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Aqueous Polymerization of Acrylonitrile Initiated by Ce^{4+}-Ethyl Methyl Ketone Redox System

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ABSTRACT

The kinetics of polymerization of acrylonitrile (AN) initiated by the Ce^{4+}- ethyl methyl ketone (EMK) redox system has been studied. The rate of ceric disappearance was found to be directly proportional to [EMK] and $[Ce^{4+}]$. The rate of polymerization was found to be proportional to $[AN]^{1.5}$, $[Ce^{4+}]^{0.5}$, and $[EMK]^{0.5}$. At higher concentrations of Ce^{4+}, the rate was independent of $[Ce^{4+}]$. A probable mechanism involving primary radical initiation and mutual termination is proposed to explain the results.

Ceric salts or ceric salt reducing agent systems have been used as initiators of vinyl polymerization [1-5] in different acid media. It was concluded that initiation was both by Ce^{4+} and the primary radical obtained by the oxidation of the substrate, and termination was extensively by Ce^{4+}. It was envisaged that in the vinyl systems polymerized by a redox-type initiator involving Ce^{4+}, the direct interaction of Ce^{4+} with the monomer and the growing polymer radical could be brought under control by suitable adjustments in the concentration of the reactants, temperature, etc., so that such reactions

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could be either suppressed or eliminated whenever necessary. To elucidate this aspect, a study of the kinetics of polymerization of acrylonitrile (AN) initiated by the ceric ammonium sulfate-ethyl methyl ketone (EMK) redox system in sulfuric acid medium has been undertaken.

EXPERIMENTAL

All reagents used were AnalaR samples. Ethyl methyl ketone was dried over anhydrous sodium sulfate and fractionally distilled, always collecting the middle fraction. Acrylonitrile was washed with dilute acid and alkali followed by water. This was then dried over anhydrous calcium chloride and distilled under reduced pressure. Doubly distilled deionized water was used for the preparation of stock solutions. The experimental procedures employed for polymerization have been detailed elsewhere [6, 7]. The polymerization reactions were heterogeneous, with polymer precipitating continuously. Rates of polymerization were obtained by gravimetry, while rates of oxidant consumption were obtained by cerimetry on reaction mixtures arrested by the addition of excess standard ferrous sulfate.

RESULTS AND DISCUSSION

Under the experimental conditions, no polymerization of the monomer was found even after 30 min when ceric ammonium sulfate alone was used as an initiator. Polymerization started without any induction period in the presence of the substrate.

Rate of Ceric Disappearance ($-R_{Ce^{4+}}$)

The rate was found to be directly proportional to $[Ce^{4+}]$ as evidenced by the linear plot of $-R_{Ce^{4+}}$ vs $[Ce^{4+}]$ which passed through the origin (Fig. 1A). The rate was independent of monomer concentration, which meant ceric ions were not involved in the initiation reaction of the type $M + Ce^{4+}$ or in termination reaction of the type $(M_n)^{\cdot} + Ce^{4+}$. The rate increased with the first power of [EMK] (Fig. 1B), and the plot of $-R_{Ce^{4+}}$ vs [EMK] was linear, passing through the origin, and indicating the order in [EMK] also to be one.

The absence of complex formation between the substrate and ceric ion was revealed by the straight line plot of the rate against [EMK] which passed through the origin (Fig. 1B). On the other hand, formation of a complex and obedience to Michaelis-Menton [8] kinetics would mean that a plot of 1/rate vs 1/[EMK] would be linear with

