

Effects of Inorganic Anions on the Photopolymerization of Acrylamide Sensitized by 2,3-Butanedione in Aqueous Solutions

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ABSTRACT: In aqueous solutions, 2,3-butanedione (biacetyl: BA) served as a sensitizer for the photopolymerization of acrylamide (AA). The presence of inorganic salts such as KSCN, KSeCN, and NaN_3 increased not only the rate of polymerization but also the molecular weight of the polymer. On the other hand, Na_2SeO_3 increased the rate of polymerization markedly with apparently normal kinetic behavior. In the absence of any salt, the triplet excited state of BA was shown to act as a degradative chain transfer agent as well as a photo-sensitizer. The mechanism of this characteristic photosensitized polymerization is discussed.

KEY WORDS Photopolymerization / Sensitizer / Acrylamide / 2,3-Butanedione / Biacetyl / Triplet Excited State / Inorganic Anion / Degradative Chain Transfer /

The photopolymerization of vinyl monomers sensitized by organic carbonyl compounds has been investigated by many workers.¹ Most of these studies were carried out in organic solvents. 2,3-Butanedione (Biacetyl: BA), an α -diketone soluble both in water and organic media, was used as an efficient sensitizer for the polymerizations of monomers such as styrene and methyl methacrylate.²⁻⁵ But there has been little study on BA-sensitized polymerization in an aqueous medium. Recently, Encina and his coworkers⁶ reported that in the polymerization of *N*-vinyl-2-pyrrolidone and vinyl acetate, BA was a poor initiator and relatively high photoinitiation efficiencies were achieved only in the presence of methanol or water, by which BA was solvated giving a hydroxy-substituted alkanone effective at 300 nm irradiation.

We studied the photopolymerizations of vinyl monomers such as acrylonitrile, styrene,

methyl methacrylate, and acrylamide (AA) sensitized by organic dyes⁷ and metal complexes.⁸⁻¹⁴ In a previous paper,¹³ we reported the photopolymerization of AA sensitized by the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ or $[\text{Co}(\text{en})_3]\text{Cl}_3$ (en: ethylenediamine)-KSCN system in aqueous medium. These metal complexes alone could not initiate the photopolymerization of AA, but could sensitize the polymerization markedly in the presence of KSCN.

We thus studied such effects of inorganic salts on the photopolymerizations in aqueous solutions. BA is soluble in water and has a relatively unique property of exhibiting phosphorescence as well as fluorescence in a fluid solution at room temperature. Then, the effects of inorganic salts on the photopolymerization of AA sensitized by BA were studied kinetically and spectroscopically.

Contrary to the normal kinetic behavior of radical polymerization,¹⁵ the addition of some

salts was found to increase not only the rates of polymerization but also the molecular weights of the polymer obtained. The mechanism of the polymerization is discussed in detail to account for this anomalous behavior.

EXPERIMENTAL

Materials

Acrylamide (AA) was recrystallized twice from benzene. 2,3-Butanedione (biacetyl; BA) was purified by vacuum distillation before use. Inorganic salts were of reagent grade and used without further purification.

Experimental Procedures

A freshly prepared sample solution was degassed by four freeze-pump-thaw cycles on a vacuum line, and then sealed into a standard 1-cm spectrophotometer quartz cell (capacity, 4 ml).

The photopolymerization was carried out under irradiation at 30°C. As a stationary light source, 500 W ultra-high pressure mercury lamp (Ushio USH-500D) was used together with a cutoff glass filter (Toshiba UV-D2 85% transmittance at 365 nm). The polymers were isolated by precipitation with methanol.

The rate of polymerization was determined from the weight of the polymer obtained in the reaction time, since the conversion almost linearly increased with time. The molecular weight of the polymer was measured by GPC calibrated by poly(ethylene oxide) in water or by an Ostward viscosimeter using the following equation, $[\eta] = 6.8 \times 10^{-4} \bar{M}_n^{0.66}$.¹⁶

Measurements

Absorption spectra were measured with a Hitachi model 124 spectrophotometer. Emission spectra were recorded with a Hitachi model EPS-2 spectrophotometer (λ_{ex} , 365 nm). Since BA-phosphorescence was observable only in an oxygen-free solution at room temperature, sample solutions were deaerated in sealed cells. The flash photolysis apparatus

was the same as described previously.¹³ The light intensities were measured with potassium tris(oxalato)ferrate(III) actinometer¹⁷.

RESULTS AND DISCUSSION

Photopolymerization of AA Sensitized by BA and Effects of Inorganic Salt Additives

Using BA as a sensitizer in aqueous solutions, both the rates of photopolymerization (R_p) of AA and molecular weights of the polymers obtained were nearly proportional to the concentrations of the monomer over the range of 0.3 to 1.5 M at a given concentration of BA (0.1 M).

