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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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To cite this Article Kaliyamurthy, K. , Elayaperumal, P. , Balakrishnan, T. and Santappa, M.(1982) 'Kinetics of Polymerization of Vinyl Monomers Initiated by Manganese(lll) Acetate. I', Journal of Macromolecular Science, Part A, 18: 2, 219 — 236

To link to this Article: DOI: 10.1080/00222338208074420

URL: http://dx.doi.org/10.1080/00222338208074420

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J. MACROMOL. SCI.–CHEM., A18(2), pp. 219-236 (1982)

Kinetics of Polymerization of Vinyl Monomers Initiated by Manganese(III) Acetate. I

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ABSTRACT

The kinetics of thermal polymerization of acrylic acid (AA), methacrylic acid (MAA), acrylonitrile (AN), and methacrylamide (MAM) in aqueous sulfuric acid using manganic acetate was studied. The effect of variations in [monomer], [Mn^{3+}], [H^+], μ, and temperature on the rates of monomer disappearance (R_p), Mn^{3+} disappearance ($-R_m$), and the degree of polymerization ($\bar{X}_n$) were studied. Based on the kinetic results, a suitable reaction scheme is proposed and rate expressions are derived. The rate constants, such as k_i, k_p/k_t, and thermodynamic parameters, corresponding to these are evaluated.

INTRODUCTION

Mn(III) chelate complexes initiate polymerization of vinyl monomers by a free radical mechanism in nonaqueous media [1]. Manganic ions coupled with reducing agents like Mn^{3+} + malonic acid [2], Mn^{3+} + pinacol [3], and Mn^{3+} + cyclohexanone [4] were used to initiate

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vinyl polymerization in aqueous media. Santappa et al. [5] studied the polymerization of acrylamide, acrylic acid, and acrylonitrile in the temperature range 20-45° C using Mn^{3+} + diglycolic acid and Mn^{3+} + isobutyric acid redox systems. At elevated temperatures (40-45° C) they could observe initiation both by Mn^{3+} and the primary radical produced by the redox reaction. A search of the literature indicated no reference regarding the initiation by Mn^{3+} salts alone in aqueous medium. This is to establish the fact that vinyl polymerization could be initiated by Mn^{3+} alone in the absence of a reducing agent.

EXPERIMENTAL

The reaction tubes are Pyrex glass tubes with a B24 quickfit socket fitted with a B24 cone carrying an inlet and outlet for nitrogen. Monomers were purified as follows. Acrylic acid was twice distilled over cupric chloride under reduced pressure (15 mmHg) in an atmosphere of nitrogen. The middle cuts (bp 50° C) were used [6]. Methacrylic acid was purified by distillation in an atmosphere of nitrogen under reduced pressure (7 mmHg, 50° C) over ferrous sulfate and copper powder, and the middle cuts were used [7]. Acrylonitrile (American Cyanamide Co., New York) was washed with 5% sodium hydroxide to remove the inhibitor and then with 3% o-phosphoric acid to remove the basic impurities. It was washed with water, dried over anhydrous $CaCl_2$, distilled under reduced pressure, and stored in dark brown bottles at 5° C [8]. Methacrylamide was recrystallized twice from a mixture of absolute alcohol and benzene mixed in a ratio of 1:4 (v/v) [9]. All the experiments were conducted in aqueous sulfuric acid medium. The organic solvents (e.g., chloroform, benzene, dimethylformamide) were distilled immediately before use and the middle cuts of the distillates were used. Sodium bisulfate (E. Merck) was used to maintain the ionic strength. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared by a known method [10].

The rate of polymerization (R_p) and the rate of disappearance of Mn^{3+} ($-R_m$) were determined as described below. Inhibitor-free monomer, sulfuric acid and sodium bisulfate solutions were placed in a reaction tube and thermostated at a definite temperature. The system was flushed with oxygen-free nitrogen for about 30 min. In order to minimize the loss of monomer, another tube containing an aqueous solution of the monomer of the same concentration as in the reaction mixture was interposed between the nitrogen train and the reaction tube. At the end of the deaeration, Mn^{3+} solution was added to the reaction tube. The reaction mixture was shaken well so that the mixing was effective. The tube was then sealed with rubber gaskets to ensure an inert atmosphere. At the end of the reaction time (30 min) the reaction tube was cooled in a freezing mixture and

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air was blown through the solution to arrest the polymerization. A known volume of the reaction mixture was added to 25 mL of bromide-bromate solution kept in an iodine flask. Then sulfuric acid (5 M, 10 mL) was added and the flask was tightly stoppered and kept in the dark for about 15 min. Potassium iodide solution was then added to the reaction mixture, the flask was cooled in ice, and the liberated iodine was then titrated against a standard sodium thiosulfate solution (0.1 N). A blank titration was run before the monomer was polymerized, and from the differences in titre values the final monomer concentration and R_p were calculated. A known volume of the same reaction mixture was run into another flask and mixed with 2% potassium iodide solution. The liberated iodine was titrated against 0.0025 N sodium thiosulfate solution. A blank titration was carried out, and from these titre values the $-R_m$ was evaluated. The degree of polymerization ($\overline{X}_n$) was determined by viscometry using an Ubbelohde suspended level dilution viscometer in a thermostat with a temperature control of ±0.01°C. The Mark-Houwink relationships for the polymers are the following:

