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Redox Photochromism of Waterproof Viologen-Matrix Polymer System

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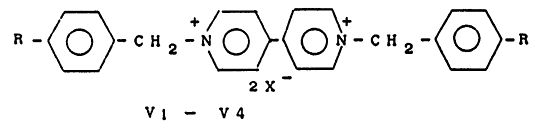
Synopsis. A waterproof viologen-matrix polymer system exhibiting redox photochromism in thin films was devised using water-insoluble viologens embedded in *N*-vinyl-2-pyrrolidone(VP)-methyl acrylate (MA) copolymers also insoluble in water. Both the photosensitivity and the stability of the colors developed decreased with decrease in the VP-content.

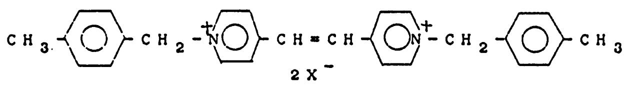
In previous publications,[1—7] it has been reported that bipyridinium salts (viologens) embedded in the poly(1-vinyl-2-pyrrolidone) (PVP) matrix film reversibly develop visible intense colors with radiation of the solar level (redox photochromism).

It is required for some purposes, however, that these photochromic systems are waterproof, since both conventional viologens and PVP are water-soluble. Accordingly, waterproof thin films consisting of the viologen-matrix polymer system have been prepared and their reversible color-developing behaviors induced by near UV-irradiation of the solar level have been investigated.

Water-insoluble viologens employed in the present study were 1,1′-bis(arylmethyl)-4,4′-bipyridinium bis(tetrafluoroborate) and bis(hexafluorophosphate) (**V1—V4**) and *trans*-4,4′-vinylenebis[1-(*p*-methylbenzyl)pyridinium] bis(tetrafluoroborate) (**V5**) and bis(hexafluorophosphate) (**V6**).



V1 – V4



V5 – V6

	R	X
V1 :	CH_3	BF_4
V2 :	CH_3	PF_6
V3 :	Cl	BF_4
V4 :	Cl	PF_6
V5 :	-	BF_4
V6 :	-	PF_6

Viologens bearing 4,4′-bipyridinium and *trans*-4,4′-vinylenebispyridinium units were adopted as typical of exhibiting intense visible colors upon near UV irradiation.

Matrix polymers, in which the viologens were to be embedded, were copolymers of 1-vinyl-2-pyrrolidone (VP) with methyl acrylate (MA) in less than 1 : 1 molar ratios, which were insoluble in water.

Experimental

Water-Insoluble Viologens (V1—V6). 1,1′-Bis(*p*-methyl- or *p*-chlorobenzyl)-4,4′-bipyridinium dichloride or *trans*-4,4′-vinylenebis[1-(*p*-methylbenzyl)pyridinium] dichloride (11 mmol) were dissolved in water (200 ml). Aqueous HBF_4 (42 wt%; 4.8 g, 23 mmol) or aqueous HPF_6 (60 wt%; 5.6 g, 23 mmol) was then added to precipitate white to yellowish white crystalline powder (**V1—V6**) in more than 90% yield (mp 240, 238, 254, 249 °C for **V1—V4**; decomp for **V5**, **V6**). The results of IR (KBr) and elemental analyses were satisfactory.

Matrix VP-MA Copolymers. Prepared in dioxane solutions kept at 80 °C for 72 h with α,α'-azobisisobutyronitrile as initiator, in the conventional manner using glass ampules sealed under N_2. The VP-contents in copolymers were determined by elemental analyses to afford satisfactory agreements with the initial monomer ratios. Values of intrinsic viscosity $[\eta]$ in DMF at 25 °C for the 1 : 5, 1 : 7, and 1 : 10 copolymers, which were insoluble in water, were 0.22, 0.24, and 0.22 dl g^{-1}, respectively.

