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Photochromic Properties of 2-Hydroxychalcones in Solution and Polymers[1]

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A series of substituted 2-hydroxychalcones (HC) were prepared, most of which underwent efficient and clean photochemical conversion into flavylium cations (FV) in acidic solution and polymer film, although strongly dependent on the pH and medium conditions as well as the HC structures. 4′-Methoxy and 4′-dimethylamino derivatives showed relatively high thermal stabilities of the colored mixtures, well-separated absorption bands of the HC and FV forms, almost quantitative conversion from HC to FV in the photostationary-state mixtures, and good photochromic performances in solution and polymer film, without suffering from the dissolved oxygen or moisture. A few of them showed relatively high reversibilities in the HC–FV interconversions under special pH and medium conditions.

The color stabilization of the naturally occurring anthocyanins have been recently proposed to include special complexation or association phenomena, such as copigmentation, self-association, and intramolecular stacking in aqueous solution,[2] though their aglycons (flavylium cations FV) are generally unstable and in equilibrium with 2-hydroxychalcones (HC) in acid solution.[3] In spite of the considerable studies on the spectroscopic and photochemical properties[4] as well as the thermal equilibria,[5] systematic and/or quantitative studies on the photochromic HC–FV system seem to have been scarcely reported. Both HC and FV forms should be thermodynamically or kineticaly stabilized by controlling the medium conditions and/or by the removal of the hydroxyl (alkoxyl) group at the 4- or 6-position of HC.[3] Therefore, a new type of photochromic system could be developed if their interconversions are controlled by photochemical and other means,[1,3] although its photochromic properties are yet poor compared with those of the well-developed photochromic spiropyrans,[6] fulgides,[7] and 1,2-diarylethenes.[8]

In the present work, HC with different structures (Scheme 1) were prepared to investigate the effects of substrate structures and medium conditions on the photochromic properties of the HC–FV system, thus searching for a new and unique photochromic system.

Results and Discussion

Photochromic Properties in Organic Acid Media. Figure 1 illustrates photochemical coloration (PC) of 2-hydroxy-4′-methoxychalcone (**4H**) and 2-hydroxy-4′-(dimethylamino)chalcone (**6H**) in organic acid media, showing good separation of the absorption bands between HC and FV forms. On irradiation with 334—366 nm light in acetic acid solution (a), the

HC FV

Substrate	R1	R2	R3	Ar
1	H	H	H	Phenyl
2	H	H	H	*o*-Methoxyphenyl
3	H	H	H	*m*-Methoxyphenyl
4	H	H	H	*p*-Methoxyphenyl
5	Methoxy	H	H	*p*-Methoxyphenyl
6	H	H	H	*p*-(Dimethylamino)phenyl
7	H	5,6-Benzo		*p*-(Dimethylamino)phenyl
8	H	H	H	2-Furyl
9	H	H	H	2-Thienyl
10	H	H	H	2,5-Dimethyl-3-thienyl
11	H	H	H	2-Cyano-1,5-dimethyl-3-pyrrolyl
12	H	H	H	2-Methylbenzo[*b*]thienyl

Scheme 1.