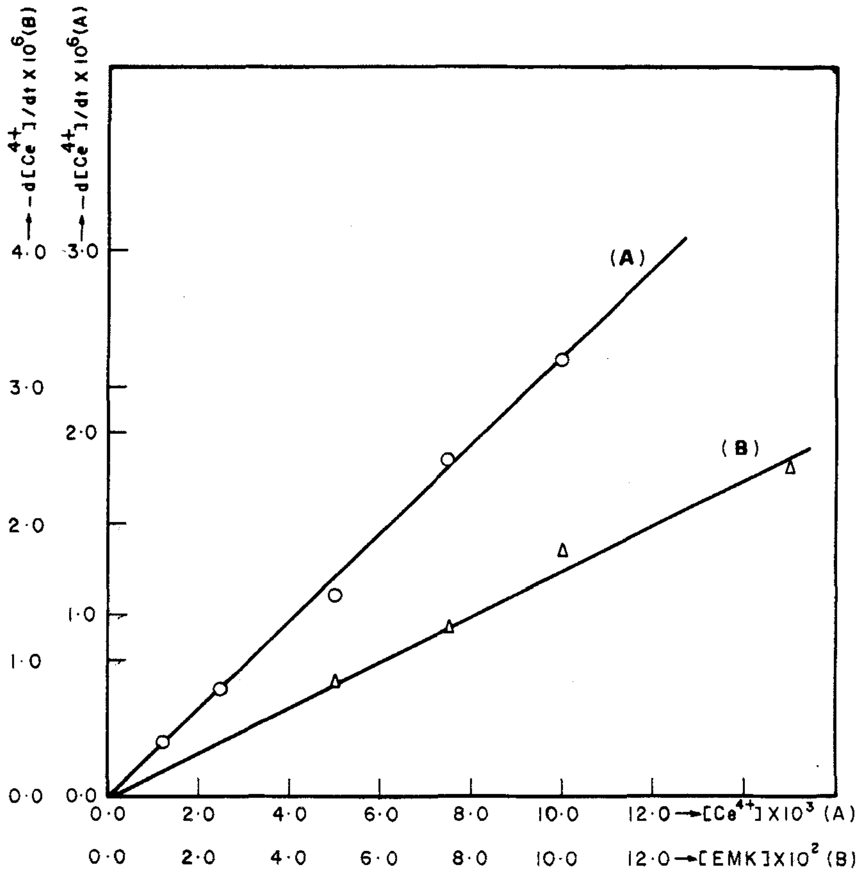

FIG. 1. (A) Plot of -d[Ce^{4+}]/dt vs [Ce^{4+}] × 10^3; [EMK] = 0.05 M; [H_2SO_4] = 1.00 M; [AN] = 0.608 M; 313 K. (B) Plot of -d[Ce^{4+}]/dt vs [EMK] × 10^2; [Ce^{4+}] = 0.005 M; [H_2SO_4] = 1.00 M; [AN] = 0.608 M; 313 K.

an intercept on the ordinate. The rate was found to increase with increasing [H_2SO_4] at constant ionic strength.

Rates of Monomer Disappearance

Oxidation of EMK proceeds via a free radical mechanism, the evidence for which has been provided by the induced polymerization of acrylonitrile.

