

PHOTOREDUCTION OF ALKYL VIOLOGENS AND POLYVIOLOGENS IN 2-PROPANOL AQUEOUS SOLUTION

LIANG Zhaoxi (梁兆熙) LI Wen (黎文) and LI Manfu (李曼孚)

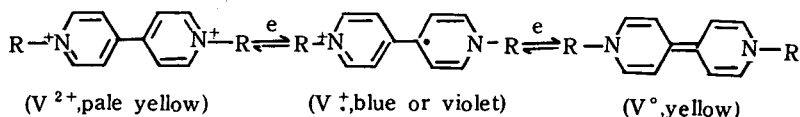
(Institute of Polymer Science, Zhongshan University, Guangzhou)

ABSTRACT

In order to study the effect of alkyl chain length and the polymer effect on the photoreduction behavior of some viologens, a series of alkyl viologen, polyviologen and bisviologen compounds have been synthesized. In the presence of excess 2-propanol, the initial photoreduction of alkyl viologens and polyviologens follow the pseudo-second-order reaction, the calculated rate constants are related to the alkyl chain length. In addition, the intramolecular association of radical cations of polyviologens has been found even in dilute solution. However the extent of association is varied with the alkyl chain length. The observed polymer effect of polyviologens in the photoreduction is significant which can be explained in terms of the nature of second order reaction.

INTRODUCTION

The N, N-disubstituted 4, 4'-dipyridinium compound known as the viologen is a kind of redox compound which can undergo two-step reduction with obvious color changes by chemical, electrochemical or photochemical methods.



Viologen has been of great interest not only for its photochromic character but also for its use as an electrochromic display material, and electron-transfer catalyst, as well as in photochemical system designed for solar energy conversion.

In 1970 Ledwith studied the photoreduction of paraquat dihalides in aqueous alcoholic solutions and proposed a mechanism for these reactions^[1,2]. Later in 1981 Furue investigated the photoreduction of viologen containing vinyl polymers, such as polystyrene attached with pendant viologen and some bisviologen compounds^[3,4]. They interpreted all observed results, including the variation of rate and structure of reduced species, in terms of "local concentration effect".

Since 1981, we have synthesized some main chain viologen containing polymers^[5] and investigated their chemical reduction behaviors^[6]. Further, we studied the photo-reduction rate of polyviologens in PVA (polyvinylalcohol) or other water-soluble polymer matrices^[7].

In this paper, we have directed our attention to the photo reduction of alkyl viologen compounds in 2-propanol aqueous solution. In order to study the effect of alkyl chain length of viologens and polymer effect on the photoreduction, a series of viologen compounds, such as alkyl

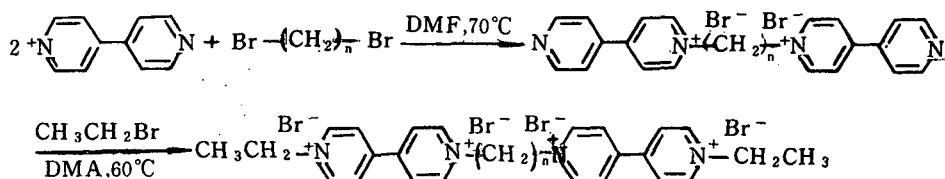
viologen $\text{H}-\text{CH}_2\text{N}^+\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\text{H}$ ($n=1, 2, 3, 4, 5, 6, 7, 8, 9$ MV, EV, PrV, BV, PeV, HxV, HpV, OV, NV, respectively); polyviologen $\left[\text{N}^+\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\right]_m$ ($n=1, 2, 3, 4, 5, 6, 7, 8, 9, 10$ PMV, PEV, PPrV, PBV, PPeV, PHxV, POV, PNV, PDV, respectively); and bisviologen $\text{CH}_3\text{CH}_2\text{N}^+\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\text{N}^+\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\text{CH}_3$ ($\text{V}-(\text{CH}_2)_n-\text{V}$, $n=1, 2, 3, 4, 5, 6, 7, 8, 9, 10$) have been synthesized. The photoreduction behavior of these compounds in 2-propanol aqueous solution has been investigated by means of electro spectroscopy.

EXPERIMENTAL

Materials

Alkyl viologens and polyviologens were prepared using Menshutkin reaction as described in our previous article^[5]. The products were recrystallized from acetonitrile or washed with ethyl ether and dried under vacuum.

