

Photopolymerization of Methyl Methacrylate with Methyl Viologen- $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in Aqueous-Organic, Two-Phase System

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ABSTRACT: The photopolymerization of methylmethacrylate (MMA) with methyl viologen (MV^{2+})- $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 initiator was studied in aqueous-organic two-phase system. The initial rate (R_p) of photopolymerization was proportional to the square root of fed quantity of initiator components, MV^{2+} , $\text{Na}_2\text{S}_2\text{O}_4$, and CCl_4 , respectively. R_p , however, decreased when MV^{2+} or CCl_4 was fed beyond a certain value. R_p also gradually decreased in the presence of a large excess of CCl_4 . A cyclic phase-transfer initiation system has been proposed for this photopolymerization on the basis of MV^+ cation radical disproportionation.

KEY WORDS Photopolymerization / Methyl Methacrylate / Methyl Viologen / Sodium Dithionite / Carbon Tetrachloride / Phase Transfer /

In the previous paper¹ authors reported that methyl methacrylate (MMA) was photopolymerized with 1-benzyl-1,4-dihydronicotinamide (BNAH) and CCl_4 in CH_2Cl_2 . The polymerization was suggested to be initiated according to the following mechanism: A hydrogen atom transfers from the photoexcited BNAH* to CCl_4 yielding BNA· radical and CCl_3 · radical. The BNA· reacts with CCl_4 to produce 1-benzyl nicotinamide chloride (BNA^+Cl^-) together with CCl_3 · radical. The produced BNA^+Cl^- also photodecomposes into BNA· and Cl · radicals. Both the CCl_3 · and Cl · initiate the polymerization.

The authors also reported that MMA was photopolymerized with 1-benzyl nicotinamide chloride (BNA^+Cl^-)- $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 as an initiator system in MMA-water two-phase system and that the following cyclic phase-transfer photoinitiation was suggested for this photopolymerization.

BNA^+Cl^- produced in organic phase by the reaction of the photoexcited BNAH* with CCl_4 transfers to aqueous phase, in which BNA^+Cl^- is reduced with $\text{Na}_2\text{S}_2\text{O}_4$ to BNAH under alkaline condition.

In this paper, authors used methyl viologen (MV^{2+}) instead of BNA^+Cl^- in the initiator system for the photopolymerization of MMA, because MV^{2+} has been known to be reduced easily to MV^+ cation radical.² MV^{2+} - Na_2O_4 - CCl_4 was also found to act as an initiator system in a similar manner as BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 , and the initiation mechanism with MV^{2+} - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic two-phase system will be suggested according to the results of the kinetic studies.

EXPERIMENTAL

Materials

MMA was purified by usual method just

before use. Water was deionized and distilled. Methyl viologen dichloride ($MV^{2+}Cl^{2-}$) of reagent grade (Tokyo Kasei Kogyo Co.) was used without further purification. All other chemicals used in the study were also reagent grade.

Photopolymerization

Two-phase photopolymerizations were performed by the use of photochemical reaction apparatus which was described in detail in the previous paper.³ A 150 cm³ reaction vessel was charged with 20 cm³ of MMA solution containing CCl₄ (10 mmol) and 80 cm³ of aqueous solution containing $MV^{2+}Cl^{2-}$ (0.1 mmol), Na₂S₂O₄ (45 mmol), and Na₂CO₃ (45 mmol). The contents in the reaction vessel was blown with pure nitrogen and was irradiated by a Fuji Glass High Pressure Mercury Lamp HL-100 (100W). After irradiation, the reaction mixture was poured into a large quantity of methanol and the precipitated polymer was filtered, washed with water and methanol, and dried *in vacuo*.

RESULTS AND DISCUSSION

Methyl viologen (MV^{2+}) dichloride, known as paraquat, is widely used as a herbicide, and has also attracted much attention in the studies of solar energy system,^{4,5} since the one-electron reduction product, methyl viologen cation radical ($MV^{+\cdot}$) is a strong reductant capable of reducing protons to molecular hydrogen in the presence of ruthenium(II)-tris(bipyridine).⁶ 1,1'-Dimethyl-4,4'-bipyridylidene (MV) is also produced by two-electron reduction with a suitable reducing agent from MV^{2+} (Figure 1). Therefore, methyl viologen (MV^{2+}) acts as an

effective electron transfer catalyst at room temperature in the reduction of aromatic aldehydes⁷ and ketones⁸ by Na₂S₂O₄.