Films for Irradiation. Films open to air (A) and those tightly sandwiched between two glass plates (B) were prepared in the same manners as in previous studies,[6,7] except that DMF and an elevated temperature (40 °C) were employed

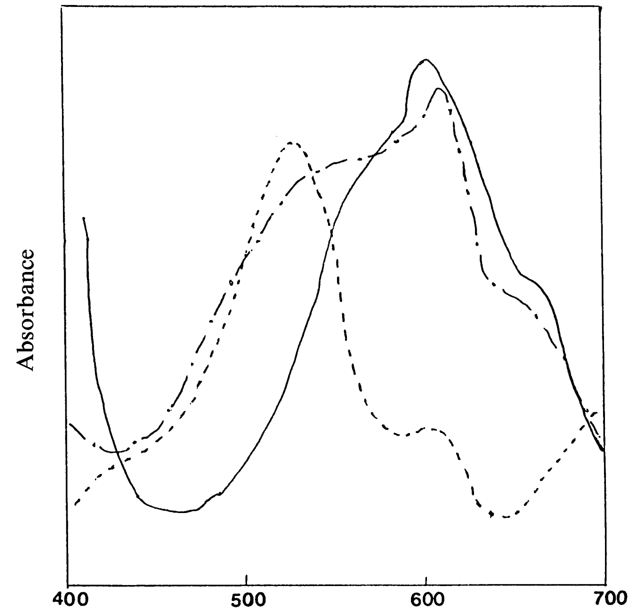


Fig. 1. Typical visible absorption spectra developed for water-insoluble viologens embedded in VP–MA copolymer matrix films with irradiation by near UV light.
—— For **V2** embedded in VP–MA (1 : 5) copolymer; ----- for **V5** in VP–MA (1 : 7) copolymer; —·— for 1, 1′-bis(*p*-methylbenzyl)-4,4′-bipyridinium dichloride in VP homopolymer. Measures of ordinates are arbitrary only to show the shapes of spectra.

instead of water as solvent and evaporation at room temperature, respectively.

Absorption Change. Radiation through a glass plate from a 75 W high pressure Hg lamp (Toshiba SHL-UV100) was applied to either films A or B placed at the distance of 5 cm from the light source, and the resulting visible absorption changes of films were determined by means of a Hitachi 200-10 recording spectrophotometer.

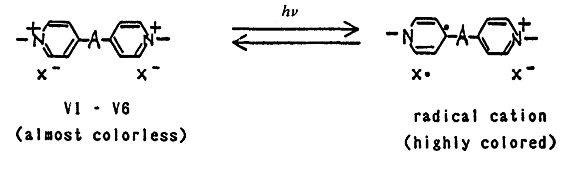
Results and Discussion

Viologens **V1**—**V6** were prepared by the anion exchange reaction of the respective chlorides with excess tetrafluoroboric and hexafluorophosphoric acids without any difficulty.

MA was chosen as the comonomer, since it provides not only water-proofness but also transparency and toughness to copolymer films. Films less than 0.1 mm in thickness were prepared on glass plates by evaporating DMF solutions at 40 °C. In Fig. 1 are given typical absorption spectra developed for the films upon irradiating near UV light of the solar level.

It can be recognized from Fig. 1 that the shapes and absorption maxima (λ_{max}) of the visible absorption spectra developed for the waterproof viologen–VP–MA copolymer system by near UV irradiation are almost identical with those of the radical cations produced in the water-soluble viologen–VP homopolymer one,[1–7] except that, in the latter system, absorptions attributable to associated radical cations[8] are also discernible, e.g. between ca. 500 and 600 nm for 4,4′-bipyridinium. This fact suggests that the species causing these absorption changes were also viologen radical cations generated by the photo-redox reaction, as demonstrated in previous studies.[9,10]

Equation 1 indicates this relationship in the absence of air where A is intended to represent none and -CH=CH- for **V1**—**V4** and **V5**, **V6**, respectively.



(1)

A remarkable fact in the present case is that almost no

Table 1. Reversible Visible Absorption Change (Photochromism) for **V1**—**V4** Embedded in Matrix Polymer Film with Irradiation by UV[a]

Viologen	Matrix polymer (VP:MA) mol/mol	Film[b]	A_t[c] 3 min	A_t[c] 4 min	A_t[c] 5 min	$t_{1/2}$[d] min
V1	1:5	A	0.069	0.160	0.253	13
		B	0.069	0.153	0.244	27
V2	1:5	A	0.086	0.205	0.351	10
		B	0.087	0.194	0.351	30
V3	1:5	A	0.127	0.198	0.251	6
		B	0.121	0.190	0.245	60
V4	1:5	A	0.088	0.205	0.272	6
		B	0.113	0.206	0.275	60
V1	1:7	A	0.040	0.100	0.116	8
		B	0.043	0.091	0.116	30
V2	1:7	A	0.037	0.085	0.125	8
		B	0.037	0.099	0.127	25
V3	1:7	A	0.050	0.104	0.158	8
		B	0.040	0.098	0.148	70
V4	1:7	A	0.044	0.156	0.204	7
		B	0.049	0.160	0.206	60
V1	1:10	A	0.014	0.088	0.105	7
		B	0.013	0.080	0.097	10
V2	1:10	A	0.039	0.081	0.093	6
		B	0.040	0.086	0.102	10
V3	1:10	A	0.041	0.084	0.103	7
		B	0.040	0.088	0.106	40
V4	1:10	A	0.039	0.076	0.094	8
		B	0.044	0.083	0.103	40

