**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Liang, Zh. X. , Li, W. and Chen, Y. L.(1990) 'Photoreduction of Alkyl Polyviologens and Their Low Molecular Analogs in PVA Matrix', Journal of Macromolecular Science, Part A, 27: 6, 699 — 709
**To link to this Article: DOI:** 10.1080/00222339009349652
**URL:** http://dx.doi.org/10.1080/00222339009349652

J. MACROMOL. SCI.—CHEM., A27(6), pp. 699–709 (1990)

# PHOTOREDUCTION OF ALKYL POLYVIOLOGENS AND THEIR LOW MOLECULAR ANALOGS IN PVA MATRIX

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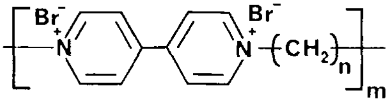
## ABSTRACT

The photoreduction behavior of alkyl viologen compounds in a PVA matrix was investigated. The initial photoreduction of alkyl viologens and related polyviologens follows second-order reaction kinetics, and the respective rate constants, which vary only slightly with alkyl chain length, were determined. While the polymer effect was not remarkable in a PVA matrix, the association behavior of radical cations was similar to that found in a 2-propanol aqueous solution.

## INTRODUCTION

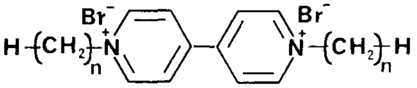
In the presence of a donor, viologen compounds undergo reversible one-electron reduction to form radical cations accompanied with obvious color change. They have therefore been of great interest for use as photochromic materials [1].

Since 1981, we have synthesized some alkyl polyviologens with the main chain structure of (I) [2] and investigated their chemical reduction [3], photoreduction in 2-propanol aqueous solution [4], and photochromism in polymer matrices [5].



(I)

This paper is mainly concerned with the photoreduction behavior of alkyl viologen compounds in a PVA matrix. In order to study the effect of alkyl chain length and the polymer effect on photoreduction, a series of alkyl viologen compounds such as alkyl viologens (II, *n* = 1–9, abbreviated MV, EV, PrV, BV, PeV, HxV, HpV, OV, and NV, respectively), polyviologens (I, *n* = 2–6, 8–10, abbreviated PEV, PPrV, PBV, PPeV, PHxV, POV, PNV, and PDV, respectively), and bisviologens (III, *n* = 1-6, 8–10) has been synthesized and investigated.



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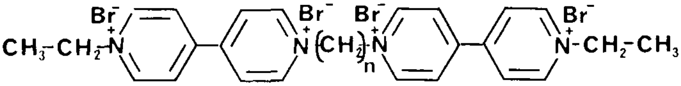


(III)

## EXPERIMENTAL

### Materials

Alkyl viologens, polyviologens, and bisviologens were prepared as described in previous papers [2, 4]. For polyviologens, the intrinsic viscosities were measured in formamide at 30°C and are listed in Table 1.

Polyvinyl alcohol (PVA) was a product with *DP* = 1000–1200 and a degree of hydrolysis of 90%.

### Photoreduction

Photoreduction plates were prepared according to the following procedure. The viologen compound was dissolved in 10% PVA solution at a concentration of $4.5 \times 10^{-3}$ *M*. The solution was coated on a quartz plate and air dried overnight in the dark. The plate was then kept in a desicca-

TABLE 1. The Pseudo-Second-Order Rate Constant $k_m$ of Viologens, Polyviologens, and Bisviologens[a]

| | $k_m \times 10^{-2}$ | | |
|---|---|---|---|
| $n$ | Viologen | Polyviologen ($[\eta]$)[b] | Bisviologen |
| 1 | 0.61 | | |
| 2 | 0.82 | 1.50 (0.084) | 1.78 |
| 3 | 0.87 | 1.58 (0.121) | 1.11 |
| 4 | 0.96 | 1.45 (0.179) | 1.26 |
| 5 | 0.98 | 1.43 (0.221) | 1.38 |
| 6 | 1.08 | 1.41 (0.319)<br>1.16 (0.250)<br>0.91 (0.202) | 1.21 |
| 7 | 1.09 | | |
| 8 | 0.91 | 1.30 (0.308) | 1.46 |
| 9 | 1.01 | 1.56 (0.375) | 1.61 |
| 10 | | 1.61 (0.462) | 1.80 |

[a] RH = 30%.