For poly(acrylic acid) [12]:

$$[\eta] = 7.6 \times 10^{-4} (\overline{M}_v)^{0.5} \text{ in dioxane at } 30^\circ\text{C}$$

For poly(methacrylic acid) [13]:

$$[\eta] = 6.6 \times 10^{-4} (\overline{M}_v)^{0.5} \text{ in } 0.002\ \underline{M} \text{ aqueous HCl at } 30^\circ\text{C}$$

For poly(acrylonitrile) [14]:

$$[\eta] = 3.35 \times 10^{-4} (\overline{M}_v)^{0.72} \text{ in dimethylformamide at } 30^\circ\text{C}$$

RESULTS AND DISCUSSION

Preliminary Experiments

In our reaction conditions the photochemical initiation of the above-mentioned monomers was not noticed. On the other hand, thermal polymerization could be easily initiated by Mn^{3+}. No induction period was observed under deaerated conditions. The polymerization was inhibited by the presence of air or oxygen or hydroquinone. This indicated that the reaction was free radical in nature. Steady state was attained within 20 min in all these cases. [Mn^{2+}] was kept

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nearly 20 times higher than [Mn^{3+}] in order to prevent the disproportionation of Mn^{3+} to Mn^{2+} and Mn^{4+}. An increase of [Mn^{2+}] above this ratio caused no change in rates. The oxidation of water by Mn^{3+} under our experimental conditions was negligible. Since the kinetics for all four systems are the same, the results are grouped together in the following sections.

Rate of Polymerization, R_p

In the case of all these systems the rate of polymerization depended on the square of the monomer concentration. Log R_p vs log [M] plots were linear with a slope of 2 in all four systems. Plots of R_p against $[M]^2$ were linear and passed through the origin (Fig. 1).

The manganic ion concentration was varied from 1.6×10^{-3} to 8.2×10^{-3} M, and R_p was found to be independent of [Mn^{3+}] in this range of concentrations.

The hydrogen ion concentration was varied from 1 to 3.5 M at constant ionic strength (μ2.7-3.7). R_p decreased with an increase of [H^+]. Linear plots of log R_p vs log 1/[H^+] with unit slopes as well as R_p vs 1/[H^+] plots (Fig. 2) with zero intercepts indicated that the rate was inversely proportional to [H^+]. The ionic strength was varied from 1.2 to 3.7 M at constant [H^+]. There was little change in the rate of polymerization with an increase of μ.

Rate of Mn^{3+} Disappearance, $-R_m$

A direct proportionality between $-R_m$ and [M] was observed. Plots of $-R_m$ against [M] were linear and passed through the origin (Fig. 3). An increase of [Mn^{3+}] increased $-R_m$, and plots of log $-R_m$ vs log [Mn^{3+}] were linear with unit slopes. Plots of $-R_m$ vs [Mn^{3+}] were linear and passed through the origin (Fig. 4), indicating that the order with respect to [Mn^{3+}] was unity. $-R_m$ decreased with the increase of [H^+] in all four systems. Plots of 1/$-R_m$ vs [H^+] were linear with an intercept on the 1/$-R_m$ axis (Figs. 5 and 6). An increase of ionic strength at constant [H^+] had a negligible effect on $-R_m$.

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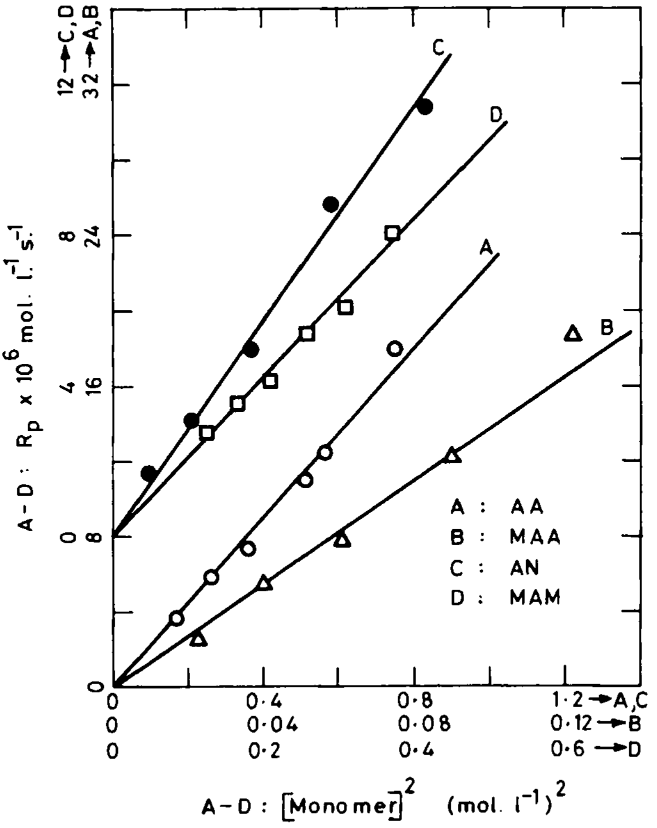

