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Polymerization of Acrylonitrile Initiated by the Mn^{3+} /Tartaric Acid Redox System*

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ABSTRACT

Vinyl polymerization of acrylonitrile initiated by the redox system Mn^{3+} /tartaric acid was investigated in aqueous sulfuric acid in the temperature range 30-50°C, and the initial rates of polymerization, Mn^{3+} disappearance, etc. were measured. The effects of certain water-miscible organic solvents, neutral electrolytes, dyes, and solid substances on the rate of polymerization have been investigated. A mechanism involving the formation of a complex between Mn^{3+} and tartaric acid, whose decomposition yields the initiating free radical with the polymer chain being terminated by mutual interaction of growing radicals, has been suggested.

*Dedicated to Dr. M. K. Rout, Principal, Ravenshaw College, Cuttack, Orissa, India.

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INTRODUCTION

Kinetic investigations of aqueous vinyl polymerization initiated by metal ions in their higher valence states, Co^{3+} , Ce^{4+} , V^{5+} , Cr^{6+} , Fe^{3+} , and Mn^{3+} , have provided valuable information regarding the mechanistic details of individual steps [1-7]. A series of interesting communications made by Waters et al. [8, 9] reports that dibasic acids like malonic acid can be oxidized by manganese pyrophosphate and manganic sulfate through a free radical mechanism. Singh et al. [10] and Namasivayam et al. [11] have reported that manganic sulfate in excess of sulfuric acid may form an effective redox system for grafting of poly(methyl methacrylate) onto cellulose and polyvinyl alcohol (PVA). Recently Nayudamma et al. [12] have reported Mn^{3+} -initiated graft copolymerization of vinyl monomers onto collagen. Nayak et al. have reported the polymerization of acrylonitrile [12-19] and methyl methacrylate [20] by the use of Mn^{3+} and a multitude of organic substrates. We have reported the aqueous polymerization of acrylonitrile [21] initiated by the Mn^{3+} -mannitol redox system. In this laboratory there is an ambitious research program to carry out chemical initiation graft copolymerization of vinyl monomers onto wool, silk, nylon 6, cellulose, etc. by the use of the Mn^{3+} ion. As a part of the research program, this communication presents the results of studies of vinyl polymerization of acrylonitrile (AN) initiated by the Mn^{3+} -tartaric acid (TA) redox system. From the experimental observations, a suitable reaction scheme has been suggested involving the initial complex formation between the substrate and the metal ion whose decomposition yields the initiating free radical with the polymerization being terminated by mutual combination of the growing chains.

EXPERIMENTAL

Acrylonitrile (American Cyanamid) was purified according to the method of Bamford et al. [22]. It was further purified by distillation in a nitrogen atmosphere under reduced pressure. Mn(II) sulfate and tartaric acid were EM-GR products. All other reagents (e.g., ferrous ammonium sulfate, O-phenanthroline) were commercial products. Mn^{3+} stock solutions were prepared by electrolytic oxidation of the appropriate Mn^{2+} solution (0.4-0.6 M) in 4-6 M sulfuric acid at a platinum anode [23, 24]. Freshly prepared solutions which were immediately used were analyzed for Mn^{3+} content by cerimetry for total manganese content by EDTA titration. Water distilled three times over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing through several columns of Fieser solution [16], a column of saturated lead acetate solution, and finally a wash bottle containing distilled water. The polymerization reactions

were heterogeneous with the polymer precipitating continuously. Rates of polymerization were determined from the weight of the polymer obtained, while the rates of oxidant consumption were determined by cerimetry on reaction mixtures arrested by the addition of excess standard ferrous ammonium sulfate solution.

The molecular weights \bar{M}_w of the purified polymers were determined by the appropriate Mark-Houwink relationship. The viscosities of the polymer solution (0.1%) were determined in an Ubbelohde suspended-level dilution viscometer in N,N-dimethylformamide at 30°C by using the relationship [25]

$$(\eta) = 3.335 \times 10^{-4} \bar{M}_w^{0.72}$$

RESULTS AND DISCUSSIONS

Acrylonitrile (AN) was polymerized in aqueous sulfuric acid solution at 35-50°C and in presence of the Mn^{3+} -tartaric acid redox system. A typical set of time conversion curves at 35°C and at various tartaric acid concentrations (0.5×10^{-3} to 2.5×10^{-3} M) at constant $[Mn^{3+}]$ concentration (7×10^{-3} M) are shown in Fig. 1.