[b] Intrinsic viscosity measured in formamide at 30°C.

tor (containing saturated $CaCl_2$ aqueous solution) at room temperature for 24 h to control the humidity (relative humidity 30% at 25°C).

Irradiation was carried out by using a 250-W high-pressure Hg lamp at a distance of 20 cm. A quartz plate coated only with PVA was used as a reference.

## Measurement

The absorption spectra used for monitoring the formation of radical cations $V^{\dagger}$ or $PV^{\dagger}$ were measured with a Shimadzu UV-240 UV-visible spectrophotometer at ambient temperature (25 ± 2°C).

The ESR spectra were recorded by using a JEOL-FEIXG ESR spectrometer. Samples were prepared by dissolving the viologen compound in 2-propanol/$H_2O$ (volume ratio = $^2/_3$) at a concentration of $5.0 \times 10^{-4}$ *M*. The solution was added to an ESR tube, and $N_2$ was passed through for 20 min. The sample tube was then irradiated using a 250-W high-pressure Hg lamp. The appearance of blue color was an indication of the formation of radical cations.

## RESULTS AND DISCUSSION

### The Absorption Spectra of Photoreduced Species

Figure 1 shows typical spectral changes of methyl viologen with irradiation. The absorption maxima at 398 and 608 nm, attributed to the formation of radical cations, increase gradually with time. The spectra of other alkyl viologens in a PVA matrix normally change in the same manner. Compared with the monomeric analogs, the photoreduced radical cations of alkyl polyviologens may exist in dimeric form with maxima at 350, 503, and 880 nm (Fig. 2). Thus the color of the film may appear as blue, purplish blue, or purplish red according to the extent of association, which in turn depends on the alkyl chain length. These interesting results indicate that the radical cations of polypropyl viologen have a strong tendency to associate either in dilute aqueous solution or in the solid state (Fig. 2c). When $n = 8$–$10$, the spectra are similar to Fig. 2(f), that is to say, when $n > 3$, the longer the intervening polymethylene chain, the less probable is the association. However, when $n \leq 2$, the radical cations mainly exist in monomeric form, probably owing to the conformation difficulty to associate. These results are similar to that of photoreduction carried out in 2-propanol aqueous solution. Moreover, as the model compounds of alkyl polyviologens, alkyl bisviologens show a similar photoreduction behavior in a PVA matrix as do their polymeric analogs (Fig. 3).

In order to obtain further evidence for the association of radical cations, we investigated the ESR spectra of reduced species produced by photoreduction in 2-propanol aqueous solution. As expected, MV and EV exhibited strong ESR signals (Figs. 4a and 4b) with hyperfine structures similar to the results reported by Johnson and Gutowsky [6]. An interesting finding was that PEV shows an ill-resolved spectrum compared with EV (Fig. 4c). In contrast, no ESR signal of PPrV was detected, which means that PPrV has a strong tendency to associate because