To an aqueous solution of MV^{2+} was added an aqueous solution of Na₂S₂O₄ and Na₂CO₃ under nitrogen, then the blue color of viologen cation radical was observed. The blue color disappeared immediately by the addition of CCl₄-containing MMA. By the irradiation of UV light MMA polymerized without induction period, and the conversion reached to 12.7% after one hour (Table I). In every case where one of these components was excluded the rate

Table I. Photopolymerization of MMA with MV^{2+} -Na₂S₂O₄-CCl₄ in aqueous organic, two-phase system^a

MV^{2+}	Na ₂ S ₂ O ₄	CCl ₄	Conversion
mmol	mmol	mmol	%
0.1	45	10	12.7
—	45	10	3.7
0.1	—	10	2.7
0.1	45	—	0

^a MMA, 20 cm³; H₂O, 80 cm³; Na₂CO₃, 45 mmol; temp, 303 K; time, 1 h; blowing rate of N₂, 0.5 cm³ s⁻¹.

Table II. Photopolymerization of MMA with MV^{2+} -reductant-CCl₄ in aqueous-organic two phase system^a

Reductant	mmol	Conversion/%
Na ₂ S ₂ O ₄	45	12.7
NaHSO ₃	45	3.4
Na ₂ SO ₃	45	1.1
—	—	2.1

^a MMA, 20 cm³; H₂O, 80 cm³; MV^{2+} , 0.1 mmol; CCl₄, 10 mmol; Na₂CO₃, 45 mmol; temp, 303 K; time, 1 h; blowing rate of N₂, 0.5 cm³ s⁻¹.

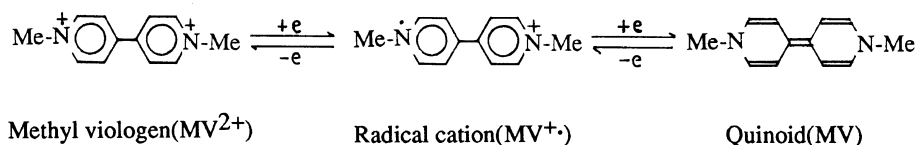


Figure 1. Redox system of Methyl viologen.

of polymerization was remarkably suppressed. In particular the polymerization was not induced at all without CCl_4 . When NaHSO_3 or Na_2SO_3 was used instead of $\text{Na}_2\text{S}_2\text{O}_4$, the rate of photopolymerization was also very slow as expected from their reducing activities (Table II).

For the photopolymerization of MMA with MV^{2+} – $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 , all the conversion–time relations were linear. The initial rates of photopolymerization (R_p) were plotted against the square root of fed quantity of initiator

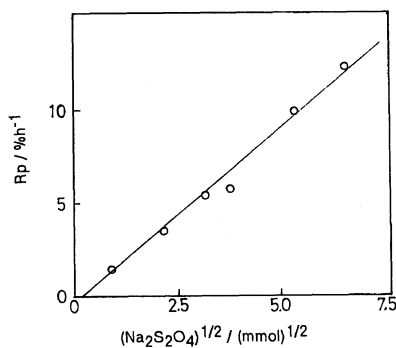


Figure 2. Relation of R_p vs. $(\text{Na}_2\text{S}_2\text{O}_4)^{1/2}$ for the photopolymerization of MMA with MV^{2+} – $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in aqueous–organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; MV^{2+} , 0.1 mmol ; Na_2CO_3 , 45 mmol ; CCl_4 , 10 mmol ; temp, 303 K .

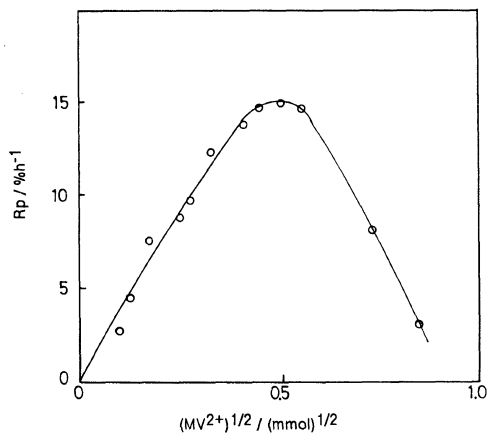


Figure 3. Relation of R_p vs. $(\text{MV}^{2+})^{1/2}$ for the photopolymerization of MMA with MV^{2+} – $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in aqueous–organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; $\text{Na}_2\text{S}_2\text{O}_4$, 45 mmol ; Na_2CO_3 , 45 mmol ; CCl_4 , 10 mmol ; temp, 303 K .

