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Effect of Temperature on the Color Developed by Near Ultraviolet Light for 4,4′-Bipyridinium Salts (Viologens) Embedded in Poly(1-vinyl-2-pyrrolidone) Matrix

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Synopsis. Thermal stability of the colors developed by UV light for 4,4′-bipyridinium salts (viologens) embedded in the glass-sandwiched poly(1-vinyl-2-pyrrolidone) is dominated by the kind of counter anion. Temperature increase resulted in either no or slight changes of the colors developed for the major viologens, whereas it resulted in bleaching for some viologen sulfonates.

It was reported previously[1)] that 4,4′-bipyridinium salts (viologens), when embedded in a tightly glass-sandwiched poly(1-vinyl-2-pyrrolidone) (PVP) film, developed intense colors with a short-second irradiation by a solar level UV-light and that the developed colors were remarkably stable at room temperature.

However, it has been also reported[2—5)] that, as for films solely made of the viologens with alkyl(C_8—C_{14}) benzenesulfonates as counter anion as well as for some viologen crystals with sulfonate anions, both with exclusion of air, bleaching of the colors thus developed takes place, especially at elevated temperatures (solid-state redox photochromism).

Such being the case, the tightly glass-sandwiched films of PVP or poly(vinyl alcohol) (PVA) bearing various viologens were prepared in the present study and subjected to a solar level UV-irradiation, and thermal stabilities of the colors thus developed have been investigated.

As for the major viologens the colors have been thermally stable within the scope of the present experimental conditions, whereas for some viologens with sulfonate counter anions bleaching has been observed.

Results and Discussion

Figure 1 gives typical thermal behaviors of the visible absorption spectra developed with irradiation by UV light for the glass-sandwiched films indicated in Table 1.

Thus, the absorption spectrum (blue color) developed by UV for film 9 almost disappeared on heating at 100 °C for one hour (spectra 2 and 2′), whereas that for film 1 was not affected at all (1 and 1′). Thermal behaviors of the colors developed for various viologens are summarized in Table 2.

It can be seen that films 3, 8, and 9, all bearing sulfonates as viologen counter anions as well as employing PVP as matrix, develop blue colors with satisfactory photosensitivities by a solar level UV-irradiation and that the colors can be bleached by the application of heat. This color development by UV and subsequent thermal bleaching of the color developed can be repeated.

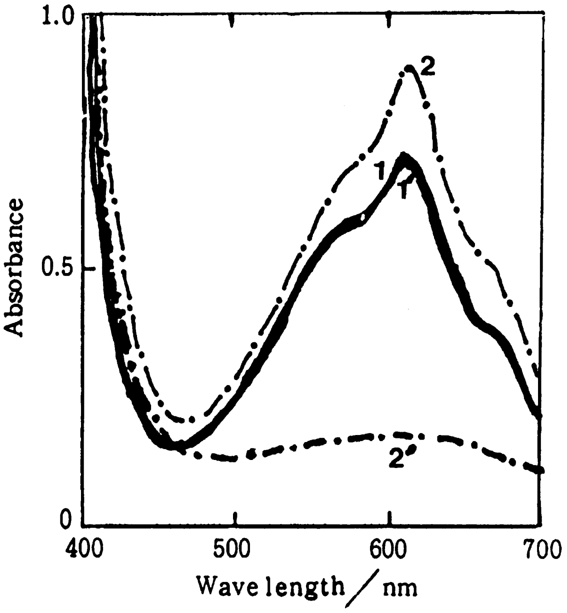
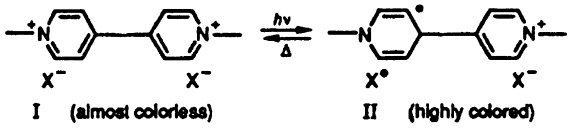


Fig. 1. Typical thermal behaviors of the colors developed by the UV light for the glass-sandwiched films. —— 1: Visible absorption spectrum of the color developed by UV for film 1;
1′: that upon heating the color developed film at 100 °C one hour in dark. —•— 2: Visible absorption spectrum of the color developed by UV for film 9;
2′: that upon heating the color-developed film at 100 °C for one hour in dark.

