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Polymerization of Acrylonitrile: Kinetics of the Reaction Initiated by the Mn^{3+}/Ascorbic Acid Redox System

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ABSTRACT

Vinyl polymerization of acrylonitrile initiated by the Mn^{3+}/ascorbic acid redox system was investigated in aqueous sulfuric acid in the temperature range of 30-45°C. The rate of polymerization R_p and the rate of Mn^{3+} ion disappearance were measured. The effect of additives like water-miscible organic solvents, neutral salts, complexing agents and different surfactants on the initial rate of polymerization were investigated. Depending on the results obtained, a suitable reaction mechanism is suggested which involves the formation of a complex between Mn^{3+} ion and the acid whose decomposition generates the initiating free radical, with the polymer chain being terminated by mutual combination of the growing chains.

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INTRODUCTION

Detailed kinetic investigations of aqueous vinyl polymerization initiated by metal ions in their higher valence states, Co(III), Ce(IV), V(V), Cr(VI), Fe(III), Mn^{3+}, have provided valuable information regarding the mechanistic details of individual steps [1-7]. In a series of interesting communications, Waters et al. [8, 9] have reported 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 an excess of sulfuric acid may form an effective redox system for grafting of poly(methyl methacrylate) onto cellulose and poly(vinyl alcohol) (PVA). Recently Nayudamma et al. [12] have reported Mn^{3+}-initiated graft copolymerization of vinyl monomers onto collagen. We have reported the aqueous polymerization of acrylonitrile [12-18] methyl methacrylate [19], and acrylamide [6] by use of Cr(VI), V(V), Mn^{3+} and a multitude of organic substrates. In this laboratory there is an ambitious research program to carry out chemical initiation graft copolymerization of vinyl monomers onto some natural and synthetic macromolecules such as wool, silk, nylon 6, etc., by use of Mn^{3+} ion. As a part of the research program, this communication presents results of the studies of vinyl polymerization of acrylonitrile (AN) initiated by the Mn^{3+}-ascorbic acid redox system. From the experimental observation, a suitable reaction scheme has been suggested involving the initial complex formation between the acidic hydroxyl group of ascorbic acid and the metal ion, whose decomposition yields the initiating free radical with the polymerization being terminated by mutual combination of the growing chains. Various kinetic parameters were evaluated.

EXPERIMENTAL

Acrylonitrile (American Cyanamid) was washed with 5% NaOH, dilute H_2SO_4, and finally with distilled water and dried over anhydrous calcium chloride. It was further purified by distillation in a nitrogen atmosphere under reduced pressure. Mn(II) sulfate was an EM-GR product. All other reagents like cerric ammonium sulfate, ferrous ammonium sulfate, o-phenanthroline, citric acid, tartaric acid, ascorbic acid, oxalic acid, glutaric acid, and adipic acid were AR grade. Mn(III) stock solutions were prepared by electrolytic oxidation of the appropriate Mn^{2+} salt solution (0.4-0.6 $\underline{M}$) in 4-6 $\underline{M}$ sulfuric acid at a platinum anode [20, 21]. 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 passage 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 [15] solution, 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 was 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 $\overline{M}_w$ of the purified polymers were determined by using the appropriate Mark-Houwink relationship. The viscosities of the polymer solution (0.1%) were determined in an Ubbelohde suspended-level dilution viscometer in DMF at 30°C by using the relationship [22]:

$$[\eta] = 3.335 \times 10^{-4} \, \overline{M}_w^{\,0.72}$$

RESULTS AND DISCUSSION

Acrylonitrile (AN) was polymerized in aqueous sulfuric acid solution at 30-45°C and in presence of the Mn^{3+}-ascorbic acid redox system. A typical set of time-conversion curves at 40°C and at various ascorbic acid concentrations (0.5×10^{-3} to 2.0×10^{-3} M), at constant $[Mn^{3+}]$ concentration (7.0×10^{-3} M) are shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions with Mn^{3+} in presence of other carboxlic acids like tartaric acid, oxalic acid, citric acid, succinic acid, glutaric acid, and adipic acid. There is an induction period involved in each case and the point of appearance of the turbidity in the reaction mixture is taken as the starting point of polymerization. The results are recorded in Table 1, which shows under identical conditions, the reactivity of the carboxylic acids are: citric acid > tartaric acid > ascorbic acid > oxalic acid > succinic acid > glutaric acid > adipic acid.

