Tris(2,2'-Bipyridine)Ruthenium(II)-Sensitized Photopolymerization of Acrylamide

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ABSTRACT: Photopolymerization of vinyl monomers sensitized by tris(2,2'-bipyridine)-ruthenium(II) complex ($Ru(bpy)_3^{2+}$) was studied in polar solvents. No vinyl monomer tested was photopolymerized in the presence of sensitizer $Ru(bpy)_3^{2+}$ alone under irradiation of visible light. Acrylamide (AA) was found to be photopolymerized in the presence of both the sensitizer and an electron donor triethylamine. The photopolymerization of AA did not occur in the presence of the sensitizer and methylviologen as an electron acceptor, but did in the coexistence of KSCN. In these systems the photosensitizer $Ru(bpy)_3^{2+}$ was not consumed during the polymerization. The photopolymerization mechanisms for the $Ru(bpy)_3^{2+}$-sensitized systems are discussed.

KEY WORDS   Tris(2,2'-Bipyridine)Ruthenium(II) Complex / Photo-sensitizer / Acrylamide / Photopolymerization / Photoredox Reaction / Photoinduced Electron-Transfer Reaction / Flash Photolysis /
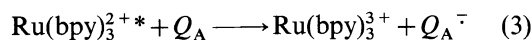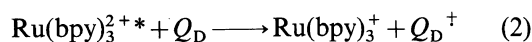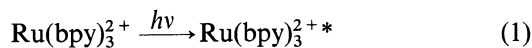
Many papers have been published on the metal complex-sensitized photopolymerization of vinyl monomers.[1,2] We have studied the photopolymerization of vinyl monomers using amminecobalt(III) complexes as sensitizers which can absorb light in the visible region.[3-7] Most of the excited metal complexes such as amminecobalt(III) complex decompose to form active species which can initiate the polymerization of vinyl monomers, and are consumed during the photopolymerization. If such complexes act as electron-transfer type photosensitizers as shown in Scheme 1, where A and D are an electron-accepting and an electron-donating molecule or monomer, respectively, the complexes would be regenerated by the two successive electron-transfer processes and would not be consumed. Therefore, we investigated the photopolymerization of vinyl monomers using tris(2,2'-bipyridine)ruthenium(II) complex $Ru(bpy)_3^{2+}$ as a photosensitizer which could absorb light in the visible region.
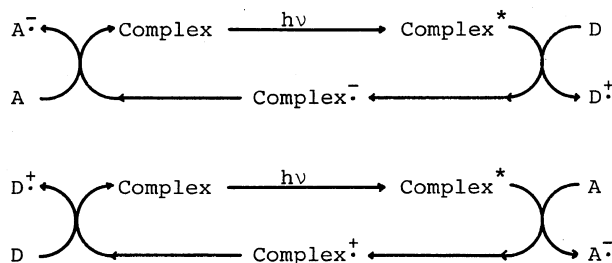
Scheme 1.

Ruthenium complexes are familiar and useful photosensitizers in the conversion and storage of light energy.[8,9] The ruthenium complex $Ru(bpy)_3^{2+}$ is chemically stable and does not readily undergo photochemical loss of ligands unlike many other metal complexes. Visible light absorption by $Ru(bpy)_3^{2+}$ yields the metal-to-ligand charge-transfer excited state $Ru(bpy)_3^{2+}*$. It reacts with electron donors and acceptors, and these electron-transfer reactions convert $Ru(bpy)_3^{2+}*$ into $Ru(bpy)_3^+$ and $Ru(bpy)_3^{3+}$, respectively, according to the following equations,

$$Ru(bpy)_3^{2+} \xrightarrow{hv} Ru(bpy)_3^{2+}* \qquad (1)$$

$$Ru(bpy)_3^{2+}* + Q_D \longrightarrow Ru(bpy)_3^+ + Q_D^+ \qquad (2)$$

$$Ru(bpy)_3^{2+}* + Q_A \longrightarrow Ru(bpy)_3^{3+} + Q_A^- \qquad (3)$$

where Q_D and Q_A are an electron-donating and an electron-accepting quencher, respectively. The former resulting ruthenium complex is a more powerful reductant and the latter is a more powerful oxidant than $Ru(bpy)_3^{2+}*$ itself.

