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Kinetics of Polymerization of Ethyl Acrylate Initiated by Manganese(III)

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ABSTRACT

The kinetics of the thermal polymerization of ethyl acrylate initiated by Mn^{3+} in sulfuric acid at 50 to 60°C have been studied. The rate of monomer disappearance is found to bear a square dependence on [M] and is independent of both $[Mn^{3+}]$ and $[H^+]$. The rate of manganic disappearance is found to be directly proportional to [M], $[Mn^{3+}]$, and $[H^+]$. The degree of polymerization is directly proportional to [M] and inversely proportional to $[Mn^{3+}]$ and $[H^+]$. A kinetic scheme involving the initiation and termination of polymerization by Mn^{3+} is proposed.

INTRODUCTION

A literature survey reveals that the kinetics of polymerization of several vinyl monomers initiated by Mn^{3+} coupled with reducing agents have been extensively studied [1-6]. This paper presents the results obtained in the kinetics of polymerization of ethyl acrylate initiated by Mn^{3+} in the absence of any reducing agent in sulfuric acid medium.

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EXPERIMENTAL

Manganese(III) acetate was prepared by the method of Andrulis et al. [7]. Ethyl acrylate was purified according to the Santappa et al. [8] method. Sulfuric acid (BDH, AR) and sodium bisulfate (E. Merck) were used to maintain hydrogen ion concentration and ionic strength, respectively. Other chemicals used were extra pure samples.

Procedure

In a typical experiment, appropriate quantities of monomer, sulfuric acid, and sodium bisulfate solution were taken in a reaction tube and thermostated at the required temperature. The reaction mixture was flushed with oxygen-free nitrogen for about 40 min. After deaeration, Mn^{3+} solution was added to the reaction mixture, thoroughly shaken, and the tube was closed immediately to ensure an inert atmosphere. After a specified time, the reaction tube was cooled in a freezing mixture, and air was blown through the reaction solution to arrest the polymerization.

Rate Measurements

The polymerization rate was followed by determining the concentration of monomer in the reaction mixture before and after polymerization by the method of Wallace and Young [9]. The rate of manganic disappearance was followed iodometrically. The degree of polymerization of poly(ethyl acrylate) was calculated using the equation $[\eta] = 2.6 \times 10^{-4} M_v^{0.66}$ in ethyl acetate [10] at 30°C.

RESULTS AND DISCUSSION

Rate of Polymerization (R_p)

The plot of R_p vs $[\text{monomer}]^2$ (Fig. 1) is linear, passing through the origin and thus indicating that the rate is second order with respect to [monomer]. R_p is found to be independent of $[Mn^{3+}]$, $[H^+]$, and μ.

Rate of Manganic Disappearance ($-R_m$)

$-R_m$ increased linearly with [M] and $[Mn^{3+}]$. The linear plots of $-R_m$ vs [M] (Fig. 2, Curve A) and $-R_m$ vs $[Mn^{3+}]$ (Fig. 2, Curve B)

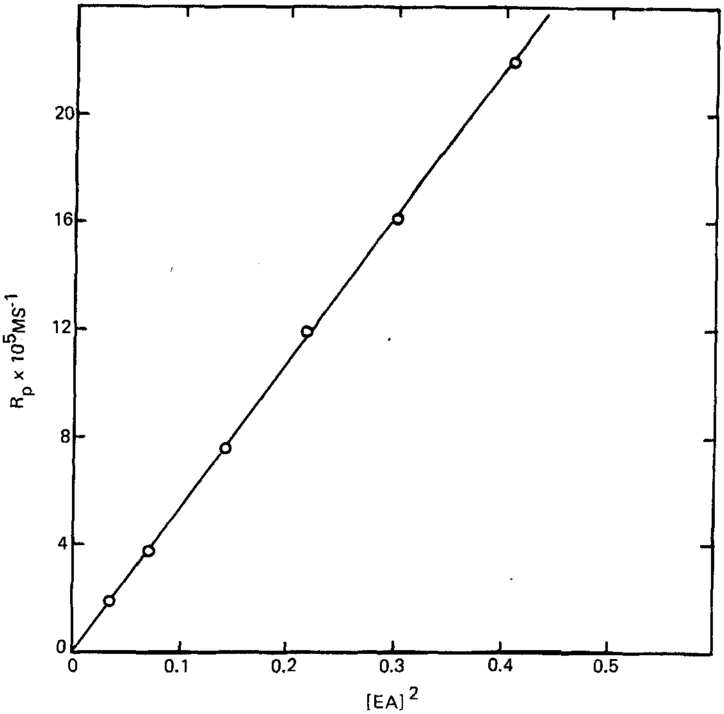

FIG. 1. Variation of R_p with [M]. R_p vs $[M]^2$ at $[Mn^{3+}] = 1.698 \times 10^{-3}$ M, $[H^+] = 2.4$ M, $\mu = 3.2$ M, and T = 50°C.

with zero intercept show that the order with respect to [M] and $[Mn^{3+}]$ is unity. $-R_m$ is directly proportional to $[H^+]$ (Fig. 2, Curve C). Ionic strength has no significant effect on $-R_m$.

