

Dye-sensitized photopolymerization of *N,N'*-methylenebisacrylamide by initiation with eosin–ascorbic acid system

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Abstract. The dye-sensitized photopolymerization of *N,N'*-methylenebisacrylamide (MBA) in aqueous medium initiated by eosin–ascorbic acid (AH₂) was studied at 25°C. The polymerization takes place only at higher concentration of AH₂ (>10⁻³ mol/L) and its rate increases rapidly as [AH₂] is increased. The rate of polymerization is proportional to [MBA] and [AH₂]. Kinetic results indicate that semi-quinone (DH) dye radical and semi-oxidized form (Ā) of ascorbic acid are unable to initiate polymerization. Formation of H₂O₂ is proposed and confirmed. A suitable mechanism is proposed in accordance with experimental results obtained.

Keywords. *N,N'*-methylenebisacrylamide (MBA); eosin dye (D); ascorbic acid (AH₂); semi-quinone dye (DH); semi-oxidized form of ascorbic acid (Ā); hydrogen peroxide (H₂O₂).

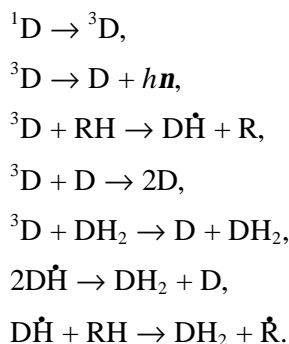
1. Introduction

Generally in a photo initiating system consisting of a dye and a reducing agent, the excited triplet state of the dye, abstracts the hydrogen from the reducing agent. This results in the formation of reduced dye and a primary radical derived from the reducing agent. This radical initiates the vinyl polymerization (scheme 1).

In scheme 1, D is the dye, ¹D the first excited singlet state, ³D the triplet state, DH• the semi-quinone dye, DH₂ the leuco dye, RH the reducing agent and R• the initiating radical. Similar schemes

have been proposed for other classes of dye^{1–3}. (See chart 1 for structures.)

It is well documented that ascorbic acid (AH₂) acts as a powerful reducing agent.^{4–7} In our preliminary experiment, we found that this reducing agent in combination with eosin dye could not initiate vinyl polymerization in a nitrogen atmosphere. However, the same system initiated the vinyl polymerization in an oxygen atmosphere. In order to



Scheme 1.

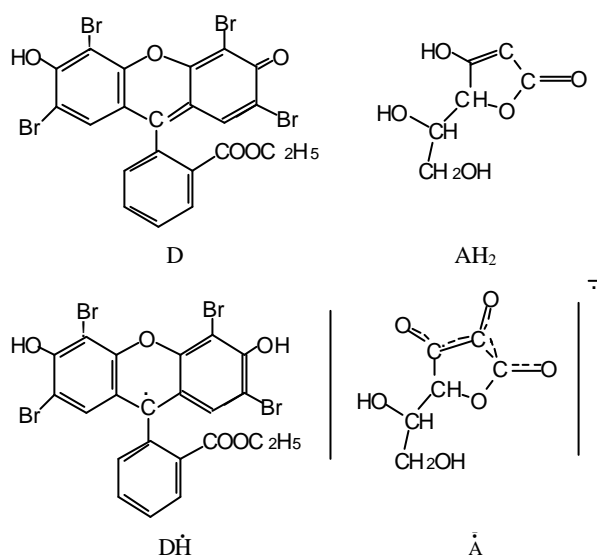


Chart 1.

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elucidate the role of AH_2 and oxygen, the polymerization of N,N' -methylenebisacrylamide (MBA) has been taken up. This monomer is a non-conjugated diolefin with double bonds at the terminal positions. Normally such divinyl monomers yield only cross-linked insoluble polymers. Co-polymers of MBA with other vinyl monomers are reported to be used in the separation and characterization of proteins.⁸ MBA can also undergo cyclization during polymerization^{9,10} without cross-linking and hence is of special interest.

2. Experimental

All the reagents used were of analar grade. MBA (Aldrich) was recrystallised from hot water. Photolysis was carried out using a 500-W tungsten lamp, and its output was stabilized by an automatic line-voltage corrector (Instruments Techniques Limited, Hyderabad). Standard ferrioxalate actinometry was employed for measuring the light intensity. The procedure¹¹ followed for a typical kinetic run is as follows.