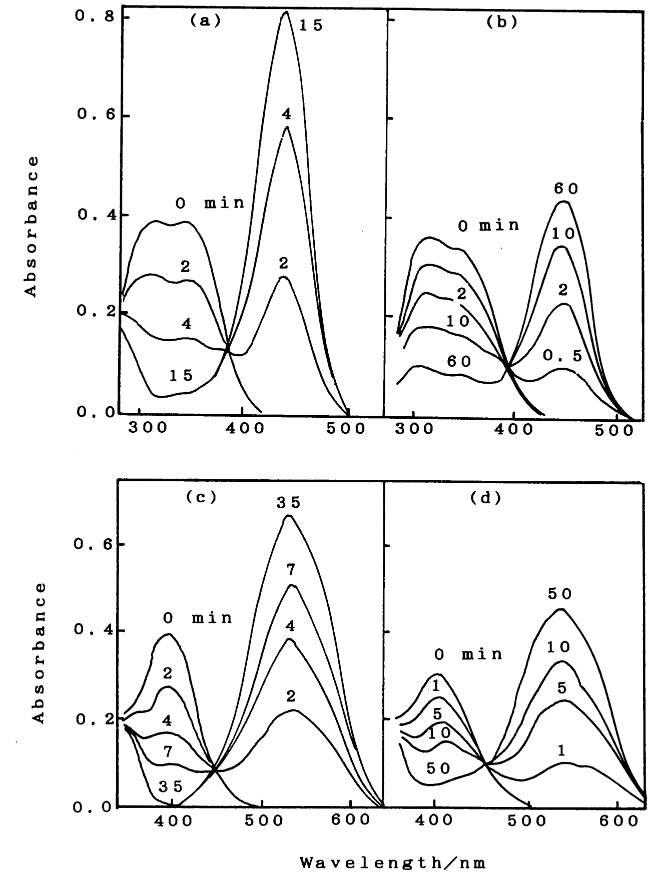


Fig. 1. Photochemical coloration of **4** in acetic acid solution (a), **4** in poly(acrylic acid) film (b), **6** in acetic acid solution (c), and **6** in poly(acrylic acid) film (d). Initial concentrations of the substrates were 1.5×10^{-5} mol dm^{-3} in acetic acid solution, and 2.0 wt% in poly(acrylic acid) film.

absorption band of **4H** (yellow) decreased and strong absorption band of **4F** appeared in the region of 400—500(orange) with isosbestic points (ISP) at 386 and 282 nm. On 15 min irradiation, a photostationary state (PSS) was attained, where the absorption band of **4H** was substantially disappeared and thereafter the spectrum remained unchanged on further irradiation.

The quantum yield for PC was estimated to be 0.29 at 365—366 nm, using (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride in toluene as a chemical actinometer. The influence of the dissolved oxygen was negligible. The colored solution at PSS was stable at room temperature in the absence or presence of visible light, though slowly decolorized on heating at 50 °C. In a solid polymer film, poly(acrylic acid) containing 2.0 wt% of **4H** was spin-coated on a silica glass plate, similar response was observed with lower rate and completeness (b).

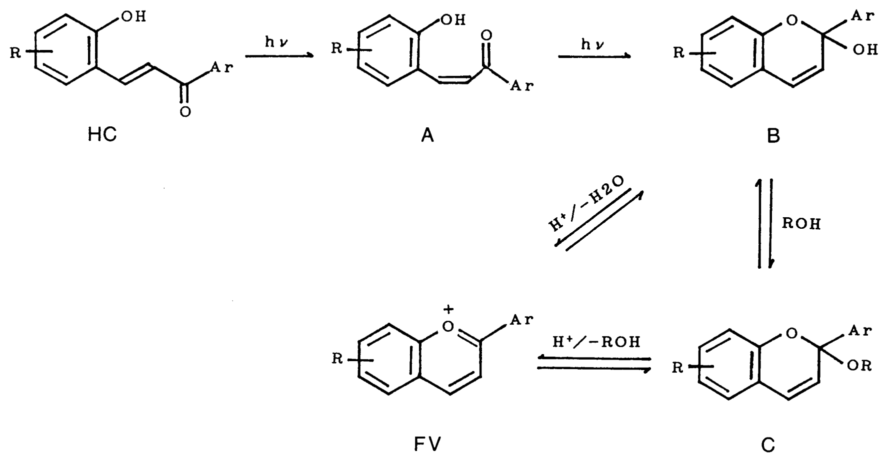
Though the photochemical response of **6H** was slightly lower than **4H**, the absorption spectra were significantly red-shifted (c and d) due to the stronger electron-donating dimethylamino group. Further, the absorption of **6H** was completely disappeared at PSS, implying quantitative conversion. Photochemical responce was somewhat lower in poly(acrylic acid) film (d).

In order to see the structure-activity relationships, the influences of the types and/or positions of substituents in the aryl ring (Ar) at C-2 were examined with phenyl (**1**—**6**) and heteroaromatic (**8**—**12**) ring derivatives. Table 1 summarizes photochromic properties of **1**—**12** in acetic acid solution obtained by similar experiments. The mole fraction of FV at PSS, F/(F+H), was evaluated as a measure for the completeness of the photochemical conversion, on the assumption that the absorption of FV forms has no tail in the maximum region of the HC bands and that other species such as B and C in the equilibrium (Scheme 2) is negligible.

