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### Homopolymerization of Ethyl Methacrylate

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## Homopolymerization of Ethyl Methacrylate

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### ABSTRACT

The kinetics of polymerization of ethyl methacrylate initiated by manganese(III) in sulfuric acid have been investigated. The overall rates of polymerization ( $R_p$ ), disappearance of manganic ion ( $-R_m$ ), and degree of polymerization ( $\bar{X}_n$ ) were measured with variation in [monomer],  $[Mn^{3+}]$ ,  $[H^+]$ ,  $\mu$ , and temperature. Various rate parameters and thermodynamic parameters were evaluated and are discussed.

### INTRODUCTION

A few papers have appeared on the polymerization of ethyl methacrylate. The studies of Kapur and Gadkary [1] and Khanna et al. [2] are mainly concerned with the evaluation of solvent transfer and monomer transfer parameters as a sort of comparison with similar vinyl monomer systems. Otsu et al. [3] studied the polymerization of ethyl methacrylate while studying the effect of alkyl groups on the radical polymerization of alkyl methacrylate. Cardenas and O'Driscoll [4] have investigated the kinetics of polymerization of ethyl methacrylate in connection with their studies on high conversion polymerizations and the effect of monomer transfer on the autoacceleration effect. The present investigation has been carried out

to throw light on the mechanism of polymerization of ethyl methacrylate initiated by manganese(III) in aqueous sulfuric acid medium.

## EXPERIMENTAL

Manganese(III) acetate was prepared by the method of Andrulis et al. [5]. Ethyl methacrylate was washed repeatedly with 5% sodium hydroxide and then with distilled water to remove the inhibitor. After drying over calcium sulfate, the monomer was distilled at a pressure of 49 mm at 45-48°C under pure nitrogen atmosphere. The other reagents, experimental procedure, estimations, and kinetic measurements were covered in an earlier paper [6]. The degree of polymerization of poly(ethyl methacrylate) was calculated using the equation  $[\eta] = (8.6 \times 10^{-5}) \bar{M}_v^{0.71}$  in ethyl acetate [7] at 35°C.

## RESULTS AND DISCUSSION

### Rate of Polymerization ( $R_p$ )

The rate of polymerization has a square dependence on monomer concentration, indicating that the rate is second-order with respect to  $[M]$ .  $R_p$  was found to be independent of  $[Mn^{3+}]$  and  $\mu$ , and decreases linearly with an increase of  $[H^+]$  (Fig. 1).

### Rate of Manganic Ion Disappearance ( $-R_m$ )

The rate of disappearance of manganic ion was found to increase linearly with  $[M]$  and  $[Mn^{3+}]$  and decrease with an increase of  $[H^+]$  (Fig. 2). Ionic strength has no effect on  $-R_m$ .

### Degree of Polymerization ( $\bar{X}_n$ )

The degree of polymerization was directly proportional to  $[M]$  and inversely proportional to  $[Mn^{3+}]$  and  $[H^+]$  (Fig. 3).

The square dependence of  $R_p$  on  $[M]$ , inverse proportionality of  $R_p$  on  $[H^+]$ , and the independent nature of  $R_p$  on  $[Mn^{3+}]$  indicate that the termination was affected by  $Mn^{3+}$  ions. Termination by  $Mn^{3+}$  ion has been reported in the literature [8-10]. The direct proportionality of  $-R_m$  on  $[M]$  and  $[Mn^{3+}]$  shows that initiation was either by  $Mn^{3+}OH^-$  or  $Mn^{3+}$  ions. The inverse proportionality of  $-R_m$  on  $[H^+]$  reveals that the initiation was effected by  $Mn^{3+}OH^-$  species and not by  $Mn^{3+}$  ions. If  $Mn^{3+}$  is the initiating agent,  $-R_m$  should increase with the

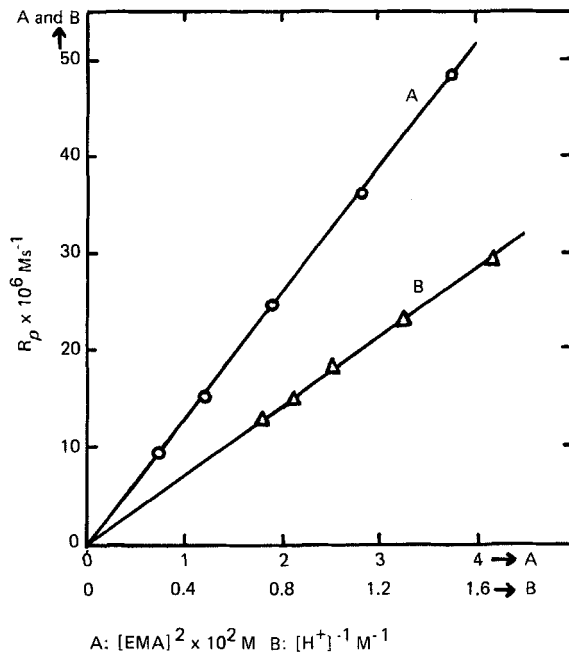
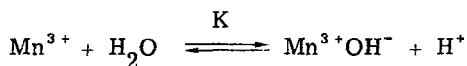


