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## Kinetics of Aqueous Polymerization of Acrylamide Initiated by Ceric Ammonium Sulfate/2-Mercaptoethanol Redox System

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### ABSTRACT

Polymerization of acrylamide monomer, initiated by the redox system involving acidified ceric ammonium sulfate and 2-mercaptoethanol (2-ME) was carried out in an aqueous medium at 25°C. White, rigid polyacrylamide, isolated under controlled experimental conditions, showed a molecular weight of  $1.5 \times 10^4$  from viscosity measurements. The rate of monomer (M) conversion to polymer was found to be proportional to  $[M]^{1.5}$ ,  $[2-ME]^{0.5}$ , and  $[Ce(IV)]^{0.4}$ . Further, the rate of disappearance of ceric ion was observed to be directly proportional to  $[2-ME]$  and independent of  $[M]$  in the range of 0.16-0.48 mole/liter. The explanation of the above proportionalities is given in terms of a proposed reaction mechanism. Values of the usual rate constants,  $k_r$ ,  $k_0/k_t$ , and  $k_t/k_p^{1/2}$  have been computed.

## INTRODUCTION

A number of studies have been reported in literature to deal with the mechanism and kinetics of polymerization of different monomers, initiated either by ceric salts alone or ceric salt-reductant couples. The reducing agents used have been alcohols [1-6], aldehyde [7], secondary and tertiary amines [8], triethyl borate [9], and malonic acid [10]. Typical graft copolymers of acrylamide have also been prepared by using ceric ion-poly(vinyl alcohol) [11] and ceric ion-dextran [12] redox systems as well. The redox system produces cerous ions and transient free radicals to initiate the chain polymerization of vinyl monomers.

2-Mercaptoethanol was recently coupled with the oxidant potassium persulfate in order to polymerize acrylamide [13]. The above redox pair has been reported to be a potent initiator of polymerization of this monomer. It was, therefore, thought interesting to study the role of the Ce(IV)/2-ME redox pair in polymerization of acrylamide in order to gather some necessary information on different steps of polymerization.

## EXPERIMENTAL

### Chemicals

Acrylamide (HPCL, Japan) was recrystallized twice from methanol and kept dry by storage in a vacuum desiccator. 2-Mercaptoethanol (Koch Light Labs, Ltd., England) was used as received. Ceric ammonium sulfate and other reagents employed in this investigation were all of BDH (Analar) grade. Potassium hydrogen sulfate was used to maintain a desired constant ionic strength, and all the required solutions were prepared in double distilled water.

### Rate Measurement

The polymerization method and rate measurement of monomer conversion to polymer under purified nitrogen have been described in an earlier communication [14].

### Ceric Ion Estimation

Ceric ion concentration at different intervals of time was determined by quenching the aliquots in a suitable excess of ferrous

ammonium sulfate to back-titrate the excess of ferrous ions with a known concentration of ceric ammonium sulfate. The indicator used was N-phenylanthranilic acid.

### Molecular Weight of Polyacrylamide from Viscosity Measurements

Under controlled concentrations of monomer and redox couple, the polymer was isolated after 3 hr by adding pure methanol to the above system. Aqueous solutions of suitable concentrations of purified polyacrylamide samples were subjected to viscosity measurements, from which the viscosity-average molecular weight was obtained by utilizing the equation of Collinson et al [ 15]. The molecular weight of polyacrylamide, thus determined, was  $1.5 \times 10^4$ .

## RESULTS AND DISCUSSION

### Rate of Monomer Disappearance

The rate of polymerization  $R_p$  increases with an increasing concentration of acrylamide in the range of  $6.5 \times 10^{-2}$  to  $18.0 \times 10^{-2}$  mole/liter. The  $R_p$  versus  $[M]^{1.5}$  plot is linear and passes through the origin (Fig. 1). The dependence of  $R_p$  on the 1.5 exponent of monomer concentration shows, therefore, that the termination occurs by mutual interaction of the growing polymer radicals rather than by linear reaction.

The rate has also been observed to be proportional to the 0.5 power of the reductant (2-ME) concentration (Fig. 2), which appears to confirm again the mutual termination; for linear termination, the rate would have been proportional to  $[2\text{-ME}]$ .

Further, the rate of disappearance of monomer is found to be proportional to  $[\text{Ce(IV)}]^{0.4}$  within the concentration range  $0.3 \times 10^{-3}$  to  $1.5 \times 10^{-3}$  mole/liter (Fig. 3). The rate, however, appeared to decrease with increasing concentration of ceric ions beyond  $1.5 \times 10^{-3}$  mole/liter. Now, the increase of rate at lower concentration may be explained in terms of the formation of free radicals as a result of  $\text{Ce(IV)} + 2\text{-ME}$  interaction along with the termination by mutual interaction of growing free radicals. At higher concentrations of the oxidant  $\text{Ce(IV)}$ , a linear termination appears to be one of the probabilities.