We have designed the $Ru(bpy)_3^{2+}$-sensitized photopolymerization systems where the sensitizer could be regenerated by two successive electron-transfer reactions. In the present paper, the photopolymerization of vinyl monomers such as acrylamide (AA) sensitized by $Ru(bpy)_3^{2+}$ was studied in polar solvents such as H_2O and N,N-dimethylformamide (DMF). We found two kinds of the photopolymerization systems where $Ru(bpy)_3^{2+}$ as the photosensitizer was not consumed during the polymerization. The polymerization mechanisms for these systems are discussed.

EXPERIMENTAL

Materials

$[Ru(bpy)_3^{2+}]Cl_2 \cdot 6H_2O$ was prepared from $RuCl_3$ and $2,2'$-bipyridine according to the method of Barstall.[10] Acrylamide (AA) was recrystallized twice from benzene. Methacrylamide and N-vinylcarbazole were recrystallized from CH_2Cl_2 and methanol, re-

spectively. Acrylonitrile, methacrylonitrile, acrylic acid, and styrene were treated in the usual way and distilled under reduced pressure. Triethylamine (TEA, Nakarai Chemicals, GR) and methylviologen (MV^{2+}, Aldrich) were used without further purifications. N,N-Dimethylformamide (DMF) was distilled after drying over CaH_2. CH_3CN was of Dotite Spectrosol Grade and was used without further purification.

Polymerization Procedure

A freshly prepared sample solution was degassed by four freeze-pump-thaw cycles on a vacuum line, and then sealed into a quartz reaction cell with a volume of 4 ml, 1 cm in thickness. The photopolymerization was carried out under irradiation at 30°C. An Ushio 500 W Xenon lamp was used for a stationary light source through a cutoff filter (Toshiba UV-39) for the selective excitation of $Ru(bpy)_3^{2+}$. All of these procedures were carried out in a dark room. The polymers were isolated by precipitation with appropriate precipitants such as methanol. The rate of polymerization was estimated by weighing the precipitated polymer. The molecular weight of poly(AA) was measured by GPC and calibrated by poly(ethylene oxide) standards.

Measurements

Absorption spectra were recorded on a Hitachi model 124 spectrophotometer. The emission intensities were measured with a Shimadzu RF-502A spectrofluorometer. The flash photolysis apparatus was the same in previous papers.[7,11] A freshly prepared sample solution was degassed by four freeze-pump-thaw cycles on a vacuum line and then sealed into a cylindrical Pyrex cell with an optically flat quartz bottom, about 1 cm in diameter and 10 cm in length. The decay curve was measured by a grating spectrophotometer (Narumi RM-23-I) with a photomultiplier (Hamamatsu TV 1P28) and a synchroscope (Iwatsu SS-5157).
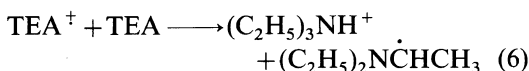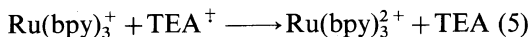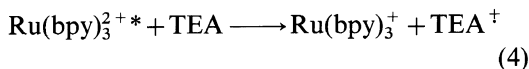
RESULTS AND DISCUSSION

Initiation by $Ru(bpy)_3^{2+*}$

Photopolymerization of electron-accepting monomers such as AA, acrylic acid, and methacrylamide, and of electron-donating monomers such as N-vinylcarbazole and styrene was studied in polar solvents such as DMF and H_2O in the presence of $Ru(bpy)_3^{2+}$. No polymer was obtained in our experimental conditions ($[Ru(bpy)_3^{2+}] = 1 \times 10^{-4}$ M, [monomer] ≥ 1 M). These findings indicate that $Ru(bpy)_3^{2+*}$ cannot initiate the polymerization of these monomers directly. In fact, the emission of $Ru(bpy)_3^{2+*}$ located about 615 nm in DMF was not substantially quenched by any monomers tested. The interactions between $Ru(bpy)_3^{2+*}$ and the monomers were not observed in the experiments of emission and polymerization. Therefore, we designed the photopolymerization systems where active $Ru(bpy)_3^+$ or $Ru(bpy)_3^{3+}$ would be formed by the electron-transfer reactions between $Ru(bpy)_3^{2+*}$ and an electron-donor or -acceptor.

