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

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ABSTRACT: The kinetics of the thermal polymerization of methyl acrylate (MA) and acrylamide (AAM) initiated by manganic ion in aqueous sulfuric acid medium has been studied. The rate of disappearance of [monomer] (R_p) was found to bear a square dependence on monomer and to be independent of [Mn^{2+}] in the case of both the systems. R_p for acrylamide increased with the increase in [H^+] but that for methyl acrylate remained almost constant. The degree of polymerization of the polymers ($\bar{X}_n$) determined viscometrically was directly proportional to the [monomer] and inversely proportional to [Mn^{3+}], for both systems. $\bar{X}_n$ increased with an increase in [H^+] in the case of acrylamide and decreased in the case of methyl acrylate. Suitable reaction schemes to explain these experimentally observed facts have been proposed. Kinetic and thermodynamic parameters are also evaluated.
KEY WORDS Kinetics / Polymerization / Acrylamide / Methyl Acrylate / Manganic Ion / Reaction Scheme / Degree of Polymerization /

The oxidation kinetics of inorganic and organic substrates by [Mn^{3+}] has already been reported.[1-3] Literature survey revealed that chelate complexes of Mn(III) initiate the polymerization of vinyl monomers *via* free radical mechanism in non-aqueous media.[4] Redox systems containing Mn^{3+} and an organic substrate like Mn^{3+} + malonic acid,[5] Mn^{3+} + pinacol[6] and Mn^{3+} + cyclohexanone[7] have been found to initiate vinyl polymerization. Santappa *et al.*[8] studied the polymerization of acrylamide, acrylic acid, and acrylonitrile in the temperature range from 20—45°C using Mn^{3+} + diglycolic acid and Mn^{3+} + isobutyric acid redox systems. At elevated temperatures 40—45°C they observed the initiation of polymerization both by Mn^{3+} and primary radicals produced by redox reactions. The literature indicates no reference regarding initiation by only Mn^{3+} salts in an aqueous medium. It was therefore proposed to establish by the present investigation that vinyl polymerization could be initiated by Mn^{3+} without any reducing agents. In Part I[9] we report the kinetics of polymerization of acrylic acid, methacrylic acid, acrylonitrile and methacrylamide initiated by Mn^{3+}.
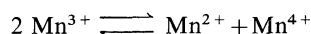
EXPERIMENTAL

Materials

Acrylamide[10] (American Cyanamide Co., New York) was recrystallized twice from warm chloroform. The resulting product was a crystalline white solid; mp, 84.5°C. Methyl acrylate was purified[11] by washing with 5% aqueous sodium hydroxide to remove the inhibitor and then washed with water. It was then dried over anhydrous sodium sulphate and distilled twice at reduced pressure in an atmosphere of nitrogen. The distilled product was stored in a refrigerator at about 5°C. All experiments were conducted in an aqueous sulphuric acid medium. Solutions of sulphuric acid were prepared by suitable dilutions of concentrated acid (A.R., B.D.H.) with double-distilled water and standardized against sodium hydroxide solution. Organic solvents such as chloroform, methyl ethyl ketone, etc., were distilled immediately before use and the middle cuts of the distillates were used.