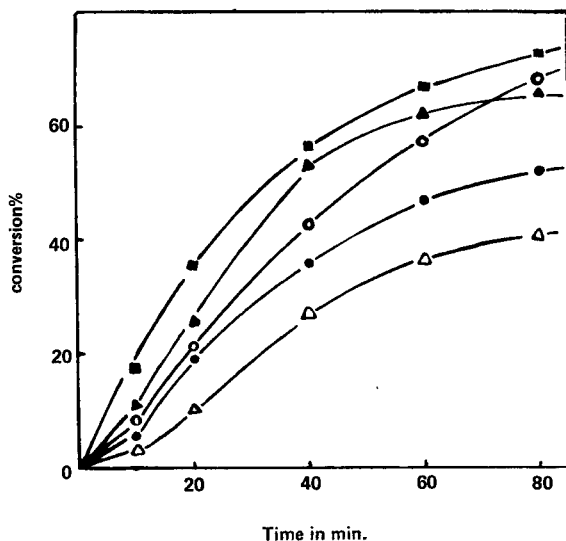


FIG. 1. Variation of % conversion with time: effect of activator concentration. $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.7$ M, $[AN] = 0.754$ M, $\mu = 1.8$ M, and temperature = 35°C. [TA] values: (●) 0.5×10^{-3} , (▲) 1×10^{-3} , (■) 1.5×10^{-3} , (○) 2×10^{-3} , and (△) 2.5×10^{-3} M.

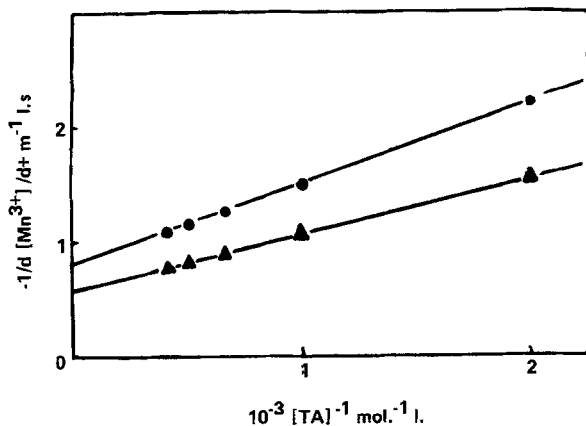


FIG. 2. Variation of $-d[\text{Mn}^{3+}]/dt$ with substrate at different temperatures. $[\text{Mn}^{3+}] = 7 \times 10^{-3} \text{ M}$, $[\text{H}^+] = 0.7 \text{ M}$, $[\text{AN}] = 0.754 \text{ M}$, and $\mu = 1.8 \text{ M}$. Temperatures: (●) 30°C and (▲) 35°C .

Rate of Manganic Ion Disappearance

The rate of manganic ion disappearance ($-d[\text{Mn}^{3+}]/dt$) was first order in $[\text{Mn}^{3+}]$ and independent of monomer concentration $[\text{AN}]$. The plots of $(-d[\text{Mn}^{3+}]/dt)^{-1}$ vs $[\text{TA}]^{-1}$ (where TA stands for tartaric acid) were linear with the intercept on the rate axis (Fig. 2), showing Lineweaver-Burk kinetics [26] for complex formation. Similar complex formation between Mn^{3+} and malonic acid has been shown by Waters et al. [27]. The rate of reaction is catalyzed both by sulfuric acid and by perchloric acid.

Rate of Polymerization

The rate of polymerization R_p was found to increase linearly with the increase of monomer concentration (0.1508-0.9048 M). Plots of R_p vs $[\text{AN}]^{3/2}$ were linear and passed through the origin (Fig. 3), indicating that the order with respect to $[\text{AN}]$ was three by two. R_p also increased linearly with an increase in the catalyst $[\text{Mn}^{3+}]$ concentration up to a certain limit, after which a decreasing trend was noticed. The initial rate of polymerization was found to increase linearly with increasing tartaric acid concentration. The plots of $1/R_p^2$ vs $[\text{TA}]^{-1}$ were linear with the intercept on the rate axis (Fig. 4).

