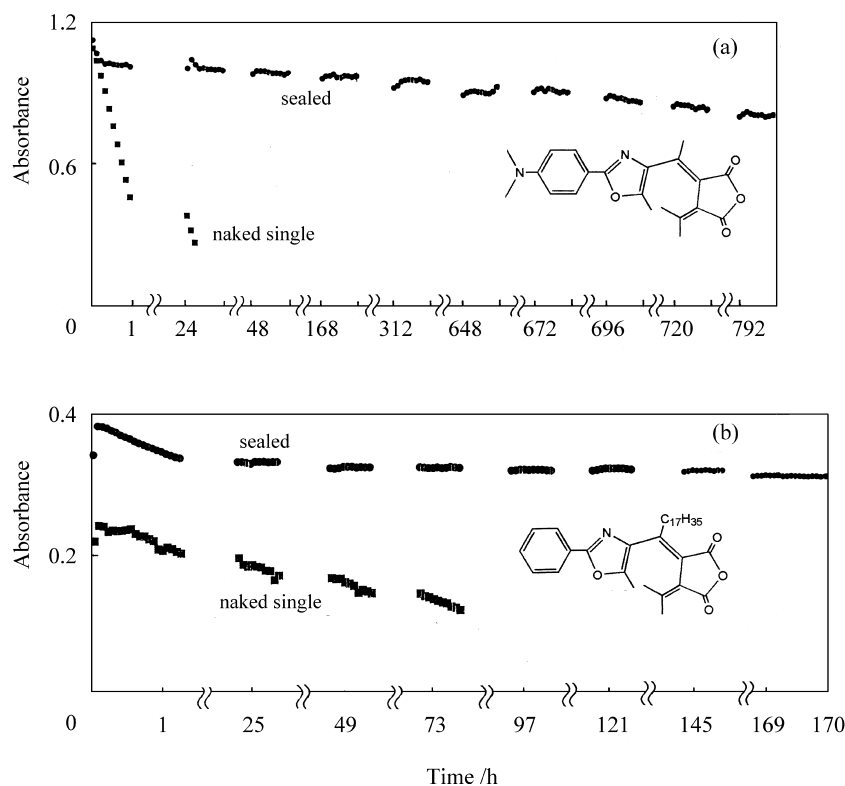


Fig. 4. Improvements in the photochemical fatigue resistances of fulgides **5** (a) and **6** (b), in sealed PS films as compared with unsealed or naked single film. (a) Absorbances at 520 nm measured on irradiation with UV for 180 s and Vis for 180 s. (b) Absorbances at 465 nm measured on irradiation with UV for 120 s and Vis for 120 s, in each cycle.

and shorter irradiation times for the coloration and discoloration reactions. The sealed film still exhibits rapid degradations in the initial stages (up to 20 cycles), which might be caused by the dissolved oxygen (air) during the preparation of the film before sealing. The photochemical fatigue resistances (retainment of the maximum absorbance of the colored forms after repeated cycles: A_{100}/A_{20}) are listed in Table 1 with some fulgides in sealed films, together with the quantum yields and irradiation times (per cycle). Very similar improvements were obtained in sealed films of PMMA.

The sealing treatment also improved the thermal stabilities at 80°C to some extent, as illustrated in Table 2: the colored

forms are significantly stabilized while the erased forms are little stabilized.

3.2. Photochemical fatigue resistances of fulgides in silica sol-gel matrices

Photochromic properties of fulgides have been examined in silica sol-gel matrices. The UV and Vis absorption spectra of fulgides **1** and **2** in the silica sol-gel matrices were comparable to those in the PMMA film, but significantly red-shifted (colored and erased forms of **1** were shifted from 342 and 501 nm in PMMA to 350 and 520 nm in the sol-gel matrix), in a similar tendency as reported with indolyl fulgide [21]. The quantum yields for coloration were also comparable to those in PMMA film.