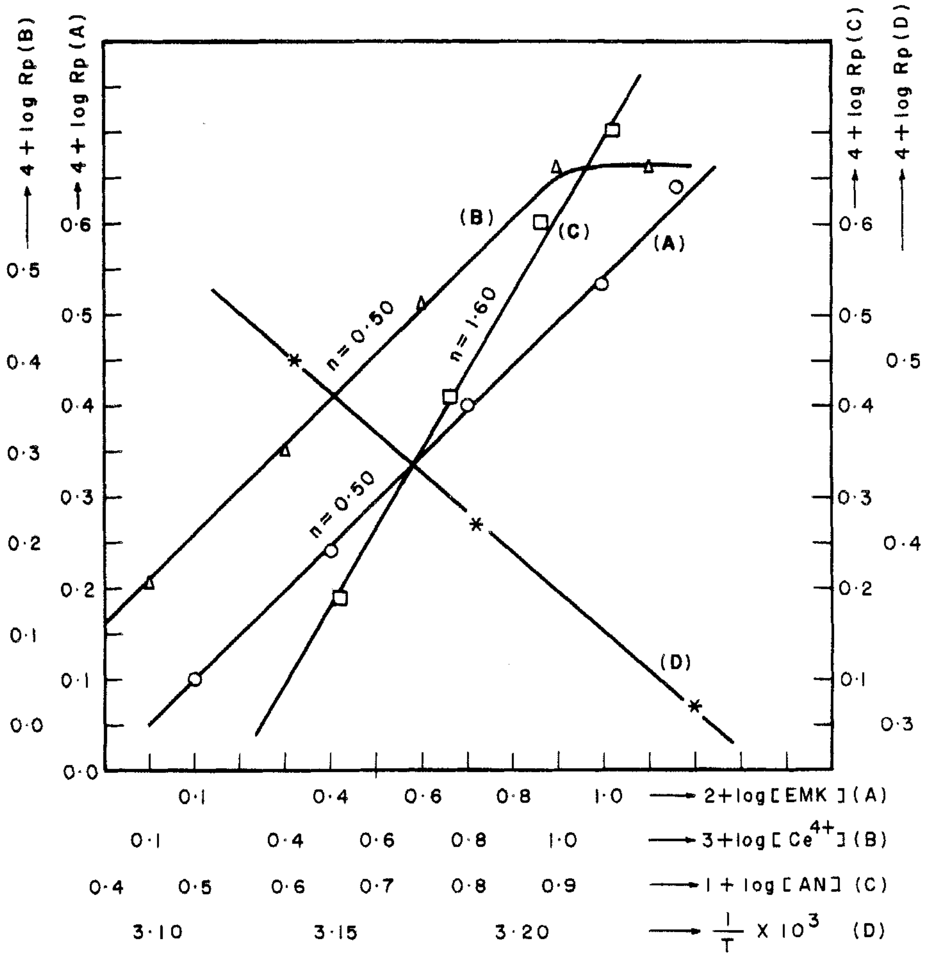

FIG. 2. (A) Plot of 2 + log [EMK] vs 4 + log R_p; [Ce^{4+}] = 0.005 M; [H_2SO_4] = 1.00 M; [AN] = 0.608 M; 313 K. (B) Plot of 3 + log [Ce^{4+}] vs 4 + log R_p; [EMK] = 0.005 M; other conditions same as in A. (C) Plot of 1 + log [AN] vs 4 + log R_p; [Ce^{4+}] = 0.005 M; [H_2SO_4] = 1.00 M; [EMK] = 0.050 M; 313 K. (D) Plot of $10^3/T$ vs 4 + log R_p; [AN] = 0.608 M; other conditions same as in C.

Because the rate depends on $[M]^{1.5}$ (Fig. 2C), there is strong evidence for mutual termination rather than linear termination. The rate was directly proportional to $[EMK]^{0.5}$ (Fig. 2A). If the linear termination were effective, the rate would have been directly proportional to [EMK]. Increasing $[Ce^{4+}]$ (1.25×10^{-3} to 1.00×10^{-2} M) increased the rate; however, at higher concentrations ($> 1.00 \times 10^{-2}$ M) the rate was independent of $[Ce^{4+}]$ (Fig. 2B). In the lower concentration range a double logarithmic plot gave a straight line with a slope of 0.5, indicating the order in $[Ce^{4+}]$ to be 0.5. The increase in rate with $[Ce^{4+}]$ may be understood in terms of initiation by Ce^{4+} + EMK and mutual termination. The rate of polymerization increased with an increase in temperature, and the overall activation energy was found to be 34.6 kJ/mol (Fig. 2D).

The following scheme was found to explain satisfactorily all the kinetic results obtained.

Reaction of ceric ion with EMK to produce a radical $R^{\cdot}$:

$$Ce^{4+} + EMK \xrightarrow{k_1} R^{\cdot} + Ce^{3+} + H^+ \qquad (1)$$

Reaction of primary radicals with Ce^{4+} to give the products:

$$Ce^{4+} + R^{\cdot} \xrightarrow[\text{fast}]{k_2} \text{products} + Ce^{3+} + H^+ \qquad (2)$$

Initiation of polymerization, say reaction of primary radicals with monomer (M):

$$R^{\cdot} + M \xrightarrow{k_i} R\text{–}M^{\cdot} \qquad (3)$$

Propagation:

$$R\text{–}M^{\cdot} + M \xrightarrow{k_p} R\text{–}M\text{–}M^{\cdot} \qquad (4)$$