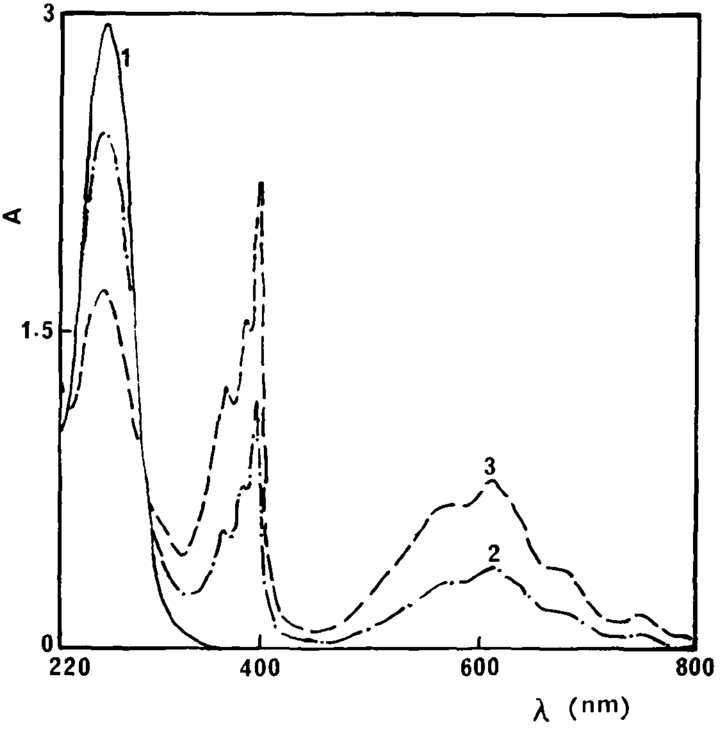
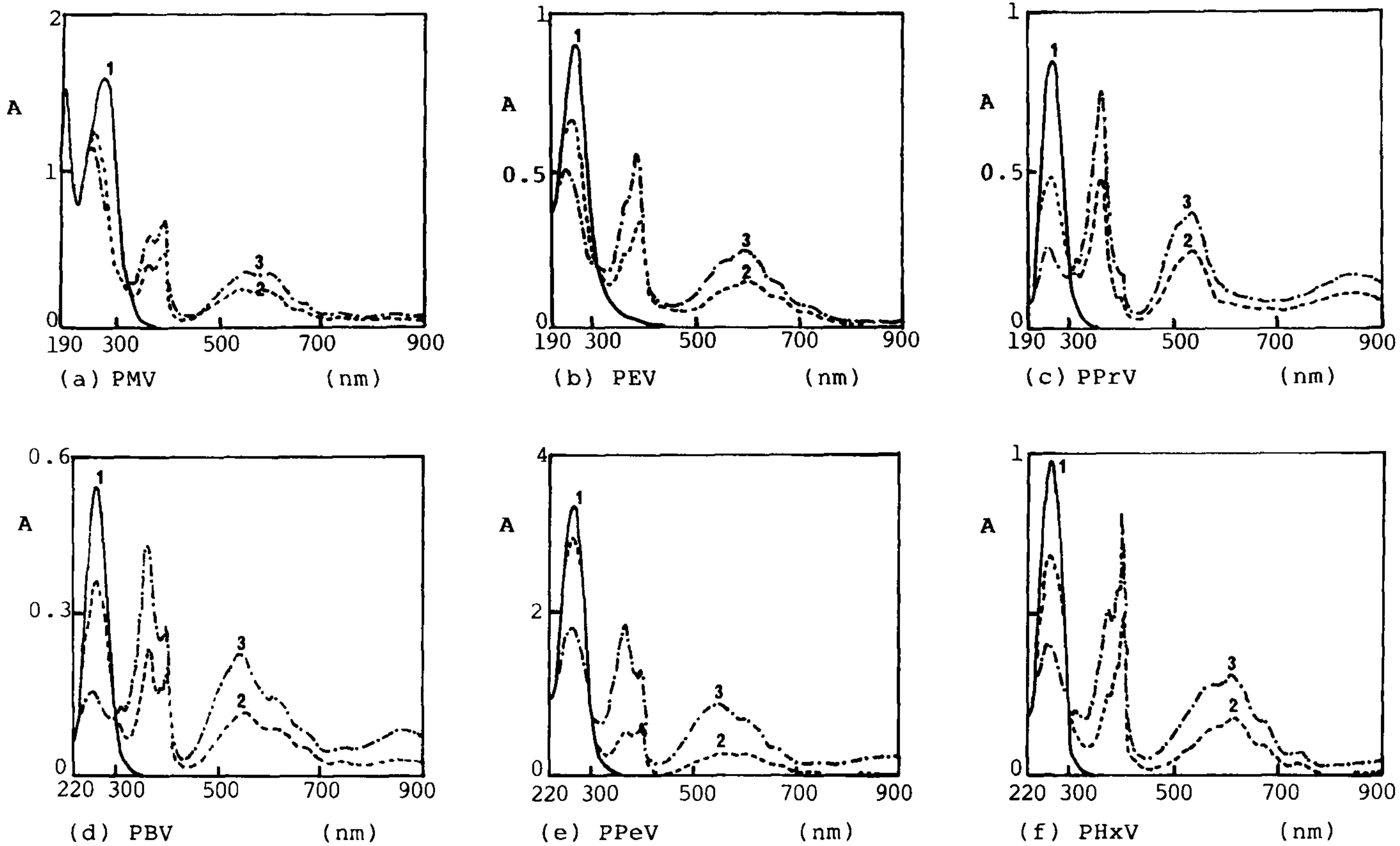