Bisviologens were prepared according to the following procedure:



All the viologen compounds were characterized by elemental analyses, ^1H NMR and IR spectroscopy.

Photoreduction

A viologen sample in aqueous solution of 2-propanol at pH 6.8 (phosphate buffer) was introduced into a quartz cell, then oxygen-free nitrogen was bubbled through for 10 min., and sealed. The solution was irradiated for different time intervals by a 250 W high pressure mercury lamp.

Measurement

The formation of radical cations $\text{V}^{\cdot+}$ or $\text{PV}^{\cdot+}$ was monitored with a Shimadzu UV-240 UV-visible spectrophotometer at ambient temperature ($25 \pm 2^\circ\text{C}$). The absorption spectral characteristic of viologen compounds are shown in [6].

Other measurement

A Model 384 Polarographic Analyzer was used for the measurement of reduction potentials. A Model 303 static mercury drop electrode was used as working electrode, Ag/AgCl electrode as reference and Pt wire as counter electrode.

RESULTS AND DISCUSSION

The absorption spectra of photoreduced species

Fig. 1a, 1b show the absorption spectra of hexylviologen under UV irradiation. The absorption maxima at 396, 603nm, attributed to the formation of radical cation, increased gradually with

time (Fig. 1a). However, under prolonged exposure, the absorbance of radical cation decreases gradually and peaks at 230 and 375nm arise simultaneously which indicate the further reduction of the radical cation (Fig. 1b). In addition, similar results are also observed for other alkyl viologens.

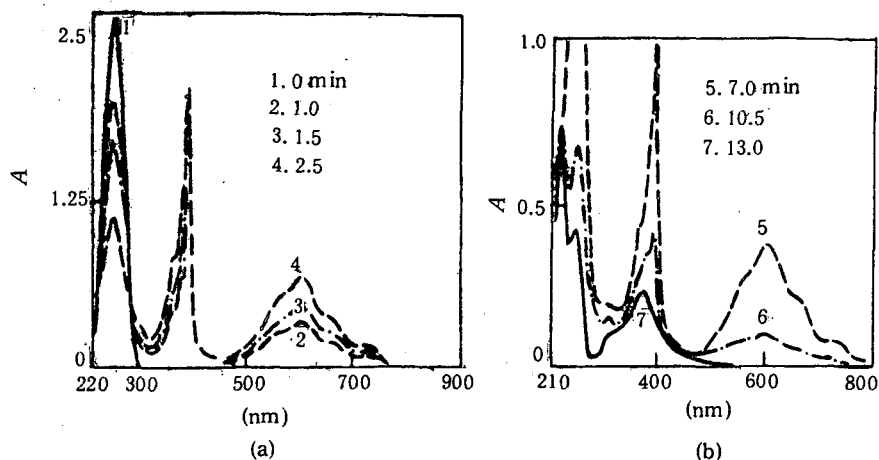


Fig. 1 Absorption spectra of H_xV in photoreduction $[H_xV^{2+}] = 1.13 \times 10^{-4}M$, $[2-PrOH] = 1.0M$, pH 6.8

The UV-visible absorption spectra of some polyviologens in 2-propanol aqueous solutions before and after irradiation are shown in Fig. 2.