Degree of Polymerization ($\overline{X}_n$)

The degree of polymerization is directly proportional to [M] and inversely proportional to $[Mn^{3+}]$ and $[H^+]$ (Fig. 3, Curves A, B, and C).

The square dependence of R_p on $[M]^2$ and independence of $[H^+]$ shows that initiation and termination is caused by the same ionic species of manganese. The metal ion species which can produce such results under the experimental conditions is either Mn^{3+} or $Mn^{3+}OH^-$. The direct proportionality of $-R_m$ on $[H^+]$ indicates that both the initiation and the termination are caused by Mn^{3+} in an unhydrolyzed form. If $Mn^{3+}OH^-$

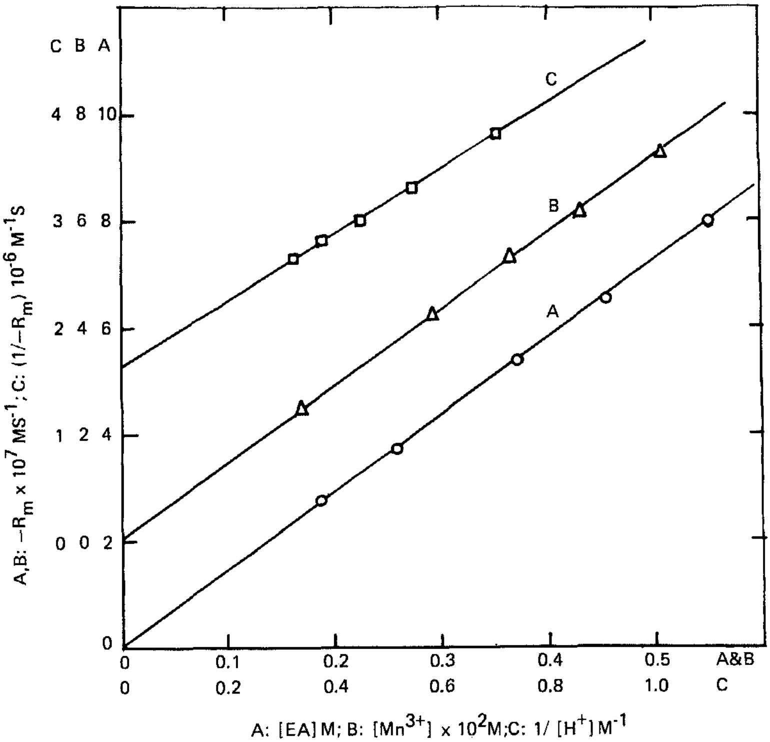

FIG. 2. Variation of $-R_m$ with [M], [Mn^{3+}], and [H^+]. A: $-R_m$ vs [M] at [Mn^{3+}] = 1.698×10^{-3} M, [H^+] = 2.4 M, μ = 3.2 M, and T = 50°C. B: $-R_m$ vs [Mn^{3+}] at [M] = 0.1919 M, [H^+] = 2.2 M, μ = 3.0 M, and T = 50°C. C: $1/-R_m$ vs $1/H^+$] at [M] = 0.1919 M, [Mn^{3+}] = 1.698×10^{-3} M, μ = 3.0 M, and T = 50°C.

species causes both initiation and termination, $-R_m$ should decrease with an increase of [H^+]. Since such a trend in $-R_m$ is not observed, it is concluded that Mn^{3+} is responsible for both initiation and termination. Katai et al. [11] reported the same trend in the polymerization of acrylonitrile initiated by the Ce^{4+}-ethylene glycol redox system and concluded that both initiation and termination are caused by Ce^{4+}. Balakrishnan et al. [12] reported the initiation and termination of methyl acrylate polymerization by Mn^{3+}. Subramanian [13] observed Ce^{4+} initiation and termination of ethyl acrylate polymerization. Mino et al. [14] and Santappa et al. [15] also reported the metal ion initiation and termination of polymerization.