Rate of Manganic Ion Disappearance

The rate of manganic ion disappearance ($-d[Mn^{3+}]/dt$) was first-order in $[Mn^{3+}]$ and independent of monomer concentration [AN]. The plot of $(-d[Mn^{3+}]/dt)^{-1}$ versus $[AA]^{-1}$ (where AA stands for ascorbic acid) were linear with intercept on the rate axis (Fig. 1) showing Lineweaver-Burk kinetics [23] for complex formation.

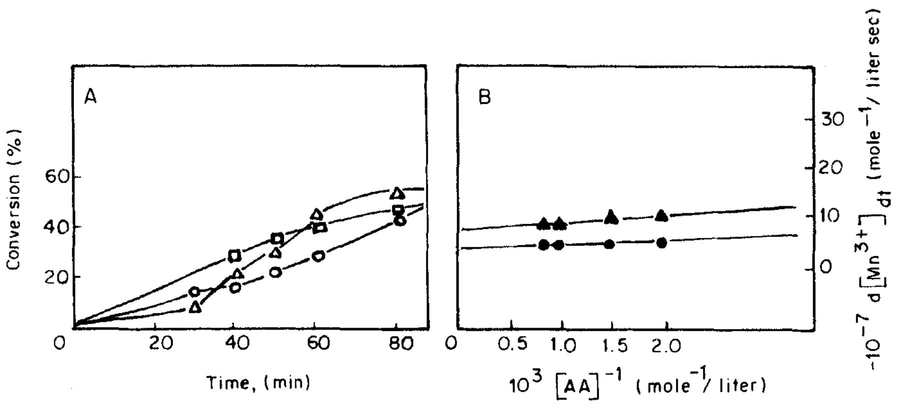

FIG. 1. Plots of (a) conversion vs. time (effect of activator concentration) at 40°C at (○) [AA] = 0.5×10^{-3} M, (△) [AA] = 1.0×10^{-3} M, and (□) [AA] = 1.25×10^{-3} M and (b) $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[AA]^{-1}$ at (▲) 35°C and (●) 40°C. $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.4$ M, [AN] = 0.754 M.

TABLE 1. Polymerization of Acrylonitrile (AN) Initiated by Various Mn^{+3}-Carboxylic Acid Redox Systems at 20 ± 0.1°C[a]

Acid	Concentration (M)	Induction period (min)	$R_p \times 10^5$ (min^{-1})
Citric acid	3×10^{-3}	2	12.05
Tartaric acid	3×10^{-3}	8	2.83
Ascorbic acid	3×10^{-3}	0	0.7452
Oxalic acid	3×10^{-3}	3	0.5047
Succinic acid	3×10^{-3}	15	0.3254
Glutanic acid	3×10^{-3}	40	0.2825
Adipic acid	3×10^{-3}	60	0.2157

[a] Recipe: $[Mn^{3+}] = 1.75 \times 10^{-3}$ M; $[H^+] = 1.83$ M; $\mu = 1.957$ M; [AN] = 0.754 M.