The rate of polymerization also showed an increasing trend with decreasing  $[\text{H}_3\text{O}^+]$  at a constant ionic strength ( $\mu$ ) of the system; it

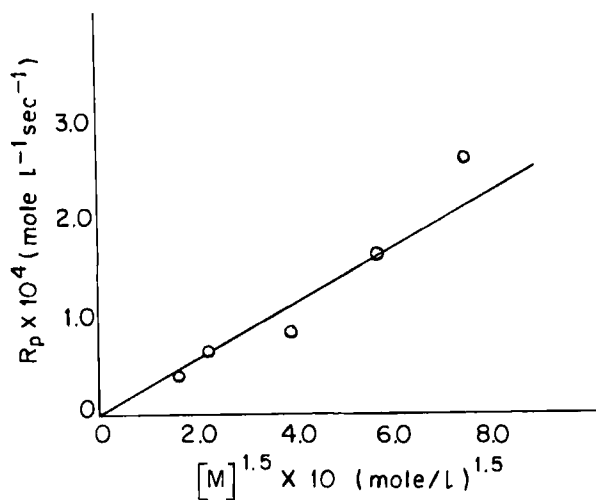


FIG. 1. Rate of polymerization as a function of monomer concentration at constant  $[2\text{-ME}] = 1.0 \times 10^{-3}$  mole/liter;  $[\text{Ce(IV)}] = 2.0 \times 10^{-3}$  mole/liter;  $[\text{H}_2\text{SO}_4] = 1.0 \times 10^{-2}$  mole/liter;  $\mu = 0.066 \text{ M}$ .

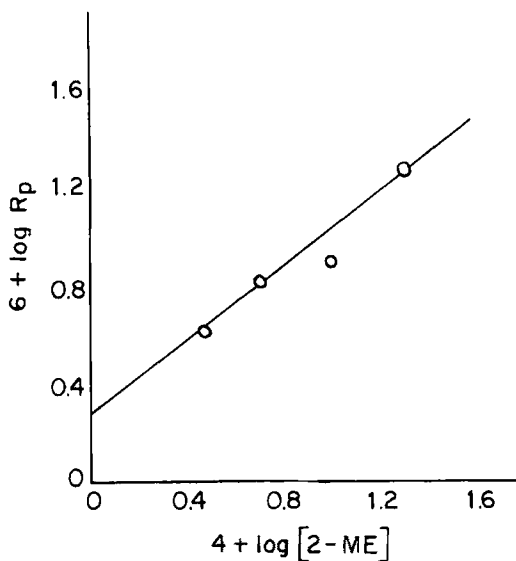


FIG. 2. Plot of  $\log R_p$  vs.  $\log [2\text{-ME}]$  at constant  $[M] = 0.12$  mole/liter;  $[\text{H}_2\text{SO}_4] = 1.0 \times 10^{-2}$  mole/liter;  $[\text{Ce(IV)}] = 2.0 \times 10^{-3}$  mole/liter;  $\mu = 0.066 \text{ M}$ .

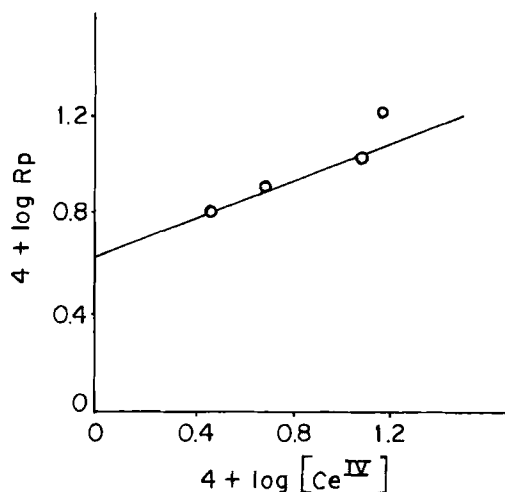


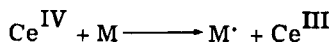
FIG. 3. Plot of  $\log R_p$  vs.  $\log [\text{Ce(IV)}]$  at constant  $[M] = 0.12$  mole/liter;  $[2\text{-ME}] = 1.0 \times 10^{-3}$  mole/liter;  $[\text{H}_2\text{SO}_4] = 1.0 \times 10^{-3}$  mole/liter;  $\mu = 0.066$  M.

decreased with increasing  $\mu$  values at a fixed concentration of  $\text{H}_3\text{O}^+$  ions, and was found to be independent of the variation of both pH and  $\mu$  values. A similar pattern of results has been obtained by Santappa et al. [10] in case of the Ce(IV)-malonic acid system towards the polymerization of MA and MMA monomers.