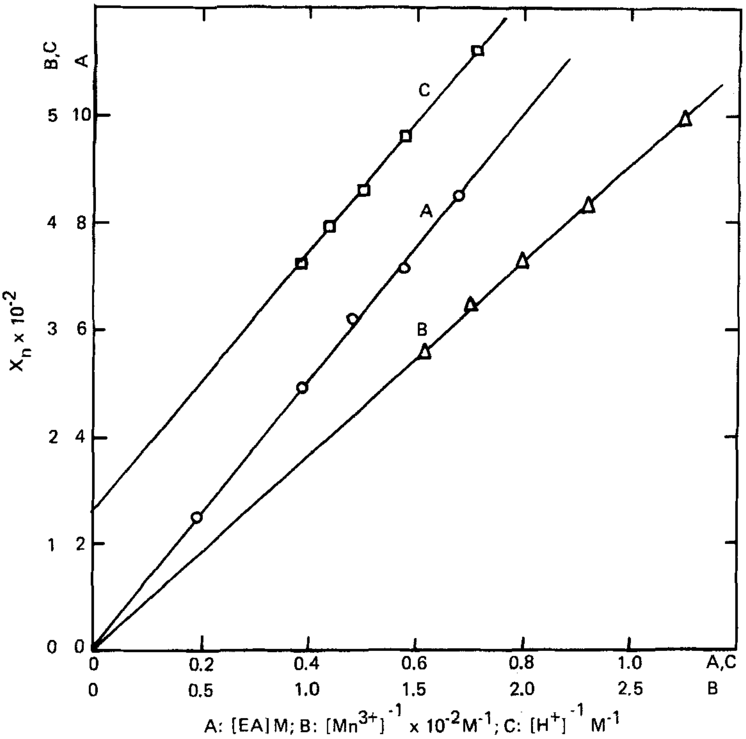

FIG. 3. Variation of $\overline{X}_n$ with [M], [Mn^{3+}], and [H^+]. A: $\overline{X}_n$ vs [M] at [Mn^{3+}] = 2.884×10^{-3} M, [H^+] = 1.4 M, μ = 2.4 M, and T = 50°C. B: $\overline{X}_n$ vs 1/[Mn^{3+}] at [M] = 0.3838 M, [H^+] = 1.5 M, μ = 2.5 M, and T = 50°C. C: $\overline{X}_n$ vs 1/[H^+] at [M] = 0.3838 M, [Mn^{3+}] = 2.884×10^{-3} M, μ = 2.7 M, and T = 50°C.

Kinetic Scheme and Rate Laws

The experimental results discussed above can be explained adequately on the basis of the following reaction scheme.

Initiation:

$$M + Mn^{3+} \xrightarrow{k_i} M^{\bullet} + Mn^{2+} + H^+$$

Propagation:

$$M + M^{\bullet} \xrightarrow{k_p} M{-}M^{\bullet}$$

-   -   -

-   -   -

$$(M)^{\bullet}_{n-1} + M \xrightarrow{k_p} (M)_n^{\bullet} \text{ etc.}$$

Termination:

$$(M)_n^{\bullet} + Mn^{3+} \xrightarrow{k_t} P_n + Mn^{2+} + H^+$$

The hydrolytic equilibrium is

$$Mn^{3+} + H_2O \overset{K}{\rightleftharpoons} Mn^{3+}OH^- + H^+$$

Applying the steady-state principle for radicals and assuming the nondependence of the rate constants (k_p and k_t) on chain length, we obtain the following rate expressions for R_p, $-R_m$, and $\overline{X}_n$ from the scheme presented above.

$$R_p = k_p k_i [M]^2/k_t$$

$$-R_m = 2k_i[Mn^{3+}][M][H^+]/(K + [H^+])$$

$$\overline{X}_n = \frac{k_p[M](K + [H^+])}{k_t[Mn^{3+}][H^+]}$$

Evaluation of Rate Constants and Thermodynamic Parameters

The rate constants calculated from the plot of $1/-R_m$ vs $1/[H^+]$ are $k_1 = 1.316$ mol/L, $k_i = 8.10 \times 10^{-4}\ s^{-1}$, and $k_p/k_t = 0.7735$ at 50°C and $k_1 = 1.373$ mol/L, $k_i = 1.80 \times 10^{-3}\ s^{-1}$, and $k_p/k_t = 0.6678$ at 55°C.

Thermodynamic parameters calculated are $E_a = 26.11$ kcal/mol, $\Delta S^\dagger = 30.54$ e.u., $\Delta^\ddagger = 16.39$ kcal/mol, and $A = 3.02 \times 10^{19}$.

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