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Photochromism of 2-Hydroxychalcones in Solid Hydrogel Matrices

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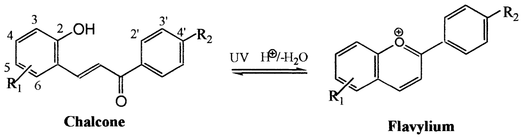
Photochromic reactions of some substituted 2-hydroxychalcones [3-(2-hydroxyphenyl)-1-phenyl-2-propen-1-ones] have been studied in solid hydrogel matrices. The results demonstrated good reversibilities for the chalcone-flavylium interconversion. Thus, in an agar-gel matrix the coloration-decoloration could be repeated over 50 cycles without significant fatigue. In a silica sol-gel matrix, a fairly good reversibility was obtained up to ca. 30 cycles; in the later cycles, however, extensive degradations took place.



Scheme 1. Photochromic interconversions between chalcones **1H** (R_2 = NMe_2), **2H** (R_2 = NEt_2), **3H** (R_2 = NHC_8H_{17}) and flavylium ions **1F** (R_2 = NMe_2), **2F** (R_2 = NEt_2), **3F** (R_2 = NHC_8H_{17}).

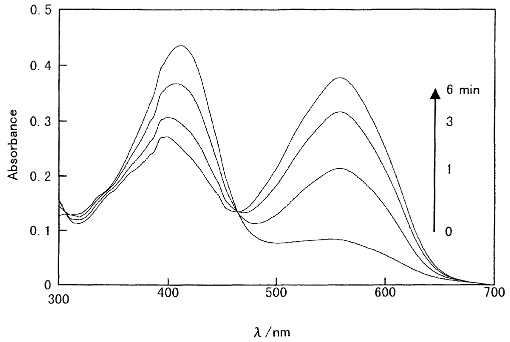


Fig. 1. Photochemical coloration (b) of chalcone **1H** in agar-gel matrix. Concentrations were **1H** in 15 μM and agar in 0.3 wt%, in 1 : 1 aqueous ethanol at pH 6.0.

The unique photochromic system involving chalcone-flavylium interconversion, as a simplified model of the naturally occurring anthocyanin dyes,[1–3] has some favorable features. Thus, the colored forms (flavylium ions) exhibit sharp and strong absorption bands in the yellow,[4,5] mazenta,[6–9] and blue[10,11] regions (depending on the substituents) well separated from the chalcone bands. They are significantly soluble in aqueous media, and the lifetimes of the colored forms can be adjusted by the acidity of the medium. Recently, the photochemical decoloration process has been achieved in the system, leading to a photon-mode erasable optical memory with nondestructive readout ability.[12,13] While good photochromic reversibilities have been demonstrated in fluid solutions, no good reversibility has been obtained yet in solid films or matrices where extensive degradations took place after several cycles.[7] Continued examinations, however, indicated that fairly good photochromic reversibilities could be achieved for the first time with the system in solid hydrogels such as agar-gel and silica sol-gel matrices.[10] The present paper briefly reports on the photochromic properties of some 2-hydroxychalcone derivatives (Scheme 1) in environmentally more suitable agar-gel and silica sol-gel matrices.

Figure 1 illustrates photochemical coloration of an agar-gel matrix containing 15 μM of chalcone **1H** upon irradiation with 405–436 nm light beams; such a gel was thermostable in the dark at room temperature (25 ± 3 °C) for over 20 days. The colored gel was thermally bleached at room temperature in an hour. Similar photochromic reactions were observed in the absence of agar in a 1 : 1 aqueous ethanol solution at pH 6.0. Figure 2(a) illustrates the photochromic reversibility of chalcone **1H** in the agar-gel matrix, demonstrating an excellent fatigue resistance over 50 cycles. Under similar conditions, agar-gels of chalcones **2H** and **3H** revealed rather poor fatigue resistances (Table 1).

Similar photocoloration and thermal bleaching has been observed with **1H** in the silica sol-gel matrix, without thermal coloration in the dark. Upon repeated photocoloration and thermal bleaching, however, chalcone **1H** underwent extensive degradations, and the thermal bleaching became slower and less complete (bleached baseline became higher) in the later cycles. During the gel-drying process, structural changes of the substrate become significantly restricted in the gel matrix so as to depress both photochemical and thermal response rates, due to the reduction in the size of the effective free volume as well as to the strong hydrogen bonds to the silanols of the silica cage.[14] In addition, an increase in the acidity of the silica cavity would increase the thermal stability of the colored form (flavylium ion), reducing the thermal bleaching rate. Thus, the longer reaction times needed for photochemical and/or thermal bleaching should enhance side reactions and decompositions. Under similar conditions, silica gel of chalcone **2H** revealed moderate photochromic reversibility up to 10 cycles, but underwent rapid degradations after ca. 20 cycles. By contrast, chalcone **3H** revealed a good photochromic reversibility up to 35 cycles under similar conditions, as shown in Fig. 2(b), though extensive degradations were observed in the later cycles. The results are numerically compared in Table 1. Substrates with longer and more flexible alkyl substituents (R_2) seem to give better reversibility in the silica sol-gel matrix, while the reverse is true in the agar-gel. The substrate with a longer alkyl group would retain a larger molecular volume in the silica-gel cavity, allowing easier conformational changes in the chromophore due to an excess flexibility of the alkyl group. On the other hand, the substituent effects in the