FIG. 1. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) by Mn^{3+} in aqueous sulfuric acid medium. (A): R_p vs $[AA]^2$ at constant $[Mn^{3+}] = 0.001985$ M, $[H^+] = 1.00$ M, $\mu = 1.4$ M, T = 50°C. (B): R_p vs $[MAA]^2$ at constant $[Mn^{3+}] = 0.002212$ M, $[H^+] = 1.5$ M, $\mu = 1.7$ M, T = 30°C. (C): R_p vs $[AN]^2$ at constant $[Mn^{3+}] = 0.00428$ M, $[H^+] = 3.0$ M, $\mu = 3.1$ M, T = 45°C. (D): R_p vs $[MAM]^2$ at constant $[Mn^{3+}] = 0.00555$ M, $[H^+] = 3.0$ M, $\mu = 3.2$ M, and T = 30°C.

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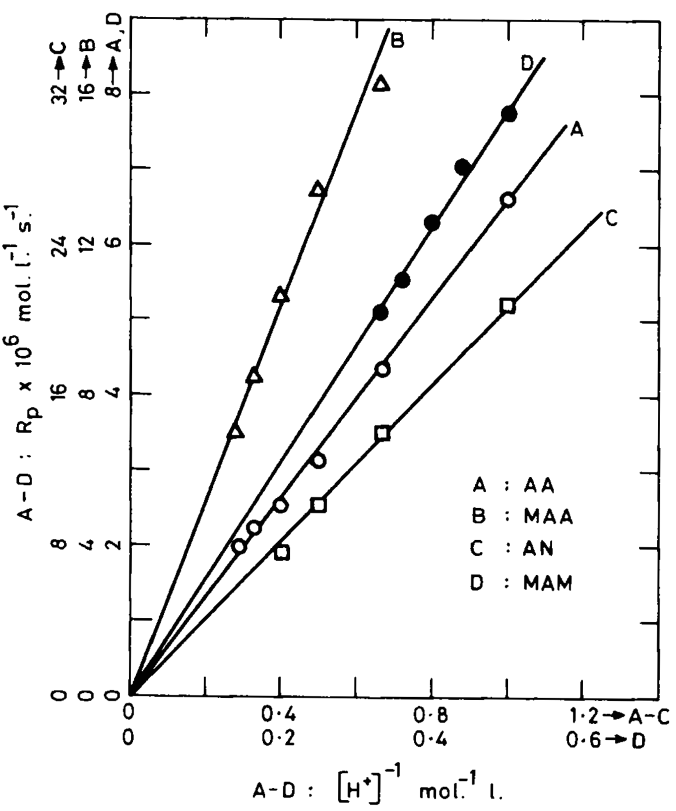

FIG. 2. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) by Mn^{3+} in aqueous sulfuric acid medium. Plots of R_p vs $[H^+]^{-1}$. (A): At constant $[AA] = 0.5426$ M, $[Mn^{3+}] = 0.002069$ M, $\mu = 3.7$ M, T = 50°C. (B): At constant $[MMA] = 0.3488$ M, $[Mn^{3+}] = 0.002005$ M, $\mu = 3.2$ M, T = 30°C. (C): At constant $[AN] = 0.7595$ M, $[Mn^{3+}] = 0.002117$ M, $\mu = 2.7$ M, T = 45°C. (D): At constant $[MAM] = 0.5005$ M, $[Mn^{3+}] = 0.006081$ M, $\mu = 3.25$ M, T = 30°C.

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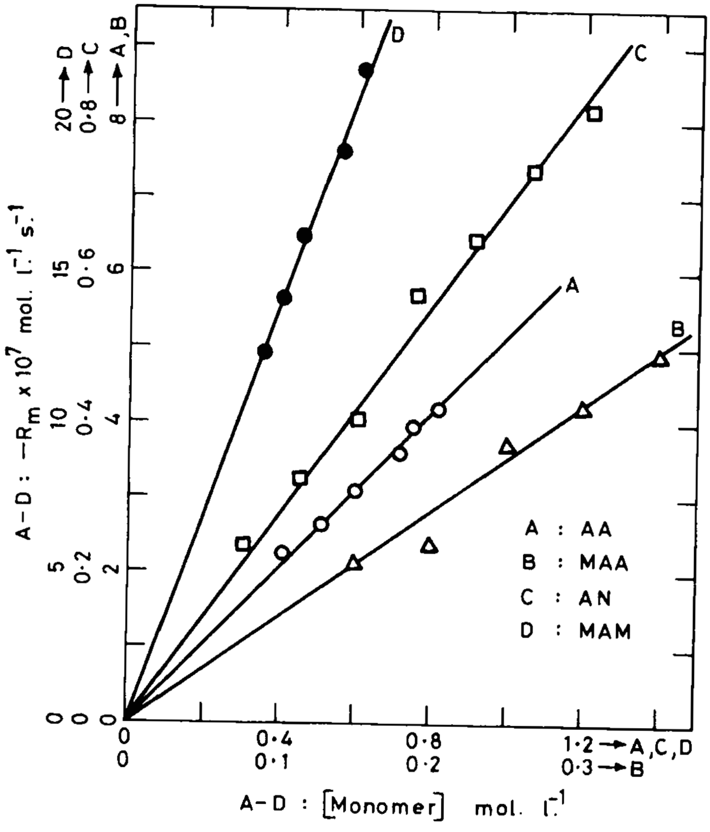