As shown in Figure 1, R_p was linear to the square root of the absorbed light intensity. This observation appeared in agreement with that for the normal radical polymerization terminated bimolecularly.

Under the same conditions, the presence of potassium thiocyanate ($[\text{KSCN}] = 0.01 \text{ M}$) brought about an increase of the rate by a factor of about 4 (Figure 1). The effects of

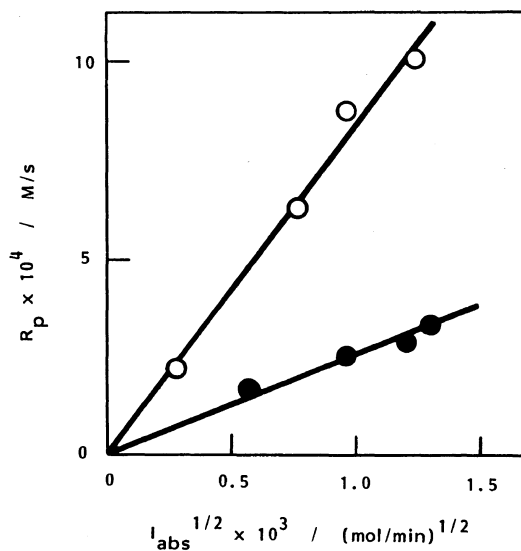


Figure 1. Dependence of the rate of photopolymerization on the square root of the absorbed light intensity in the absence (●) and presence (○) of KSCN: $[\text{AA}] = 1 \text{ mol l}^{-1}$, $[\text{BA}] = 0.1 \text{ mol l}^{-1}$, and $[\text{KSCN}] = 0.01 \text{ mol l}^{-1}$.

various inorganic salts such as NaN_3 , KSeCN , and Na_2SeO_3 as well as KSCN are shown in Figure 2, in which R_p is plotted against the square root of salt concentration. With respect

to KSCN , a linear relation between R_p and $[\text{KSCN}]^{1/2}$ was observed throughout a concentration of the salt (*ca.* 1×10^{-4} M), above which R_p was held almost constant and the

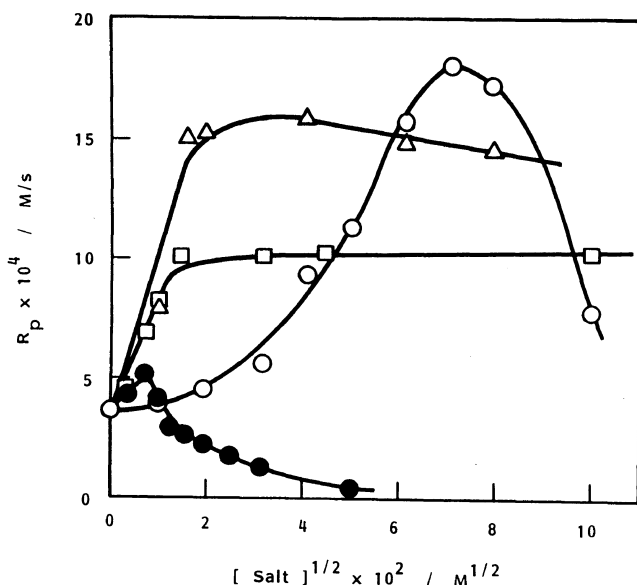


Figure 2. Dependence of the rate of photopolymerization on the square root of the concentration of the added salts: (\square), KSCN ; (\triangle), NaN_3 ; (\bullet), KSeCN ; (\circ), Na_2SeO_3 ; $[\text{AA}] = 1 \text{ mol l}^{-1}$ and $[\text{BA}] = 0.1 \text{ mol l}^{-1}$.