Table 1. Photochemical Coloration (PC) and Thermal Decolorization (TD) in Acetic Acid Solution[a)]

Substrate	Absorption maxima		ISP	F/(F+H) at pss	Apparent rates for PC and TD	
	λ_H/nm	λ_F/nm	nm		δA_F/min	$-\delta A_F$/day
1	353	394	374	b)	b)	b)
2	345	438	364	0.94	0.24	0.028
3	348	385	366	0.97	0.18	0.087
4	345	442	386	0.93	0.47	0.019
5	347	463	390	0.95	0.55	0.013
6	395	533	447	0.98	0.12	0.010
7	410	558	466	1.00	0.48	0.002
8	355	430	386	0.95	0.49	0.54
9	353	432	385	0.83	0.27	0.19
10	347	435	368	0.94	0.06	0.44
11	345	436	375	0.90	0.09	0.003
12	347	470	400	0.85	0.06	0.16

a) λ_H and λ_F are the absorption maxima of the HC and FV forms, respectively, while ISP stands for the isosbestic points. F/(F+H) refers to the mole fraction of FV at the photostationary state. δA_F and $-\delta A_F$ refer to the rates of increase and decrease in the absorbance of FV for the photochemical coloration and thermal (50 °C) decolorization, respectively. b) Not measured because of the poor separation of the absorption bands of the HC and FV forms.



Scheme 2.

Further, as a rough measure for relative rates of PC and TD (thermal decolorization), the rates of increase and decrease in the absorbance of the FV band, δA_F and $-\delta A_F$, were measured. Th derivatives with Ar=phenyl (**1**) and *p*-chlorophenyl (not cited in the Table) groups showed slow PC response and poor separation of the absorption bands between HC and FV, e.g., less than 50 nm. Among *o*-, *m*-, and *p*-methoxy derivatives (**2**—**4**), photochemical response of HC and thermal stability of FV, as well as the separation of the absorption bands between HC and FV, tend to increase in the order *m*-MeO<*o*-MeO<*p*-MeO derivatives, reflecting the electron-donating ability of Ar. The tendency is the most evident with the *p*-dimethylamino derivatives (**6** and **7**) which show the highest thermal stability of FV and the larget separation of the absorption bands between HC and FV.

As is often the case with photochromic fulgides and 1,2-diarylethenes, heteroaromatic ring (as compared with phenyl ring) derivatives show remarkable improvements in the photochromic properties.[7,8] Although the reaction mode of the HC-FV system is essentially different from those of fulgides and 1,2-diarylethenes, we also investigated some heteroaromatic ring derivatives (**8**—**12**) expecting some improvements in the photochromic properties. However, these derivatives showed relatively poor PC rates, poor separation of the absorption bands between HC and FV, and poor thermal stabilities of FV, as listed in Table 1. Though the PC rates are fairly high, thermal stabilities of FV are low with **8** and **9**. While the thermal stability of **11F** is high, the PC rates of **10**—**12H** are very low.

Influence of pH and Solvents. Table 2 illustrates the influence of pH on the photochromic properties in 1:1

Table 2. Effects of pH on the Photochromic Properties in Aqueous Ethanol[a)]

Substrate	pH	Absorption maxima		F	Apparent rates for PC and TD	
		λ_H/nm	λ_F/nm	F+H	δA_F/min	$-\delta A_F$/day
4[a)]	1.6	350	440	0.97	0.063	0.20
	2.4	350	440	0.75	0.052	1.06
	3.3	350	440	0.26	0.007	2.36
	4.2	350	440	0.16	0.001	0.48
6[b)]	2.1	402	530	0.97	0.033	0.01
	3.1	402	530	0.83	0.005	0.02
	4.3	402	530	0.66	0.003	0.03
	5.0	402	530	0.39	0.002	0.04
	5.5	402	—	0.00	0.000	—
7[c)]	2.0	410	558	1.00	0.230	0.003
	3.0	410	558	1.00	0.230	0.007
	4.0	410	558	0.98	0.228	0.009
	5.0	410	558	0.98	0.227	0.035
	6.0	410	558	0.97	0.229	0.105
	6.4	407	558	0.48	0.064	0.049
	7.0	400	558	0.10	0.001	0.025
	8.0	395	558	0.05	0.000	0.004

a) For notations see footnote in Table 1. b) Initial concentrations of **4H** and **6H** were 1.50×10^{-5} mol dm^{-3} in 1:1 aqueous ethanol solution. b) Initial concentration of **7H** was 0.83×10^{-5} mol dm^{-3} in 1:1 aqueous ethanol solution.