Polymerization of MBA monomer under thermal conditions, using eosin-ascorbic acid redox system was carried out by the following method. Requisite amount of ascorbic acid and monomer was taken in a reaction vessel and thermostatted at 25°C, during this time purified oxygen gas was bubbled through the reaction mixture for one half hour. The appropriate amount of eosin solution was added to the reaction vessel. The light source was switched on and zero time was noted. Formation of polymer was noticed after an induction period. Rate of polymerization (R_p) was calculated from the weight of the polymer formed at different intervals of time. For determining this at the fixed time, the entire reaction mixture (10 ml) was quenched by adding excess ice-cold hydroquinone. The polymer formed was filtered through sintered glass gouche crucible (G_4 type) and washed several times with distilled water. The filtered polymer was then dried at 50°C in an air oven to constant weight. This was repeated over several time intervals and R_p vs time and percentage conversion of polymer vs time were plotted to get the steady state condition, which was found to be 20 min. The values of R_p were measured at different monomer concentrations (after 20 min). From the slope of the linear plot of $\log R_p$ vs \log [monomer], the order in [monomer] was calculated. The orders in [eosin] and in $[AH_2]$ were estimated similarly by

varying [eosin] and $[AH_2]$ separately. The rate of polymerization (R_p) was calculated from the weight of the polymer by making use of the following equation.

$$R_p = -d[M]/dt = 1000 w/vtm,$$

where w is the weight of polymer, v is the total volume of the reaction mixture, t is the reaction time and m is the molecular weight of the monomer.

The percentage conversion of the polymer was calculated by the following equation.

$$\text{Percentage of conversion (\%)} = 100 w/g,$$

where w is the weight of polymer and g is the weight of the monomer used.

3. Results and discussion

Polymerization studies were conducted at 298 K in an oxygen atmosphere. Steady state was attained within 20 min (table 1).

3.1 Effect of $[AH_2]$ on R_p

Rate of polymerization increases with increase in $[AH_2]$ and the order of reaction is unity (figure 1B). At low concentration ($<10^{-3}$ mol/L) of AH_2 , polymerization is not observed even when its concentration is ten times greater than the dye concentration. This could be due to complete consumption of AH_2 to form H_2O_2 . H_2O_2 is generated during dye-sensitized reactions when dye, reducing agent and oxygen are present.⁷ H_2O_2 subsequently reacts with the reducing agent to produce hydroxyl radicals which then initiate the vinyl polymerization. Evidence for this comes from the fact that the polymer obtained

Table 1. Polymerisation studies.

Time (min)	Conversion (%)	$R_p \times 10^5$ mol/L
15.0	22.0	1.22
20.0	39.8	1.62
25.0	46.7	1.55
30.0	51.8	1.44
35.0	54.4	1.29

$[MBA] = 5.00 \times 10^{-2}$ mol/L; $[AH_2] = 1.00 \times 10^{-2}$ mol/L;
 $[eosin] = 5.00 \times 10^{-4}$ mol/L; $I_a = 6.30 \times 10^7$ quanta/L.s;
 temp. = 298 K

with the $\text{H}_2\text{O}_2\text{-AH}_2$ redox system under thermal conditions also gives a polymer with similar superimposable IR spectra. In both cases, the characteristic peak of the $-\text{OH}$ group is found at about 3600 cm^{-1} .

3.2 Effects of [MBA] on R_p

Rate of polymerization increases with increase in [MBA] and the order in [MBA] is unity (figure 1A). The polymer obtained shows characteristic properties similar to the ones obtained with other initiating systems.^{8,9} Hence, in the present case also a cyclo-polymerization mechanism is assumed to be operative.

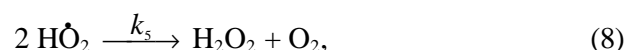
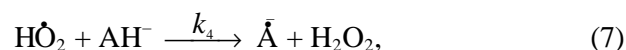
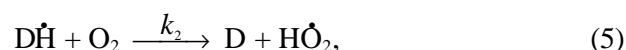
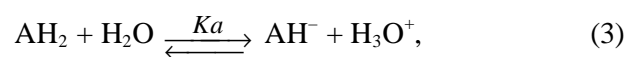
3.3 Effect of [eosin] on R_p

The rate of polymerization is found to be independent of [eosin]. When the concentration of eosin is varied from 1.00×10^{-4} to 10.0×10^{-4} mol/L, the reason is the reappearance of dye molecules from the semi-reduced form of the dye. As mentioned earlier at low concentration of AH_2 , polymerization is not observed. This is due to the complete consumption of ascorbic acid in producing H_2O_2 . As the

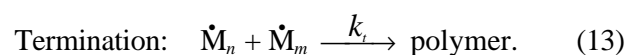
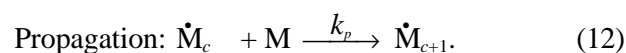
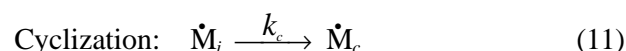
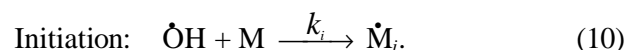
concentration of AH_2 increases, polymerization takes place and its rate increases rapidly.

This indicates that primary radicals (semi-quinones), dye radicals ($\text{D}\dot{\text{H}}$) and semi-oxidized forms of ascorbic acid ($\bar{\text{A}}$) are unable to initiate polymerization.

It is an established fact that such type of highly stabilized radicals are incapable of initiating polymerization.⁷ The formation of H_2O_2 is proposed and confirmed.¹² The production of initiating hydroxyl radicals from H_2O_2 is proposed as the possible initiating step.



The hydroxyl radical initiates the polymerization due to its high reactivity compared to $\bar{\text{A}}$ which is a resonance-stabilized species. The following mechanism is proposed to explain the observed results.