Sodium hydrogen sulphate (E. Merck, Germany) was used to maintain the ionic strength. Manganese(II) acetate (L.R., B.D.H.) was used to prepare manganese(III) acetate by a known method.[12] The reaction vessel was a pyrex glass tube fitted with a B-24 quickfit socket. A B-24 cone provided with an inlet and outlet tube for nitrogen was fitted into the tube. The reaction mixture containing appropriate quantities of inhibitor free monomer, sulphuric acid, and sodium bisulphate solution was thermostated and deaerated for 30 min. Another reaction vessel containing a blank solution of the same concentraion of monomer as the reaction mixture was interposed between the nitrogen train and the reaction tube to minimize the loss of monomer during deaeration by passing pure dry nitrogen. At the end of the deaeration a Mn^{3+} solution was added to the reaction mixture and shaken well. The inlet and outlet were then closed by rubber gaskets to maintain the nitrogen atmosphere. After 30 min the reaction was arrested by cooling the reaction tube in freezing mixture and blowing air slightly through the solution. A known volume of the reaction mixture was added to 25 ml of a bromide-bromate solution. The 10 ml of 5 M sulphuric acid were added and the flask was tightly stoppered and kept in the dark for about 15 minutes. It was mixed with an excess of potassium iodide solution and the liberated iodine was titrated with 0.1 M sodium thiosulphate solution. The same volume of solution from the blank vessel was also titrated and from the differences in titre values, R_p was computed. 10 ml of the reaction mixture were introduced into another conical flask and mixed with 2% potassium iodide solution and the liberated iodine was titrated with 0.0025 M sodium thiosulphate. A blank titration was also done and the rate of disappearance of Mn^{3+} ($-R_m$) was calculated from these titre values. The degree of polymerization was determined viscometrically using appropriate Mark–Houwink relationships. For poly-(acrylamide)[13] $[\eta]=6.8\times10^{-4}$ $(M_v)^{0.66}$ in water at 30°C. For poly(methyl acrylate)[14] $[\eta]=0.397\times10^{-4}$ $(M_v)^{0.772}$ in butanone at 30°C. The viscosity measurements were made with a Ubbelohde suspended level dilution viscometer (fitted with sinter) in a thermostat with a temperature contol of ±0.01°C.

Preliminary Experiments

Before discussing the experimental results, a brief analysis of the preliminary experiments will now be made: (i) under our reaction conditions, no photochemical initiation of acrylamide or methyl acrylate was noticed. On the other hand, thermal polymerization could be easily initiated by Mn^{3+}; (ii) no induction period was observed under deaerated conditions. Polymerization was found to be inhibited by the presence of air or oxygen or hydroquinone. This indicates that the reaction is free radical in nature. (iii) a steady-state rate was reached within 20 minutes in both cases; (iv) [Mn^{2+}] was about 20 times higher than [Mn^{3+}] in order to prevent the following disproportionation reaction:

$$2\ Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+}$$

An increase in [Mn^{2+}] above this ratio caused no change in the rates and (v) the oxidation of water by Mn^{3+} under our experimental conditions was negligible.

RESULTS AND DISCUSSION

(A) Mn^{3+} + Acrylamide + Aqueous Sulphuric Acid System

Rate of Disappearance of Monomer, R_p

The concentration of monomer was varied from 0.3858 M to 0.7717 M. R_p had square dependence on the [monomer]. The log R_p vs. log [M] plot gave a slope of two and the plot of R_p against [M]^2 was linear with zero intercept indicating that the order with respect to monomer was two (Figure 1A). The concentration of Mn^{3+} was varied from 0.001875 M to 0.005625 M. The rate R_p remained almost constant in this range of [Mn^{3+}]. The hydrogen ion concentration was varied from 1.5 M to 3.5 M at constant ionic strength. The plot of R_p vs. H$^+$ was a straight line passing through the origin, indicating that the order with respect to [H$^+$] was unity (Figure 1C). The effect of ionic strength on the rate of polymerization was not very significant.