Initiation by $Ru(bpy)_3^{2+*}$–Donor System

Triethylamine (TEA) was used as a reductive quencher for $Ru(bpy)_3^{2+*}$.[12] In the $Ru(bpy)_3^{2+}$–TEA system, $Ru(bpy)_3^{2+}$ excited by visible light is reduced by TEA, yielding $Ru(bpy)_3^+$ and TEA$^+$(eq 4).

$$Ru(bpy)_3^{2+*} + TEA \longrightarrow Ru(bpy)_3^+ + TEA^+ \tag{4}$$

$$Ru(bpy)_3^+ + TEA^+ \longrightarrow Ru(bpy)_3^{2+} + TEA \tag{5}$$

$$TEA^+ + TEA \longrightarrow (C_2H_5)_3NH^+ + (C_2H_5)_2N\overset{\cdot}{C}HCH_3 \tag{6}$$

In CH_3CN and DMF, the accumulation of $Ru(bpy)_3^+$, which had an absorption band located about 510 nm, was observed as shown in Figure 1, since TEA$^+$ reacted with TEA (eq 6)[13] irreversibly. In the case of the addition of vinyl monomers to the photoredox system, some monomers such as AA and acrylonitrile were polymerized, whereas some monomers
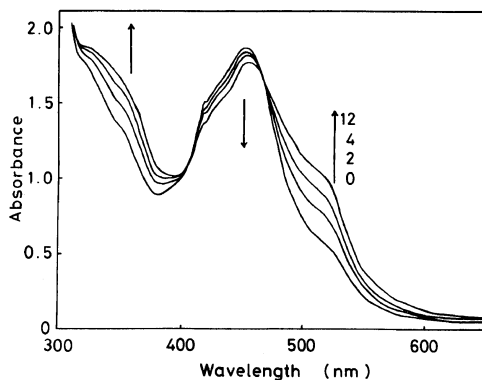

Figure 1. Absorption spectra of $Ru(bpy)_3^{2+}$–TEA system in CH_3CN during visible light irradiation. Inserted numerals are irradiation times in min: $[Ru(bpy)_3^{2+}]$, 1×10^{-4} mol l^{-1}; [TEA], 0.5 mol l^{-1}.

such as styrene and methacrylonitrile were not. Although the emission of $Ru(bpy)_3^{2+*}$ at 615 nm was not quenched by AA and acrylonitrile as described before, it was quenched by TEA in DMF. Therefore, these photopolymerizations of AA and acrylonitrile were not initiated by $Ru(bpy)_3^{2+*}$ directly, but would be initiated by the photoredox products between $Ru(bpy)_3^{2+*}$ and TEA such as $Ru(bpy)_3^+$, TEA$^+$, and its derivatives. When AA and acrylonitrile polymers were obtained, neither the accmulation of $Ru(bpy)_3^+$ nor the decrease of $Ru(bpy)_3^{2+}$ were observed. Because of its high polymerizability, consequently, we studied the $Ru(bpy)_3^{2+}$–TEA–AA system in detail.