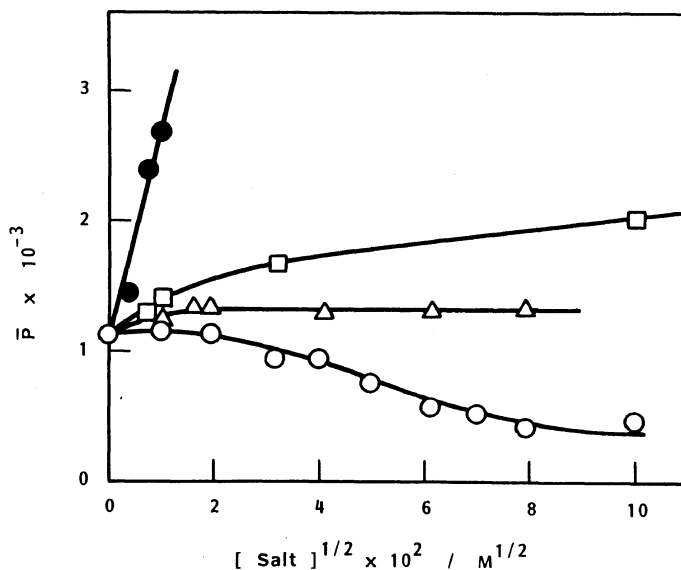


Figure 3. Dependence of the degree of polymerization (\bar{P}) on the square root of the concentration of the added salts: (\square), KSCN ; (\triangle), NaN_3 ; (\bullet), KSeCN ; (\circ), Na_2SeO_3 ; $[\text{AA}] = 1 \text{ mol l}^{-1}$ and $[\text{BA}] = 0.1 \text{ mol l}^{-1}$.

phosphorescence of BA was quenched completely. The observation with NaN_3 was similar to that with KSCN . With KSeCN , R_p increased at lower concentrations, although R_p decreased considerably at high concentrations. In the presence of Na_2SeO_3 , on the other hand, R_p increased gradually but progressively with increasing concentration of the salt, and then decreased at very high concentrations where BA might be squeezed out by salting-out.

In Figure 3, the degree of polymerization (DP) of the polymers obtained in the above experiments is plotted against the same abscissa as that in Figure 2. It is well known that in the normal radical polymerization of a monomer, the molecular weight of the polymer obtained decreases with increasing R_p at a constant concentration of the monomer because of faster bimolecular radical termination. Nevertheless, the salt additives tested except Na_2SeO_3 enlarged the molecular weights of polymers along with increasing R_p . These observations have not been reported as far as we know. On the other hand, the

polymers obtained in the presence of Na_2SeO_3 became shortened gradually with increasing concentration of the salt. This behavior is apparently of a well-known type.

Relation between R_p and DP of the Polymer

As is well known, almost all examples of photopolymerization are of free-radical character and R_p can be expressed as

$$R_p = k_p \left(\frac{2 \times 2.3 \phi \epsilon d I_0}{k_t} \right)^{1/2} [\text{BA}]^{1/2} [\text{M}] \quad (1)$$

and DP for the case of no chain transfer is

$$\text{DP} = \frac{k_p [\text{M}]}{(2 \times 2.3 \phi \epsilon d I_0 k_t)^{1/2} [\text{BA}]^{1/2}} = \frac{(k_p [\text{M}])^2}{k_t R_p} \quad (2)$$

where notations for the rate constants of propagation and termination and for the concentration of monomer are the same as usual, and ϕ , ϵ , d , and I_0 are the quantum yield, extinction coefficient, light-pass length in cm, and light intensity, respectively. Then, at a

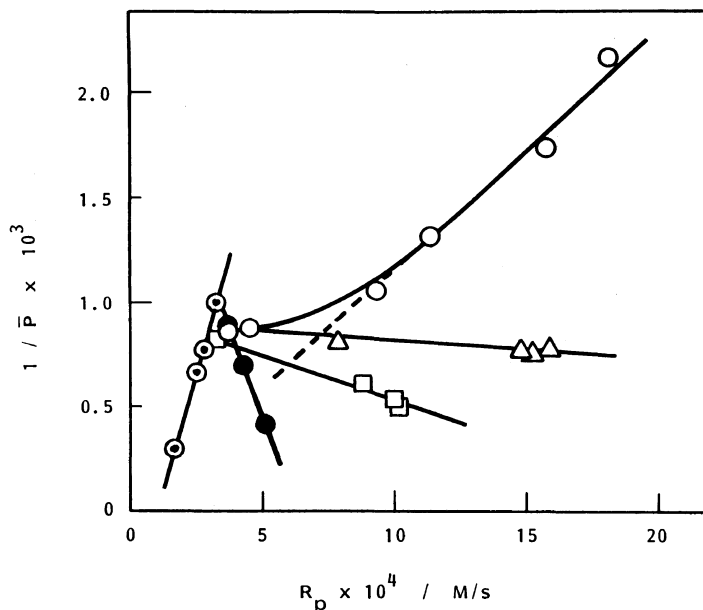


Figure 4. Plots of the reciprocal of the degree of polymerization ($1/\bar{P}$) against the rate of polymerization: (\square), KSCN ; (\triangle), NaN_3 ; (\bullet), KSeCN ; (\circ), Na_2SeO_3 ; (\odot), Non.

stationary light intensity and constant concentration of monomer, R_p should be proportional to the square root of the concentration of sensitizer and DP inversely proportional to R_p .

In Figure 4, the reciprocals of DP are plotted against R_p in the absence and presence of various inorganic salts. Some interesting features are seen in the figure.