$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}$$

Termination by Ce^{4+}:

$$(M_n)^{\cdot} + Ce^{4+} \xrightarrow{k_t'} \text{polymer} + Ce^{3+} + H^+ \qquad (5a)$$

Mutual termination:

$$(M_n)^{\cdot} + (M_m)^{\cdot} \xrightarrow{k_t} \text{polymer} \tag{5b}$$

Making the usual assumptions for the steady-state concentrations of free radicals (primary and growing polymer radicals) and considering only the mutual type of termination to be effective under the experimental conditions, we arrive at Eqs. (6) and (7) for the rate of ceric disappearance and the rate of monomer disappearance, respectively.

$$-\frac{d[\mathrm{Ce}^{4+}]}{dt} = k_1[\mathrm{Ce}^{4+}][\mathrm{EMK}] \tag{6}$$

$$R_p = -\frac{d[M]}{dt} = \frac{k_p[M]^{3/2}}{k_t^{1/2}}\left(\frac{k_i k_1[\mathrm{EMK}][\mathrm{Ce}^{4+}]}{k_i[M] + k_2[\mathrm{Ce}^{4+}]}\right)^{1/2} \tag{7}$$

At high $[\mathrm{Ce}^{4+}]$ it can be assumed that $k_2[\mathrm{Ce}^{4+}] > k_i[M]$, i.e., most of the primary radicals are converting into products. Equation (7) reduces to

$$= -\frac{d[M]}{dt} = k_p(k_1k_i/k_2k_t)^{1/2}[M]^{1.5}[\mathrm{EMK}]^{1/2} \tag{8}$$

TABLE 1. Effect of Varying Solvents and $[\mathrm{Cu}^{2+}]$ on the Rate of Polymerization (R_p)[a]

% of acetic acid (v/v)	$R_p \times 10^4$	% of acetonitrile (v/v)	$R_p \times 10^4$	$[\mathrm{Cu}^{2+}] \times 10^2$ M	$R_p \times 10^4$
0.00	2.60	0.00	2.60	0.00	2.60
5.00	2.20	5.00	1.80	0.05	2.25
10.0	1.95	10.0	1.20	0.10	1.90
15.0	1.82	15.0	0.85	0.15	1.73
20.0	1.69	20.0	0.70	0.20	1.67

[a] $[\mathrm{Ce}^{4+}] = 5.00 \times 10^{-3}$ M, $[\mathrm{EMK}] = 5.00 \times 10^{-2}$ M, $[\mathrm{AN}] = 0.608$ M, $[\mathrm{H}^+] = 1.00$ M, temperature = 313 K.

Under these conditions, $k_2[Ce^{4+}] > k_i[M]$, assuming linear termination (5a) in preference to mutual termination. The rate would be independent of $[Ce^{4+}]$ and dependent on $[M]^2$ and [EMK]. Since the experimental rate is strictly dependent on $[EMK]^{1/2}$ and $[M]^{1.5}$, termination by Ce^{4+} must be ruled out.

Rate equations (6), (7) and (8) satisfactorily explain all the results obtained for the rate of ceric disappearance and monomer disappearance at low as well as high $[Ce^{4+}]$. Cu^{2+} ion was proved to be a good terminating species in vinyl polymerizations [9]. Addition of these ions decreased the rate of polymerization in this system (Table 1). This is attributed to the reaction of polymer radicals with Cu^{2+} ion to produce dead polymer and Cu^{+}.

Water-soluble solvents such as acetic acid and acetonitrile also decrease the rate of polymerization considerably (Table 1). This behavior can be interpreted by assuming that the presence of solvents increases the regulated rate of production of primary radicals which makes the termination rate relatively fast compared to the growing polymer chain rate. It also decreases the area of shielding by the strong hydration layer in aqueous medium, resulting in termination by growing chains, in accordance with the view of Kern et al. [10].

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