The overall polymerization may be represented by the following equation,

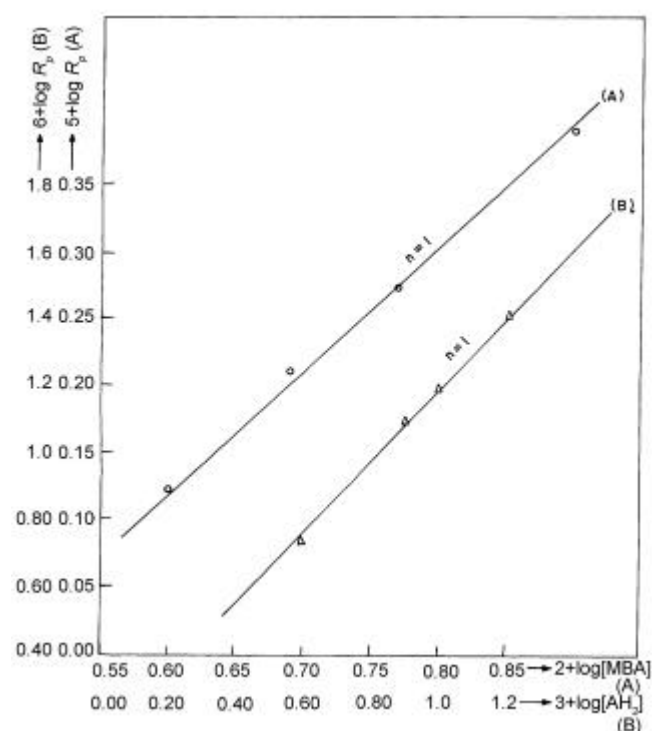


Figure 1. Plot of $\log [\text{MBA}]$ vs $\log R_p$ (A), $\log [\text{AH}_2]$ vs $\log R_p$ (B).

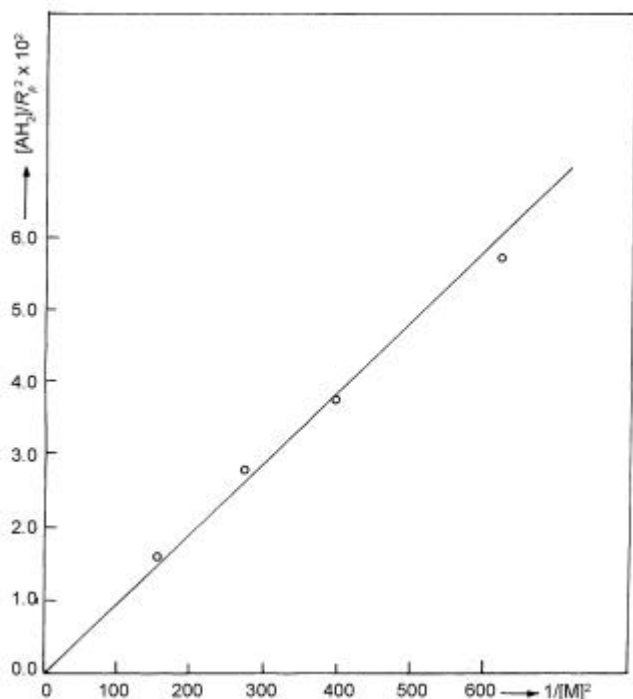
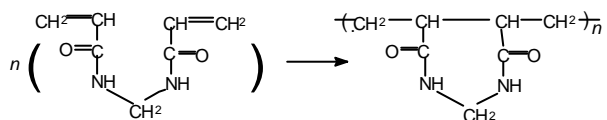


Figure 2. Plot of $[AH_2]/R_p^2$ vs $1/[M]^2$. ($[MBA] = 5.00 \times 10^{-2}$ mol/L; $[AH_2] = 1.00 \times 10^{-2}$ mol/L; $[eosin] = 5.00 \times 10^{-4}$ mol/L; $I_a = 6.30 \times 10^{-7}$ quanta/L.s; temp. = 298 K.

$nM \rightarrow \text{polymer}$,



Applying the steady state principle to the above mechanism a rate law for the rate of polymerization, R_p , may be obtained as

$$R_p = k_p [M] \left\{ \frac{k_6 [AH_2][H_2O_2]}{k_t} \right\}^{1/2}. \quad (14)$$

Equation (14) agrees well with the experimental results. Similar kinetic behaviour was observed in vinyl acetate polymerization sensitized by ethyl eosin-ascorbic acid system as reported by Pemberton and Johnson.⁷ Squaring both sides of (14) and rearranging the terms (15) is obtained,

$$[AH_2]/R_p^2 = \frac{k_t}{k_6 k_p [H_2O_2]} \cdot \frac{1}{[M]^2}. \quad (15)$$

Equation (15) predicts a linear relationship between $[AH_2]/R_p^2$ and $1/[M]^2$. When the observed data is used, a plot of $[AH_2]/R_p^2$ vs $1/[M]^2$ gives a straight line passing through the origin (figure 2), in keeping with the prediction as per (15). This validates the proposed kinetic scheme.

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