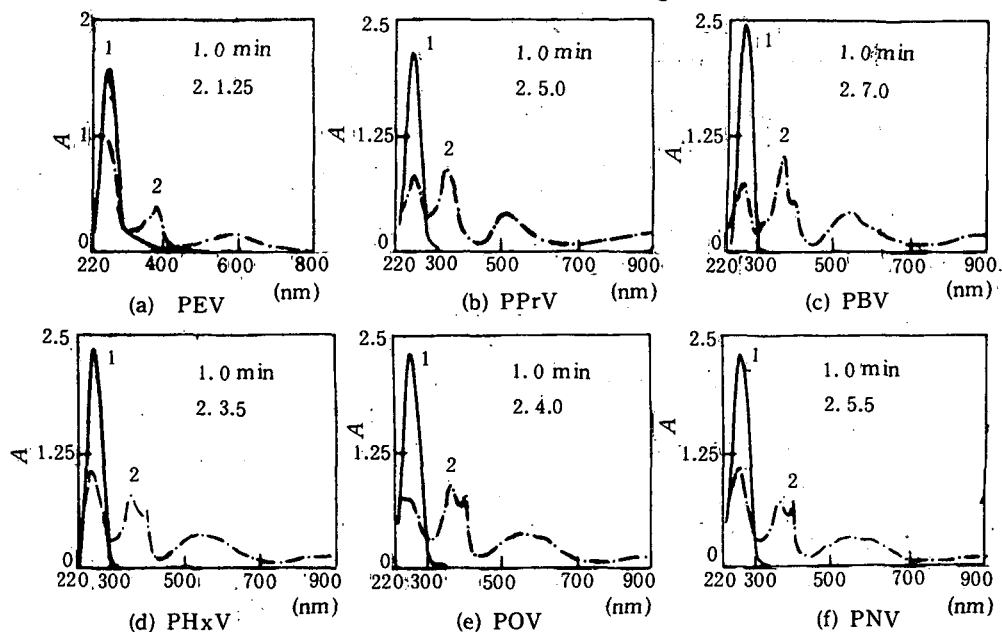
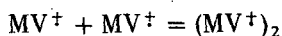


Fig. 2 Absorption spectra of some polyviologens in photoreduction $[PV^{2+}] = 1 \times 10^{-4}M$, $[2-PrOH] = 1.0M$, pH 6.8

In the case of MV, it is known that an equilibrium exists between monomeric and dimeric associated species: [8]



The monomeric form has maxima at 393 and 603nm and the dimeric at 350, 503 and 880nm respectively. The appreciable hypsochromic absorption shifts clearly show that some kind of intramolecular association of V^+ groups occurs in the polymer chain. In the case of $n = 3$, the absorption spectrum shown maxima at 350, 503, 880nm indicates the radical cations having a strong tendency to associate (Fig. 2b). Since the concentration of polyviologen is so low, then, only the intramolecular but not intermolecular association is possible to take place. When $n > 3$, the longer intervening polymethylene chain, the less probability of association. But an exception is $n = 2$, only the monomeric form is observed. It is believed that the conformational difficulty precludes the radical cation from association.

Fig. 3 shows the changes of absorption spectra of polyhexylviologen with irradiation time. In both concentration ranges, peak at 350nm increase gradually with increasing time, which indicates the associated form of polyviologen increasing with time. These provide further evidences of intramolecular association of radical cation in dilute solution.

Similar to the hexylviologen, prolonged irradiation of polyhexylviologen leads to further reduction of polyradical cation, as shown in Fig. 4. But, as compared to monomeric analogues, the radical cation of the polymer is more stable because a longer irradiation time is necessary for further reduction. These facts are further confirmed by the measurement of their reduction potentials.

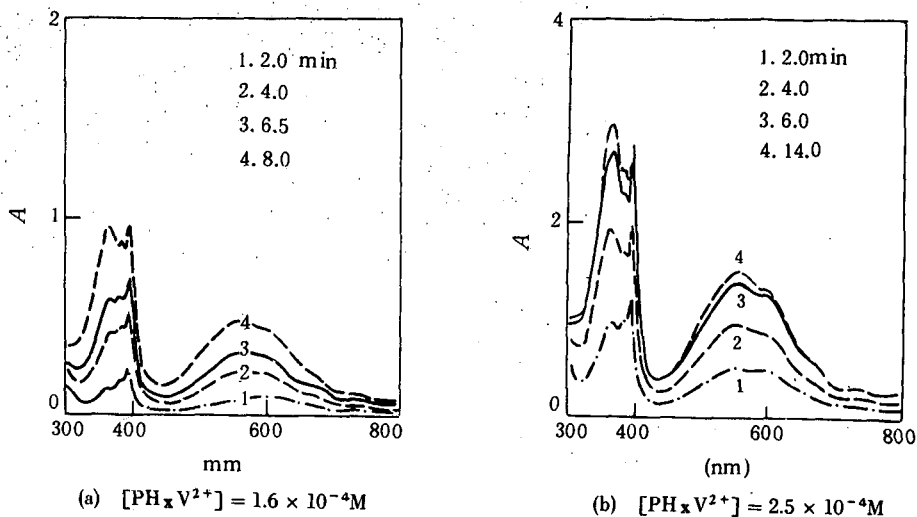


Fig. 3 Absorption spectra of $PH_x V$ in photoreduction
[2-PrOH] = 1.0M, pH 6.8

The photoreduction rates in 2-propanol aqueous solution

In the presence of large amount of 2-propanol, a typical plot of $1/A$ with irradiation time is shown in Fig. 5 where the absorbance A at 262nm represents the concentration of viologen.

