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THE PHOTOCHROMIC BEHAVIOR OF VIOLOGENS AND POLYVIOLOGENS IN POLYMER MATRICES

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ABSTRACT

The photochromic behavior of viologens (V^{2+}) and polyviologens (PV^{2+}) was investigated using poly(*N*-vinyl pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) as matrices. In the PVP matrix the coloration rate of butylviologen bromide increases with decreasing humidity, but no influence of humidity on coloration rate was observed in the PVA matrix. The coloration rate in the PVA matrix follows a second-order plot while in the PVP matrix it does not. These results imply that, for the coloration process of viologens in polymer matrices, the effect of the matrix polymer as an electron donor must be considered. The fading rate of colored poly(butylviologen bromide) in PVP matrix increases remarkably with humidity. The fading reaction obeys a first-order relation at the very beginning and permits the determination of the rate constant. The fading rate increases with temperature with an activation energy of 13 kcal/mol. The fatigue of viologens and polyviologens was evaluated by the half-decay flash number. Polyviologens are more durable than their lower homologs.

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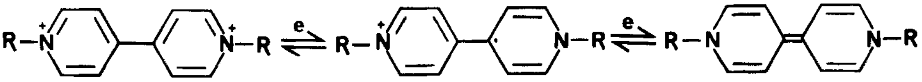
INTRODUCTION

Viologens (1,1′-disubstituted-4,4′-bipyridinium salts) are known as herbicides and are used as electron-transfer agents in the photodecomposition of water, they are also known as photochromic and electrochromic materials. All these properties are attributable to the following redox reactions:



(R – BPy – R)

(oxidation state V^{2+}, usually light yellow)	(first reduction state V^{+}, usually purplish-blue or violet)	(second reduction state V^{0}, usually yellow)

We synthesized some polyviologens by the Menschutkin reaction with a main-chain structure of $\left[\begin{array}{c}-\mathrm{BPy}-\mathrm{R}-\\ 2X^{-}\end{array}\right]_n$ in which R is alkyl, aryl, or aralkyl, and X^- is an anion such as chloride or bromide [1]. It has been found that the photoreduction (coloration) rate of polyviologen is much faster than that of the corresponding low molecular viologen, and the difference of the reduction potentials in the first and second steps (ΔE) is also larger for polyviologen, which may inhibit the less reversible second reduction step. As a photochromic material, the fatigue behavior is an important property, but no such information has yet been reported in the literature. We have therefore investigated the photochromic behavior of viologens and polyviologens in polymer matrices.

EXPERIMENTAL

Viologens (V^{2+}) and polyviologens (PV^{2+}) were synthesized in this laboratory and identified by elemental analysis. The intrinsic viscosity was measured in formamide at 30°C.

The poly(vinylpyrrolidone) (PVP) was a product of the GAF Corporation, MW 360 000.

The poly(vinyl alcohol) (PVA) had a DP of 500 and a degree of hydrolysis of 88%.

For the preparation of photochromic plates, the V^{2+} or PV^{2+} was dissolved in a 5% solution of polymer (PVP or PVA) to a concentration of 0.1%. This solution was then coated on quartz or glass plates, dried, and kept in a desiccator at predetermined humidity. The film thickness was controlled by coating a fixed amount of the solution on a fixed coated area (around 1.2 X 3.0 cm).

Humidity control was achieved by placing saturated solutions of different salts in the desiccator. The relative humidity (RH) measured with a hair hygrometer at 25°C was 18% for $CaCl_2$ (anhydrous), 55% for $Ca(NO_3)_2.4H_2O$, 73% for $Mg(OAc)_2$, and 82% for KBr.

The irradiation was carried out with a 300-W high-pressure Hg lamp at a distance of 30 cm. The sample was placed in a closed box with a quartz window for the UV light to pass through. The humidity in the box was adjusted similarly to that in the desiccator.

The UV-VIS spectra were recorded with a Shimadzu UV-240 spectrophotometer.

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RESULTS AND DISCUSSION

A. The Coloration Rate

Previous study [2] of the effect of different polymer matrices on the coloration and fading rate of polyviologens showed that the fastest rate of coloration and fading occurs in a PVP matrix. This result is in accordance with the findings of Kamogawa et al. [3] for low molecular weight viologens. They also reported that the coloration rate decreases with increasing humidity in PVP, PVA, and other polymer matrices. The result was interpreted by a mechanism in which the anion acts as an electron donor in the reduction of the viologens, and the greater humidity causes stronger hydration of ions, thus lowering the electron donating ability and hence the coloration rate.