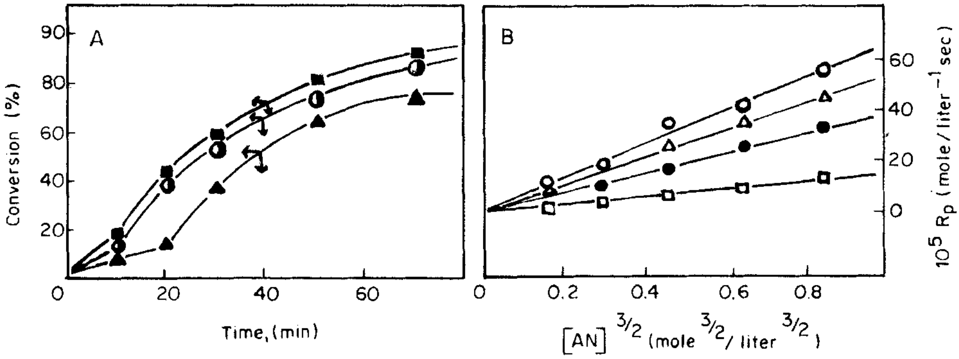

FIG. 2. Plot of (a) conversion vs. time at [AA] = 0.001 M, [AN] = 0.754, μ = 1.17 M, 40°C: (▲) [Mn^{3+}] = 7 × 10^{-3} M, (■) [Mn^{3+}] = 10.4 × 10^{-3} M, (◑) [Mn^{3+}] = 10.7 × 10^{-3} M and (b) R_p vs. $[AN]^{3/2}$ at [Mn^{3+}] = 7 × 10^{-3} M, [H^+] = 0.4 M, [AA] = 1 × 10^{-3} M: (□) 30°C, (●) 35°C, (△) 40°C, and (○) 45°C.

Similar complex formation between Mn^{3+} and malonic acid has been shown by Waters et al. [24]. The rate of the reaction is catalyzed both by sulfuric and perchloric acid.

Rate of Polymerization

The rate of polymerization R_p was found to increase linearly with increase of monomer concentration (0.0314-0.9042 M). Plots of R_p versus $[AN]^{3/2}$ were linear and passed through the origin (Fig. 2), indicating that the order with respect to [AN] was three halves. R_p also increased linearly with increase in the catalyst (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 ascorbic acid concentration. The plots of $1/R_p^2$ versus $[AA]^{-1}$ were linear with intercept on the rate axis.

Effect of Water-Miscible Organic Solvents. Addition of 10% (v/v) water-miscible organic solvents such as acetic acid, acetone, dimethylformamide (DMF), and chloroform to the reaction mixture depresses the initial rate as well as the maximum conversion (Fig. 3). This is probably caused by the decrease in area of shielding of a strong hydration layer in the aqueous medium, resulting in the

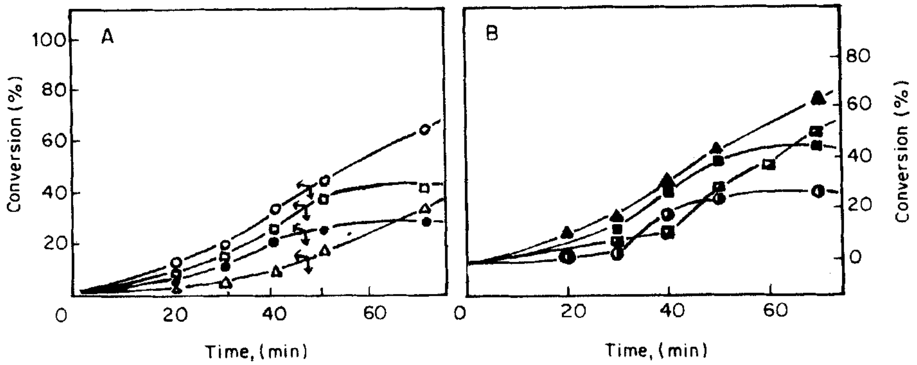

FIG. 3. Plots of conversion % vs. time (a) showing effect of complexing agents at [Mn^{3+}] = 7 × 10^{-3} M, [H^+] = 0.4 M, [AA] = 1.0 10^{-3} M [AN] = 0.754 M, 40°C: (○) control, (△) pyridine = 0.02 M, (□) piperidine = 0.02 M, (●) lutidine = 0.02 M and (b) showing effect of water-soluble organic solvents at [Mn^{3+}] = 7 × 10^{-3} M, [H^+] = 0.4 M, [AA] = 1.0 × 10^{-3} M, [AN] = 0.754 M, 40°C: (▲) = control, (■) 10% acetic acid; (◪) 10% DMF; (◑) 10% chloroform.

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 existing experimental conditions renders the termination rate relatively fast compared to the rate of growth of the polymer chains, as pointed out by Kern et al. [25]. Palit et al. [26] have noticed similar observations even for the homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid, which causes a premature mutual combination of the polymer chains.

Effect of Added Electrolytes. The addition of certain neutral electrolytes such as $CuSO_4$, Na_2SO_4, KCl, or $ZnSO_4$, to the reaction mixture reduces both the initial rate of polymerization and the maximum conversion to a considerable extent. This might be due to the following two reasons: (1) the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain, and (2) the great reduction of the activity of the manganic ion due to ion-pair coupling with the added electrolytes as suggested by Nayak et al. [5].