Obviously, the initial photoreduction of hexylviologen follows the pseudo-second order reaction law. However, at the later stage, the photoreduction does not follow second order relationship. This deviation probably comes from the side reaction of viologen according to the following sequence:

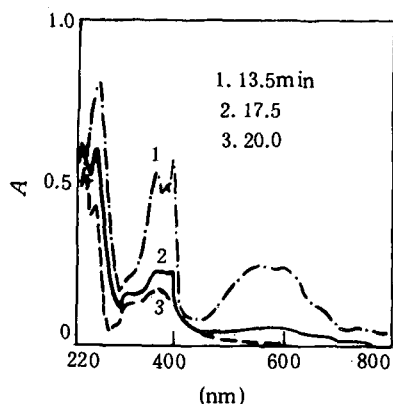
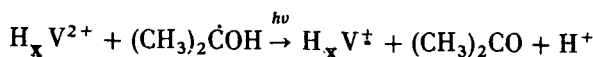
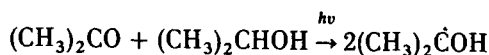


Fig. 4 Absorption spectra of PH_xV in continuous photolysis
 $[\text{PH}_x\text{V}^{2+}] = 1.0 \times 10^{-4} \text{M}$,
 $\text{pH } 6.8$ $[2\text{-PrOH}] = 1.0 \text{M}$

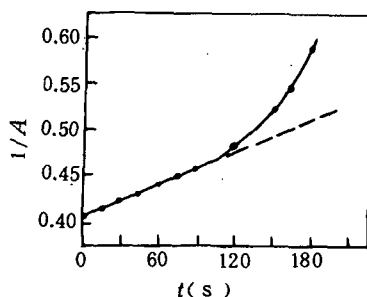


Fig. 5 Plot of $1/[\text{H}_x\text{V}^{2+}]$ vs. irradiation time for photoreduction of H_xV
 A is the absorbance of 262 nm of H_xV^{2+} ($\epsilon = 2.32 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$)
 $[\text{H}_x\text{V}^{2+}] = 1.06 \times 10^{-4} \text{M}$,
 $\text{pH } 6.8$, $[2\text{-PrOH}] = 5.0 \text{M}$

The produced acetone can react with 2-propanol under UV light to form alkoxy radical which can further reduce viologen readily, thus causes the additional consumption of the latter. Moreover, we have observed similar results with other alkyl viologens.

From Eq.1, the pseudo-second order rate constants of alkyl viologen with different alkyl chain length n are calculated.

$$-\frac{d[\text{V}^{2+}]}{dt} = k_0 [2\text{-PrOH}] [\text{V}^{2+}]^2 = k [\text{V}^{2+}]^2 \quad (\text{eq. 1})$$

The results mentioned in Table 1 show that the rate constant k is related to the alkyl chain length n , especially when n is long enough. It seems likely that these viologens with long hydrophobic chains form micellar assemblies in aqueous solution which significantly enhance the photoreduction rates.

Table 1 The pseudo-second-order rate constant k of alkyl viologens

n	1	2	3	4	5	6	7	8	9
$k \times 10^{-1} \text{ (mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}\text{)}$	0.46	0.60	0.61	0.60	0.76	1.33	2.40	3.43	3.40

$$[\text{V}^{2+}] = 1.0 \times 10^{-4} \text{M}, [2\text{-PrOH}] = 5.0 \text{M}, \text{pH } 6.8$$

Similarly, the rate constants of polyviologens and their model compounds — bisviologens are determined and collected in Tables 2 and 3.