#### Rate of Ce(IV) Disappearance

In the absence of 2-ME, the rate was found to be independent of  $[M]$ . This is shown in Table 1. It appears, therefore, quite clear that there are no initiation or termination steps of the following types:

Initiation:



Termination:

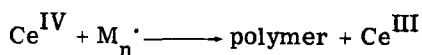


TABLE 1. Effect of Monomer Concentration on the Rate of Ceric Ion Disappearance in the Absence of 2-ME<sup>a</sup>

Monomer concentration [M] (mole/liter)	Reduction of [Ce(IV)] after 3 hr (mole/liter × 10 <sup>4</sup> )
0.16	1.40
0.32	1.50
0.48	1.45

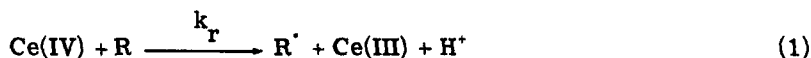
<sup>a</sup>Recipe: initial [Ce(IV)] =  $3.56 \times 10^{-3}$  mole/liter; [H<sub>2</sub>SO<sub>4</sub>] =  $2.0 \times 10^{-2}$  mole/liter;  $\mu = 0.124$  M; 25°C.

In the presence of reductant, the rate of ceric ion disappearance viz,  $-d[\text{Ce(IV)}]/dt$ , showed an increasing trend with an increasing concentration of 2-ME within the range of  $0.4 \times 10^{-4}$  to  $8.0 \times 10^{-4}$  mole/liter. The linear plot of rate versus concentration of 2-ME (as in Fig. 4) passing through the origin appears to confirm the absence of complex formation between the substrate and ceric ions supporting, thereby, the views of Subramanian and Santappa [10] in case of Ce(IV) and malonic acid-initiated redox polymerization of MA, MMA, and AN monomers.

### Reaction Mechanism and Rate Laws

On the basis of the above results, an attempt has been made to propose here the following reaction scheme for the polymerization of acrylamide, initiated by the acidified ceric ammonium sulfate 2-mercaptoethanol redox system in aqueous medium.

The interaction of ceric ions with the reductant (R) is



in which R stands for 2-ME and R' is a primary radical generated to initiate the polymerization.

Next, the reaction of these primary radicals with Ce(IV) ions involves the possibility (2):



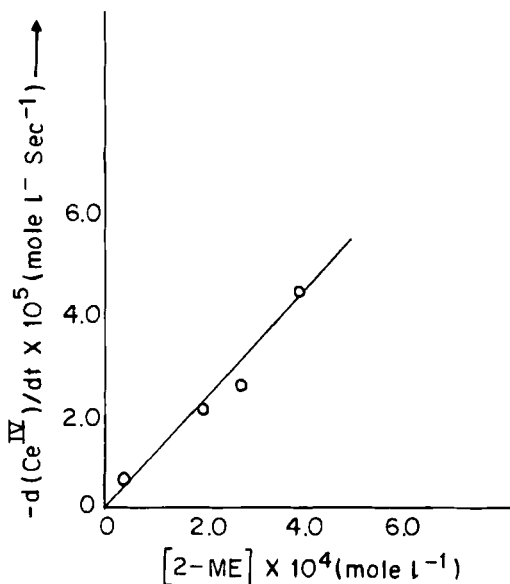


FIG. 4. Variation of rate of ceric ion disappearance with [2-ME] at constant [M] = 0.12 mole/liter; [H<sub>2</sub>SO<sub>4</sub>] = 2.0 × 10<sup>-2</sup> mole/liter; [Ce(IV)] = 3.56 × 10<sup>-3</sup> mole/liter; μ = 0.124 M.

The initiation of polymerization thus stands as,



followed by propagation,



and finally leading to the mutual termination as:



On applying now the usual steady-state principle to both [R'] and [M'], the rate equation for the monomer disappearance has been worked out as Eq. (6):



$$-d[M]/dt = k_p[M] \left\{ (k_i k_r / k_t) ([M][\text{Ce(IV)}][R] / (k_0[\text{Ce(IV)}] + k_i[M])) \right\}^{1/2} \quad (6)$$

For much higher concentration of Ce(IV) as compared to monomer concentration, i.e.,  $k_0[\text{Ce(IV)}] \gg k_i[M]$ , one may write Eq. (6) as:

$$-d[M]/dt = k_p[M]^{3/2} (k_i k_r / k_0 k_t)^{1/2} [R]^{1/2} \quad (7)$$

Thus, at high concentration of ceric ions, according to Eq. (7), the rate of polymerization should be independent of ceric ion concentration and proportional to  $[M]^{1.5}$  and  $[R]^{0.5}$ , as has been observed.