FIG. 1. Variation of  $R_p$  with  $[M]$  and  $[H^+]$ . A:  $R_p$  vs  $[M]^2$  at  $[Mn^{3+}] = 2.219 \times 10^{-3} \text{ M}$ ,  $[H^+] = 1.8 \text{ M}$ ,  $\mu = 2.0 \text{ M}$ , and  $T = 55^\circ\text{C}$ .  
 B:  $R_p$  vs  $1/[H^+]$  at  $[M] = 0.1098 \text{ M}$ ,  $[Mn^{3+}] = 2.958 \times 10^{-3} \text{ M}$ ,  $\mu = 1.4 \text{ M}$ , and  $T = 55^\circ\text{C}$ .

increase of  $[H^+]$ . Hence, it was concluded that initiation was effected by  $Mn^{3+}OH^-$  species and termination by  $Mn^{3+}$  ions. Jijie et al. [11] reported the initiation of polymerization by  $Co^{3+}OH^-$  species and termination by  $Co^{3+}$  ions.

#### Kinetic Scheme and Rate Laws

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



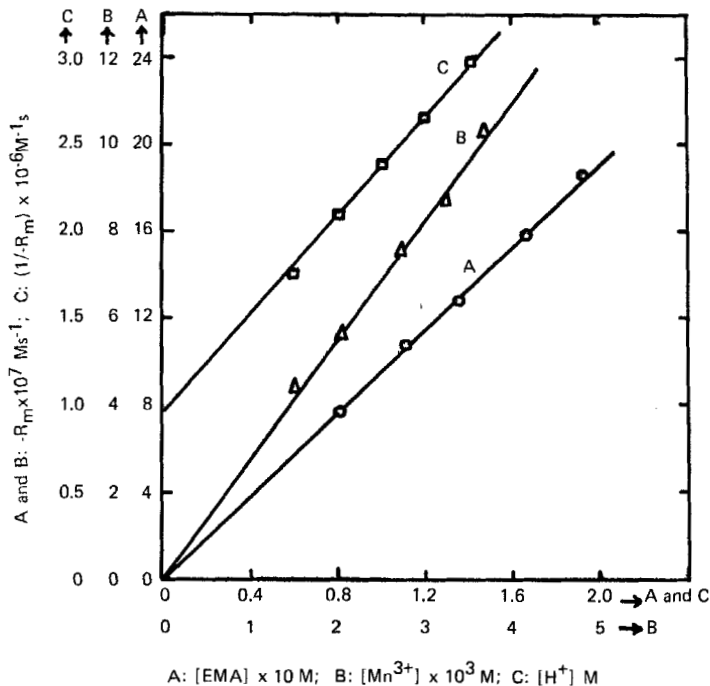
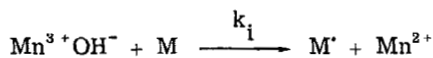
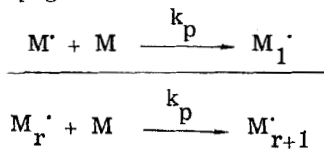


FIG. 2. Variation of  $-R_m$  with  $[M]$ ,  $[Mn^{3+}]$ , and  $[H^+]$ . A:  $-R_m$  vs  $[M]$  at  $[Mn^{3+}] = 2.219 \times 10^{-3} \text{ M}$ ,  $[H^+] = 1.8 \text{ M}$ ,  $\mu = 2.0 \text{ M}$ , and  $T = 55^\circ\text{C}$ . B:  $-R_m$  vs  $[Mn^{3+}]$  at  $[M] = 0.1295 \text{ M}$ ,  $[H^+] = 1.5 \text{ M}$ ,  $\mu = 1.6 \text{ M}$ , and  $T = 55^\circ\text{C}$ . C:  $-R_m$  vs  $[H^+]$  at  $[M] = 0.1098 \text{ M}$ ,  $[Mn^{3+}] = 2.958 \times 10^{-3} \text{ M}$ ,  $\mu = 1.4 \text{ M}$ , and  $T = 55^\circ\text{C}$ .