FIG. 3. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) by Mn^{3+} in aqueous sulfuric acid medium. (A): $-R_m$ vs [AA] at constant [Mn^{3+}] = 0.001985 M, [H^+] = 1.0 M, μ = 1.4 M, T = 50° C. (B): $-R_m$ vs [MAA] at constant [Mn^{3+}] = 0.002212 M, [H^+] = 1.5 M, μ = 1.7 M, T = 30° C. (C): $-R_m$ vs [AN] at constant [Mn^{3+}] = 0.00428 M, [H^+] = 3.0 M, μ = 3.1 M, T = 45° C. (D): $-R_m$ vs [MAM] at constant [Mn^{3+}] = 0.00555 M, [H^+] = 3.0 M, μ = 3.2 M, T = 30° C.

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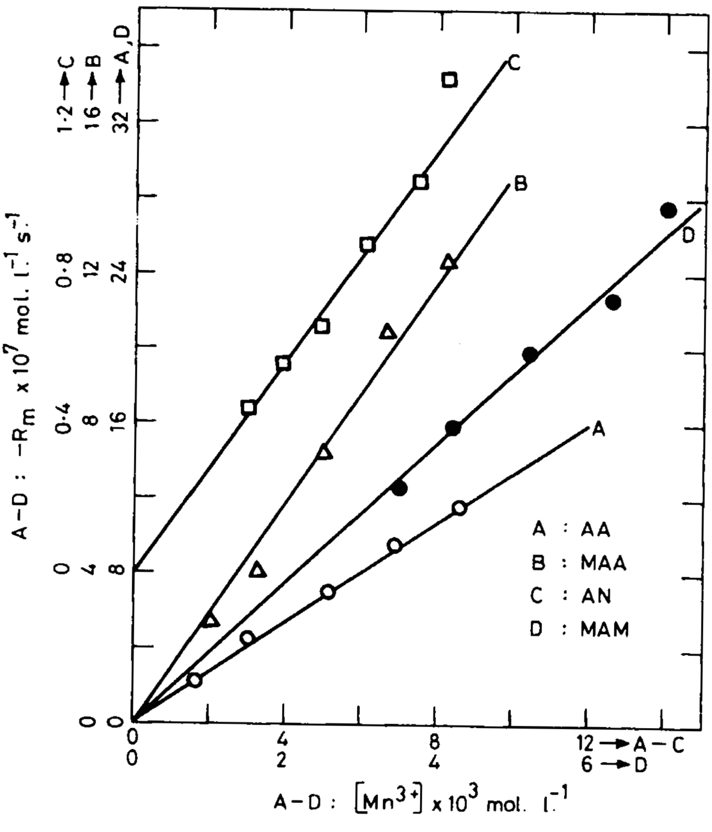

FIG. 4. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) by Mn^{3+} in aqueous sulfuric acid. Plots of $-R_m$ vs $[Mn^{3+}]$. (A): At constant [AA] = 0.5372 M, $[H^+]$ = 2.0 M, μ = 3.6 M, T = 50°C. (B): At constant [MAA] = 0.2488 M, $[H^+]$ = 1.5 M, μ = 1.9 M, T = 30°C. (C): At constant [AN] = 0.7595 M, $[H^+]$ = 3.0 M, μ = 3.1 M, T = 45°C. (D): At constant [MAM] = 0.6087 M, $[H^+]$ = 3.0 M, μ = 3.2 M, T = 30°C.

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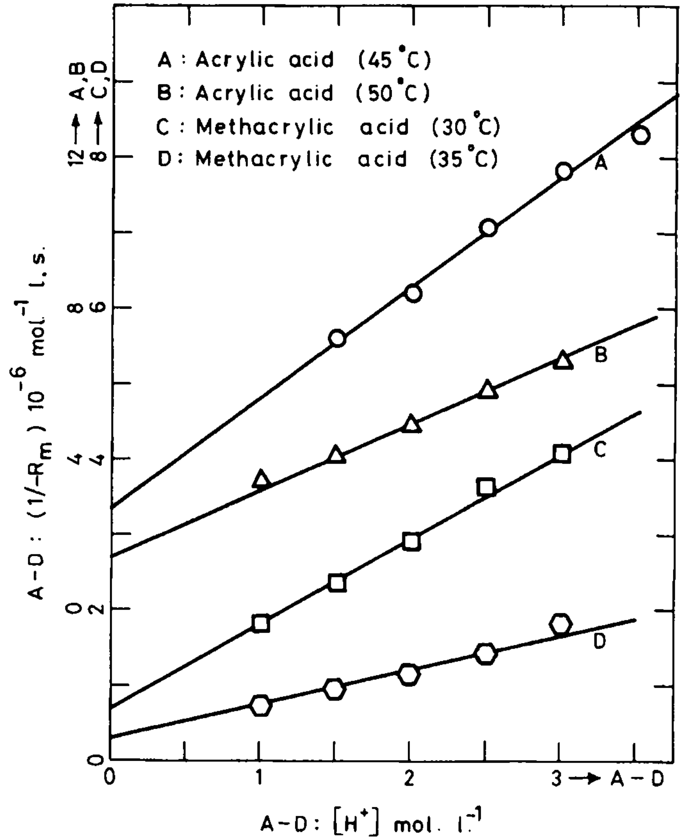