FIG. 1. Spectral changes of methyl viologen with irradiation. Curves 1, 2, and 3 correspond to irradiation times of 0, 1, and 2 min, respectively.

the dimeric form was known to be diamagnetic. It is very interesting that the same association tendency of polyviologen radical cations was observed either in solution or in a polymer matrix. However, the molecular motions are quite different in these two cases. Thus the mechanism of association is worthy of further investigation.

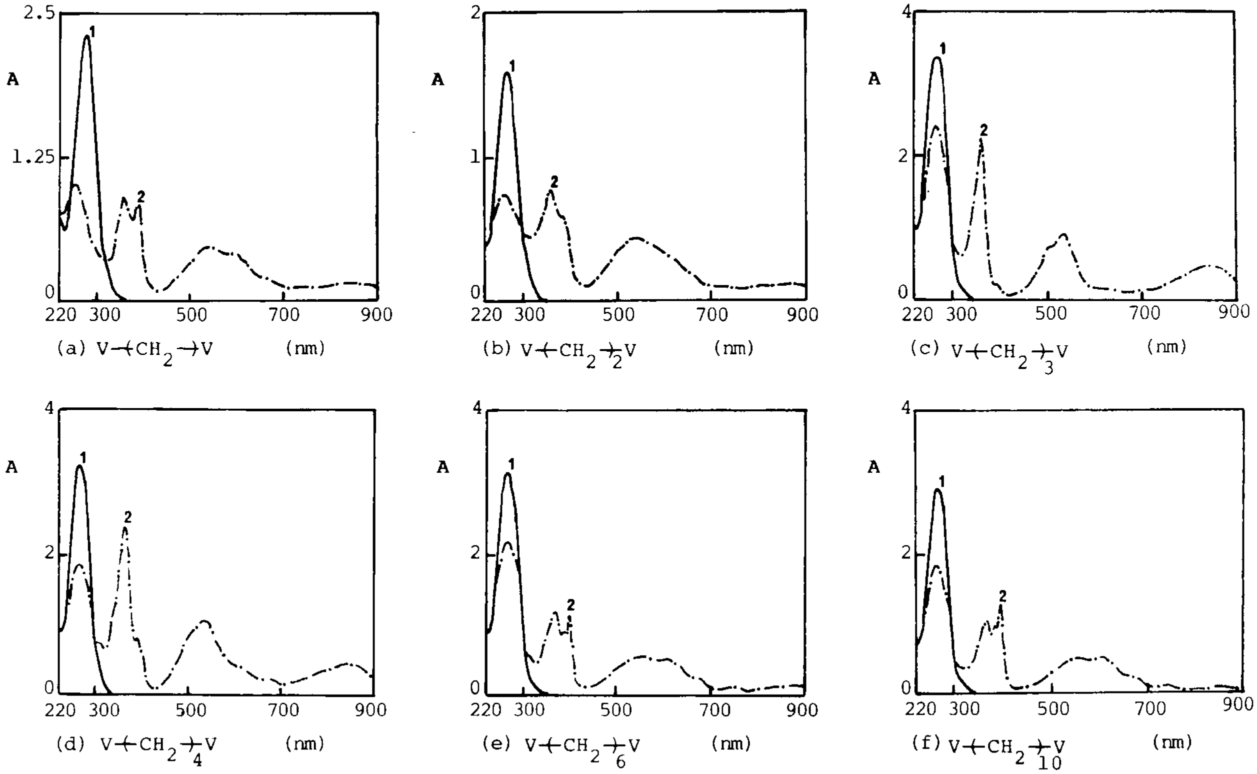
## The Photoreduction Rates in PVA Matrix