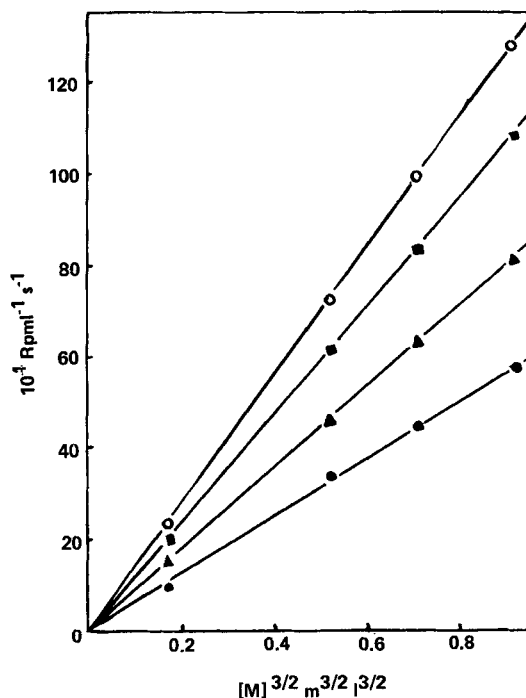


FIG. 3. Variation of R_p with monomer at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $\mu = 1.8 M$, and $[TA] = 1.5 \times 10^{-3} M$. Temperatures: (●) 30°C, (▲) 35°C, (■) 40°C, and (○) 45°C.

Effect of Temperature

With an increase of temperature the initial rate as well as the maximum conversion increased appreciably (Fig. 5). The dependence of the rate of polymerization with the increase of temperature could be ascribed to the greater activation energy.

Effect of Water-Miscible Organic Solvents

Addition of 10% (v/v) water-miscible organic solvents such as acetic acid, acetone, and ethanol to the reaction mixture depresses the initial rate as well as the maximum conversion. This is probably caused by the decrease in area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical and of the growing chain, or the increase in the regulated rate of production of primary radicals caused by the solvents which under the

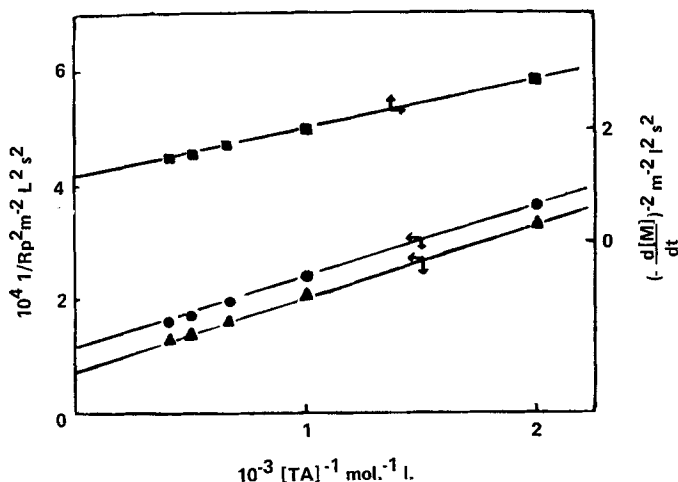


FIG. 4. (a) Variation of R_p with substrate concentration at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[AN] = 0.754 M$, and $\mu = 1.8 M$. Temperatures: (●) $30^\circ C$ and (▲) $35^\circ C$. Plot of $(-d[Mn^{3+}]/dt)^{-2}$ vs $[TA]^{-1}$. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[AN] = 0.754 M$, $\mu = 1.8 M$, and temperature (■) $35^\circ C$.

existing experimental conditions render the termination rate relatively fast compared to the rate of growth of the polymer chains as pointed out by Kern et al. [28]. Palit et al. [29] have noticed similar observations even for the homogeneous medium in which water is an additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid, which causes a premature mutual combination of the polymer chains. The effect of higher solvents composition results in a still greater decrease in the initial rate as well as in the maximum conversion (Fig. 6).

Effect of Added Electrolytes

The addition of certain neutral electrolytes such as $CuSO_4$, Na_2SO_4 , KCl , and $ZnSO_4$ to the reaction mixture reduces both the initial rate of polymerization and the maximum conversion to a considerable extent (Fig. 5). This might be due to the following two reasons.

(1) The ionic dissociation of the added electrolytes interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain, and (2) there is great reduction of activity of the manganic ion due to ion-pair coupling with the added electrolytes as suggested by Nayak et al. [5].