FIG. 5. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) in aqueous sulfuric acid medium. Plots of $1/\text{-}R_m$ vs $[H^+]$. (A): At constant [AA] = 0.5426 $\underline{M}$, $[Mn^{3+}]$ = 0.0021 $\underline{M}$, μ = 3.9 $\underline{M}$, T = 45° C. (B): At constant [AA] = 0.5426 $\underline{M}$, $[Mn^{3+}]$ = 0.002069 M, μ = 3.9 $\underline{M}$, T = 50° C. (C): At constant [MAA] = 0.3488 $\underline{M}$, $[Mn^{3+}]$ = 0.002005 $\underline{M}$, μ = 3.2 $\underline{M}$, T = 30° C. (D): At constant [MAA] = 0.3488 $\underline{M}$, $[Mn^{3+}]$ = 0.002005 $\underline{M}$, μ = 3.2 $\underline{M}$, T = 35° C.

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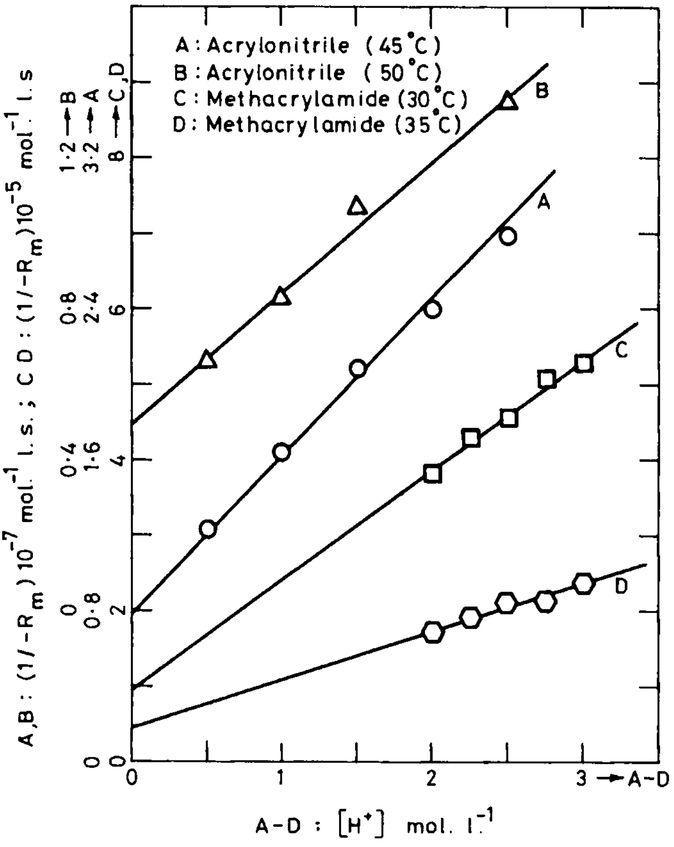

FIG. 6. Polymerization of vinyl monomers (AA, MAA, AN, and MAM) in aqueous sulfuric acid system. Plots of $1/\text{-}R_m$ vs $[H^+]$. (A): At constant [AN] = 0.7595 M, $[Mn^{3+}]$ = 0.002117 M, μ = 3.2 M, T = 45°C. (B): At constant [AN] = 0.7595 M, $[Mn^{3+}]$ = 0.002117 M, μ = 3.2 M, T = 50°C. (C): At constant [MAM] = 0.5005 M, $[Mn^{3+}]$ = 0.006081 M, μ = 3.25 M, T = 30°C. (D): At constant [MAM] = 0.5005 M, $[Mn^{3+}]$ = 0.006081 M, μ = 3.25 M, T = 35°C.