a) At a distance of 5 cm from a 75 W high pressure Hg lamp, with a glass filter fitted so as to obtain the light >300 nm. b) 5% **V1**—**V4** on the basis of matrix polymer. A: Open to air; B: Tightly glass-sandwiched. c) Absorbance increase in irradiation time t. Values reduced to 0.1 mm film thickness at λ_{max} (605 nm). Absorptions were negligible for films before and long after irradiation. Irrad iation times are indicated in min. d) Half-bleaching time at 20 °C.

Table 2. Photochromism for **V5** and **V6** Embedded in Matrix Polymer Film with Irradiation by UV[a]

Viologen	Matrix polymer (VP:MA) mol/mol	Film	A_t[b] 15 s	A_t[b] 30 s	$t_{1/2}$ s
V5	1:5	A	0.531	0.563	15
		B	0.632	0.671	20
V6	1:5	A	0.524	0.559	17
		B	0.789	0.801	23
V5	1:7	A	0.497	0.527	13
		B	0.587	0.613	16
V6	1:7	A	0.481	0.499	16
		B	0.630	0.660	17
V5	1:10	A	0.228	0.283	13
		B	0.354	0.403	16
V6	1:10	A	0.216	0.249	14
		B	0.370	0.428	16

a) Notations are identical with those in Table 1, unless otherwise noted. b) Values reduced to 0.1 mm thickness at λ_{max} (525 nm).

absorptions attributable to associated radical cations exist especially in the spectra for **V1**—**V4** as exemplified in Fig. 1 (——), presumably suggesting that the species are in thermodynamically less stable states when compared with those generated in VP-homopolymer (—·—). This less stable characteristic is also observed in half-bleaching time ($t_{1/2}$) in Table 1.

Thus, it is known from the values of $t_{1/2}$ that complete bleachings take place even for air-tight films (B), whereas, in the case of VP-homopolymer as matrix, the colors developed by light persist for a long term (life of months to years) under the same film-forming conditions.[7]

The results in Tables 1 and 2 indicate that the absorbance increase (A_t) at λ_{max} in irradiation time t becomes remarkably smaller with decrease of the VP-content in the copolymers, so that the values of A_t for the 1 : 10 (VP : MA) copolymers open to air (A) amount to less than half (5 min irrad.) and approximately half (30 s irrad.) those for the 1 : 5 copolymers in the cases of **V1**—**V4** and **V5**, **V6**, respectively; $t_{1/2}$ for the tightly glass-sandwiched films (B) appear to show the same tendency.

These facts are considered to demonstrate that the principal mechanism of the photo-reaction in this case is, as shown in Eq. 1, the reductive attack of the X^- highly activated by the VP-portion of the copolymers against the photo-excited viologen dication to produce a highly colored radical cation, which is stabilized in its turn by binding to the VP-portion, by the same reason as for 1-methyl-2-pyrrolidone, a highly efficient polar aprotic solvents.[1]

Thus, the decrease of the VP-content in polymer may lead to decreases of both reactivity of the counter anion and stability of the radical cation, thereby bringing about decreases of both A_t and $t_{1/2}$.

The photochromic behaviors investigated above were waterproof, as expected, and did not much differ among **V1**—**V4** in Table 1 and between **V5** and **V6** in Table 2 each other, with exception that **V3** and **V4** [1,1′-bis(*p*-chlorobenzyl) derivatives] provided considerably larger values of $t_{1/2}$ than **V1** and **V2** [1,1′-bis(*p*-methylbenzyl) ones] did.

Features of **V5**, **V6** in Table 2, other than providing a λ_{max} at 525 nm (red) instead of 605 nm (blue) for **V1**—**V4**,[1-7], are high photosensitivities as well as rapid bleachings in dark. The presence of air oxygen (A) also afforded A_t always smaller than the almost absence of air (B) did.

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