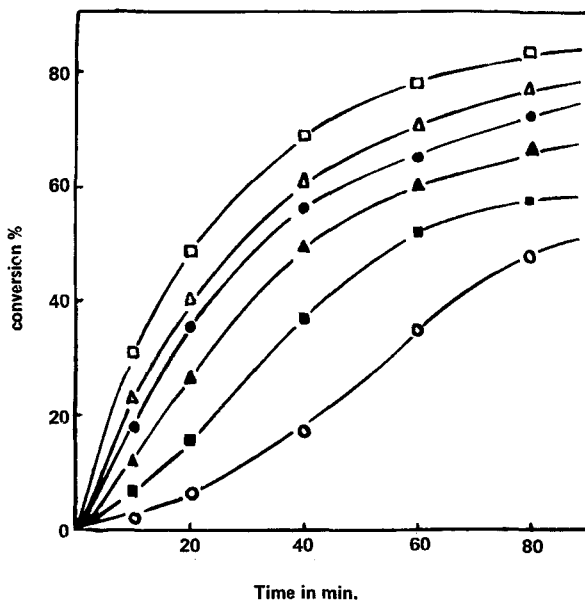


FIG. 5. Plots of % conversion vs time, effect of temperature. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[TA] = 1.5 \times 10^{-3} M$, $[AN] = 0.754 M$, and $\mu = 1.8 M$, Temperatures. (\bullet) $35^\circ C$, (Δ) $40^\circ C$, and (\square) $45^\circ C$. Plots of % conversion vs time, effect of neutral electrolytes. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[TA] = 1.5 \times 10^{-3} M$, $[AN] = 0.754 M$, $\mu = 1.8 M$, and temperature = $35^\circ C$. (\bullet) Control, (\blacktriangle) $[KCl] = 0.02 M$, (\blacksquare) $[Na_2SO_4] = 0.02 M$, and (\circ) $[ZnSO_4] = 0.02 M$.

Effect of Complexing Agents

The addition of 0.02 M complexing agents like NaF, succinic acid, lutidine, and α -picoline resulted in considerable depression of the initial rate and the maximum conversion, and with aniline as the complexing agent the reaction was completely inhibited. The most probable explanations for this type of behavior are that the pH of the medium changes due to consumption of H^+ ion by the amines and that the activity of the Mn^{3+} ion is greatly reduced due to the complex formation with amines behaving as ligands.

Effect of Certain Dyes

On addition of $4.5 \times 10^{-4} M$ methyl red and fluorescein dyes, the initial rate and the maximum conversion were depressed considerably

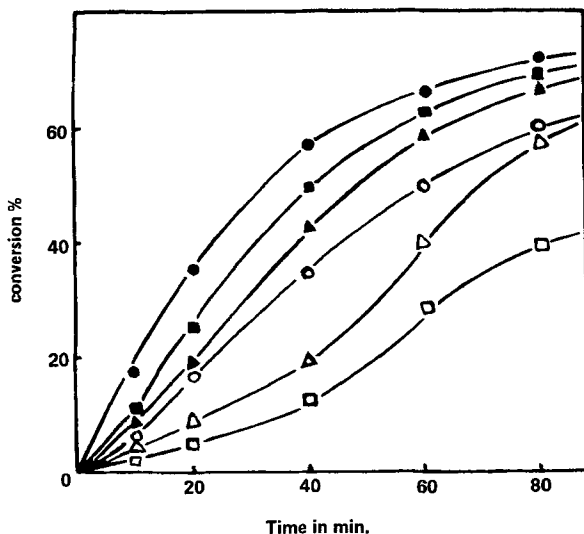


FIG. 6. Variation of % conversion with time at different acetone compositions. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[TA] = 1.5 \times 10^{-3} M$, $[AN] = 0.754 M$, $\mu = 1.8 M$, and temperature $= 35^\circ C$. (●) Control. [Acetone] values: (■) = 10%, (▲) 20%, (○) 30%, (△) 40%, and (□) 50% (v/v).

(Fig. 7) and the color of the dyes was retained with the polymer formed.

Effect of Solid Substances

The initial rate and maximum conversion were increased when the reaction was carried out in the presence of silica (Fig. 7). A similar observation was noticed by Maustafa et al. [30] in the polymerization of methyl methacrylate in the presence of graphite. The behavior of silica in the polymerization of AN is complex, and the catalytic effect may be attributed to the fact that it decreases the apparent activation energy for the polymerization of AN and increases the active centers present at certain spots.