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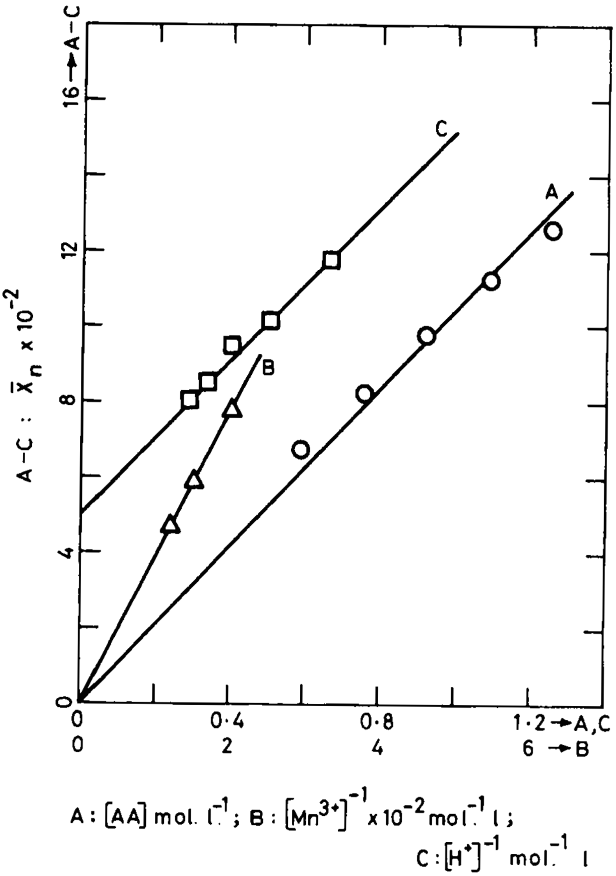

FIG. 7. Polymerization of acrylic acid by Mn^{3+} in aqueous sulfuric acid. (A) Plot of $\bar{X}_n$ vs [AA] at constant $[Mn^{3+}]$ = 0.001935 $\underline{M}$, $[H^+]$ = 1.0 $\underline{M}$, μ = 1.52 $\underline{M}$, T = 45°C. (B) Plot of $\bar{X}_n$ vs $[Mn^{3+}]^{-1}$ at constant [AA] = 0.7755 $\underline{M}$, $[H^+]$ = 2.5 $\underline{M}$, μ = 3.3 $\underline{M}$, T = 45°C. (C) Plot of $\bar{X}_n$ vs $[H^+]^{-1}$ at constant [AA] = 0.7755 $\underline{M}$, $[Mn^{3+}]$ = 0.002003 $\underline{M}$, μ = 3.7 $\underline{M}$, T = 45°C.

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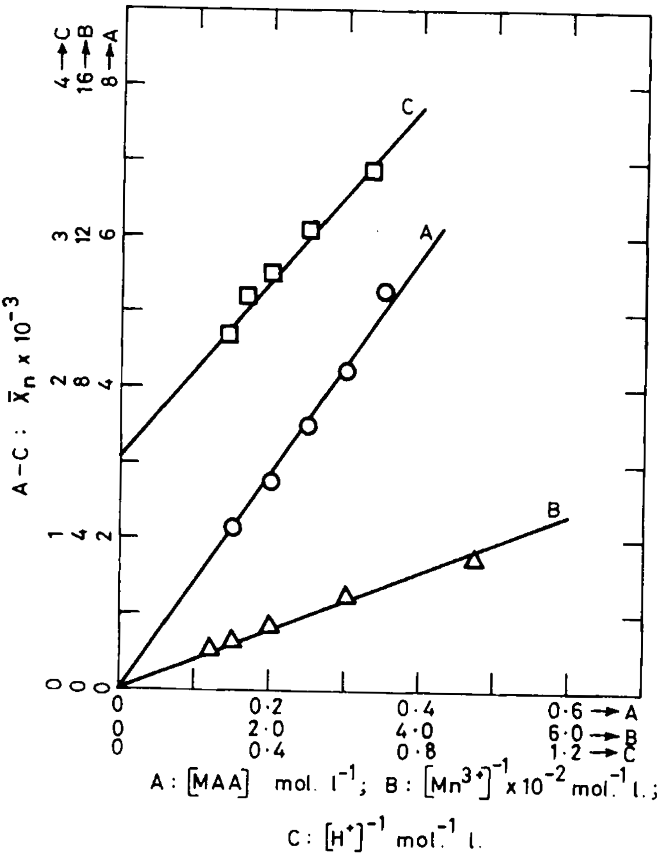

FIG. 8. Polymerization of methacrylic acid by Mn^{3+} in aqueous sulfuric acid. (A) Plot of $\bar{X}_n$ vs [MAA] at constant [Mn^{3+}] = 0.002005 M, [H^+] = 1.5 M, μ = 1.9 M, T = 35° C. (B) Plot of $\bar{X}_n$ vs [Mn^{3+}] at constant [MAA] = 0.2502 M, [H^+] = 1.5 M, μ = 1.9 M, T = 35° C. (C) Plot of $\bar{X}_n$ vs $[H^+]^{-1}$ at constant [MAA] = 0.2496 M. [Mn^{3+}] = 0.002005 M, μ = 3.7 M, T = 35° C.