Polymerization Behavior of $Ru(bpy)_3^{2+*}$–TEA–AA System

The photopolymerization of the $Ru(bpy)_3^{2+}$–TEA–AA system was carried out by the selective excitation of $Ru(bpy)_3^{2+}$ under the experimental conditions ($[Ru(bpy)_3^{2+}] = 1 \times 10^{-4}$ M, [TEA] = 0.5 M, and [AA] = 2 M). In the polymerization of DMF solutions poly(AA) with a smaller molecular weight of 10^4 order was precipitated, whereas in aqueous solutions water-soluble poly(AA) with a larger molecular weight of 10^5 or-
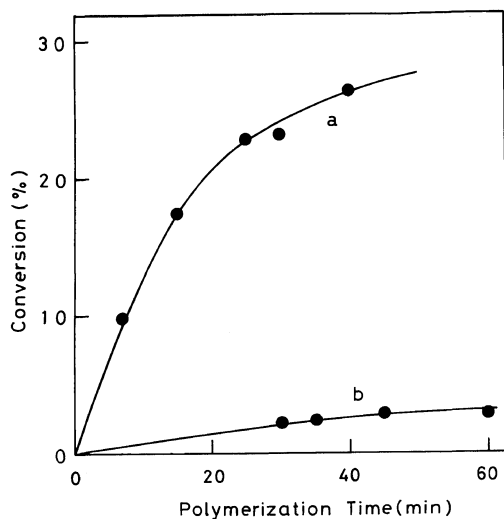
Figure 2. Polymerization time–conversion plots in Ru(bpy)$_3^{2+}$–TEA–AA system in a) H$_2$O and b) DMF: [Ru(bpy)$_3^{2+}$], 1×10^{-4} mol l^{-1}; [TEA], 0.5 mol l^{-1}; [AA], 2 mol l^{-1}.
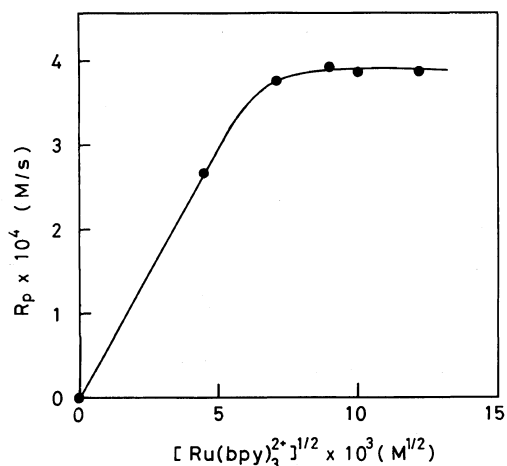
Figure 3. Effects of Ru(bpy)$_3^{2+}$ concentration on R_p: [TEA], 0.5 mol l^{-1}; [AA], 2 mol l^{-1}; solvent, H$_2$O.

der was obtained. The rate of the photopolymerization in H$_2$O was much larger than that in DMF as shown in Figure 2. Consequently, we studied the photopolymerization behavior of the Ru(bpy)$_3^{2+}$–TEA–AA in aqueous soluion systems in detail. As linear relationships between the polymer conversion and the polymerization time were not ob-
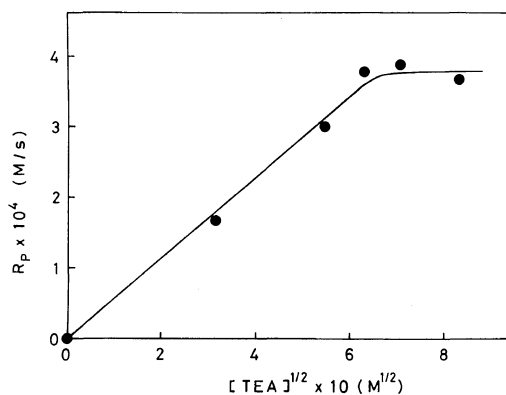

Figure 4. Effects of TEA concentration on R_p: [Ru(bpy)$_3^{2+}$], 1×10^{-4} mol l^{-1}; [AA], 2 mol l^{-1}; solvent, H$_2$O.

Table I. Effects of irradiation mode on polymer conversion[a]

Irradiation mode	Conversion %
Continuous irradiation (40 min)	26.4
Irradiation (30 min) + in dark (20 min) + irradiation (10 min)	27.8

[a] [Ru(bpy)$_3^{2+}$], 1×10^{-4} mol l^{-1}; [TEA], 0.5 mol l^{-1}; [AA], 2 mol l^{-1}; solvent, H$_2$O; temp, 30°C.

tained as seen in Figure 2, the polymerization rate R_p was estimated from the initial slope below 15 min of polymerization time. In Figures 3 and 4 are shown the Ru(bpy)$_3^{2+}$- and TEA-concentration dependence of R_p, respectively. There apperared to be saturation phenomena, probably indicating that R_p depended on the effective concentration of Ru(bpy)$_3^{2+}$* and was not effected by the TEA concentration beyond the complete quenching concentration for Ru(bpy)$_3^{2+}$*. Poly(AA) was not obtained in the dark or in the absence of either Ru(bpy)$_3^{2+}$ or TEA.