aqueous ethanol solution. Most substrates revealed good photochemical responces in the pH region below 2. The quantum yield of PC was 0.12 with **4** at pH 2 in aqueous ethanol. With the increase in pH, the rate of PC and the completeness of coloration at PSS (or the stability of FV) tended to decrease. It is notable that each substrate shows different pH-dependence; while the methoxy derivative **4** reveals poor photochromic activity at pH above 3, *p*-dimethylamino derivatives **6** and **7** retained good performances in the pH region up to 4 and 6, respectively. The photochromic response of **7** is relatively high and essentially constant in the pH region of 2.0—6.0.

A series of 1:1 aqueous organic mixed solvents were examined at constant pH 2.0 (except with acetic acid and poly(acrylic acid) media). As seen in Table 3, photochromic properties were significantly influenced by the nature of solvents, though no convincing explanation for the results have been obtained. In glycerol–water solution the absorbances (both $A_{\rm H}$ and $A_{\rm F}$) as well as the PC and TD rates are particularly low, suggesting some other species than HC or FV forms are present in significant amounts. In solid poly(acrylic acid) (PAA) the PC response of **6** is comparable with that of **4**, while in other solvents **6** shows considerably lower responces. Table 4 compares the photochromic properties of **6** in some solid polymer films in the absence and presence of added benzoic acid. While PAA and SMA (copolymer

Table 3. Solvent Effects on the Photochromic Properties of **4** and **6**[a)]

Substrate	Solvent[b)]	Absorption spectra of **H** and **F**				Time for PSS/min[c)]	Apparent rates for PC and TD	
		$\lambda_{\rm H}$/nm	$A_{\rm H}$	$\lambda_{\rm F}$/nm	$A_{\rm F}$		$\delta A_{\rm F}$/min	$-\delta A_{\rm F}$/day
4	Methanol–water	350	0.491	438	0.975	25	0.103	0.352
	Ethanol–water	353	0.435	440	0.873	25	0.130	0.648
	2-Propanol–water	352	0.278	439	0.544	10	0.124	0.544
	t-Butyl alcohol–water	351	0.393	440	0.848	25	0.154	0.749
	Glycerine–water	350	0.115	436	0.309	25	0.030	0.044
	Dioxane–water	350	0.374	439	0.735	25	0.142	0.640
	THF–water	350	0.428	439	0.470	10	0.154	0.468
	Acetonitrile–water	347	0.334	437	0.697	10	0.119	0.286
	Acetic acid	345	0.381	441	0.873	15	0.142	0.067
	Poly(acrylic acid)	350	0.339	448	0.438	60	0.089	N.D.
6	Methanol–water	395	0.226	532	0.563	140	0.026	0.012
	Ethanol–water	392	0.366	535	0.682	70	0.033	0.010
	2-Propanol–water	388	0.281	535	0.554	140	0.030	0.035
	t-Butyl alcohol–water	385	0.393	534	0.442	140	0.030	0.017
	Glycerine–water	360	0.085	531	0.339	140	0.006	0.027
	Dioxane–water	393	0.270	536	0.538	80	0.026	0.023
	THF–water	385	0.282	537	0.459	80	0.028	0.039
	Acetonitrile–water	387	0.318	533	0.687	80	0.040	0.076
	Acetic acid	394	0.391	533	0.660	35	0.11	0.073
	Poly(acrylic acid)	400	0.304	540	0.466	50	0.075	N.D.

a) Initial concentration of **4H** was 2.0×10^{-5} mol dm^{-3}, while poly(acrylic acid) film contained 2.0 wt% of **4H**. Initial concentration of **6H** was 1.5×10^{-5} mol dm^{-3}, while poly(acrylic acid) film contained 2.6 wt% of **6H**. $A_{\rm H}$ and $A_{\rm F}$ are the absorbances at the maxima of HC and FV, respectively. For other notations see footnotes in Table 1. b) Except for acetic acid and poly(acrylic acid) media, each organic–water solvent was of 1:1 in volume and pH was adjusted at 2.0 with 0.1 equiv sulfuric acid. c) Irradiation time needed to attain photostationary state of coloration.