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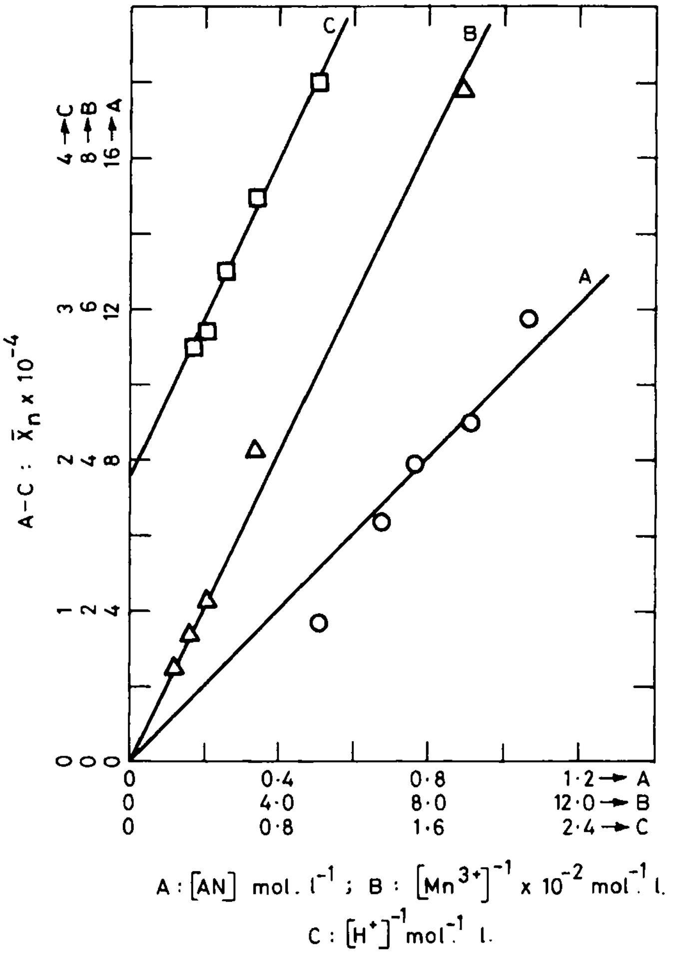

FIG. 9. Polymerization of acrylonitrile by Mn^{3+} in aqueous sulfuric acid. (A) Plot of $\overline{X}_n$ vs [AN] at constant [Mn^{3+}] = 0.002050 M, [H^+] = 1.5 M, μ = 1.9 M, T = 45°C. (B) Plot of $\overline{X}_n$ vs $[Mn^{3+}]^{-1}$ at constant [AN] = 0.6076 M, [H^+] = 1.5 M, μ = 1.9 M, T = 45°C. (C) Plot of $\overline{X}_n$ vs $[H^+]^{-1}$ at constant [AN] = 0.5010 M, [Mn^{3+}] 0.002050 M, μ = 3.2 M, T = 45°C.

Degree of Polymerization, $\bar{X}_n$

The degree of polymerization for acrylic acid, methacrylic acid, and acrylonitrile increased with the increase in [monomer]. Plots of $\bar{X}_n$ vs [M] were linear and passed through the origin (Figs. 7A, 8A, and 9A). It was observed that there was an inverse proportionality between $\bar{X}_n$ and $[Mn^{3+}]$, and plots of $\bar{X}_n$ vs $1/[Mn^{3+}]$ gave straight lines passing through the origin (Figs. 7B, 8B, and 9B). $\bar{X}_n$ decreased with an increase of $[H^+]$, and plots of $\bar{X}_n$ vs $1/[H^+]$ were linear with an intercept on the $\bar{X}_n$ axis (Figs. 7C, 8C and 9C). Since the values of K and "a" of the Mark-Houwink equation were not available for methacrylamide, we were unable to carry out degree of polymerization studies for this monomer.

REACTION SCHEME AND RATE LAW

It was noticed that there is a direct proportionality between R_p and the square of the monomer concentration. This could be the case only when the polymer chains are terminated by $\dot{O}H$ or MN^{3+} or $Mn^{3+}OH^-$, whereas if the chains are terminated by the mutual type (combination or disproportionation), R_p should be proportional to $[M]^{3/2}$. Therefore, the possibility of the mutual type of termination is ruled out. It is found that R_p is independent of $[Mn^{3+}]$. This fact is significant in the sense that it provides strong evidence for termination by Mn^{3+} ions. Similar cases of metal ion termination in which R_p is independent of metal ion concentration have been reported in the literature [15-23]. Mino et al. [15], who studied the kinetics of polymerization of the acrylamide-3-chloro-1-propanol-ceric nitrate system, have shown that termination of chains was effected by ceric ions in complete preference to a mutual type of termination. Santappa et al. [16] also reported termination by ceric ions in the polymerization of acrylonitrile. They also noticed the termination of polymerization caused exclusively by Mn^{3+} in the Mn^{3+}-acrylamide-diglycolic acid [17] system. In the polymerization of acrylonitrile initiated by the redox system V^{5+}-organic substrate, the terminating species was V^{5+} [18, 19]. Other metal ions reported to be acting as terminating species are Fe^{3+}, Cu^{2+}, Tl^{3+} [20-22], vanadyl, and uranyl [23] ions. The rate of polymerization was found to decrease linearly with $[H^+]$, and this could be possible only under the conditions of initiation by $Mn^{3+}OH^-$ and termination by Mn^{3+}. The reaction scheme explaining most of the experimental results is