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

It was observed that a direct proportionality exists between the rate of Mn^{3+} disappearance and monomer concentration. The plot of $-R_m$ against [M] was linear and passed through the origin (Figure 2A). $-R_m$ was also directly proportional to the Mn^{3+} concentration. The plot of $-R_m$ against [Mn^{3+}] was linear and passed through the origin
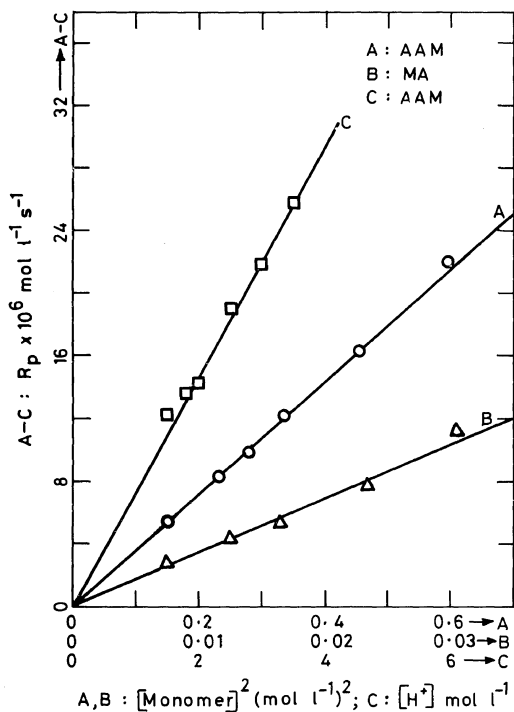
Figure 1. Polymerization of vinyl monomers (AAM and MA) by Mn^{3+} in aqueous sulphuric acid. (A): R_p vs. $[AAM]^2$ at constant $[Mn^{3+}]=0.001962$ M; $[H^+]=1.5$ M; $\mu=1.9$ M; $T=50°C$. (B): R_p vs. $[MA]^2$ at constant $[Mn^{3+}]=0.0016$ M; $[H^+]=1.0$ M; $\mu=1.32$ M; $T=45°C$. (C): R_p vs. $[H^+]$ at constant $[AAM]=0.5804$ M; $[Mn^{3+}]=0.002005$ M; $\mu=3.7$ M; $T=50°C$.
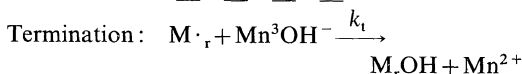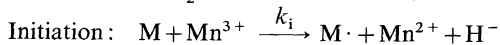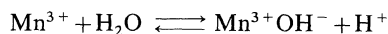
(Figure 2C). $-R_m$ increased with an increase in $[H^+]$ and the plots of $-1/R_m$ vs. $1/[H^+]$ were linear with an intercept on the $-1/R_m$ axis (Figure 3A, B). $-R_m$ was not appreciably affected by change in ionic strength at constant hydrogen ion concentration.

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

A direct proportionality between $\bar{X}_n$ and monomer concentration was observed. The plot of $\bar{X}_n$ against [M] was linear, passing through origin (Figure 4A). It was observed that an increase in $[Mn^{3+}]$ lessened the degree of polymerization. A plot of $\bar{X}_n$ vs. $1/[Mn^{3+}]$ was linear and passed through origin (Figure 4B). $\bar{X}_n$ increased with an increase in $[H^+]$ and the plot of $\bar{X}_n$ vs. $[H^+]$ was linear with an intercept on the $\bar{X}_n$ axis (Figure 4C).

Mechanism and Rate Law

Based on the above observations, a plausible mechanism may be formulated for the polymeri-

zation of acrylamide as shown below.

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

Initiation: $\quad M+Mn^{3+} \xrightarrow{k_i} M\cdot +Mn^{2+}+H^-$

Propagation: $\quad M\cdot +M \xrightarrow{k_p} M\cdot_1$

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Termination: $\quad M\cdot_r+Mn^3OH^- \xrightarrow{k_t}$
$$M_rOH+Mn^{2+}$$
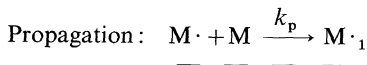
Assuming the steady state condition for the radical concentrations and also the principle of non-variation of rate constants with the size of the polymer radical, the following expressions were derived.

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

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

where

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

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

The rate of polymerization shows a square dependence on [M]. This perhaps may be the trend only when the polymer chains are terminated by $OH\cdot$ 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 $[M]^{3/2}$. So the observed dependence of R_p on monomer concentration rules out the possibility of termination by mutual type. If $OH\cdot$ is the species responsible for the termination, $-R_m$ should be independent of the monomer concentration. Since the observed trend in $-R_m$ is contrary to this, the probability of termination by $OH\cdot$ is excluded.