1) The line for the absence of any salt, on which the concentration of BA is over the range of 0.001 to 0.1 M, has a steep positive slope. Further, when the light intensity was lowered through a neutral density filter at 0.1 M BA, the plot of $1/DP$ against R_p was almost on the same line as shown above. Therefore, the excited state of BA may be responsible for this behavior.

2) In the presence of Na_2SeO_3 , the line was of moderate positive slope in higher rate region but the slope became gentle in relatively low rate region. The extrapolation of the linear part of the plots passed through the original point of axes, indicating a normal behavior of radical polymerization in that region.

3) For cases in the presence of NaN_3 , KSCN, and KSeCN, the lines had more negative slopes in this order, that is, DP also increased with increasing R_p in contrast to usual cases.

4) The molecular weight of the polymer, obtained at a given concentration of BA (0.1 M) in the absence of any salt, was significantly small in spite of the low rate of polymerization. This shows that BA also may act as a retarder in the process although it played a role in sensitization on the other hand. Therefore, the addition of salts seems to weaken the retarding effect of BA.

In the absence and presence of KSCN, R_p is plotted against the square root of the concentration of BA in Figure 5. It was shown that at higher concentrations of BA, the polymerization was suppressed because of degradative chain transfer by BA, but the retarding effect was removed by the presence of KSCN (0.01 M).

Thermal polymerization of AA initiated by azobisisobutyronitrile (AIBN) in aqueous solution was found to be significantly retarded

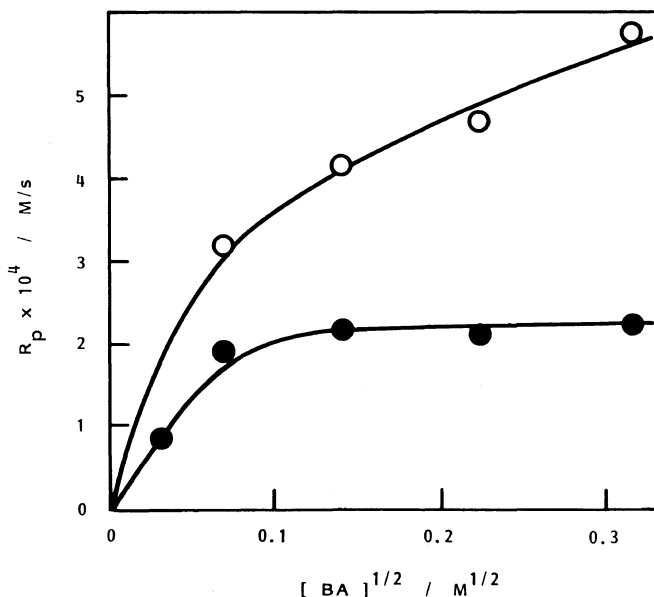


Figure 5. Plots of the rate of polymerization against the square root of the concentration of 2,3-butanedione in the absence (●) and presence (○) of KSCN: $[AA] = 1 \text{ mol l}^{-1}$ and $[KSCN] = 0.01 \text{ mol l}^{-1}$.

by a small amount of BA in the dark as shown in Table I. This finding also shows BA itself to be a retarder of the polymerization of AA in aqueous solution.

Quenching of BA Phosphorescence by Inorganic Anions

BA is one of a few examples which exhibit phosphorescence in a fluid solution at room temperature. On irradiation ($\lambda = 365$ nm) BA undergoes $n \rightarrow \pi^*$ transition to give the corresponding singlet excited state, from which the triplet state is formed with a quantum yield of nearly unity. As the triplet lifetime (0.145 ms) is about 2×10^4 times greater than the singlet lifetime (6.3 ns),¹⁸ the concentrations of anions

which efficiently quench phosphorescence leave fluorescence unaffected.

To study the interactions between the excited BA and inorganic anions, the intensities of BA-phosphorescence at 512 nm were measured in the presence of these salts and are plotted against their concentrations in Figure 6 (Stern–Volmer plot). The triplet excited state was quenched by SeCN^- , SCN^- , and N_3^- , but not by SeO_3^{2-} . From the values of the quenching rate constant k_q in Table II, calculated from K_{SV} and the triplet lifetime (0.145 ms), the behavior of the anions except SeO_3^{2-} appears to be correlated with their redox potentials, indicating that a charge

Table I. Effects of biacetyl on the AIBN-initiated thermal polymerization of acrylamide^a

Initiator	$R_p \times 10^5 / \text{M s}^{-1}$
AIBN ^b	29.8
AIBN ^b + BA ^c	1.95
BA ^c	1.71

^a [AA] = 1.0 M in aqueous solution at 60°C.

^b AIBN was saturated in the solution.

^c [BA] = 0.1 M.

