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# UNUSUAL PHOTOREDUCTION OF VIOLOGEN BY DIMETHYL SULFOXIDE ON A NEW POLYMER HAVING DIRECT PENDANTS OF VIOLOGEN AND BENZOPHENONE STRUCTURES

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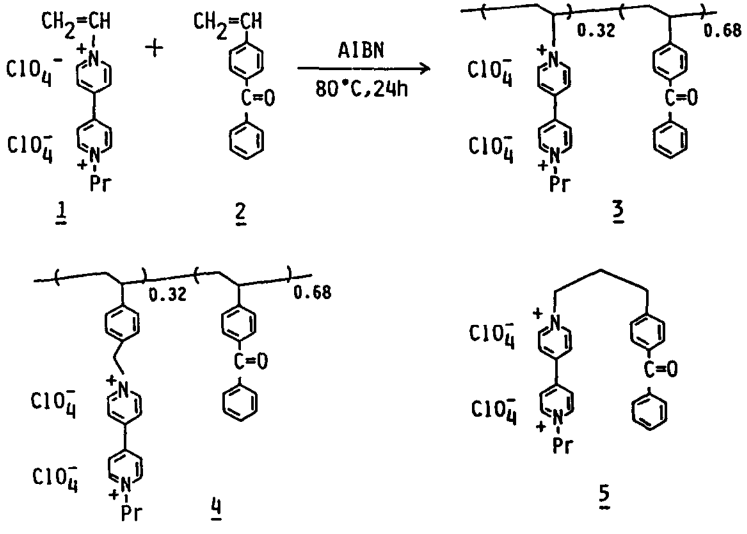
Summary: A new viologen copolymer with direct pendants of viologen and benzophenone structures was effectively photoreduced by dimethyl sulfoxide for the first time derived by the cooperative functional group interactions.

Viologen ($V^{2+}$) is known as an efficient electron transfer mediator in the conversion of photoenergy into chemical energy.[1,2] The photoreduction of viologen by 2-propanol, EDTA and so on sensitized by benzophenone or $Ru(bpy)_3^{2+}$, have been extensively studied.[3,4] In this letter, we describe the unusual photoreduction of viologen in an aprotic medium for the first time on the newly synthesized viologen copolymer.

The copolymer (**3**) having viologen and benzophenone structures as direct pendants was prepared by the radical copolymerization of a new viologen monomer, 1-propyl-1'-vinyl-4,4'-bipyridinium diperchlorate (**1**),[5] and vinyl benzophenone (**2**) with the $V^{2+}$ content of 32.4 mol%.[6] Another copolymer (**4**) having a benzyl group as a spacer between a polymer main chain and the viologen structure was also prepared by the copolymerization of 1-propyl-1'-vinylbenzyl-4,4'-bipyridinium diperchlorate and monomer (**2**) with the $V^{2+}$ content of 32.1 mol%. As a model compound, viologen-benzophenone model (**5**) was also prepared.



**Scheme 1**

A dimethyl sulfoxide (DMSO) solution of copolymer 3 showed a visible absorption ($\lambda_{max}$: 480 and 700 nm, Figure 1) and its maximum wavelength and intensity were linearly correlated with the solvent donacity. In addition, this absorption disappeared by the addition of protic acid (perchloric acid). These results suggested that the charge transfer complexation assisted by the solvent was occurred between the viologen and benzophenone moieties in copolymer 3.[7] A weaker visible absorption was also observed in the model compound at 480 nm but not in copolymer **4** or propyl viologen diperchlorate ($PrV^{2+}$) - benzophenone mixture.

The copolymer solution in DMSO was in turn photoirradiated by xenon lamp ( $\lambda$ > 302 nm).[8] The solution turned to deep blue and the electronic spectrum showed the absorption of the viologen radical cation ($V^{\dot{+}}$) at 610 nm mainly in the monomeric form (Figure 1).

