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PHOTOCHEMICALLY INDUCED REDUCTION OF VIOLOGENS IN SOLID POLAR APROTIC POLYMER MATRICES

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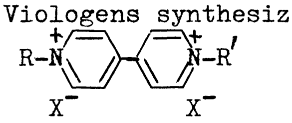
Photochemically induced reversible reduction of viologens in solid polar aprotic polymer matrices proceeds much more efficiently than that in protic ones. The effects of the N-substituent and anionic part of viologens were also considerable.

It is well known that viologens such as 1,1'-dimethyl-4,4'-bipyridilium dichloride are reduced reversibly to afford highly colored cation radicals.[1,2] Photochemically induced generations of viologen cation radicals have been reported for alcoholic solutions of viologens[3,4,5] and for polymeric viologens both in aqueous solutions[6] and in solid state.[7,8]

In this report, we wish to present the results of investigation conducted on the photochemical behavior of viologens in solid polymer matrices, especially in polar aprotic ones.

In Tables 1 and 2 are given the viologens prepared by the Menschutkin reaction in conventional manners and the polymers employed as matrix, respectively. Generally, a matrix polymer (0.5g) was dissolved in water (5 ml). A viologen was then dissolved in the solution to afford 0.099 mole/l concentration. The resulting solution was spread over a glass plate of 1.2 cm width so as to afford a 1.2 x 2.0 cm area, followed by drying overnight at room temperature. The plate was then stored in a desiccator of 30% RH (sat.$CaCl_2$ solution) at least overnight before use. The plate taken out of the desiccator was immediately irradiated at a distance of either 5 or 15 cm from a 75W-mercury lamp (Toshiba SHL-100UV) and the resulting color-development was recorded on a Hitachi 200-10 spectrophotometer.

Table 1. Viologens synthesized and used



Compd	R	R'	X^-
1a	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Br^-
1b	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Cl^-
1c	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	I^-
2	$PhCH_2$	$n\text{-}C_3H_7$	Br^-
3a	$PhCH_2$	$PhCH_2$	Br^-
3b	$PhCH_2$	$PhCH_2$	Cl^-
3c	$PhCH_2$	$PhCH_2$	BF_4^-
4	CH_3OOCCH_2	CH_3OOCCH_2	Cl^-

As exemplified in Figure 1 and Table 3, the absorbance at the absorption maximum (610 nm) which appeared as the result of the formation of cation radicals in the

Table 2. Polymers used as matrix

Polymer	Abbreviation	Average MW	Remark
Poly(acrylamide)	PAM	$[\eta] = 1.9$ dl/g[a]	Aqueous polymerization
Poly(N,N-dimethyl acrylamide)	PMAM	$[\eta] = 0.8$ dl/g[a]	Ethanolic polymerization
Poly(vinyl alcohol)	PVA	20,000	Iwai Chem. Co.
Poly(N-vinyl pyrrolidone)	PVP	10,000	Tokyo Kasei Co.

a. Intrinsic viscosity in water at 30°C.

Table 3. Effect of matrix on color development

Viologen	Matrix	Irrad. distance cm	Absorbance[a] at irrad. time 30	60	90 sec	$t_{\frac{1}{2}}$[b]
1a	PVA	5	0.12	0.24	0.34	60
	PAM	5	0.00	0.04	0.04	40
	PMAM	5	0.13	0.38	0.56	10
	PVP	5	0.49	1.18	1.47	10
3b	PVA	15	-	0.13	-	600
	PVP	15	-	0.90	-	70

a. Value at abs.max.(610 nm). b. Half-recovery time(min).

solid polymer films containing viologen by UV-irradiation is affected profoundly by the kind of matrix. The effect of matrix on the color-developing rate was in the decreasing order: PVP, PMAM, PVA, and PAM. It is also to be noted that PVP and PMAM, polar aprotic matrices, provided much higher color-fading rates ($t_{\frac{1}{2}}$) than PVA and PAM, protic ones.

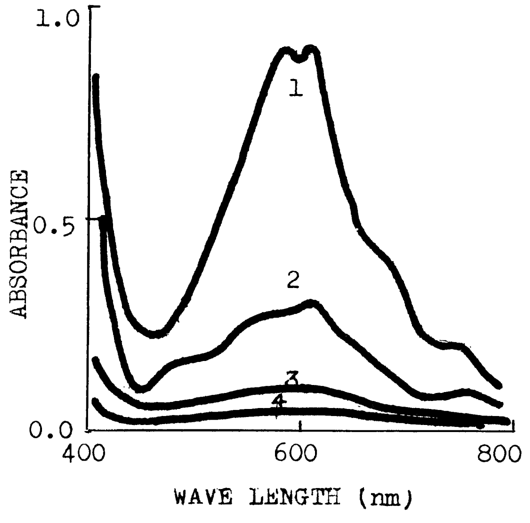


Figure 1. Effect of matrix on the color-development of the film containing 3a and exposed to UV-light for 90 sec at the distance of 15 cm from the lamp: 1 PVP; 2 PMAM; 3 PVA; 4 PAM.