Table 1
Photochemical fatigue resistances of fulgides in sealed PS films

Fulgide	Quantum yield		Irradiation time (s) ^a		Retainment A_{100}/A_{20} ^b
	ϕ_{EC}	ϕ_{CE}	UV	Vis	
2	0.16	0.12	240	40	0.15
3	0.18	0.054	60	180	0.80
5	0.28	0.011	180	180	0.78
6	0.42	–	120	120	0.96

^a Irradiation times in each coloration–discoloration cycle.

^b A_{100} and A_{20} refer to the absorbances of the colored forms at the 100th and 20th cycles, respectively, in the repeated coloration–discoloration reactions.

Table 2
Sealing effects on the thermal stabilities in PS films at 80°C

Fulgide	Film conditions	Heating time (day)	Retainment A/A_0	
			Colored form	Erased form
1	Sealed	27	0.68	0.52
	Unsealed	27	0.06	0.57
5	Sealed	127	0.83	0.88
	Unsealed	159	0.56	0.70

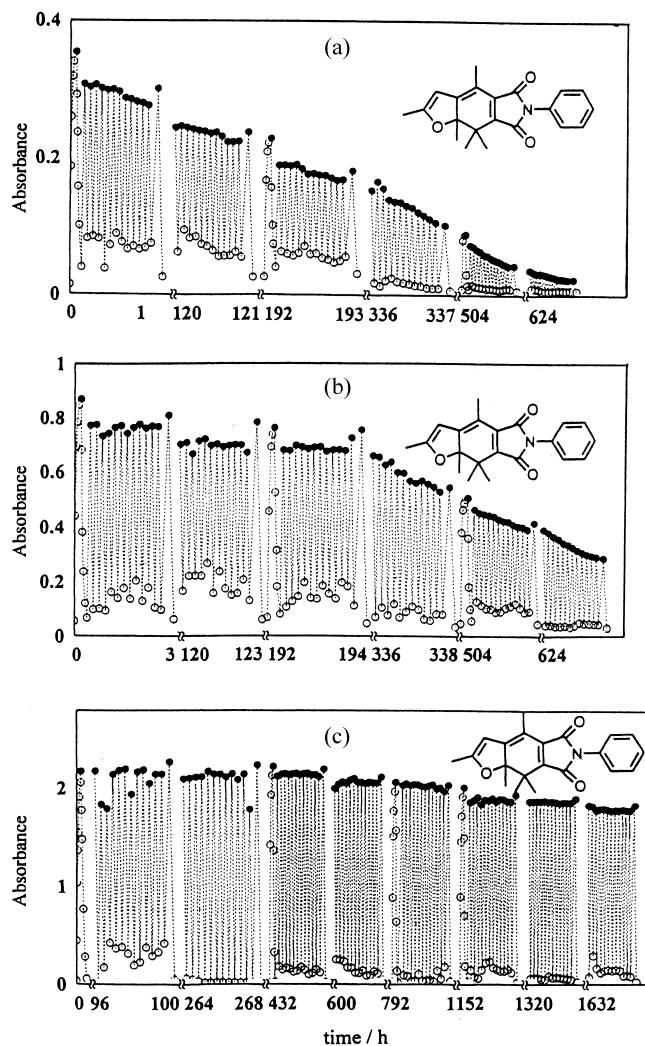


Fig. 5. Improvements in the photochemical fatigue resistances of fulgimide 7 (ca. 1.5 wt.%) in sealed gels (b) and (c) as compared with those in a naked single gel (a). (b) Sealed gel prepared under the air. (c) Sealed gel prepared in a dry nitrogen balloon.

Fig. 5 illustrates the photochromic reversibilities of fulgimide 7 in a naked single gel (Fig. 5a), in a sealed gel prepared under the air (Fig. 5b), and in a sealed gel prepared under nitrogen atmosphere (Fig. 5c), demonstrating large sealing effects in the gel matrices. As expected, fulgide 1 underwent extensive degradations and was little improved by the sealing treatment, mainly because of the extensive hydrolytic degradations in such media [26]. By contrast, a high fatigue resistance was demonstrated with fulgimide 8 toward hydrolytic degradations in a sealed gel whose surfaces were wetted with water before stacking and sealing (data not shown), as compared with fulgide 1 which suffered from extensive hydrolytic degradations under similar conditions.