Effect of Surfactants. In the recent past micellar catalysis has played an important role in the kinetic investigations of the mechanism of certain polymerization reactions [27, 28]. The hydrophobic interactions and electrostatic attractions are mainly responsible for the spectacular rate enhancement or inhibition exhibited by the micelles on the polymerization reactions. Addition of anionic surfactant sodium lauryl sulfate to the reaction mixture below and above CMC reduced the rate of polymerization. The retarding effect of the anions may be explained by specific ion-pair binding of the cation Mn^{3+} with the anion RSO_4^- which lowers the rate of primary radical generation. Alexander et al. [28] have proposed such ion-pair binding between cationics and $S_2O_8^{2-}$ ions only above CMC leading to the formation of an insoluble complex, which could be dispersed by further addition of cationics and hence the rate is reduced. The nonionic surfactant, Triton-X-100, has no effect on the rate of polymerization.

Effect of Complexing Agents. On addition of 0.02 M complexing agents like pyridine, piperidine, and dimethylaniline, the initial rate and the maximum conversion were depressed considerably (Fig. 3) 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 the consumption of the 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 Catalyst Concentration. The initial rate as well as the maximum conversion decreased with increasing concentration of the catalyst over the range 7×10^{-3} - 10.4×10^{-3} M. A set of time-conversion plots at a definite temperature are shown in Fig. 2a. At higher concentration of the catalyst (above 10.7×10^{-3} M) a decrease in the rate was noticed. This might be due to the fact that at higher concentration of the catalyst, the oxidation rate becomes relatively fast compared to the polymerization rate as pointed out by Nayak et al. [5].

Reaction Mechanism and Rate Law

Heterogeneity is a characteristic feature of aqueous polymerization of acrylonitrile initiated by Mn^{3+} ion in the presence of ascorbic acid as the activator. The reaction mixture, though homogeneous before the initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the 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 ascorbic acid and termination by mutual combination of the polymer chain has been suggested.

$$Mn^{3+} + AA \xrightleftharpoons{K} \text{Complex} \tag{1}$$

$$\text{Complex} \xrightarrow{k_r} R^{\cdot} + Mn^{2+} + H^{+} \tag{2}$$

$$R^{\cdot} + Mn^{3+} \xrightarrow{k_0} Mn^{2+} + \text{product} \tag{3}$$

$$R^{\cdot} + M \xrightarrow{k_i} R - M_1^{\cdot} \tag{4}$$

$$R - M_1^{\cdot} + M \xrightarrow{k_p} R - M_2^{\cdot} \tag{5}$$

$$\vdots$$

$$R - Mn\cdot + R - Mn \xrightarrow{k_t} \text{Polymer} \tag{6}$$

On applying the steady-state principle to the primary radical $R^{\cdot}$ as well as to the growing radical $R - Mn^{\cdot}$ and making the usual assumption that the radical reactivity is independent of radical size we arrive at the following rate expression:

$$-\frac{d[Mn^{3+}]}{dt} = k_r K [Mn^{3+}] [AA] + \frac{k_0 k_r K [Mn^{3+}]^2 [AA]}{(k_0 [Mn^{3+}] + k_i [M])} \tag{7}$$

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

$$- d[Mn^{3+}]/dt = 2 k_r K [Mn^{3+}] [AA] \tag{8}$$

Since the measured rate $- d[Mn^{3+}]/dt$ applies to total $[Mn^{3+}]$ regardless of the species and since