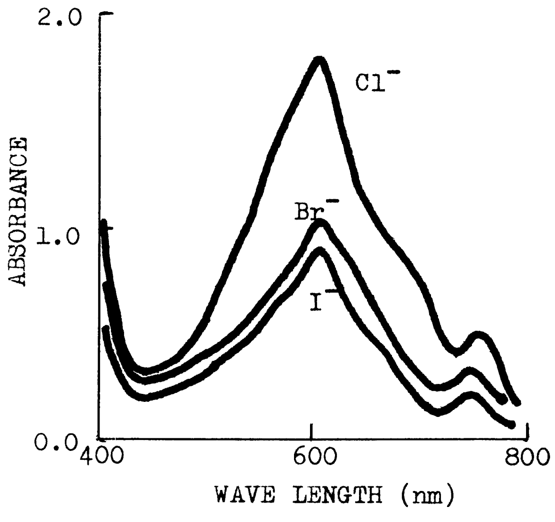


Figure 2. Effect of the anionic part of viologen on the color-development of PVP films containing 1a, 1b, and 1c and exposed to UV-light for 60 sec at the distance of 5 cm from the lamp.

In Figure 2 and in Table 4 are exemplified the effect of the anionic part of viologen on the spectral changes caused by the reduction. The kind of anion considerably affects the rate of reduction with the decreasing order of Cl^-, Br^-, and I^- and BF_4^- in PVP-matrix.

Table 5 exemplifies the effect of the N-substituent (R and R' in Table 1) in viologen cation on the color-developing rate in PVP-matrix. The order obtained:

dibenzyl > benzyl-propyl > dipropyl is consistent with that of dark normal redox potentials.[9] As regards viologen 4 with methyl ester groups, a somewhat different tendency is observed: absorption maximum at 605 nm which is different from others (610 nm) and rather lower absorbances developed. The value of A_{20}/A_{60}, however, is rational.

Table 4. Effect of the anionic part of viologen on the photochemically induced reduction[a]

Viologen	Absorbance[b] at irrad. time[c]		
	0	20	60 sec
3a	0.00	0.88	1.58
3c	0.00	0.35	0.88
1c	0.00	0.16	0.58

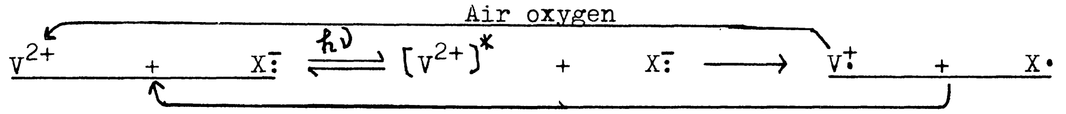
a. Matrix PVP. b. Value at abs.max.(610 nm). c. 5 cm from UV-lamp.

Table 5. Effect of N-substituent (R and R') on reduction rate[a]

Viologen	Absorbance[b] at irrad. time[c]			A_{20}/A_{60} x100[d]
	20	40	60 sec	
1a	0.40	1.18	1.58	25
2	0.71	-	1.50	47
3a	0.88	1.50	1.58	56
4	0.52[e]	0.63[e]	1.07[e]	49

a. Matrix PVP. b. Value at abs.max. c. 5 cm from UV-lamp. d. A: Absorbance. e. At 605 nm (abs.max.).

The results presented above might suggest that the photochemically induced reduction of viologen cation in a solid polar aprotic matrix to afford a highly colored cation radical proceeds at least partially as indicated in eq. 1 under the present experimental condition.



$$V^{2+} + X^{\overline{\cdot}} \underset{}{\overset{h\nu}{\rightleftharpoons}} [V^{2+}]^{*} + X^{\overline{\cdot}} \longrightarrow V^{\dot{+}} + X\cdot \qquad (1)$$

Air oxygen

where V and [ ]* represent viologen cation and the photoexcited state, respectively. Thus, anion $X^{\overline{\cdot}}$ may be in the "naked" state in polar aprotic matrices such as PVP and PMAM, especially when the ambient RH and therefore the moisture contents of films are low, since such matrices would hardly solvate anions just like their liquid equivalents.[10] Accordingly, such naked anions will attack V^{2+} more efficiently than the solvated ones such as those in PVA and PAM, protic matrices, thereby providing much higher rates of reduction (Figure 1 and Table 3). The rate order as for anion in PVP, a typical polar aprotic matrix: $Cl^- > Br^- > I^-$ and BF_4^- (Figure 2 and Table 4) is consistent with the usual order of nucleophilicity for these anions in liquid polar aprotic solvents.[11] The abstractions of hydrogen radicals from matrices may also occur, especially for PVA, but a large difference in photoreduction efficiency found between PMAM and PAM in which the structure difference lies only in the N-substituent (Figure 1 and Table 3) also suggests that the mechanism of color-development indicated in eq. 1 can not be disregarded. The fact that color-fading rates ($t\frac{1}{2}$) in protic matrices such as PVA are much lower than those in polar aprotic ones such as PVP (Table 3) excludes the presence of air oxygen, which promotes color-fading (back reaction), in larger amounts in the former matrices. The fact that lower ambient RHs down to

30% afford higher photoreduction rates, as exemplified in Table 6, may also suggest that lower contents of water, a typical protic solvent, enhance the activating effect of solid polar aprotic matrices.

Table 6. Effect of relative humidity (RH) on photoreduction rate

Viologen	Irrad. distance cm	Irrad. time sec	RH[a] %	Absorbance(610 nm)	Matrix
3a	5	20	30	0.91	PVP
			58	0.74	
			84	0.72	
3a	5	40	30	0.43	PMAM
			58	0.33	
			84	0.29	
3a	5	20	30	0.09	PVA
			58	0.06	
			84	0.06	
3b	15	60	30	0.91	PVP
			58	0.77	
			84	0.69	
1b	5	40	30	1.08	PVP
			58	1.04	
			84	0.96	

a. 58% RH: over sat. NaBr solution; 84% RH: over sat. KBr solution.

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