components, MV^{2+} , $\text{Na}_2\text{S}_2\text{O}_4$, and CCl_4 , respectively and linear relationships were observed between them (Figures 2–4). R_p , however, remarkably decreased when MV^{2+} increased beyond a certain value. These results showed that the growing polymer radical would be terminated by 1,1'-dimethyl-4,4-bipyridylidene (MV) or stable $\text{MV}^{\cdot+}$ cation radical. In the presence of a large excess of CCl_4 R_p gradually decreased. This would imply that the growing polymer radical could be also terminated by CCl_3^{\cdot} .

Willner and coworkers⁹ reported on the

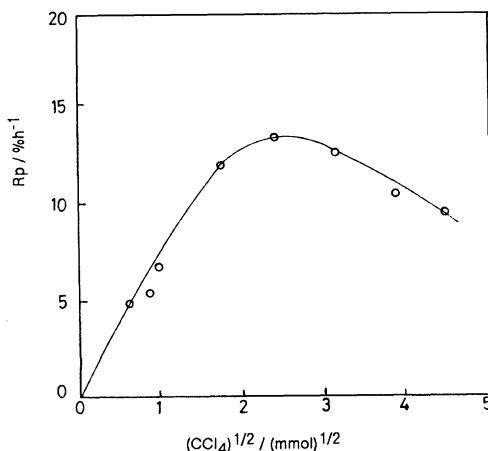


Figure 4. Relation of R_p vs. $(\text{CCl}_4)^{1/2}$ for the photopolymerization of MMA with MV^{2+} – $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in aqueous–organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; MV^{2+} , 0.1 mmol ; $\text{Na}_2\text{S}_2\text{O}_4$, 45 mmol ; Na_2CO_3 , 45 mmol ; temp, 303 K .

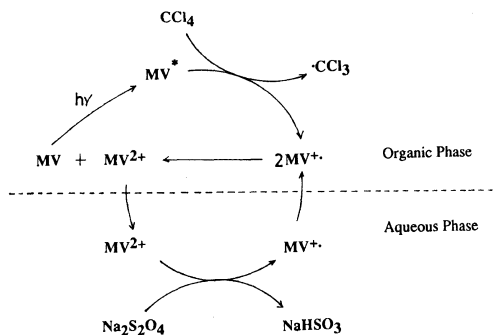
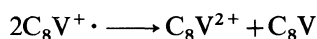


Figure 5. Scheme for polymerization of MMA with MV^{2+} – $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in aqueous–organic, two phase system.

chemical and photochemical debromination of 1,2-dibromodiarylethanes to 1,2-diarylethyl- enes *via* phase transfer system consisted of dioctyl viologen (C_8V^{2+}) and $Na_2S_2O_4$, and emphasized that the active species in the reduction process is a two-electron reduction product, dioctylbipyridylidene (C_8V) which is derived from the radical disproportionation according to the following equation rather than dioctyl viologen cation radical ($C_8V^{+\cdot}$).



The radical disproportionation like this would be also expected in $MV^{2+}-Na_2S_2O_4-CCl_4$ system, which allows us to suggest an initiation mechanism as shown in Figure 5. MV^{2+} in aqueous phase was reduced by $Na_2S_2O_4$ into $MV^{+\cdot}$, which transferred from aqueous phase into organic phase due to its hydrophobic property. In organic phase, $MV^{+\cdot}$ disproportionates to give, 1,1'-dimethyl-4,4'-bipyridylidene (MV) and MV^{2+} . As the hydrophilic MV^{2+} is apt to transfer into aqueous phase, the equilibrium of the disproportionation reaction shifts to MV and MV^{2+} side due to such opposite solubility properties of $MV^{+\cdot}$ and MV^{2+} . However, MV dissolved in organic phase reacts with CCl_4 photochemically yielding $MV^{+\cdot}$ and CCl_3^{\cdot} , and the latter initiates the polymerization of MMA at once. MV, however, could not be isolated from the polymerization system because of its instability.¹⁰

In order to clarify whether $MV^{+\cdot}$ reacts with

CCl_4 or not before the disproportionation reaction the dark-polymerization was carried out under the same conditions as that of the photopolymerization. In these conditions, however, MMA did not polymerize at all.

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