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

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

$$M^{\bullet} + M \xrightarrow{k_p} M_1^{\bullet}$$

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

Using the steady-state assumption for the radical concentrations and also the principle of nonvariation of the rate constants with the size of the polymer radical, we arrived at the following expressions:

$$R_p = Kk_pk_i[M]^2/k_t[H^+]$$

$$-R_m = 2Kk_i[M][Mn^{3+}]_T/K + [H^+]$$

where

$$[Mn^{3+}]_T = [Mn^{3+}] + [Mn^{3+}OH^-]$$

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

It was found that $-R_m$ decreases with an increase of $[H^+]$ in all four cases. This is possible only when $Mn^{3+}OH^-$ acts as the initiator. The same inverse dependence of the rate of disappearance of metal ions on hydrogen ion concentration was found in the case of polymerization of vinyl monomers initiated by cobaltic ions as studied by Santappa et al. [24] where the $Co^{3+}OH^-$ species had been proposed to be the initiating species. The Mn^{3+} species mainly present in the solution under our experimental conditions are Mn^{3+} and $Mn^{3+}OH^-$. The nature of the dependence of $-R_m$ on $[H^+]$ provides an important criterion for distinguishing between initiation by Mn^{3+} and by $Mn^{3+}OH^-$. When $Mn^{3+}OH^-$ initiates and Mn^{3+} terminates, the rate expression for $-R_m$ would require the plot of $1/-R_m$ vs $[H^+]$ to be linear with an intercept on the $1/-R_m$ axis. This has indeed been observed experimentally as seen from the plots in Figs. 5 and 6. If Mn^{3+} is the initiating species and $Mn^{3+}OH^-$ is the terminating species, the trend in $-R_m$

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TABLE 1. Polymerization of Mn^{3+} (AA, MAA, AN, or MAM) Aqueous Sulfuric Acid System. Kinetic Parameters

Monomer	Temperature (°C)	k_p/k_t	k_i (s^{-1})	K (m/L)
Acrylic acid	45	0.0897	1.65×10^{-4}	0.9120
	50	0.0679	3.18×10^{-4}	1.0160
Methacrylic acid	30	0.3087	1.02×10^{-3}	0.6363
	35	0.1816	2.38×10^{-3}	0.7143
Acrylonitrile	45	0.9173	3.98×10^{-5}	0.9069
	50	0.4932	9.14×10^{-5}	1.0625
Methacrylamide	30	0.05405	1.72×10^{-3}	0.6597
	35	0.03468	3.65×10^{-3}	0.7105

TABLE 2. Polymerization of Mn^{3+} (AA, MAA, AN, and MAM) Aqueous Sulfuric Acid System. Thermodynamic Parameters

		$k_p k_i K/k_t$	k_p/k_t	k_i
Acrylic acid:	ΔE (kcal/mol)	19.85	-11.36	26.78
	$\Delta S^{\ddagger}_{318K}$(eu)	-21.77	-92.04	8.25
	$\Delta G^{\ddagger}$ (kcal/mol)	26.14	17.27	23.33
Methacrylic acid:	ΔE (kcal/mol)	17.69	-18.16	31.44
	$\Delta S^{\ddagger}_{308K}$(eu)	-22.145	-120.69	31.46
	$\Delta G^{\ddagger}$ (kcal/mol)	23.80	18.40	21.13
Acrylonitrile:	ΔE (kcal/mol)	15.10	-25.33	33.97
	$\Delta S^{\ddagger}_{318K}$(eu)	-34.60	-138.49	28.01
	$\Delta G^{\ddagger}$ (kcal/mol)	25.47	18.08	24.43
Methacrylamide:	ΔE (kcal/mol)	14.13	-16.46	27.71
	$\Delta S^{\ddagger}_{308K}$(eu)	-36.18	-118.72	20.22
	$\Delta G^{\ddagger}$ (kcal/mol)	24.66	19.49	20.87

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would be just the reverse, i.e., $-R_m$ has to increase with an increase of $[H^+]$. The experimental results pertaining to the degree of polymerization are also in agreement with the reaction scheme consisting of initiation by $Mn^{3+}OH^-$ and termination by Mn^{3+}.

Evaluation of Kinetic Parameters

The intercept and slope of the plots of $1/-R_m$ vs $[H^+]$ (Figs. 5 and 6) are $\frac{1}{2}k_i[M][Mn^{3+}]_T$ and $\frac{1}{2}Kk_i[M][Mn^{3+}]$, respectively. Hence the intercept/slope gives the value of the equilibrium constant, K. The reciprocal of the intercept multiplied by $\frac{1}{2}[M][Mn^{3+}]_T$ gives k_i. Substituting the value of k_i and K in the rate expression, $R_p = k_pk_iK[M]^2/k_t[H^+]$, the k_p/k_t values are calculated for two different temperatures and all the values have been tabulated (Table 1). From the values of the rate constants at different temperatures, the thermodynamic parameters ΔE, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ are evaluated for all four systems (Table 2).

ACKNOWLEDGMENT

One of the authors (K.K.) is grateful to the University Grants Commission, New Delhi, for the award of a Teacher Fellowship.

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Accepted by editor June 10, 1981
Received for publication July 7, 1981

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