Similarly, the rate equation for the ceric ion disappearance may be put as,

$$-d[\text{Ce(IV)}]/dt = 2k_r[R][\text{Ce(IV)}] \quad (8)$$

from which it is clear that the rate,  $-d[\text{Ce(IV)}]/dt$ , should be directly proportional to  $[R]$  and independent of  $[M]$  for a fixed concentration of Ce(IV) ions. This is, indeed, borne out by the experimental facts.

### Evaluation of Rate Constants

Under the uniform concentration of the oxidant, the rate constant  $k_r$  has been calculated by using the slope of Eq. (8). With  $k_r$  known in this way, the value of composite rate constant, viz.,  $k_p(k_i/k_0 k_t)^{1/2}$  was thus obtained from Eq. (7) at specified concentrations of the monomer and reductant.

It is now interesting to compare the value of composite rate constant as obtained above, from another alternative approach by utilizing Eq. (6).

In the concentration range where  $R_p$  is dependent on Ce(IV) ion concentration, the reciprocal of Eq. (6) gives Eq. (9):

$$\left\{ \frac{[M]}{R_p} \right\}^2 = \frac{k_t}{k_p^2 k_r} \left( \frac{1}{[\text{Ce(IV)}][R]} \right) + \frac{k_t k_0}{k_p^2 k_i k_r} \left( \frac{1}{[M][R]} \right) \quad (9)$$

A plot of  $\{[M]/R_p\}^2$  against  $1/[\text{Ce(IV)}]$  at constant concentration of monomer and reductant according to Eq. (9) was found to be a straight line (Fig. 5).

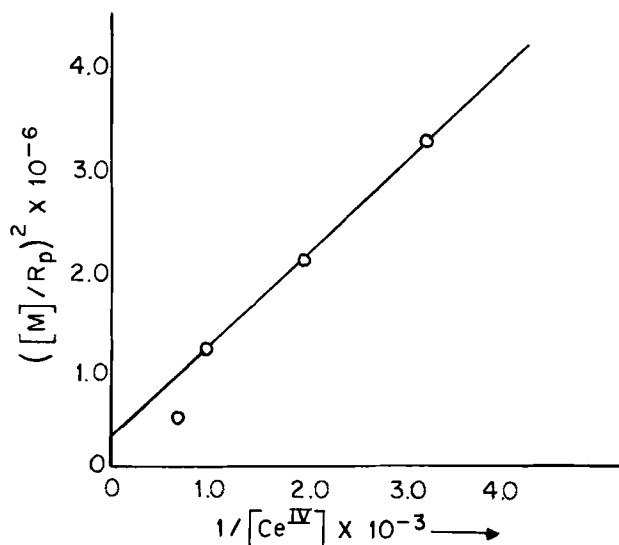


FIG. 5. Variation of  $([M]/R_p)^2$  with  $1/[Ce(IV)]$  at constant  $[M] = 0.12$  mole/liter;  $[2-ME] = 1.0 \times 10^{-3}$  mole/liter;  $[H_2SO_4] = 1.0 \times 10^{-3}$  mole/liter;  $\mu = 0.066$  M.

TABLE 2. Rate Parameters for Ce(IV)/2-ME Redox Polymerization of Acrylamide

Rate parameter	Value
$k_r$ (liter/mole-sec)	15.45
$k_p(k_i/k_0k_t)^{1/2}$	
By Eq. (7)	$2.3 \times 10^{-2}$
By Eq. (9)	$4.2 \times 10^{-2}$
$k_0/k_i$	40.8
$k_p/k_t^{1/2}$	0.27

The value of composite rate constant was thus obtained from the knowledge of  $k_r$  and the intercept of Eq. (9). The numerical value of  $k_p(k_i/k_0k_t)^{1/2}$  is very close to that obtained earlier, as is clear from Table 2.

Also, on dividing the intercept by the slope of Eq. (9), one may calculate the ratio of the rate constants  $k_0$  and  $k_1$ . Again, the slope of Eq. (9) provides yet another opportunity to estimate  $k_p/k_t^{1/2}$  from the known value of  $k_r$ . Table 2 summarizes these data for comparison.

It is evident from Table 2 that the value of ratio of rate constants for the consumption of free radicals by Ce(IV) and M, respectively,  $k_0/k_1$ , is fairly high. This eventually indicates that a comparatively small population of the free radicals tends to initiate the polymerization of acrylamide by the concerned system as shown by Eq. (3) and a larger proportion of them are used up by Ce(IV) ions according to the interaction represented by step (2).

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