In a PVA matrix the photoreduction of viologen compounds can take place readily without the addition of other donors, which indicates that PVA not only acts as a binder but also as a donor in this process. Following the mechanism proposed by Ledwith [7] for the photoreduction of



(a) PMV
(b) PEV
(c) PPrV
(d) PBV
(e) PPeV
(f) PHxV

FIG. 2. Spectral changes of alkyl polyviologens during photoreduction in a PVA matrix. Curves 1, 2, and 3 correspond to irradiation times of 0, 0.5, and 1.5 min, respectively (RH = 30%).



(a) $V-(CH_2)-V$

(b) $V-(CH_2)_2-V$

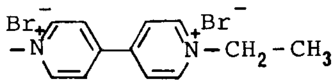
(c) $V-(CH_2)_3-V$

(d) $V-(CH_2)_4-V$

(e) $V-(CH_2)_6-V$

(f) $V-(CH_2)_{10}-V$

FIG. 3. Spectra of bisviologens in a PVA matrix before (1) and after (2) photoreduction (RH = 30%). V denotes



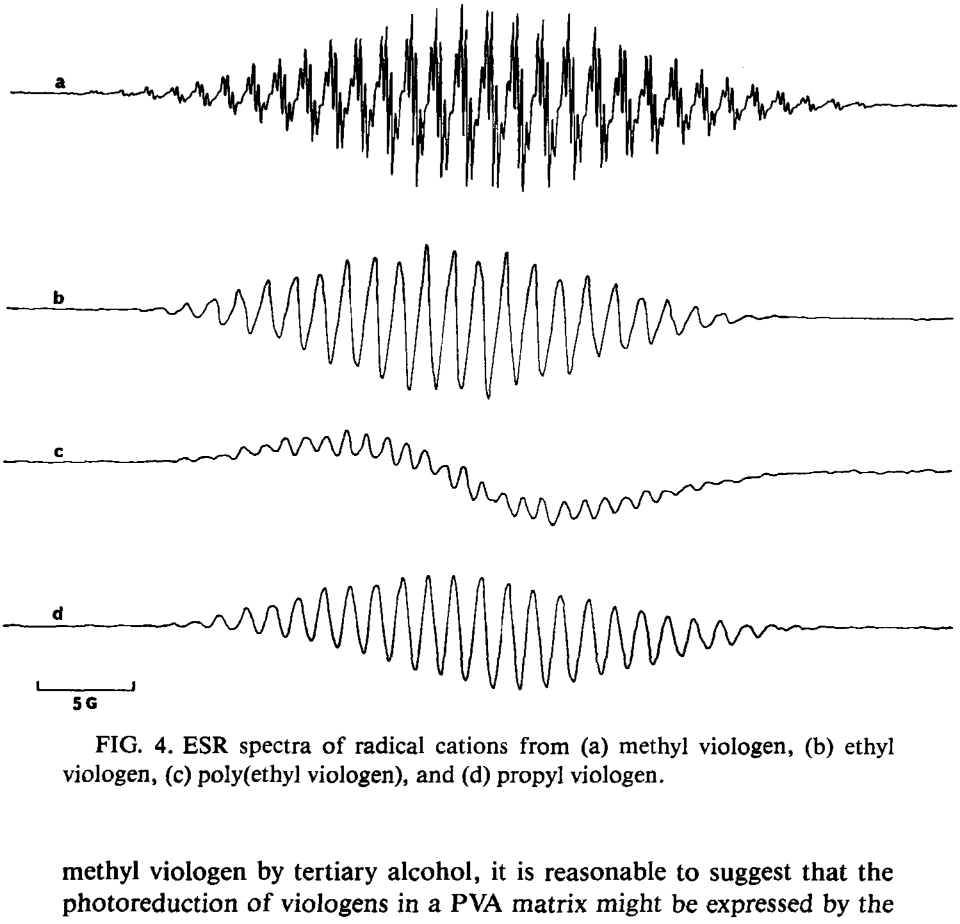
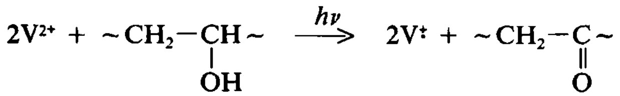