It was found that R_p is independent of $[Mn^{3+}]$. This fact is significant since it provides strong evidence for termination by manganic ion species. The manganic species mainly present under our experimental conditions are Mn^{3+} and $Mn^{3+}OH^-$. Thus, the ionic species causing initiation and termination may be identified by analysis of the dependence of R_p and $-R_m$ on $[H^+]$. R_p as well as $-R_m$ were found to increase with $[H^+]$ and this may be the trend only when Mn^{3+} acts as an initiating agent and $Mn^{3+}OH^-$ as a terminating agent. The same trend was observed in the polymerization of acrylonitrile using Ce^{4+}–ethylene glycol redox ini-
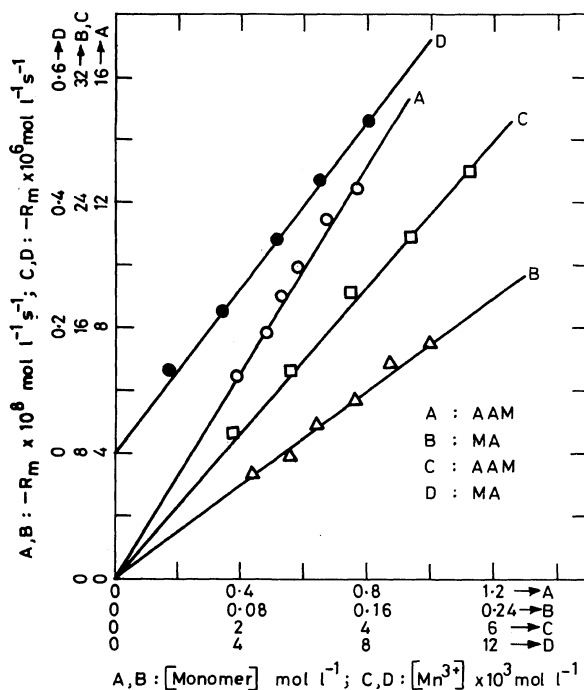
Figure 2. Polymerization of vinyl monomers (AAM and MA) by Mn^{3+} in aqueous sulphuric acid. (A): $-R_m$ *vs.* $[AAM]^2$ at constant $[Mn^{3+}] = 0.001962$ M; $[H^+] = 1.5$ M; $\mu = 1.9$ M; $T = 50°$C. (B): $-R_m$ *vs.* $[MA]^2$ at constant $[Mn^{3+}] = 0.0016$ M; $[H^+] = 1.0$ M; $\mu = 1.32$ M; $T = 45°$C. (C): $-R_m$ *vs.* $[Mn^{3+}]$ at constant $[AAM] = 0.5788$ M; $[H^+] = 20$ M; $\mu = 2.4$ M; $T = 50°$C. (D): $-R_m$ *vs.* $[Mn^{3+}]$ at constant $[MA] = 0.1370$ M; $[H^+] = 1.5$ M; $\mu = 1.9$ M; $T = 45°$C.

tiator by Katai *et al.*[15] and in the polymerization of methyl acrylate by ceric perchlorate by Santappa *et al.*[16] The trend in R_p and $-R_m$ would be just the reverse under the conditions of initiation by $Mn^{3+}OH^-$ and termination by Mn^{3+}, as observed in the polymerization of acrylic acid, acrylontrile, methacrylic acid and methacrylamide by manganic acetate in aqueous sulphuric acid.[9] Termination by metal ions has been proved beyond doubt by Dainton *et al.*[17–19] They found that in the X- and γ-ray initiated polymerization of acrylamide in an aqueous medium, ceric ions behaved as terminating agents. The oxidative and reductive termination of poly(acrylamide) radicals by metal ions such as Fe^{3+}, Cu^{2+}, Tl^{3+}, etc. were also investigated by Dainton *et al.* Vanadyl and Uranyl ions[20] were found to terminate poly(acrylamide) radicals. Watanabe and Kiuchi[21] found that cupric salts terminated poly(acrylonitrile) radicals in an aqueous solution. In the polymerization of acrylonitrile initiated by V^{5+}–organic substrates redox sys-

tems[22,23] the terminating species was V^{5+}. The dependence of $\bar{X}_n$ on [M], $[H^+]$ and $[Mn^{3+}]^{-1}$ also confirm the reaction path involving initiation by Mn^{3+} and termination by $Mn^{3+}OH^-$.