Table 4. Photochromic Properties of **6** in Polymer Films[a)]

Polymer	Benzoic acid added/wt%	Maximum absorbance		PSS time	Apparent rates for PC and TD	
		$A_{\rm H}$	$A_{\rm F}$	min	$\delta A_{\rm F}$/min	$-\delta A_{\rm F}$/day
PMMA	0	0.18	0.017	3	0.007	0.010
	5	0.18	0.032	3	0.017	0.023
	10	0.19	0.050	1	0.039	0.043
PS	0	0.20	0.013	4	0.008	0.005
	10	0.18	0.054	2	0.024	0.038
SMA	0	0.06	0.076	17	0.031	
	10	0.10	0.132	25	0.076	0.006
PAA	0	0.07	0.114	15	0.051	0.013

a) Each polymer film contained 3.0wt% of **6**. Thermal discoloration was measured at 80 °C. PMMA: poly(methyl methacrylate), PS: polystyrene, SMA: copolymer of styrene and maleic anhydride, PAA: poly(acrylic acid). For other notations see footnote in Table 1.

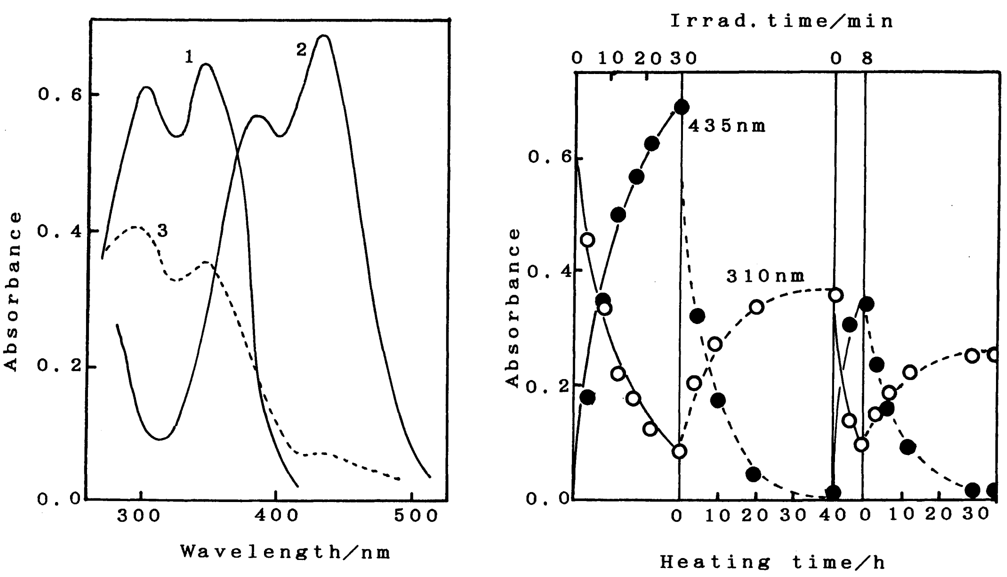


Fig. 2. Reversibility of **10** toward photochemical coloration and thermal decolorization at pH 2.1. Left: absorption spectra of **10H** before UV irradiation (1), after UV irradiation (2), and subsequent thermal decolorization (3). Right: recovery of absorbances toward photochemical coloration (solid lines) and thermal decolorization at 50°C (broken lines). Initial concentration of **10H** was 3.8×10^{-5} mol dm^{-3}.