Table 1. Photochromic Reversibilities of Chalcones in Various Media[a)]

Chalcone	Fluid solution[b)]			Agar-gel matrix			Silica sol-gel matrix		
	n	A/A_0	$\Delta A/nA_0$	n	A/A_0	$\Delta A/nA_0$	n	A/A_0	$\Delta A/nA_0$
1H	15	0.94	0.004	50	0.83	0.003	37	0.23	0.021
2H	11	0.82	0.016	50	0.69	0.006	26	0.42	0.022
3H	15	0.93	0.005	50	0.66	0.007	30	0.95	0.002
							50	0.37	0.013

a) A_0 and A refer to the absorbances (bleached baselines were subtracted) of the colored form at the initial and the n-th number of repeated cycles, respectively, and $\Delta A/nA_0$ refers to the mean degradation per cycle as a measure for relative degradability. b) Aqueous ethanol (1 : 1) solution at pH 6.0 containing each chalcone in 15 μM.

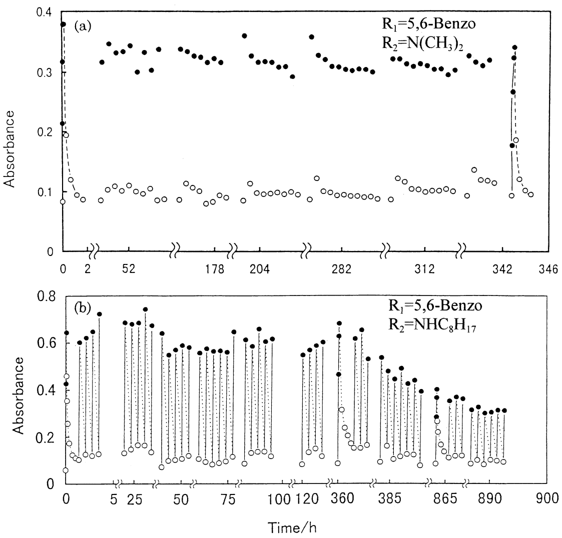


Fig. 2. (a) Photochromic reversibilities of (a) chalcone **1H** in agar-gel matrix, (b) chalcone **3H** in silica sol-gel matrix, toward repeated cycles of photocoloration and thermal reversion. (a) Photocoloration at 405 and 436 nm for 5 min, and thermal reversion at 25 °C for 30 min, (b) photocoloration at 405 and 436 nm for 2 min and thermal reversion at 25 °C for 60 min, in each cycle. The vertical axis refers to the absorbance of the flavylium ions around 550–560 nm for the colored (solid circle) or erased (open circle) state, and the horizontal axis refers to the total time of the photochemical coloration and thermal reversion processes.

agar gel, which are reverse to those observed in the silica gel, may involve special interactions with the chromophore; these cannot be explained as yet.

Experimental

Electronic absorption spectra were recorded on a Hitachi U-3000 spectrophotometer, while ^{1}H NMR spectra were obtained on a EX-90 FT-NMR spectrometer (90 MHz). 3-(2-Hydroxynaphthyl)-1-(4′-dimethylaminophenyl)-2-propen-1-one (chalcone **1H**: yield 55%, mp 189–191 °C) was prepared by a base-catalyzed aldol condensation[15] from substituted acetophenones and salicylaldehyde, while 3-(2-hydroxynaphthyl)-1-(4′-diethylaminophenyl)-2-propen-1-one (chalcone **2H**: yield 73%, mp 172-174 °C), and 3-(2-hydroxynaphthyl)-1-(4′-octylaminophenyl)-2-propen-1-one (chalcone **3H**: yield 70%, mp 110–112 °C) were obtained by treatment in basic aqueous ethanol solution of the corresponding flavylium perchlorates prepared by an acid catalyzed condensation.[16,17] The elemental analysis data and ^{1}H NMR spectra were satisfactory for each chalcone.

The agar-gel matrix was prepared from a 1 : 1 aqueous ethanol solution containing chalcone (ca. 15 μM) and agar powder (ca. 0.3 wt%) at pH 6.0 in a 10 mm-depth photometer cell. The silica sol-gel matrix was prepared from a starting mixture containing chalcone (0.002 wt%) and 0.6 mol tetraethoxysilane (TEOS), 0.4 mol trimethoxymethylsilane (MTMOS), 4.5 mol methanol or ethanol, 4.5 mol *N*,*N*′-dimethylformamide (DMF), and 4.0 mol water at pH 6.0. After the mixture was kept for 7 days at room temperature, the mixture sol was dried at 50 °C for another 7 days. The final concentration of chalcone in the dried silica gel was estimated to be ca. 0.01 wt%.

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