Evaluation of Kinetic Parameters

The rate constant for initiation, k_i was evaluated from the intercept of the plot of $-1/R_m$ *vs.* $1/[H^+]$ (Figure 3A, B) which was equal to $1/(2k_i [M][Mn^{3+}]_t)$. The slope was equal to $K/(2k_i [M][Mn^{3+}])_T$. Hence, the slope was divided by the intercept to obtain the value of the equilibrium constant, K. Substituting k_i and K in the rate expression for R_p, the value of k_p/k_t was obtained. The values of k_p/k_t, k_i, and K at 45°C were 0.4291, 3.30×10^{-5} l mol^{-1} s^{-1} and 0.89 mol l^{-1} and at 50°C were 0.3137, 7.81×10^{-5} l mol^{-1} s^{-1}, and 1.01 mol l^{-1}, respectively. ΔE for $k_p k_i/k_t K$, k_p/k_t, and k_i were 17.29, -12.79, and 34.68 kcal mol^{-1}, respectively. $\Delta S^*_{318°K}$ for these were -27.61, -105.16, and 34.47 e.u., respectively.
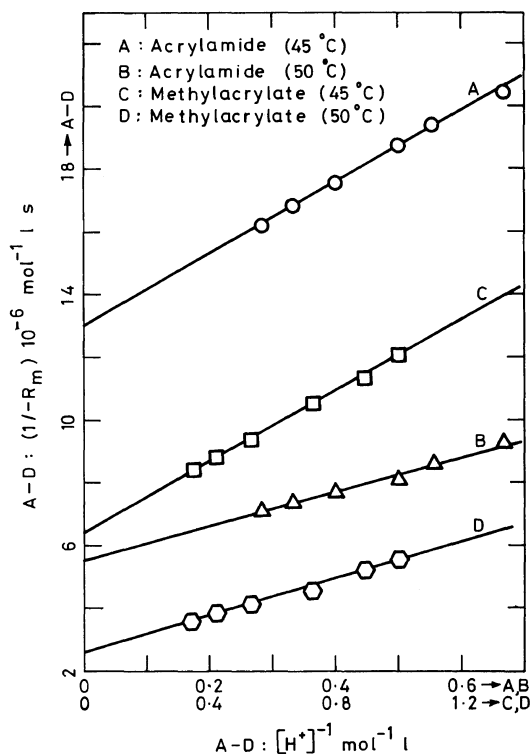
Figure 3. Polymerization of vinyl monomers (AAM and MA) by Mn^{3+} in an aqueous sulphuric acid. Plots of $-1/R_m$ vs. $[H^+]^{-1}$ (A) at constant $[AAM]=0.5804$ M, $[Mn^{3+}]=0.002005$ M, $\mu=3.7$ M, $T=45°C$, (B) at constant $[AAM]=0.5804$ M, $[Mn^{3+}]=0.002005$ M, $\mu=3.7$ M, $T=50°C$, (C) at constant $[MA]=0.1054$ M, $[Mn^{3+}]=0.00158$ M, $\mu=3.125$ M, $T=45°C$, and (D) at constant $[MA]=0.1054$ M, $[Mn^{3+}]=0.00158$ M, $\mu=3.125$ M, $T=50°C$.

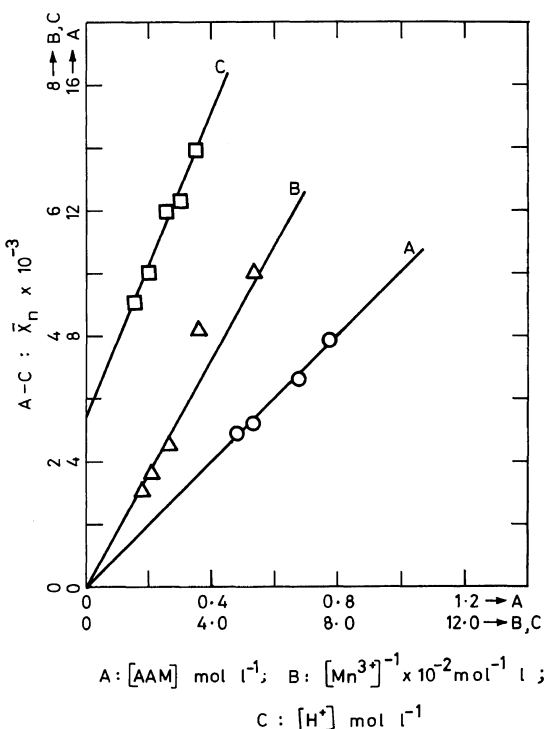**Figure 4.** Polymerization of acrylamide by Mn^{3+} in aqueous sulphuric acid (A) $\bar{X}_n$ vs. [AAM], at constant $[Mn^{3+}]=0.002004$ M, $[H^+]=1.5$ M, $\mu=1.7$ M, $T=45°C$, (B) $\bar{X}_n$ vs. $[Mn^{3+}]^{-1}$ at constant [AAM] 0.5788 M, $[H^+]=1.5$ M, $\mu=1.7$ M, $T=45°C$, and (C) $\bar{X}_n$ vs. $[H^+]$ at constant $[AAM]=0.5804$ M, $[Mn^{3+}]=0.002004$ M, $\mu=3.7$ M, $T=45°C$.