The influence of humidity on coloration rate of butylviologen bromide (BV, C_4H_9–BPy–$C_4H_9.2Br^-$) was examined both in PVP and PVA. We noticed that the film thickness affects the coloration rate appreciably. To eliminate the influence of film thickness, we adopted a method introduced in Ref. 4, i.e., several films with different thicknesses were prepared and their absorbances (A_0) at 262 nm before irradiation were measured. The 262-nm peak is the characteristic absorption of BV, hence A_0 corresponds to the film thickness. A plot of coloration rate versus ($1 - \log A_0$) will give a straight line from which the coloration rate for any film thickness can be determined.

For the BV-PVP system, $\Delta A/A_0$ was used to denote the coloration rate,

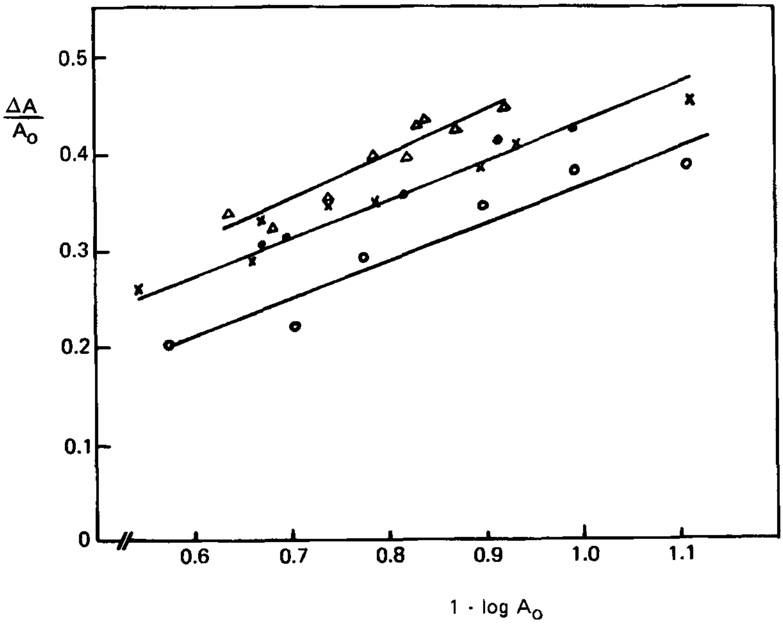

FIG. 1. Effect of humidity on BV coloration rate in PVP matrix. RH: (△) 18%, (X) 55%, (●) 73%, (○) 82%.

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where $\Delta A = A_0 - A$, A being the absorbance after 10 s of UV irradiation. A plot of $\Delta A/A_0$ versus $(1 - \log A_0)$ is shown in Fig. 1. This result confirms that obtained by Kamogawa et al., i.e., the coloration rate increases as the humidity decreases.

For the BV-PVA system, a fairly good straight line can be obtained by plotting $1/A$ against irradiation time t, and the coloration rate constant may be expressed by the slope k. A plot of k versus $(1 - \log A_0)$ is shown in Fig. 2, which, however, does not indicate any discernible difference in coloration rate at different humidities.

The linear relationship of $1/A$ to t suggests second-order reduction in the BV-PVA system, which might be interpreted [2] by a mechanism proposed by Ledwith et al. [5]. Kamogawa's mechanism fails to explain the remarkable difference of coloration rate in different polymer matrices. Therefore, the function of the polymer matrix as an electron donor must be considered.