$$[Mn^{3+}]_T = [Mn^{3+}](1 + K [AA])$$

we obtain

$$- d[Mn^{3+}]/dt = 2k_r K [Mn^{3+}]_T [AA]/(1 + K [AA]) \tag{9}$$

The polymerization rate for $k_p [RM\cdot] \gg k_i [R\cdot]$ is given by

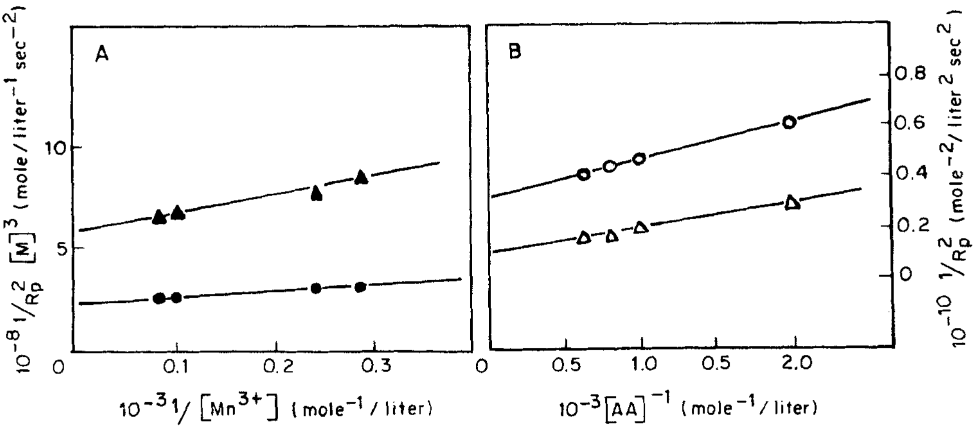

FIG. 4. Plots of (a) $(1/R_p^2\ [M]^3$ vs. $1/[Mn^{3+}]$ at $\mu = 1.17$ M, [AA] = 1.0×10^{-3} M, [AN] = 0.754 M: (▲) 35°C and (●) 40°C; (b) of $1/R_p^2$ vs. $[AA]^{-1}$ at $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.4$ M, [AN] = 0.754 M: (○) 35°C, and (△) 40°C.

$$\frac{-d[M]}{dt} = \frac{k_p k_i^{1/2} (k_r K [Mn^{3+}]\ [AA])^{1/2}\ [M]^{3/2}}{k_t^{1/2} (K_0\ [Mn^{3+}] + k_i\ [M])^{1/2}} \tag{10}$$

If $k_0\ [Mn^{3+}] \gg k_i\ [M]$, then

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

Now Eq. (10) can be rearranged to

$$\frac{- d[M]^{-2}}{dt} = \frac{k_t k_0}{k_p^2 k_i k_r k\ [AA]\ [M]^3} + \frac{k_t}{k_p^2 k_r K\ [Mn^{3+}]_T [AA]\ [M]^2} + \frac{k_t}{k_p^2 k_r\ [Mn^{3+}]_T [M]^2} \tag{12}$$

TABLE 2. Values of Rate Parameters in the Polymerization of Acrylonitrile (AN) Initiated by the Mn^{3+}-AA Redox System

Temp (°C)	$10^3 \times k_r$ (sec^{-1})	$10^{-3} \times K$ (liter/mole)	$k_p/k_t^{1/2} \times 10^{-2}$ $liter^{1/2}$-$sec^{1/2}$/$mole^{1/2}$	($k_0/k_i \times 10^{-2}$)
35	1.61	16.98	3.12	2.63
40	2.98	22.82	4.86	3.82

The plot of $(-d[M]/dt)^{-2}$ versus $[AA]^{-1}$ are linear with intercept on the ordinate (Fig. 4).

Evaluation of K, k_r, $k_p/k_t^{1/2}$ and k_0/k_i

The values of K and k_r were computed by plotting $(-d[Mn^{3+}]/dt)^{-1}$ against $[AA]^{-1}$ (Fig. 1). From the intercept and the ratio intercept/slope of these plots, the rate of unimolecular decomposition of the complex (k_r) and its formation constant (K) can be calculated. The values are presented in Table 2. Further, Eq. (12) requires that the plots of $(-d[M]/dt)^{-2}$ versus $[AA]^{-1}$ are linear with intercepts on the ordinate (Fig. 1). From the intercept of these plots, the ratio $k_p/k_t^{1/2}$ can be calculated. Equation (12) also requires that the plots of $(-d[M]^{-2}/dt\,[M]^3$ versus $[Mn^{3+}]^{-1}$ are linear with intercept equal to $k_t/k_0/k_p{}^2k_iK\,[AA]$ (Fig. 4). By using the values of k_p/k_t the ratio k_0/k_i can be calculated from these intercepts. The values of $k_p/k_t^{1/2}$ and k_0/k_i are represented in Table 2.

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