Table 2 The pseudo-second-order rate constant k of polyviologens

n	2	3	4	5	6	6	6	8	9	10
$[\eta](\text{dl/g})^a$	0.084	0.121	0.179	0.221	0.202	0.250	0.319	0.308	0.375	0.462
$k \times 10^{-1b}$ ($\text{mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}$)	5.78	1.25	1.86	2.20	1.81	2.43	2.90	4.59	5.95	8.18

A, 30°C formamide b, $[\text{PV}^{2+}] = 1.0 \times 10^{-4}M$, $[2\text{-PrOH}] = 5.0M$, pH 6.8

Table 3 The pseudo-second-order rate constant k of bisviologens:

n	2	3	4	5	6	8	9	10
$k \times 10^{-1}$ ($\text{mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}$)	1.96	1.35	0.97	0.81	1.32	2.43	4.16	5.68

$[\text{V}^{2+} - (\text{CH}_2)_n - \text{V}^{2+}] = 5.0 \times 10^{-5}M$, $[2\text{-PrOH}] = 5.0M$, pH 6.8

As regards the effect of alkyl chain length, two factors may be taken into account: First is the hydrophobicity, when n is long enough, the increase in hydrophobicity will facilitate the aggregation of viologen units through the forming of micellar assemblies and enhance the photoreduction rate, therefore the k increases with alkyl chain length as observed in the case of $n > 5$. The second factor is the distribution of concentration of V^+ unit, taking account of the second order reaction, in the case of $n < 5$, the viologens with longer intervening polymethylene chains have lower initial rates because of the difficulty for 2-propanol to react with two adjacent viologen units which are rather remotely separated.

As compared the data of Table 2 with Table 3, the same tendency of both polyviologens and bisviologens indicates that the adjacent viologen units play the important role. This fact may be explained in terms of the nature of second order reaction in dilute solution. As indicated in Tables 1 and 2, the initial rate constant of polyviologen is much larger than respective alkyl viologen, this means that the polymer effect is quite remarkable. Furthermore, for polyhexylviologen, three samples with different intrinsic viscosity were prepared for the measurement. As expected, the k value increases with the intrinsic viscosity. According to the mode of second order reaction, it is more favorable for the photoreduction of polyviologen by 2-propanol in a dilute solution because of more viologen units in vicinity within a same polymer chain.

On the other hand, in Table 4 and 5 are listed the first and second reduction potentials of alkyl viologens and relative polymers measured by differential pulse polarographic method. In general, in comparison with respective alkyl viologen, the first reduction potentials of polyviologen are more positive, but the second reduction potentials are more negative. That is to say, from the view of thermodynamics, the polymeric analogue is easier to form radical cation but more difficult to undergo second-step reduction. Therefore the chemical potential of polyviologen is higher than that of monomeric viologen.

Table 4 The reduction potentials of alkyl viologens (Differential Pulse Polarographic Potential DPP)

n	1	2	3	4	5	6	7	8	9
$-E_1(\text{V})$	0.928	0.932	0.924	0.920	0.928	0.864	0.816	0.816	
$-E_2(\text{V})$	1.252	1.212	1.172	1.120	1.052	0.988	0.986	0.984	0.912

E vs. Ag/AgCl, $[\text{V}^{2+}] = 1.0 \times 10^{-4}M$, 0.1M KCl, pH 6.8

Table 5 The reduction potentials of polyviologens

<i>n</i>	2	3	4	5	6	8	9	10
$[\eta]$ (dl/g)	0.084	0.121	0.179	0.221	0.319	0.308	0.375	0.462
$-E_1$ (V)	0.688	0.684	0.788	0.824	0.836	0.824	0.820	0.792
$-E_2$ (V)	1.232	1.192	1.192	1.104	1.124	1.124	1.236	1.028

E vs. Ag/AgCl, $[PV^{2+}] = 1.0 \times 10^{-4} M$, 0.1M KCl, pH 6.8

CONCLUSIONS

1. In the presence of large amount of 2-propanol, the initial photoreductions of alkyl viologens and related polyviologens follows a second order reaction kinetics.
2. The respective rate constants have been calculated, they are related to the alkyl chain length *n*, especially in the case of longer alkyl chain.
3. The polymer effect of polyviologens in the photoreduction is significant. In general, the initial rate constants are larger as compared with respective alkyl viologen and increased with the intrinsic viscosity of polyviologens.
4. The intramolecular association of radical cation occurs within the polymer chain, even though in the dilute solution. However, the extent of association is related to the alkyl chain length.

Keywords:

Viologen; N,N'-dialkyl 4,4'-dipyridinium dihalide; Photoreduction; 2-Propanol

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