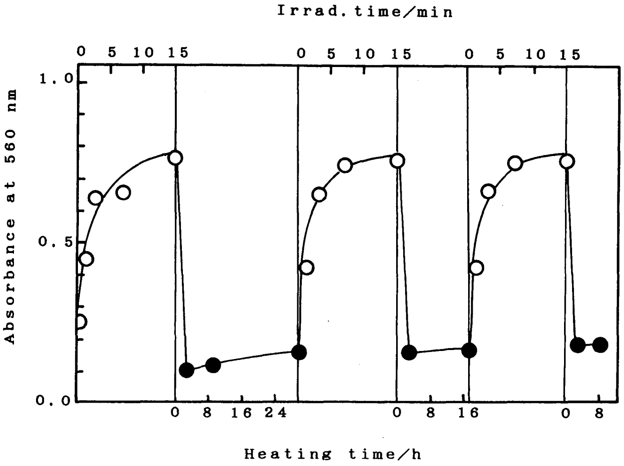


Fig. 3. Reversibility of **7** toward photochemical coloration and thermal decolorization (80°C) at pH 6.2 in 1:1 aqueous ethanol solution in the presence of boric acid (0.01 mol dm^{-3}). Initial concentration of **7** was 3.2×10^{-5} mol dm^{-3}.

of styrene and maleic anhydride) are effective as such, PMMA and PS (polystyrene) are also effective in the presence of added acid.

Reversibilities for the HC–FV Interconversions. Figure 2 illustrates the reversibility of **10** toward PC and TD cycles in 1:1 aqueous ethanol solution at pH 2.1, showing a poor reversibility. Under similar conditions, **4** showed somewhat better reversibility with ca. 8% loss of performance per cycle.[3] The colored form **6F** was thermally so stable that only 15% could be reversed to **6H** on heating at 50 °C for 3 weeks in aqueous ethanol at pH 2.1. Under similar pH and solvent conditions **7F** was even more stable (Table 2). However, after preliminary examinations of pH, solvents, and added salts etc., **7F** was substantially decolorized on heating in the presence of trichloroacetic acid or boric acid. Figure 3 illustrates the reversibility of **7** toward PC and TD (80 °C) at pH 6.2 in the presence of boric acid, showing a fair (99%) reversibility per cycle.

Unfortunately, however, no explanation for the special effect of boric acid have been obtained yet. Though trichloroacetic acid was effective for decolorization of **7F** it caused poor recyclizability for coloration–decolorization interconversions, while others including hydrochloric, sulfuric, benzoic, and acetic acids (or their salts) were ineffective.

Mechanistic and Miscellaneous Discussions. Photochemical coloration of HC has been shown to take place via rapid *E*/*Z* photoisomerization followed by cyclization to give a cyclic hemiacetal, 2-phenyl-2H-1-benzopyran-2-ol (B),[4] as shown in Scheme 2. The conversion of HC to B can occur both by thermal acid-catalyzed reaction and by photochemical reaction (in the absence or presence of acid). Alternative photochemical processes involving intramolecular transfer of the phenolic proton onto the carbonyl group followed by rotation (or *E*/*Z* isomerization) and 6π electrocyclic reaction cannot be ruled out, since it is well-established that the acidity/basicity of the intramolecular proton donor/acceptor groups increases on photochemical excitation.[9]

The hemiacetal B is subject to acid-catalyzed dehydration leading to the colored flavylium cation FV in aqueous acid solution.[5] Nucleophilic attack by water (or other nucleophiles) at the C-2 position leads back to B (or C). Both B and C are assumed to have negligible absorptions in the spectral regions of the HC and FV bands. In the presence of alcohol or hydroxylic solvents, a competitive pathway via formation of an acetal C may play a significant role, since alcohols are stronger nucleophiles than water and since acetal C is generally more stable than hemiacetal B. Thus, the PC and TD rates as well as the absorption properties are in fact significantly varied with the solvent properties at constant pH (Table 3), though attempts to correlate with the solvent nucleophilicity were unsuccessful. In glycerol-water solution, remarkably low PC and TD rates, and low absorbance values (both A_H and A_F) are observed with **4** and **6**. This may be ascribable for the high stabilities of their acetal C (R=glycerol). Alternatively, the glycerol moiety on C-2 position may play some role in association or complexation phenomena such as molecular stacking, copigmentation, and self-association which have been recently documented and have drawn wide attention in the color variation and stability of anthocyanins.[2]

The characteristic features of **4** and **5**, such as high quantum yield of PC, thermal and photochemical (against visible light) stability of the colored solution, well-separated absorption bands of the colored and uncolored forms, good performance in various solvents without suffering from the dissolved oxygen or moisture, and easy access of the materials (overall yields of the purified crystals not less than 50% starting with salicylaldehydes and *p*-methoxyacetophenone by single-step aldol condensation),[10] may be suitable for use as a convenient chemical actinometer. The related work is under investigation. Little toxicity and low cost of preparation of the compounds may be useful for photochromic ink, cosmetics, and even food additives etc..