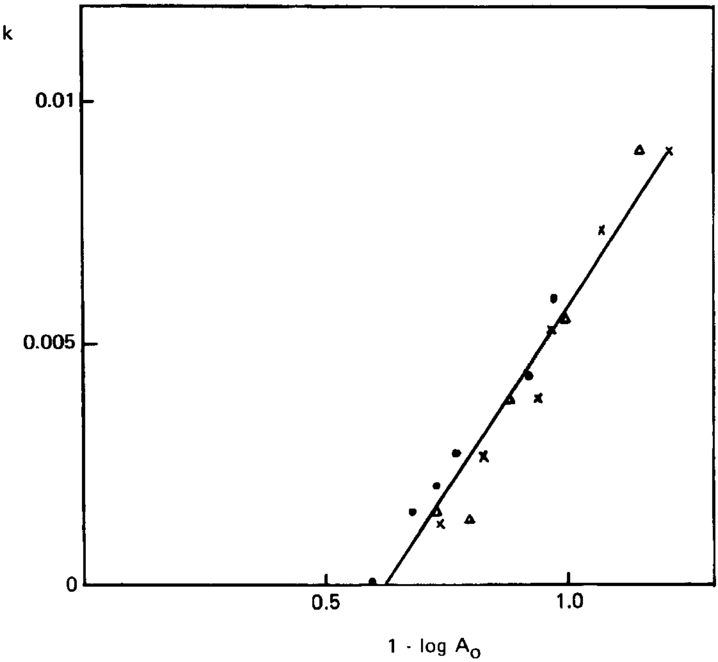

FIG. 2. Effect of humidity on BV coloration rate in PVA matrix. RH: (△) 18%, (X) 73%, (●) 82%.

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B. The Fading Rate

1. Effect of Humidity

The colored films of polybutylviologen bromide (PBV) in PVP matrix were separately placed in desiccators at different RH (18 and 73%, respectively), and the absorbances at 550 nm at certain time intervals were recorded. From the results in Fig. 3, it is obvious that, in the PVP matrix, the fading rate increases as the humidity increases. Since PVP is a highly hygroscopic polymer [6], water would act as a plasticizer and ease the segmental motion of this polymer. As a result, the oxidation of cation radicals (fading) will also be enhanced when the viologen is embedded in the PVP matrix.

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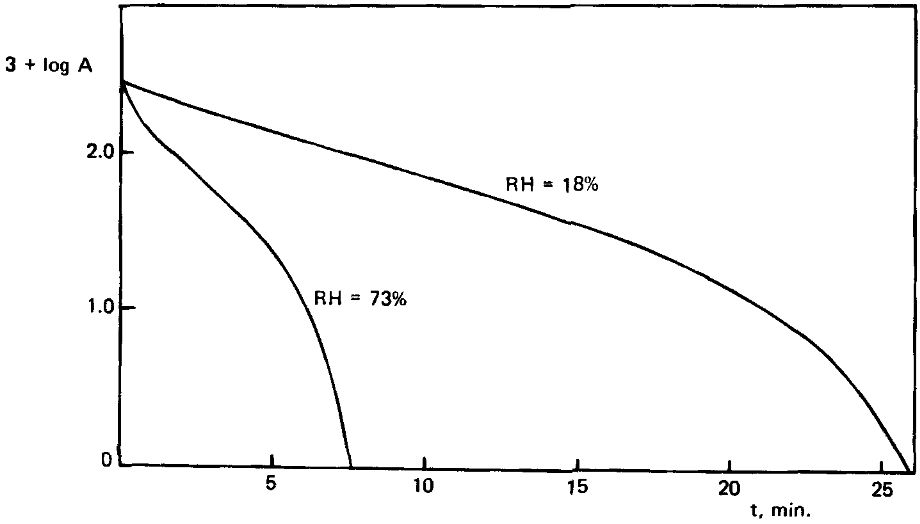

FIG. 3. The fading rate of colored PBV in PVP matrix at different humidities.

2. Effect of Temperature

It is clear from Fig. 3 that, during the initial stage of fading, there exists a linear portion in the fading curve (log A versus t plot). This implies a first-order relationship, and the fading rate constant k_f can be determined. Table 1 lists the fading rate constant k_f at different temperatures. An Arrhenius plot (Fig. 4) gives the activation energy of the fading process as 13 kcal/mol.

While studying the photochromic behavior of solid copolymers of spiropyran, Smets [7] pointed out that, below the glass transition temperature T_g, the effect of temperature on the fading rate is mainly determined by the distribution of free volume throughout the polymer, i.e., the physical state of the glassy polymer. The activation energy (below T_g) for this system was determined to be 15 kcal/mol.

C. Reversibility of Coloration-Fading (fatigue property)

Fatigue is one of the most important properties for the evaluation of photochromic materials. Although Kamogawa [8] has stated that viologens

TABLE 1. The Fading Rate Constant k_f at Different Temperatures for the PBV-PVP System[a]

Temperature, °C	k_f, min^{-1}
26.5	0.08
30	0.18
36	0.23
50	0.46

[a] RH = 73%.