FIG. 4. ESR spectra of radical cations from (a) methyl viologen, (b) ethyl viologen, (c) poly(ethyl viologen), and (d) propyl viologen.

methyl viologen by tertiary alcohol, it is reasonable to suggest that the photoreduction of viologens in a PVA matrix might be expressed by the following reaction:



$$2V^{2+} + \sim CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}\sim \xrightarrow{h\nu} 2V^{+\cdot} + \sim CH_2-\underset{\displaystyle O}{\underset{\|}{C}}\sim$$

This becomes a pseudosecond-order reaction when the concentration of viologens is quite low, and this is the case in our experiment. Figure 5 is a typical plot of $1/A$ with irradiation time, where $A$ is the absorbance of the viologen (HxV) at 262 nm in a PVA matrix, and hence $A$ represents the concentration of the viologen. The rate constant $k_m$ can be calculated

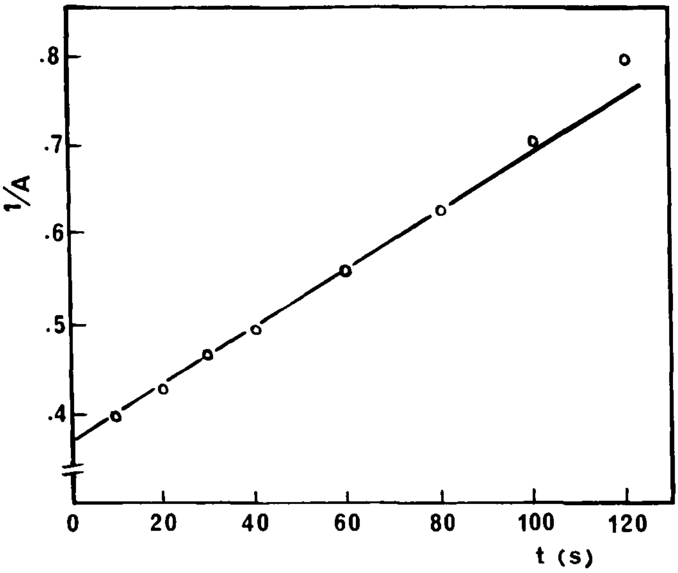


FIG. 5. The variation of the reciprocal absorbance (1/$A$) of HxV at 262 nm with time $t$. (In the PVA matrix, $A_0$ = 2.157, RH = 30%.)

from the slope of the straight line. However, the $k_m$ values thus obtained were found to vary with the initial absorbance $A_0$, which in turn was determined by the film thickness. Fortunately, we found [4] that a fairly good linear relationship exists between ln$k_m$ and ln$A_0$ (Fig. 6). Therefore, the influence of film thickness may be eliminated by taking the $k_m$ values at $A_0$ = 1. These values are summarized in Table 1.