The effect of irradiation conditions on the conversion was studied. One mode was a continuous irradiation and the other was an intermittent one. These two modes had the same total irradiation time of 40 minutes. The

results are listed in Table I. These two different irradiation modes gave similar amounts of poly(AA). This finding indicates that this photopolymerization is controlled by the expedient of turning on or off irradiation light.

In general, AA has radical and anionic polymerizabilities. From the facts that the photosensitized polymerization of AA occurred in aqueous solutions and that it was inhibited by the addition of hydroquinone $(1 \times 10^{-2}\,\text{M})$, we conclude that the visible light-induced polymerization of AA in the Ru(bpy)_3^{2+}–TEA–AA aqueous solution system occurred by the radical mechanism.

Photopolymerization Mechanism of Ru-($bpy)_3^{2+}$–TEA–AA in H_2O System

In the absence of AA the accumulation of Ru(bpy)_3^+ was observed by irradiation in DMF solutions as described before, but not in aqueous solutions. However, the μ second flash photolysis of the aqueous solution containing Ru(bpy)_3^{2+} $(5 \times 10^{-5}\,\text{M})$ and TEA $(0.5\,\text{M})$ gave the transient absorption spectrum as shown in Figure 5. The band with a maximum at *ca.* 510 nm was assigned to Ru(bpy)_3^+ owing to its identity with the spectrum of Ru(bpy)_3^+ reported.[14,15] The decay profile of Ru(bpy)_3^+ monitored at 510 nm depended on the AA concentration and the decay constant increased with increasing the concentration of
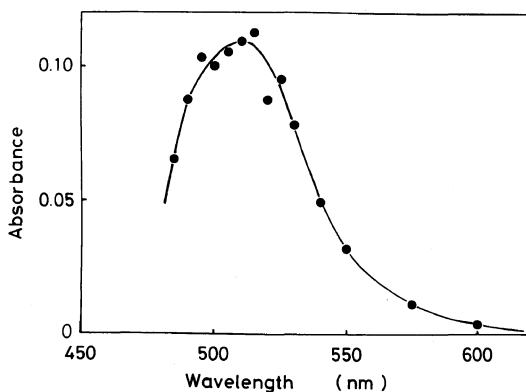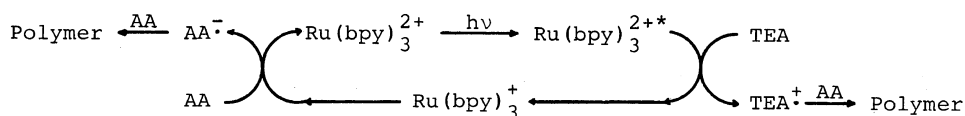

Figure 5. Transient adsorption spectrum of an aqueous solution containing Ru(bpy)_3^{2+} and TEA: $[\text{Ru(bpy)}_3^{2+}]$, $5 \times 10^{-5}\,\text{mol}\,l^{-1}$; [TEA], $0.5\,\text{mol}\,l^{-1}$.

AA added. In addition the fact that the accumulation of Ru(bpy)_3^+ was not observed in the presence of AA even in DMF solutions suggests that AA can oxidize Ru(bpy)_3^+ to Ru(bpy)_3^{2+} with concomitant production of $\text{AA}^{\overline{\cdot}}$ as seen in eq. 7.

$$\text{Ru(bpy)}_3^+ + \text{AA} \longrightarrow \text{Ru(bpy)}_3^{2+} + \text{AA}^{\overline{\cdot}} \qquad (7)$$

In this system Ru(bpy)_3^{2+} is the unconsumable photosensitizer and is regenerated by the two successive electron-transfer processes as shown in Scheme 2. The polymerization of AA is initiated by the resulting products of the photoredox reactions such as TEA^+, $\text{AA}^{\overline{\cdot}}$, and their derivatives. TEA^+ and $\text{AA}^{\overline{\cdot}}$ should

$$\text{Polymer} \xleftarrow{\text{AA}} \text{AA}^{\overline{\cdot}} \begin{array}{c} \nearrow \text{Ru(bpy)}_3^{2+} \xrightarrow{h\nu} \text{Ru(bpy)}_3^{2+*} \searrow \text{TEA} \\ \searrow \text{Ru(bpy)}_3^+ \xleftarrow{\hspace{2cm}} \text{TEA}^{+\cdot} \xrightarrow{\text{AA}} \text{Polymer} \end{array} \xleftarrow{} \text{AA}$$