Introduction of the dimethylamino group resulted in the significant improvements in the photochromic properties. Thus, through strong conjugative donor-acceptor interactions the flavylium cations, **6F** and **7F**, show significant bathochromic shifts and remakable stabilization toward solvolytic decolorization in a wide pH range. The strong absorptions and high thermal stabilities of the colored forms would allow non-destructive readout of a recorded memory. A high reversibility for the coloration–decolorization interconversion was attained with **7** by application of a "heat-mode" erase. Moreover, although reversibility was not satisfactory yet, our preliminary experiments revealed that the colored solutions are substantially erasable by electrochemical method at room temperature,[1] leading to an alternative and more desirable erase mode for a reversible memory device. Incorporation of electrochemical process in photochromic system would provide an ideal system for non-destructive information readout.[11] The efficiencies for photochemical coloration of **4**—**7H** are fairly high in solution, though somewhat lowered in solid polymers.

Experimental

The UV and visible absorption spectra were recorded on a Hitachi 200-10 spectrophotometer, while ^{1}H NMR spectra were on a Hitachi R-24 spectrometer. The UV light source was a 100-W high-pressure mercury lamp (Rico Kagaku), and the light beams of 313—366, 365—366, 405—436, or 545 nm were isolated by suitable combinations of filters, i.e., Toshiba UVD36C, UV35+UVD36C, UV-39, or aqueous $NiSO_4$ solution, respectively. The light quanta absorbed were estimated with a solution of (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (ϕ 0.20)[12] as a chemical actinometer because of the close resemblance of its absorption spectrum to those of 2-hydroxychalcones (HC).

Dilute solutions of HC, usually 1.5-3.5$\times10^{-5}$ mol dm^{-3}, were irradiated in identical Pyrex tubes without elimination of the dissolved oxygen, in a thermostat by means of a merry-go-round irradiation apparatus (Rico Kagaku). The pH values of aqueous–organic solutions were measured before and after irradiation, with a Yanaco PH-7 pH meter. Poly(acrylic acid) film of HC was prepared from a solution containing about 10 mg of HC and 0.5 g of poly(acrylic acid) (Wako Chemicals, MW: 250000, T_g: 106 °C) in 8 g of 2-butanol, by spin-coating on a silica glass plate. Polystyrene film was spin-coated from a solution containing 6 mg of HC and 0.2 g of polystyrene (Wako Chemicals, n=1600—1800) in 1.5 g of tetrahydrofuran and 1.0 g of cyclohexanone. Similarly, other polymer films of HC were spin coated with poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl alcohol), polycaprolactam, and copolymer of styrene and maleic anhydride.

The polymers were used as received while solvents were distilled before use. 2-Hydroxychalcones were prepared from substituted acetophenones and salicylaldehydes according to the literature,[10] and their ^{1}H NMR spectra and other physical constants were satisfactory.

4′-(Dimethylamino)-5,6-banzoflavylium (7F) Perchlorate. An aqueous acetone (1:1) solution of **7H** containing 15% perchloric acid was exposed to the sunlight until the yellow color of the solution turned to deep violet (after 3 h). On removal of acetone from the mixture solution violet solid (perchlorate salt of **7F**) separated out. The salt was purified by separation on silica gel with benzene followed by crystalization from aqueous acetone, yielding **7F** as perchlorate salt in 15%: Mp above 250 °C; ^{1}H NMR (60 MHz, DMSO-d_6) δ=3.2 (s, 6H), 6.9 (d, 1H, J=10 Hz), 7.4—8.9 (m, 10H), 9.6 (d, 1H, J=10 Hz). Found: C, 61.55; H, 4.70; N, 3.22%. Calcd for $C_{21}H_{18}NO_5Cl\cdot1/2\,H_2O$: C, 61.70; H, 4.68; N, 3.43%.

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