Reaction Mechanism and Rate Law

Heterogeneity is a characteristic feature of aqueous polymerization of acrylonitrile initiated by Mn^{3+} ion in the presence of tartaric acid as the activator. The reaction mixture, though homogeneous

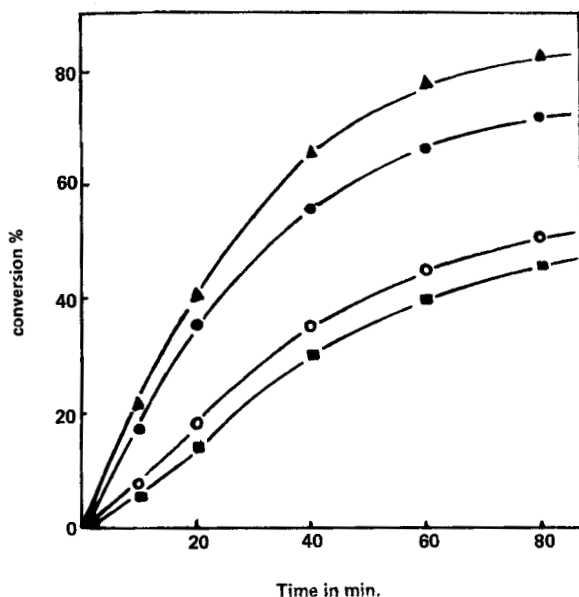
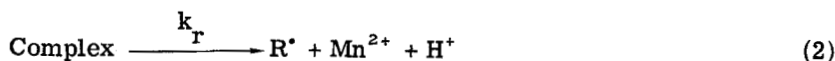


FIG. 7. Plots of conversion % vs time, effect of some dyes. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[TA] = 1.5 \times 10^{-3} M$, $[AN] = 0.754 M$, $\mu = 1.8 M$, and temperature = $35^\circ C$. (●) Control, (■) [methyl red] = $4.5 \times 10^{-4} M$, and (○) [fluorescein] = $4.5 \times 10^{-4} M$. Plots of conversion % vs time, effect of silica. $[Mn^{3+}] = 7 \times 10^{-3} M$, $[H^+] = 0.7 M$, $[TA] = 1.5 \times 10^{-3} M$, $[AN] = 0.754 M$, $\mu = 1.8 M$, and temperature = $35^\circ C$. (●) Control and (▲) silica = 1 g.

before the initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to insolubility of polyacrylonitrile (PAN) in the aqueous phase.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme involving the initiation by organic free radical produced by the interaction of Mn^{3+} with tartaric acid and termination by mutual combination of the polymer chain has been suggested.



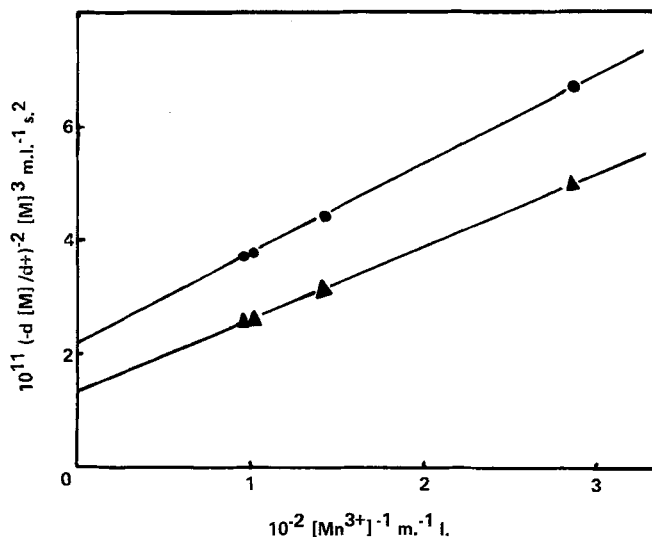
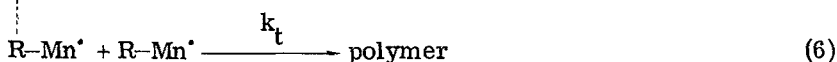


FIG. 8. Plots of $(-d[M]/dt)^{-2} [M]^3$ vs $[Mn^{3+}]^{-1}$ at different temperatures. $[TA] = 1.5 \times 10^{-3}$ M, $[AN] = 0.754$ M, and $\mu = 2.3266$ M. Temperatures: (•) 30°C and (▲) 35°C .