Scheme 2.

be extremely reactive and their reactions in aqueous media could be started by proton donation to TEA (eq 6) and by proton addition, respectively. The derived radicals $(C_2H_5)_2\text{N}\dot{\text{C}}\text{HCH}_3$ and $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$ could be capable of radical initiation. In aqueous media the radical polymerization initiated by $(C_2H_5)_2\text{N}\dot{\text{C}}\text{HCH}_3$ has not been reported so far

as we know, though the amine radical can initiate the polymerization of vinyl monomers such as methyl acrylate and acrylonitrile in organic solvents.[16-18] The photoreduction of TEA in aqueous media leads efficiently to CH_3CHO and $(C_2H_5)_2\text{NH}$.[19,20] From these we could speculate that $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$ derived from $\text{AA}^{\overline{\cdot}}$ contributes significantly to the ini-
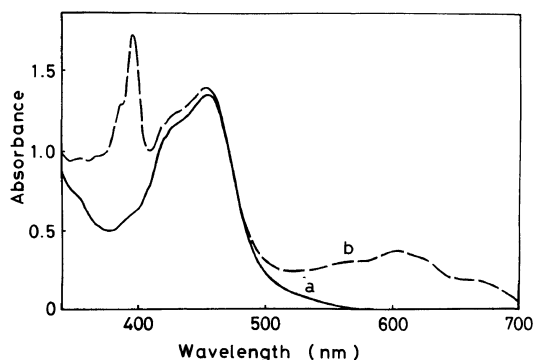
Figure 6. Absorption spectra of $Ru(bpy)_3^{2+}$–MV^{2+}–KSCN–AA system in H_2O: $[Ru(bpy)_3^{2+}]$, 1×10^{-4} mol l^{-1}; $[MV^{2+}]$, 1×10^{-2} mol l^{-1}; [KSCN], 1×10^{-2} mol l^{-1}; [AA], 1 mol l^{-1}; (a) before irradiation; (b) after irradiation for 40 min.

tiation of polymerization.

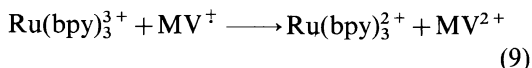*Initiation by $Ru(bpy)_3^{2+}$*–*Acceptor System*

Methylviologen (MV^{2+}) is a familiar electron acceptor for $Ru(bpy)_3^{2+}$* since it was first reported by Whitten et al.[21] In the $Ru(bpy)_3^{2+}$–MV^{2+} system $Ru(bpy)_3^{2+}$* is oxidized by MV^{2+}, yielding $Ru(bpy)_3^{3+}$ and MV^+ (eq 8).

$$Ru(bpy)_3^{2+*} + MV^{2+} \longrightarrow Ru(bpy)_3^{3+} + MV^+ \tag{8}$$

$$Ru(bpy)_3^{3+} + MV^+ \longrightarrow Ru(bpy)_3^{2+} + MV^{2+} \tag{9}$$

No spectral change in the $Ru(bpy)_3^{2+}$–MV^{2+} in H_2O system was observed during irradiation since this oxidative quenching reaction of $Ru(bpy)_3^{2+}$* was followed by the fast back reaction (eq 9). AA was not photopolymerized in the presence of only this redox pair, but was done in the presence of both the redox pair and the sacrificial electron donor KSCN. During the photopolymerization the concentration of $Ru(bpy)_3^{2+}$ did not change, but the reduction of MV^{2+} to MV^+ with an absorption maximum at 602 nm occurred as shown in Figure 6. From these results, the reaction mechanism as shown in Scheme 3 is speculated.