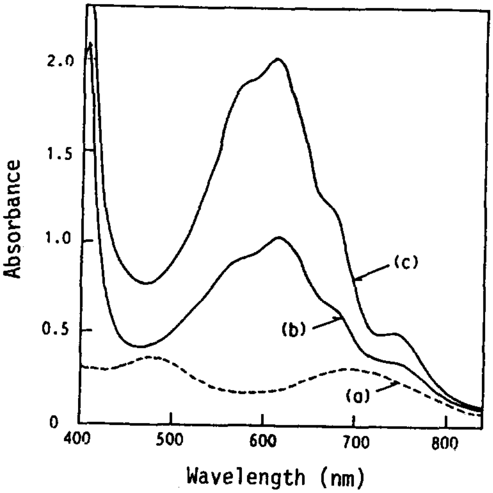


**Figure 1.** Spectral change of copolymer 3 in DMSO (0.35 mM) by photoirradiation with xenon lamp ( $\lambda$ > 302 nm): (a) initial spectrum, (b) irradiated for 3 min., (c) irradiated for 40 min.

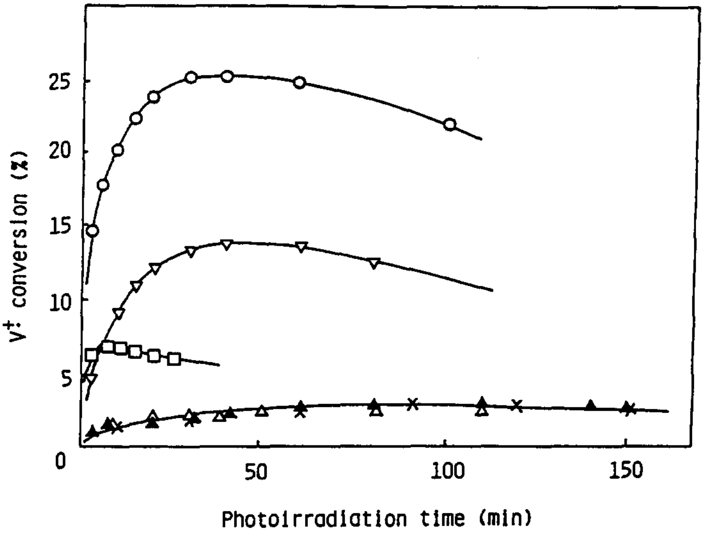


**Figure 2.** Plot of $V^{\dot{+}}$ conversion vs. photoirradiation time for various viologen derivatives in DMSO with the concentration of $V^{2+}$ unit at 0.35 mM: ( ○ ) copolymer **3** ($V^{2+}$: 32.1 mol%), ( □ ) copolymer **4** ($V^{2+}$: 32.4 mol%), ( ▽ ) model compound 5, ( × ) $PrV^{2+}$ alone, ( △ ) $PrV^{2+}$-benzophenone mixture (molar ratio 33:67), ( ▲ ) $PrV^{2+}$-benzophenone mixture (52:48).

The $V^{\ddagger}$ conversion by photoirradiation was estimated from Figure 1 and plotted against the photoirradiation time as shown in Figure 2. The results on the other viologen derivatives are plotted together. From Figure 2, it can be observed that photoirradiation of copolymer 3 gave the highest $V^{\ddagger}$ conversion (25%) followed by its model compound 5 (14%). For copolymer **4**, the $V^{\ddagger}$ conversion was comparatively lower (7%). In addition, the photoirradiation of $PrV^{2+}$ alone or the mixture of $PrV^{2+}$ and benzophenone in DMSO gave very low $V^{\ddagger}$ conversion (3%).[9]