(B) Mn^{3+}–Methyl Acrylate–Sulphuric Acid System

The reaction path of the polymerization of methyl acrylate is different from that of acrylamide discussed in part (A) and hence its kinetic results are separately discussed.

Rate of Disappearance of the Monomer, R_0

The monomer concentration was varied from 0.08752 M to 0.19690 M. R_p increased with an increase in [M]. The log R_p vs. log [M] plot yielded a slope of two and the plot of R_p against $[M]^2$ was linear, passing through the origin indicating that the order with respect to monomer concentration was two (Figure 1C). The $[Mn^{3+}]$ concentration was varied from 1.915×10^{-3} M to 8.075×10^{-3} M. The

rate of polymerization was found to decrease very slightly with $[Mn^{3+}]$ and hence no definite order could be assigned with respect to $[Mn^{3+}]$. The hydrogen ion concentration varied from 1.0 M to 2.875 M and R_p was found not appreciably influenced by a change in $[H^+]$. The ionic strength had no significant influence on R_p.

Rate of Disappearance of the Manganic Ion, $-R_m$

A direct proportionality was found between $-R_m$ and monomer concentration. A plot of $-R_m$ vs. [M] was linear and passed through the origin (Figure 2B). A plot of $-R_m$ against $[Mn^{3+}]_T$ was linear passing through origin (Figure 2D) indicating that the order with respect to $[Mn^{3+}]$ was unity. It was found that $-R_m$ increased with an increase in $[H^+]$. The plot of $-1/R_m$ vs. $1/[H^+]$ was linear with an intercept on the $-1/R_m$ axis (Figure 3C, D). Variation in ionic strength had a negligible effect on
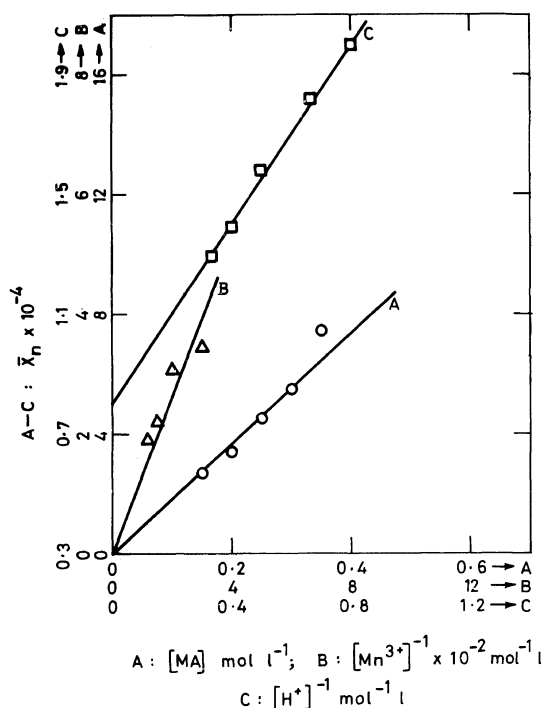
Figure 5. Polymerization of methyl acrylate by Mn^{3+} in aqueous sulphuric acid (A) $\bar{X}_n$ *vs.* [MA] at constant $[Mn^{3+}] = 0.002025$ M, $[H^+] = 1.5$ M, $\mu = 1.9\,M$, $T = 45°C$, (B) $\bar{X}_n$ *vs.* $[Mn^{3+}]^{-1}$ at constant [MA] = 0.2501 M, $[H^+] = 2.5$ M, $\mu = 2.9\,M$, $T = 45°C$, and (C) $\bar{X}_n$ *vs.* $[H^+]^{-1}$ at constant [MA] = 0.2483 M, $[Mn^{3+}] = 0.002005$ M, $\mu = 3.2\,M$, $T = 45°C$.

$-R_m$.