Generally, the $k_m$ values of alkyl polyviologens are slightly larger than those of the monomeric analogs. Furthermore, the $k_m$ value increases with the intrinsic viscosity of PHxV, which may be explained in terms of the mode of the second-order reaction.

However, as regards the effect of alkyl chain length on photoreduction rates, only a slight influence has been found as compared with the photoreduction carried out in 2-propanol aqueous solution. This difference may be attributed to the solid state where the molecular motion is assumed to be frozen.

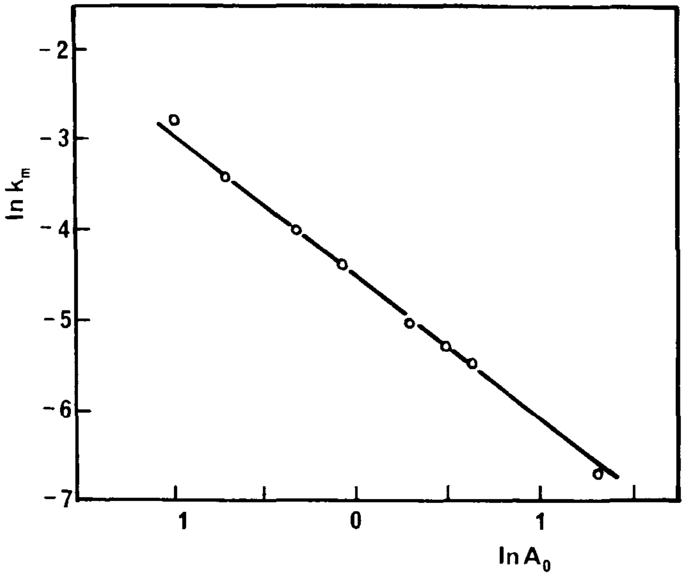


FIG. 6. A ln$k_m$ versus ln$A_0$ plot of HxV in a PVA matrix. $k_m$ is the pesudo-second-order rate constant of photoreduction, and $A_0$ is the absorbance of HxV at 262 nm before irradiation.

## CONCLUSIONS

1. The initial photoreduction of alkyl viologens and related polyviologens in a PVA matrix follows second-order reaction kinetics. The respective rate constants $k_m$ have been calculated, and they vary only slightly with the alkyl chain length.
2. The $k_m$ values of alkyl polyviologens are slightly larger than those of the monomeric analogs. This "polymer effect" is not as apparent as that observed in photoreduction carried out in 2-propanol aqueous solution.
3. Whether in PVA matrix or in dilute 2-propanol aqueous solution, a similar association behavior of radical cations of polyviologens has been observed.

## ACKNOWLEDGMENT

The authors wish to thank Mr. Liao Xi for his help in making the ESR measurements.

## REFERENCES

[1] H. Kamogawa, *J. Polym. Sci., Polym. Chem. Ed., 22*, 393 (1984).

[2] Wen Li, Xiaoming Long, Zhaoxi Liang, and Manfu Li, *Acta Scientiarum Naturalium Universitatis Sunyatseni, 4*, 105 (1985).

[3] Manfu Li, Zhaoxi Liang, and Wen Li, *Ibid., 1*, 94 (1986).

[4] Zhaoxi Liang, Wen Li, and Manfu Li, *Chinese J. Polym. Sci., 5*(3), 252 (1987).

[5] Y. L. Chen, Y. J. Guan, Y. L. Mai, W. Li, and Zh. X. Liang, *J. Macromol. Sci.—Chem., A25*(2), 201 (1988).

[6] C. S. Johnson Jr. and H. S. Gutowsky, *J. Chem. Phys., 39*(1), 58 (1963).

[7] A. S. Hopkins, A. Ledwith, and M. F. Stam, *J. Chem. Commun.*, p. 494 (1970).

Received March 31, 1989
Revision received October 4, 1989