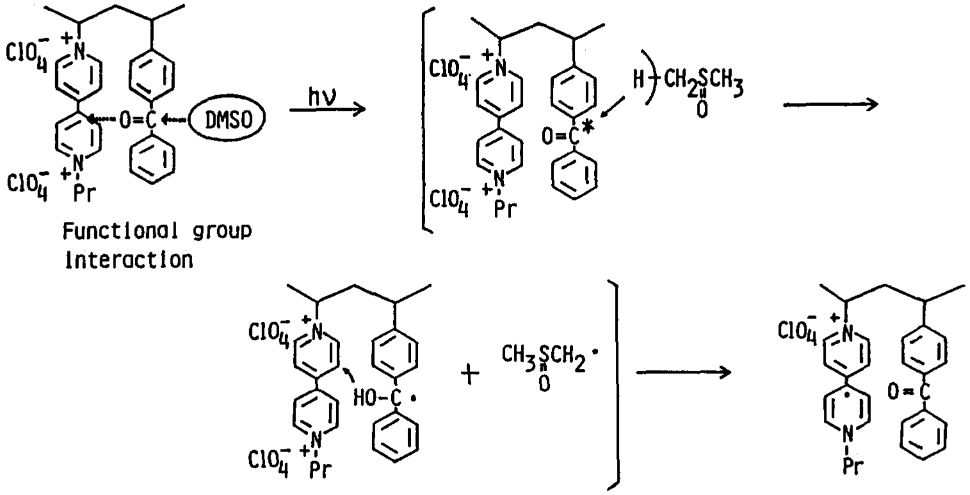
We further investigated to clarify what caused the high $V^{\ddagger}$ conversion on the photoreduction of viologen on copolymer 3 and model compound 5 contrary to the copolymer **4** or $PrV^{2+}$-benzophenone mixture. The $V^{\ddagger}$ conversion in $PrV^{2+}$-benzophenone mixture was the same as that in $PrV^{2+}$ alone and was independent on the amount of benzophenone. This agreed with Gollnick et al.'s findings[10] which stated that benzophenone was not an effective photosensitizer for DMSO dissociation. The photoirradiation of $PrV^{2+}$ with reference compound, 4-(pyridiniumpropyl)-benzophenone (**6**) was also studied, in which a pyridinium salt has the similar inductive effect to the benzophenone structure as that of model 5. But the $V^{\ddagger}$ conversion in this case was almost the same as $PrV^{2+}$-benzophenone mixture, which indicated that the inductive effect of the neighboring pyridinium structure did not enhance the benzophenone as a photosensitized electron mediator. In addition, by the photoirradiation of model compound 5 in acetonitrile, no $V^{\ddagger}$ was formed. Whereas in DMSO-acetonitrile mixture (3:97), $V^{\ddagger}$ was formed in 6 % conversion. This observation assisted that DMSO functioned as the reducing agent.

Photoirradiation of copolymer with the visible light ( $\lambda > 450$ nm) was ineffective for the formation of $V^{\ddagger}$ The CT complex formation was then affected the enhancement of the ability of hydrogen abstraction in the excited benzophenone.

Consequently, the unusual photoreduction is explained as follows. With the benzophenone structure being linked to the viologen structure by the $C_3$ linkage as occurred in copolymer 3 and the model compound 5, both groups have a favorable conformation to stack each other to show the solvent assisted charge transfer interaction as observed in its electronic spectrum, and the activated benzophenone by this interaction was able to abstract hydrogen even from DMSO to form ketyl radical effectively by photoirradiation, which then reduce the viologen to form $V^{\ddagger}$ (Scheme 2).

The enhanced photoreduction in copolymer 3 compared to the model compound is presumed that in the copolymer the benzophenone and viologen structures are directly linked to the polymer main chain to be much suitable for the stacking of both groups, and the specific functional group interaction effective for the photoreduction by Scheme 2 could be strengthened.

In conclusion, we could succeeded in the effective photoreduction of viologen by the aprotic solvent, dimethyl sulfoxide, for the first time, by designing the new viologen copolymer with viologen and benzophenone structures stacked each other. These findings are interesting in the expectation for new photochromic materials or viologen mediated new photoreactions in the aprotic medium. The detailed study on the photo efficiency irradiated by the monochromic light or photoreduction catalyzed by these copolymers are in progress.



Scheme 2

## References and Notes

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6 Radical copolymerization of monomers (**1** and **4**) and (**2**) was carried out in γ-butyrolactone (30 M) with azobisisobutyronitrile (2 mol%) as an initiator at 80 °C for 24 h to obtain powdery copolymers (**3** and **4**) in 68 % and 30 % yield, respectively.

7 The similar charge transfer spectrum was observed in the copolymer of (**1**) and methyl methacrylate, Y. Nambu, K. Yamamoto, and T. Endo, Macromolecules, 22, 3530 (1989).

8 The DMSO solution ($V^{2+}$: 0.35 mM) of copolymer (**3** or **4**), model compounds (**5**), $PrV^{2+}$, or $PrV^{2+}$-benzophenone mixture was irradiated by xenon lamp ( $\lambda > 306$ nm) in the UV cell stoppered with the three way cock after bubbling with argon gas for 10-20 min.

9 DMSO is reported to form radical species such as methyl, sulfinyl, and dimsyl radicals by photolysis[6] and these radicals may reduce viologen to its radical cation though ineffectively.

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