It should be noted that all viologens bringing about reversible color developments by UV in PVP matrix have also indicated the same characteristics by themselves either in a crystalline[3—5)] or in a film state[2)] (see also footnotes c and d).

In the reversible color developments by UV for viologens without any additives, it has been believed that the transfer of one electron to viologen dication from counter anion (X^-) by the photon mode to produce the highly colored radical cation and vice versa by the heat mode is the mechanism, as indicated in Eq. 1.[2—5)]



(1)

Table 1. Glass-Sandwiched Films Employed for the Study of Thermal Stability of the Color Developed by UV

Film	Viologen[a)]		Matrix polymer	Solvent for film
	N-substituent	Counter anion		
No.	R	X^-		preparation
1	$PhCH_2$	Cl^-	PVP (MW, 40000)	H_2O
2	n-C_3H_7	Br^-	PVP (MW, 40000)	H_2O
3	$PhCH_2$	PTS^- b)	PVP (MW, 40000)	H_2O–EtOH g)
4	n-C_3H_7	PTS^- b)	PVP (MW, 40000)	H_2O
5	n-C_3H_7	ES^- c)	PVP (MW, 40000)	H_2O
6	$PhCH_2$	BF_4^-	PVP (MW, 40000)	EtOH
7	Ph	PTS^- b)	PVP (MW, 40000)	H_2O
8 d)	$-(CH_2)_3-SO_3^-$		PVP (MW, 40000)	H_2O
9 d)	$PhCH_2$	DBS^- e)	PVP (MW, 40000)	EtOH
11	$PhCH_2$	Cl^-	PVA (DP, 2000) f)	H_2O
12	$PhCH_2$	PTS^- b)	PVA (DP, 2000) f)	H_2O–EtOH g)
13	n-C_3H_7	Br^-	PVA (MW, 2000) f)	H_2O

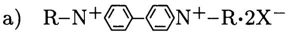
a)  b) p-Toluenesulfonate anion. c) Ethanesulfonate anion. d) A little opaque. e) p-Dodecylbenzenesulfonate anion derived from a commercially available sulfonic acid (Tokyo Kasei, D0989). f) 80% saponified. g) 50 : 50 vol/vol.

Table 2. Thermal Stability of the Colors Developed by UV for the Glass-Sandwiched Films

Film	Absorption developed by UV		Thermal stability of the absorption		Remarks
	λ_{max}	Color	$t_{1/2}$ a)		
No.	nm		25 °C	100 °C	
1	400, 610 (3.46) b)	Dark blue	>1 year	>24 h	No spectral change by heating
2	400, 605 (1.23) b)	Blue	>1 year	Slightly decreased	Slightly affected by heat
3	400, 610 (3.00) b)	Dark blue	>1 year	1 h	Some absorptions remain after prolonged heating
	(400, 610	Dark blue	0.5 h	5 min	Completely bleached) c)
4	400, 605 (1.51) b)	Blue	>1 year	>24 h	No spectral change by heating
5	400, 605 (1.38) b)	Blue	>1 year	>24 h	No spectral change by heating
6	400, 610 (2.71) b)	Dark blue	>1 year	>24 h	No spectral change by heating
7	425, 645 (2.83) b)	Dark green	>1 year	>24 h	No spectral change by heating
8	405, 605 (1.10) b)	Blue	>1 year	2 h	Some absorptions remain after prolonged heating
	(405, 605	Blue	>1 year	20 min	Completely bleached) c)
9	410, 610 (2.42) b)	Dark blue	>1 month	0.5 h	Almost completely bleached after prolonged heating
	(410, 610	Blue	>1 week	< 1 min	Completely bleached) d)
11	410, 610 (0.21) b)	Light blue	>1 year	>24 h	Rather poorly photosensitive
12	—	—	—	—	Not Photosensitive
13	410, 610 (0.05) b)	Pale blue	>1 year	>24 h	Hardly photosensitive

a) Half-bleaching time. b) Absorbance converted into 0.1 mm film thickness. c) For crystals with exclusion of air. d) For glass-sandwiched films without PVP.