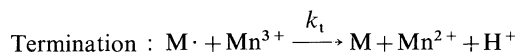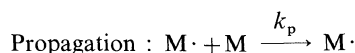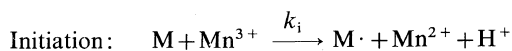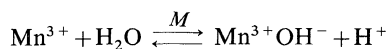### Degree of Polymrization, $\bar{X}_n$

The degree of polymerization of polymers obtained from methyl acrylate increased with an increase in monomer concentration. A plot of $\bar{X}_n$ *vs.* M was linear and passed through origin (Figure 5A). $\bar{X}_n$ decreased with an increase in $[Mn^{3+}]_T$ and a plot of $\bar{X}_n$ *vs.* $1/[Mn^{3+}]_T$ gave a straight line with a zero intercept (Figure 5B). The degree of polymerization was found to decrease with increase in $[H^+]$ and the plot of $\bar{X}_n$ *vs.* $1/[H^+]$ was linear with an intercept on the $\bar{X}_n$ axis (Figure 5C).

Mechanism and Rate Law

The following sequence of reactions appears to be the most probable to explain our results.

$$Mn^{3+} + H_2O \underset{\longleftarrow}{\overset{M}{\rightleftharpoons}} Mn^{3+}OH^- + H^+$$

Initiation: $\quad M + Mn^{3+} \xrightarrow{k_i} M\cdot + Mn^{2+} + H^+$

Propagation : $\quad M\cdot + M \xrightarrow{k_p} M\cdot$

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Termination : $\quad M\cdot + Mn^{3+} \xrightarrow{k_t} M + Mn^{2+} + H^+$

Assuming the usual stationary-state kinetics for initiation and termination by Mn^{3+}, the following equations were derived:

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

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

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

R_p is independent of [H] and $[Mn^{3+}]$ but has a square dependence on monomer concentration. These trends in R_p can be observed only under the conditions of initiation as well as termination caused by the same ionic species of manganese. The metal ion species which can produce such results in this systems is either Mn^{3+} or $Mn^{3+}OH^-$. $-R_m$ is linearly related to [M], $[Mn^{3+}]$, and $[H^+]$. These trends in $-R_m$ are possible only when Mn^{3+} acts as the initiating as well as terminating agent. If $Mn^{3+}OH^-$ ionic species causes both initiation and termination, $-R_m$ will decrease with an increase in $[H^+]$. Since such a trend in $-R_m$ is not observed, it may be concluded that Mn^{3+} is the species responsible for initiation as well as the termination of polymerization. The dependence of the degree of polymerization on [M], $[H^+]^{-1}$, and $[Mn^{3+}]^{-1}$ is also in conformity with the reaction scheme proposed and rate expressions derived on the basis of initiation and termination of polymerization caused by Mn^{3+} ion.

Evaluation of Kinetic Parameters

The initiation rate constants (k_i) at two different temperatures were evaluated from the intercept of the plots of $1/R_m$ *vs.* $1/[H^+]$ (Figures 3C, D). The intercept on the $-1/R_m$ axis was equal to $1/(2k_i [M][Mn^{3+}]_T)$ and the slope was equal to $K/(2k_i [M][Mn^{3+}]_T)$. Hence, the slope divided by the intercept gave the equilibrium constant values K. Then, using the expression $k_i = (1/\text{intercept}) \times 1/(2[M][Mn^{3+}]_T)$, k_i was evaluated. Substituting the values of k_i in the rate expression $R_p = k_p k_i [M]^2 / k_t$ the value of k_p / k_t was obtained for two different temperatures. The value of k_p / k_t, k_i, and K at 45°C were 0.7159, 4.64×10^{-4} 1 mol^{-1} s^{-1} and 0.8984

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mol 1^{-1} and at 50°C were 0.4311, 1.15×10^{-3} $1 \text{mol}^{-1} \text{s}^{-1}$ and $1.1150 \text{ mol } 1^{-1}$, respectively. ΔE for $k_p k_i / k_t$, k_p / k_t, and k_i were 16.07, -20.70, and 36.78 kcal mol^{-1}, respectively. $\Delta S^*_{318°K}$ for these were -32.97, -124.42, and 41.76 e.u., respectively.

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