Table II. Stern–Volmer constants (K_{SV}) and quenching constants (k_q) for quenching of biacetyl phosphorescence by some inorganic anions

Anions	K_{SV}	k_q	Redox potential
	M^{-1}	$\text{M}^{-1} \text{s}^{-1}$	V
SeCN^-	8.65×10^5	6.0×10^9	0.42
SCN^-	3.18×10^5	2.2×10^9	0.77
N_3^-	5.10×10^4	3.5×10^8	1.33 ^a
SeO_3^{2-}	2.4×10^2	1.7×10^6	0.03

^a For the $\text{N}_3^- / \text{N}_3^{\cdot -}$ redox couple.²¹

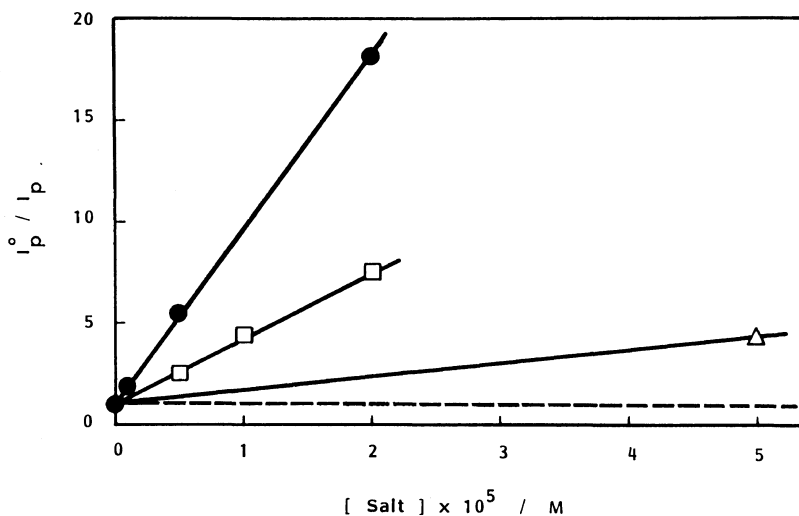


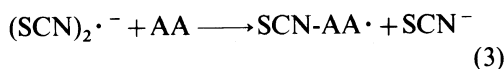
Figure 6. Plots of the intensity ratio of the phosphorescence of 2,3-butanedione (I_p^0/I_p) at 512 nm against the concentration of the added salts: (□), KSCN; (△), NaN_3 ; (●), KSeCN; ----, Na_2SeO_3 (observed point is out of range); [BA] = 0.1 mol l⁻¹.

transfer process from the anion to the triplet of BA is responsible for quenching. But the lack of quenching effect of SeO_3^{2-} in spite of its high reducing power shows that no direct interaction of the ion with the triplet state actually occurs.

In a detailed study on quenching of triplet states by inorganic ions, Treinin and Hayon¹⁹ found that the triplet states of acetophenone and acetone were quenched less effectively by SO_3^{2-} than by I^- in spite of the stronger reducing power of SO_3^{2-} . Thus, in analogy with SO_3^{2-} the triplet of BA might be hardly quenched by SeO_3^{2-} , and then the accelerating effect of the salt for the polymerization would be ascribed to the regeneration of initiating radicals from the retarding products by means of the salt.

BA-Sensitized Formation of Inorganic Anion Radicals by Flash Photolysis

The quantum yield of intercarbonyl C-C bond breakage during the photolysis of BA solution is known to be very low (0.01) as compared to that of the triplet formation (*ca.* 1).²⁰ Then, in the presence of sufficient high concentration of KSCN (0.01 M) to quench the triplet, flash photolysis of BA solution was found to give a transient radical anion $(\text{SCN})_2\cdot^-$ which had an absorption maximum at 475 nm and half-life period of about 60 μs . The half-life period of the radical anion observed in this experiment was about one-third that reported previously,¹² suggesting that the radical anion might interact with a ground state of BA. Moreover, the addition of AA monomer into the system resulted in increased decay rate of the transient with increasing concentration of the monomer. The polymerization of AA is considered to be initiated from the transient radical as follows.



Similarly, in the case of KSeCN, an analogous transient radical was confirmed to be

produced. However, the corresponding transient radical ($\text{N}_3\cdot$ or $\text{N}_6\cdot^-$)²¹ for N_3^- could not be observed owing to no absorption in the visible region, although the BA triplet was quenched by NaN_3 . In any event, the initiation of polymerization with these transient radicals increased the number of initiating species and then the net polymerization rate of AA.

Reaction Mechanisms

From the results mentioned above, we can summarize some interesting features as follows.

1) BA played a role in sensitization for the polymerization of AA in aqueous solution, but R_p was relatively low and DP of the polymer obtained in the system was considerably small.