Hence, it is suggested that, even in PVP matrix, viologen radical ion pairs (II) produced from I by UV in films 3, 8, and 9 could undergo the thermal back reaction according to Eq. 1 to significant extents to bring about bleaching of the color attributable to II (solid-state redox photochromism in the absence of air).

Such a reversible color development was also observed for the glass-sandwiched PVP film bearing *trans*-4,4′-vinylenebis(1-benzylpyridinium) dichloride, another type of viologens.⁶⁾ In this case, the photodeveloped pink color bleached completely upon standing at room temperature for one hour.

As for other viologens shown in Table 1, on the other hand, the colors developed for the glass-sandwiched films were very stable thermally within the scope of the present experimental conditions(Fig. 1 and Table 2) and the introduction of air was required for bleaching to take place (solid-state redox photochromism in the presence of air). This fact may indicate that the back reaction according to Eq. 1 hardly occurs in the absence of air and that II, particularly highly-colored radical cations, is stabilized by binding to PVP matrix. Another possible cause for this unusual stability of the photogenerated radical cation is that the also photogenerated radical X removes an electron from the matrix PVP. This consumption of X by the oxidation mechanism, if any, would not permit the progress of the back electron transfer following Eq. 1.

Thompson and a co-worker suggested a similar possibility in layered viologen compounds.⁷⁾ Accordingly, the back electron transfer from the highly-colored radical cation to provide the original colorless dication would require the presence of air.¹⁾ In this case, if the electron removal from PVP should occur, X^- would be also regenerated from the photogenerated X, thereby assuring repeating of the redox photochromism.

Poly(vinyl alcohol) (PVA) as matrix afforded no or poor, if any, color development for the reason described elsewhere (films 11, 12, and 13).⁸,⁹⁾

Dispersion of II by binding to PVP appears to be the cause of much superior thermal stabilities of the colors developed by UV for the glass-sandwiched films 3, 8, and 9 to those of the corresponding crystals and films without matrix polymer, as known from $t_{1/2}$ in Table 2.

As present time, only I with sulfonates as X^- have been able to form the glass-sandwiched films with PVP as matrix, in which the intramolecular redox back-reaction shown in Eq. 1 could take place to significant extents.

Experimental

All viologens except those in films 7 and 8 were first synthesized in either the Cl^- or the Br^- form by the Menschutkin reaction of 4,4′-bipyridine with either benzyl chloride or propyl bromide, respectively. Viologens (those in film 3—6, 9, and 12) with counter anions other than halides were prepared by the anion exchange reaction of the halide form using Amberlite IRA-40. Viologen in film 7 was synthesized by the method previously reported,¹⁰⁾ followed by the anion-exchange reaction. Viologen in film 8 was synthesized by the reaction of 4,4′-bipyridine with 1,3-propanesultone.⁴⁾

Glass-Sandwiched Films. A solution of viologen (2 mg) and matrix polymer (100 mg) in a solvent (1 ml), as shown in Table 1, was spread homogeneously on a glass plate, followed by drying at ambient temperature overnight. The plate with the resulting thin layer deposited on was heated at a temperature above 100 °C for a while until a sticky appearance was attained on the layer, followed by the immediate tight covering with another glass plate to afford an almost air-tight glass-sandwiched film ranging in thickness from 0.05 to 0.1 mm.

Photochromism Measurements. The glass-sandwiched films were subjected to the 60 s irradiation at a distance of 10 cm from a 75-W high pressure mercury lamp (Toshiba SHL-100UV). The irradiated films were placed in an air oven fitted with a thermostat for given times. Changes of visible absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer. Half-bleaching times ($t_{1/2}$) were determined for the spectra thus obtained.

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