Initiation:



Propagation:



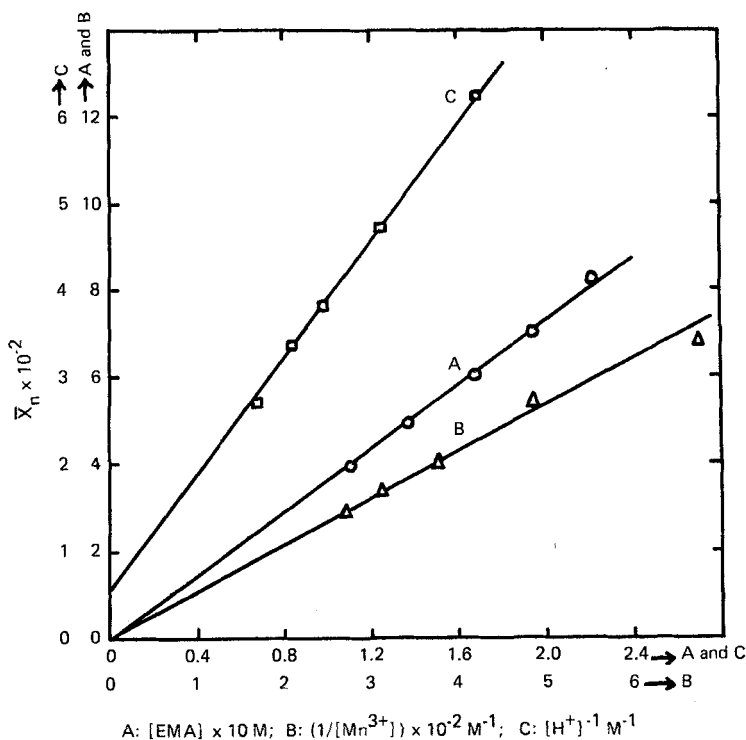
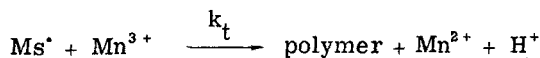


FIG. 3. Variation of  $\bar{X}_n$  with  $[M]$ ,  $[Mn^{3+}]$ , and  $[H^+]$ . A:  $\bar{X}_n$  vs  $[M]$  at  $[Mn^{3+}] = 2.219 \times 10^{-3} \text{ M}$ ,  $[H^+] = 1.8 \text{ M}$ ,  $\mu = 2.0 \text{ M}$ , and  $T = 55^\circ\text{C}$ . B:  $\bar{X}_n$  vs  $1/[Mn^{3+}]$  at  $[M] = 0.13 \text{ M}$ ,  $[H^+] = 1.5 \text{ M}$ ,  $\mu = 1.6 \text{ M}$ , and  $T = 55^\circ\text{C}$ . C:  $\bar{X}_n$  vs  $1/[H^+]$  at  $[M] = 0.1362 \text{ M}$ ,  $[Mn^{3+}] = 2.958 \times 10^{-3} \text{ M}$ ,  $[H^+] = 1.5 \text{ M}$ , and  $T = 55^\circ\text{C}$ .

Termination:



Applying the steady-state principle for free 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  $\bar{X}_n$  from the scheme presented above:

$$R_p = \frac{Kk_p k_i [M]^2}{k_t [H^+]}$$

$$-R_m = \frac{2Kk_i [M] [Mn^{3+}]}{(K + [H^+] )}$$

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

### Evaluation of Rate Constants and Thermodynamic Parameters

Plots of  $1/-R_m$  vs  $[H^+]$  were linear with a positive intercept on the  $1/-R_m$  axis. From the values of the slope and the intercept, the rate constants obtained are  $K = 0.4714$  mol/L,  $k_i = 2.05 \times 10^{-3} \text{ s}^{-1}$ , and  $k_p/k_t = 0.9952$  at  $50^\circ\text{C}$ ; and  $K = 0.5789$  mol/L,  $k_i = 6.04 \times 10^{-3} \text{ s}^{-1}$  and  $k_p/k_t = 0.5356$  at  $55^\circ\text{C}$ . Thermodynamic parameters obtained are  $E_a = 25.44$  kcal/mol,  $\Delta S^\ddagger = 23.74$  e.u.,  $\Delta G^\ddagger = 17.66$  kcal/mol, and  $A = 1.05 \times 10^{18}$ .

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