Table 3 illustrates the sealing effects on the thermal stabilities of fulgide 1 and fulgimide 8, implying only slight

Table 3

Sealing effects on the thermal stabilities in silica gel matrices

Fulgide	Conditions		Retention A/A_0		
	Glass	Temperature ($^{\circ}\text{C}$)	Time (day)	Colored form Erased form	
1	Sealed	25	88	0.70	0.70
	Naked	25	79	0.55	0.48
8	Sealed	80	28	0.83	0.86
	Naked	80	28	0.68	0.66

improvements in both colored and erased forms in the sealed gels.

3.3. Photochemical fatigue resistances of spiropyrans

Since it has been shown that the photodegradations of photochromic spiropyrans (SP) take place exclusively via triplet excited states [36,37], the sealing method was examined with SP-18 (containing ca. 10 wt.%; the structure is shown in Fig. 6) in spin-coated PMMA film. However, a preliminary experiment in a sealed film revealed degradations as extensive as those in a naked single film, as shown in Fig. 6a and b, showing nil effects of the sealing treatment. On the other hand, SP-18 (ca. 1 wt.%) in a screen-printed sheet (a naked single sheet exposed to the air) revealed significantly reduced degradations (Fig. 6c). The results may imply that the SP-concentration dependent degradations are even more dominant over oxidative degradations. It has been

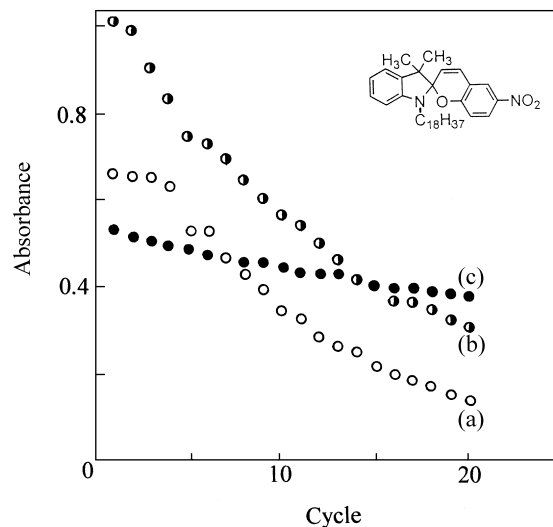


Fig. 6. Photochemical fatigues of spin-coated PMMA films containing SP-18 in ca. 10 wt.% (a) and (b) and screen-printed sheet containing SP-18 in ca. 1 wt.% (c), upon repeated irradiation with UV (365–366 nm) and Vis (>500 nm) from a 100 W high-pressure mercury lamp. The vertical axis refers to the maximum absorbance of the colored forms. (a) Naked single film. (b) Sealed film, irradiated with UV for 2 min and Vis for 1–2 min, respectively, in each cycle. (c) Naked screen-printed sheet irradiated with UV for 40 s and Vis for 20 s followed by measurement of the reflection spectra in each cycle.