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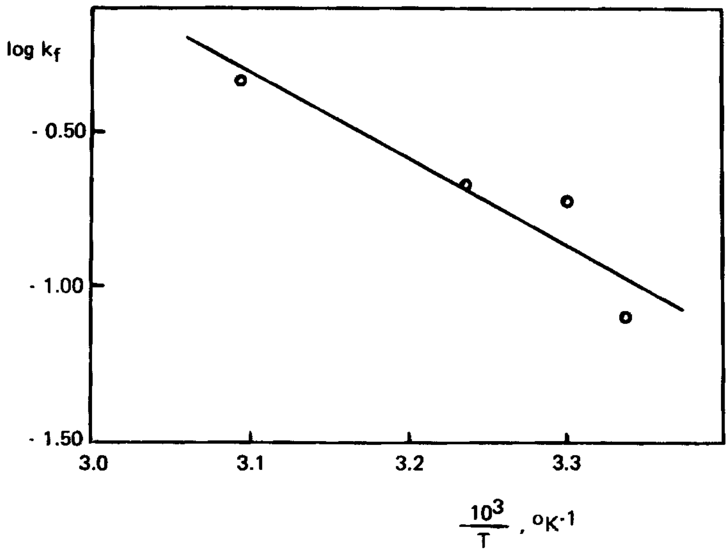

FIG. 4. Arrhenius plot of the fading process of colored PBV in PVP matrix.

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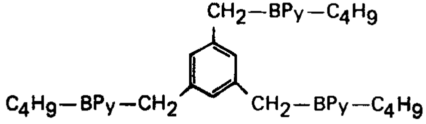
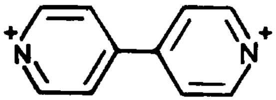
TABLE 2. The Half-Decay Flash Number *F* of Some Viologens and Polyviologens in the PVP Matrix[a]

No.	Polyviologens [b] (bromides)	Irradiation time, min	Maximum absorbance	Monitored wavelength, nm	*F*
1.	C_4H_9–BPy–C_4H_9	2	0.231	610	5
2.	C_2H_5–BPy–C_4H_8–BPy–C_2H_5	2	0.202	610	17
3.		2	0.219	600	29
4.	$\left(C_4H_8\text{–BPy}\right)_n$ (PBV, [η] = 0.160)	1	0.361	550	35
5.	PSt–CH_2–BPy–C_3H_6–BPy–C_3H_6	2	0.226	550	>80

[a] 30 ± 1°C, RH = 82%. Data averaged from three runs.

[b] BPy =



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belong to the most durable organic photochromic materials, no information is yet available in the literature.

Usually, the fatigue of a photochromic material is described in terms of the decrement in absorbance after subtracting the background. For a dilute solution ($<10^{-3}$ *M*) of a rather durable photochromic system, Gautron [9] has suggested a method for the evaluation of fatigue, but this cannot be applied to a film system. Instead, we adopted the repeated number of irradiations needed to lower the net absorbance to half of its maximum (hereafter referred to half-decay flash number and designated by *F*) to characterize the fatigue property of this system [9]. The *F* values of several low molecular viologens and polyviologens in the PVP matrix are listed in Table 2.

Table 2 clearly indicates the better reversibility for polyviologens than for the corresponding lower homologs, *F* increases with increasing number of viologen moieties (BPy) in a molecule (Nos. 1-4). Because of the difficulty in obtaining high molecular weight viologens by the Menschutkin reaction (the $[\eta]$ of PBV used in this work was 0.160), we introduced the viologen moieties as side groups into polystyrene (substitution ~ 60%) and observed a significant improvement in fatigue (No. 5). It is well known that the cation radicals of polyviologens exist mainly in associated forms [except for poly(ethylviologen)], which are more stable than the monomeric species, and it is believed that the stability of the former prevents them from being further reduced to the second reduction state which is less reversible. The yellowing of the films after repeated UV exposure reveals the existence of the second reduction states, and this is also indicated by the appearance of a new peak at 315 nm in the UV spectra.

Further study along the line of obtaining viologens with higher degrees of association of their cation radicals is now in progress.

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