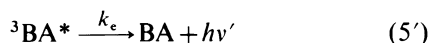
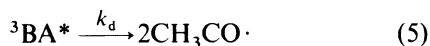
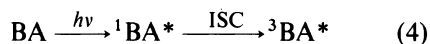
2) In the presence of KSCN, KSeCN, or NaN_3 , R_p increased with increasing concentration of the salt, but was held approximately constant in the higher concentration region where BA-phosphorescence was quenched completely. At the same time, DP of the polymer obtained also increased with R_p .

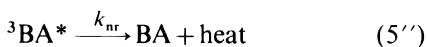
3) In spite of no quenching of BA-phosphorescence even in the high concentration of Na_2SeO_3 , R_p was allowed to increase markedly with the salt concentration and DP decreased in a similar manner as the normal free radical polymerization.

4) In the absence of any salt, BA acted as a degradative chain-transfer agent at high concentration in the polymerization of AA. However, the presence of a salt such as KSCN was found to remove the retarding effect of BA.

In its simple form, the process of a sensitized photopolymerization consists of four steps: light-absorption, initiation, propagation, and termination.

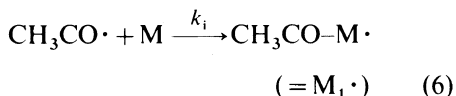
Light-absorption:



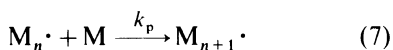


The singlet excited state of BA is almost converted to the triplet state through intersystem crossing. The triplet state may decompose into an initiating radical species with a rate constant k_d and otherwise decay with emitting phosphorescence (k_e) or thermally without emitting (k_{nr}).

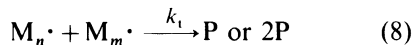
Initiation:



Propagation:

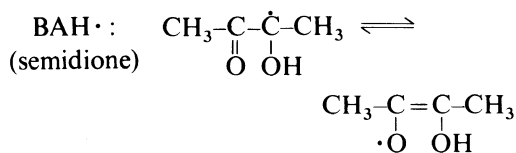


Termination:



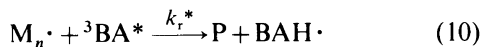
where M, $\text{M}_n\cdot$, and P indicate monomer, growing polymer radical, and stable polymer, respectively, and k_i , k_p , and k_t are the rate constants of initiation, propagation, and termination, respectively.

In the Absence of Salt. Considering the features described above, the growing polymer radical might be destroyed by the interaction with the ground and/or excited state of BA, which would give a stable polymer and a hydrogen-transferred semidione radical (BAH \cdot). Here,



The ketyl-type structure in the resulting semidione radical seems to be very important and considerably stable²² leading to termination subsequently. So, the interaction can be referred to as degradative chain transfer as shown below.

Chain transfer:



where k_r , k_r^* , and k_{td} are the rate constants for the retarding reactions by the ground and excited BA and for the termination by semidione radical, respectively.

Assuming a steady-state condition in the normal free radical polymerization without degradative chain transfer, R_p and DP are apparently expressed as well as eq 1 and 2, respectively. However, if BA and/or ${}^3\text{BA}^*$ attack the growing polymer radical and bring about degradative chain transfer, the kinetics may be as follows.

$$\begin{aligned} \frac{d[{}^3\text{BA}^*]}{dt} &= 2.3\phi\epsilon dI_0[\text{BA}] \\ &\quad - (k_d + k_e + k_{nr})[{}^3\text{BA}^*] \\ &\quad - k_r^*[\text{M}_n\cdot][{}^3\text{BA}^*] = 0 \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{d[\text{CH}_3\text{CO}\cdot]}{dt} &= 2k_d[{}^3\text{BA}^*] \\ &\quad - k_i[\text{CH}_3\text{CO}\cdot][\text{M}] = 0 \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{d[\text{M}_n\cdot]}{dt} &= k_i[\text{CH}_3\text{CO}\cdot][\text{M}] - k_t[\text{M}_n\cdot]^2 \\ &\quad - k_r[\text{M}_n\cdot][\text{BA}] - k_r^*[\text{M}_n\cdot][{}^3\text{BA}^*] \\ &\quad - k_{td}[\text{M}_n\cdot][\text{BAH}\cdot] = 0 \end{aligned} \quad (14)$$

From eq 12,

$$[{}^3\text{BA}^*] = 2.3\phi\epsilon dI_0[\text{BA}] / (k_d + k_e + k_{nr} + k_r^*[\text{M}_n\cdot])$$

If most of ${}^3\text{BA}^*$ is consumed in eq 10, the reaction may be regarded as a primary radical termination and R_p should show a zero-order dependence on the concentration of ${}^3\text{BA}^*$. As shown in Figure 1, R_p is dependent on the half order of light intensity. Therefore, it can be assumed that $k_d + k_e + k_{nr} \gg k_r^*[\text{M}_n\cdot]$ and then $[{}^3\text{BA}^*] = k[\text{BA}]/k_0$, where $k = 2.3\phi\epsilon dI_0$ and $k_0 = k_d + k_e + k_{nr}$.