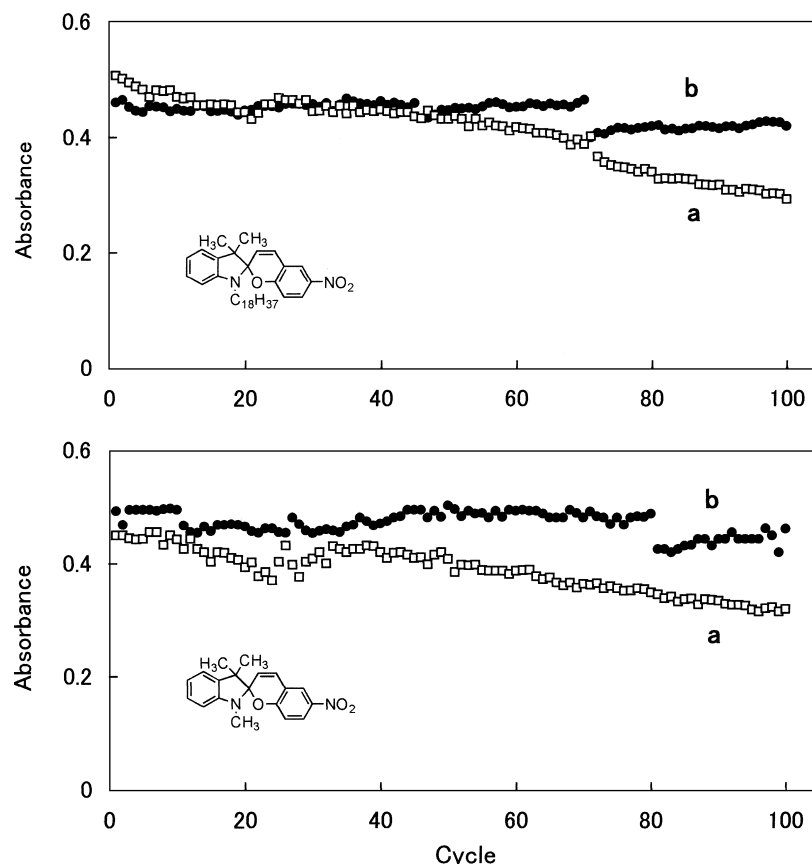


Fig. 7. Influence of the SP concentration on the photochemical fatigue resistances in dilute methanol solution. (a) Solution of SP in $400\ \mu\text{M}$ in a 1 mm-depth cell. (b) Solution of SP in $40\ \mu\text{M}$ in a 10 mm-depth cell, irradiated with UV light for 180 s and Vis for 30–60 s, in each cycle.

well known that the colored forms of SP (merocyanines) tend to aggregate in condense phases, and in PMMA film a shoulder of merocyanine aggregate has been observed around 550 nm at SP concentrations higher than 4.5 wt.% [38]. Also, it has been demonstrated that the decrease in the SP concentration can significantly reduce the photodegradations of SP [36]. To more investigate the concentration effects, dilute solutions of SP in $400\ \mu\text{M}$ (ca. 0.03 wt.%) and $40\ \mu\text{M}$ (ca. 0.003 wt.%) were prepared. Fig. 7 reveals remarkable depression of the degradations as compared with the condensed films. Further, a more dilute $40\ \mu\text{M}$ solution (b) reveals more excellent fatigue resistances than a $400\ \mu\text{M}$ solution (a). In Table 4, the effects of the conditions, including SP concentrations and irradiation times, on the fatigue resistances of SPs are summarized. From these results, the SP concentration rather than the medium properties and irradiation times seems to be the dominant factor controlling the fatigue resistances. It may be tentatively speculated that the photodegradations of SP observed in the PMMA film occurred substantially via aggregation interactions of the colored forms, although more detailed experiments (involving preparation of sealed films under nitrogen atmosphere) should be required for further confirmation. Inclusion in a suitable cavity of porous zeolites or cyclodextrins [39,40] might be expected to significantly reduce the degradations.

Table 4
Effects of the reaction conditions on the fatigue resistances of SP-18

Medium conditions	SP concentration (wt.%)	Irradiation time (s)		Retentionment A_{20}/A_1^a
		UV	Vis	
Unsealed PMMA	10	120	120	0.21
Sealed PMMA	10	120	120	0.31
Screen-printed sheet	1	40	20	0.72
Methanol solution	0.03	180	30	0.88
Methanol solution	0.003	180	45	0.97

^a A_{20} and A_1 refer to the absorbances of the colored forms at the 20th and the first cycles, respectively.

In summary, we demonstrated that the extensive photochemical degradations of fulgides and fulgimides by the dissolved oxygen can be substantially suppressed by a simple method, sealing with an adhesive to keep air-tight. The method is expected to be effective for many other photochromic compounds particularly with strong electron-donating groups which are more subject to oxidative degradations. The method may also provide a measure for the contribution of the oxidative degradations, or else when the method is little effective it may imply the involvement of some other degradation modes.

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