In this photoredox cycle two active species SCN· and MV^+ could be produced. The ability of initiation of these species was studied. One active species MV^+, which was formed by the photoreduction of MV^{2+} with isopropanol,[22] was bleached very slowly by AA, but could not initiate the polymerization of AA. On the other hand, another species SCN· was reported on its ability to initiate the polymerization of AA.[7] In an aqueous solution SCN· combines with SCN^- to form $(SCN)_2^-$ capable of initiating polymerization.

Scheme 3.

As a result, we can conclude that $Ru(bpy)_3^{2+}$ is the unconsumable photosensitizer and that the polymerization of AA is initiated by $(SCN)_2^-$. But in this polymerization system some amounts of poly(AA) was formed even in the absence of the photosensitizer $Ru(bpy)_3^{2+}$. Therefore, thermal polymerization of AA owing to the interaction among KSCN, MV^{2+}, and AA would also occur in this system.

Concluding Remarks

We have designed and found two types of the $Ru(bpy)_3^{2+}$-sensitized photopolymerization systems where the sensitizer could be regenerated by the two successive electron-transfer reactions. In these system, $Ru(bpy)_3^{2+}$ could be converted into $Ru(bpy)_3^+$ or $Ru(bpy)_3^{3+}$ transiently, but was not consumed. Many studies have been published on the photopolymerizations initiated *via* charge-transfer interac-

tions involving monomers as one component (photo-induced charge-transfer polymerization).[23] However, little has been reported on the photopolymerization systems where sensitizers do not interact with monomers directly.[24,25] These are works on the systems initiated by exciplexes. In such systems photosensitizers as one of exciplex components were not also consumed during the polymerizations. These and our mentioned $Ru(bpy)_3^{2+}$-sensitized photopolymrization systems might be one types of ideal photosensitized polymerization systems.

REFERENCES

1. G. Oster and N-L. Yang, *Chem. Rev.*, **68**, 125 (1968).
2. M. K. Mishra, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C22**, 409 (1982—1983).
3. F. Takemura, M. Omori, and H. Tanaka, *Nippon Kagaku Zasshi*, **89**, 576 (1968).
4. F. Takemura, R. Matsuyama, K. Mori, and M. Nagai, *Nippon Kagaku Zasshi*, **92**, 1102 (1971).
5. F. Takemura and E. Morita, *Nippon Kagaku Zasshi*, **92**, 1107 (1971).
6. F. Takemura, E. Morita, and J. Asakura, *Nippon Kagaku Kaishi*, 376 (1973).
7. F. Takemura and K. Sakaguchi, *Nippon Kagaku Kaishi*, 1470 (1976).
8. N. Sutin, *J. Photochem.*, **10**, 83 (1979).
9. D. G. Whitten, *Acc. Chem. Res.*, **13**, 83 (1980).
10. F. H. Barstall, *J. Chem. Soc.*, 173 (1936).
11. K. Iwai, Y. Itoh, M. Furue, and S. Nozakura, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2439 (1983).
12. P. J. DeLaive, J. T. Lee, H. W. Sprintshnik, H. Abruna, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **99**, 7094 (1977).
13. P. J. DeLaive, B. P. Sullivan, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **101**, 4007 (1979).
14. M. Maeotri and M. Grätzel, *Ber. Bunsenges. Phys. Chem.*, **81**, 504 (1977).
15. T. Miyashita and M. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 1740 (1981).
16. M. R. Sandner, C. L. Osborn, and D. J. Trecker, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3173 (1972).
17. S. R. Clarke and R. A. Shanks, *J. Macromol. Sci., Chem.*, **A14**, 69 (1980).
18. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **27**, 2683 (1982).
19. S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).
20. P. J. DeLaive, T. K. Foreman, C. Giannotti, and D. G. Whitten, *J. Am. Chem. Soc.*, **102**, 5627 (1980).
21. C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
22. A. S. Hopkins, A. Ledwith, and M. F. Stam, *J. Chem. Soc., Chem. Commun.*, 494 (1970).
23. Y. Shirota and H. Mikawa, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C16**, 129 (1977—1978).
24. S. Tazuke and N. Kitamura, *J. Chem. Soc., Chem. Commun.*, 515 (1977).
25. T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc. Chem. Commun.*, 485 (1977).