Furthermore, since the relation between

1/DP and R_p for various light intensities at 0.1 M BA was almost the same as that for various concentrations of BA at a fixed light, eq 10 might be much faster than eq 9 and immediately followed by eq 11. Consequently, two glowing polymer radicals could be substantially terminated on eq 10. Hence,

$$\frac{d[M_n \cdot]}{dt} = 2k_d[{}^3\text{BA}^*] - k_t[M_n \cdot]^2 - 2k_r^*[M_n \cdot][{}^3\text{BA}^*] = 0 \quad (15)$$

$$[M_n \cdot] = \frac{-kC[\text{BA}] + (k^2C^2[\text{BA}]^2 + 2k_t kD[\text{BA}])^{1/2}}{k_t} \quad (16)$$

where $C = k_r^*/k_0$, and $D = k_d/k_0$. C is regarded as a measure of influence of degradative chain transfer and D is the fraction of ${}^3\text{BA}^*$ decomposed in the decay processes.

As the overall rate of polymerization is expressed by eq 17,

$$R_p = k_p[M_n \cdot][M] \quad (17)$$

it is thought that if C is zero or very small, R_p follows the proportional relation between R_p and $[\text{BA}]^{1/2}$, and corresponds to that of the case involving no degradative chain transfer. As C becomes large, the exponential dependence on $[\text{BA}]$ may go down from 1/2 toward zero order and finally R_p may approach zero. Therefore, at higher concentrations of BA, R_p may be independent of concentration (Figure 5).

DP of the polymer obtained can be given as

$$\text{DP} = \frac{R_p}{R_t + R_r^*} \quad (18)$$

where R_t is the rate of production of polymer by the normal bimolecular termination and R_r^* is that by the degradative chain transfer. Then,

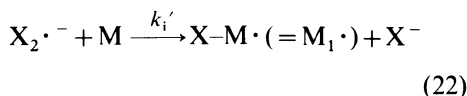
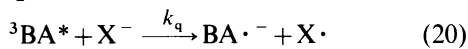
$$\frac{1}{\text{DP}} = \frac{k_t R_p}{k_p^2 [M]^2} + \frac{2kC[\text{BA}]}{k_p [M]} \quad (19)$$

In the absence of any salt, the second term of

Although Deb²³ has proposed a method for analyzing the problems associated with primary radical termination and degradative chain transfer, the treatment is not properly applicable to our results owing to different experimental conditions. Hence, solving eq 15 as a quadratic equation, the stationary concentration of growing polymer radical $[M_n \cdot]$ can be approximately expressed as follows,

the right-hand side of eq 19 may be significant for large C and then DP may be smaller than that of normal polymerization without such degradative chain transfer.

In the Presence of Salts. On the other hand, sufficient concentrations of X^- (e.g., SCN^-) to quench BA-phosphorescence can yield the initiating species $X_2 \cdot^-$ (e.g., $(\text{SCN})_2 \cdot^-$).



As the equilibrium constant K is known generally to be large, $X \cdot$ formed in eq 20 becomes immediately $X_2 \cdot^-$, which initiates the polymerization instead of $\text{CH}_3\text{CO} \cdot$ resulting from direct breakage of ${}^3\text{BA}^*$. In a similar manner as before,

$$[{}^3\text{BA}^*] = k[\text{BA}]/(k_0 + k_q[X^-])$$

$$\frac{d[M_n \cdot]}{dt} = k_q[{}^3\text{BA}^*][X^-] - k_t[M_n \cdot]^2 - 2k_r^*[M_n \cdot][{}^3\text{BA}^*] = 0 \quad (23)$$

Then,

$$[M_n \cdot] = \frac{-k_r^* [{}^3BA^*] + (k_r^* {}^2 [{}^3BA^*] + k_i k_q [{}^3BA^*][X^-])^{1/2}}{k_t} \quad (24)$$

If the scavenging of growing radicals by ${}^3BA^*$ could be neglected compared with the generation of $X_2 \cdot^-$ by eq 20,

$$\begin{aligned} R_p &= k_p [M_n \cdot] [M] \\ &= k_p \left(\frac{k_q [{}^3BA^*][X^-]}{k_t} \right)^{1/2} [M] \\ &= k_p \left(\frac{k[BA]}{k_t} \frac{k_q [X^-]}{(k_0 + k_q [X^-])} \right)^{1/2} [M] \quad (25) \end{aligned}$$

Thus,

$$\frac{1}{R_p} = \frac{1}{k_p [M]} \left(\frac{k_t}{k[BA]} \right)^{1/2} \left(1 + \frac{k_0}{k_q [X^-]} \right)^{1/2} \quad (26)$$

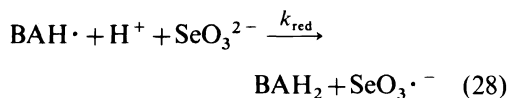
Therefore, R_p should increase with the concentration of X^- . This expectation has been well confirmed as shown in Figure 2.