On applying steady-state principles to the primary radical R^\bullet as well as to the growing radical $R-M_n^\bullet$ and making the usual assumption that the radical reactivity is independent of radical size, we arrive at the following rate expression:

$$-d[Mn^{3+}]/dt = k_r K [Mn^{3+}]_{eq} [TA] + \frac{k_0 k_r K [Mn^{3+}]_{eq} [TA]}{(k_0 [Mn^{3+}]_{eq} + k_i [M])} \quad (7)$$

The second term in Eq. (7) is due to Reaction (3). If $k_0 [Mn^{3+}] \gg k_i [M]$, this term reduces to

$$-d[\text{Mn}^{3+}]/dt = 2k_r K [\text{Mn}^{3+}]_{\text{eq}} [\text{TA}] \quad (8)$$

Since the measured rate $-d[\text{Mn}^{3+}]/dt$ applies to total $[\text{Mn}^{3+}]$ regardless of the species, and since $[\text{Mn}^{3+}]_{\text{T}} = [\text{Mn}^{3+}]_{\text{eq}}(1 + K[\text{TA}])$, we obtain

$$-d[\text{Mn}^{3+}]/dt = 2k_r K [\text{Mn}^{3+}]_{\text{T}} [\text{TA}] / (1 + K[\text{TA}]) \quad (9)$$

or

$$(-d[\text{Mn}^{3+}]/dt)^{-1} = \frac{1}{2k_r K [\text{Mn}^{3+}]_{\text{T}} [\text{TA}]} + \frac{1}{2k_r [\text{Mn}^{3+}]_{\text{T}}}$$

The polymerization rate for $k_p[\text{RM}^*] \gg k_i[\text{R}^*]$ is given by

$$-d[\text{M}]/dt = \frac{k_p k_i^{1/2} (k_r K [\text{Mn}^{3+}] [\text{TA}])^{1/2} [\text{M}]^{3/2}}{k_t^{1/2} (k_0 [\text{Mn}^{3+}] + k_i [\text{M}])^{1/2}} \quad (10)$$

If $k_0 [\text{Mn}^{3+}] \gg k_i [\text{M}]$, then Eq. (10) reduces to

$$-d[\text{M}]/dt = k_p k_i^{1/2} (k_r K [\text{TA}])^{1/2} [\text{M}]^{3/2} / k_0^{1/2} k_t^{1/2} \quad (11)$$

Now Eq. (10) can be rearranged to

$$\begin{aligned} (-d[\text{M}]/dt)^{-2} &= \frac{k_t k_0}{k_p^{1/2} k_i k_r K [\text{TA}] [\text{M}]^2} + \frac{k_t}{k_p^2 k_r K [\text{Mn}^{3+}]_{\text{T}} [\text{TA}]^2} \\ &+ \frac{k_t}{k_p^2 k_r [\text{Mn}^{3+}]_{\text{T}} [\text{M}]^2} \end{aligned} \quad (12)$$

Plots of $(-d[\text{M}]/dt)^{-2}$ vs $[\text{TA}]^{-1}$ are linear with the intercept on the ordinate (Fig. 4).

From the intercept of these plots we can calculate the ratio of $k_p/k_t^{1/2}$. The above equation also requires that the plots of $(-d[\text{M}]/dt)^{-2} [\text{M}]^3$ vs $[\text{Mn}^{3+}]^{-1}$ are linear with an intercept equal to $k_t k_0 / k_p^2 k_i k_r K [\text{TA}]$ (Fig. 8). Using the values of $k_p/k_t^{1/2}$, the ratio k_0/k_i can be calculated from these intercepts. (See Table 1).

TABLE 1. Values of Rate Parameters from the Polymerization of Acrylonitrile (AN) Initiated by the Mn^{3+} /Tartaric Acid Redox System

Temperature (°C)	$k_r \times 10^5$ (s^{-1})	$K \times 10^{-2}$ (L/mol)	$10^{-2} \times k_p/k_t^{1/2}$ ($L^{1/2}/m^{1/2}s^{1/2}$)	$(k_0/k_t) \times 10^{-2}$
30	1.41	5.13	4.16	5.98
35	3.07	6.02	8.75	8.27

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