In this case, DP may be expressed as follows from eq 18.

$$\frac{1}{DP} = \frac{k_t R_p}{k_p {}^2 [M]^2} + \frac{2k_r^* k[BA]}{k_p [M](k_0 + k_q [X^-])} \quad (27)$$

In the second term of the right-hand side in eq 27, $k_r^*/(k_0 + k_q [X^-])$ corresponds to the ratio of the degradative transfer reaction to all decay processes of ${}^3BA^*$ and DP seems to increase with the concentration of X^- . On the contrary, if the concentration of X^- decreases to zero, eq 27 might coincide with eq 19.

In the Case of SeO_3^{2-} . Although SeO_3^{2-} has strong reducing power, it can not quench ${}^3BA^*$ directly. Therefore, the action of SeO_3^{2-} seems to reduce semidone ($BAH \cdot$) yielding acetoin (BAH_2) and its own oxidized radical anion ($SeO_3 \cdot^-$). The resulting radical anion could reinitiate the polymerization smoothly.



Then, the competition for $BAH \cdot$ between $M_n \cdot$

and SeO_3^{2-} would be essentially important.

Assuming a stationary state for $BAH \cdot$, $SeO_3 \cdot^-$, and $M_n \cdot$ from eq 10, 28, and so on,

$$\begin{aligned} \frac{d[BAH \cdot]}{dt} &= k_r^* [M_n \cdot] [{}^3BA^*] \\ &\quad - k_{td} [BAH \cdot] [M_n \cdot] \\ &\quad - k_{red} [BAH \cdot] [SeO_3^{2-}] = 0 \quad (30) \end{aligned}$$

$$\begin{aligned} \frac{d[M_n \cdot]}{dt} &= 2k_d [{}^3BA^*] - k_i [M_n \cdot]^2 \\ &\quad - 2k_{td} [BAH \cdot] [M_n \cdot] = 0 \quad (31) \end{aligned}$$

But, since the kinetic solution of these equations for $[M_n \cdot]$ is really very complicated, it is instructive to consider an extreme case in which sufficient SeO_3^{2-} is added and an ideal chain transfer occurs eventually. Then, neglecting the third term in the middle of eq 31 and using the same abbreviations just as before,

$$R_p = k_p [M_n \cdot] [M] = k_p \left(\frac{2k_d k[BA]}{k_t k_0} \right)^{1/2} [M] \quad (32)$$

Therefore, R_p would be greater than that in the absence of any salt. Further, eq 10 followed by eq 28 and 29 is regarded as an ideal chain transfer reaction (k_{tr}) between $M_n \cdot$ and SeO_3^{2-} yielding a stable polymer and a reinitiating radical species.

$$\frac{1}{DP} = \frac{k_t R_p}{k_p {}^2 [M]^2} + \frac{k_{tr} [SeO_3^{2-}]}{k_p [M]} \quad (33)$$

That is to say, DP may decrease with increasing concentration of SeO_3^{2-} .

In conclusion, such effects of inorganic salt additives on the BA-sensitized photopolymerization are specific to AA in aqueous solutions and were not found for any other water-soluble vinyl monomers such as methacrylamide, *N,N*-dimethylacrylamide, and methyl

methacrylate tested. Therefore, such unique specificity to AA and BA needs to be investigated further.

CONCLUDING REMARKS

Although in aqueous solution 2,3-butanedione (biacetyl: BA) served as a photosensitizer for the polymerization of acrylamide (AA), BA itself acted as a degradative chain transfer agent and both R_p and DP of the resulting polymer were relatively low.

The addition of inorganic salts such as KSCN and NaN_3 to the aqueous BA-sensitized photopolymerization system increased not only R_p but also DP of the polymer obtained. These characteristic features were explained on the basis of the formation of initiating species with the interaction between the excited triplet state of BA and inorganic anions and the removal of influence of degradative chain transfer due to the excited BA. Moreover, the presence of SeO_3^{2-} , which has strong reducing power but no quenching ability toward the excited BA, could accelerate the photopolymerization of AA according to a normal kinetic scheme. These effects of inorganic salts on the photopolymerization were found only for AA, but not for any other vinyl monomers in aqueous solution.

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