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

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ABSTRACT

Polymerization of acrylonitrile initiated by the redox system Mn^{3+}/mannitol has been investigated in aqueous sulfuric acid in the temperature range 35-50°C. The rate of polymerization R_p and the rate of disappearance of Mn^{+3} ($-R_M$) were measured. The effect of certain water-miscible organic solvents, inorganic salts and complexing agents on the rate of polymerization have been investigated. Based on the experimental results, a suitable reaction mechanism is suggested involving the formation of complex between Mn^{3+} and the hydroxyl group of the substrate molecule, whose decomposition yields the initiating free radical; the polymer chain is terminated by the mutual combination of growing chains.

INTRODUCTION

Kinetic studies of aqueous vinyl polymerization initiated by metal ions in their higher valence states, i. e., Co(III), Ce(IV), V(V), Cr(VI), Fe(III), and Mn^{3+}, have provided valuable information regarding the mechanistic details of individual steps [1-4]. Waters et al. [5] have reported the mechanism of oxidation of a multitude of organic substrates involving trivalent manganese. Singh et al. [6] and Namasivayam et al. [7] 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. [8] reported the Mn^{3+}-initiated graft copolymerization of vinyl monomers onto collagen. Nayak et al. [9-14] have reported the aqueous polymerization of acrylonitrile and methyl methacrylate by using Mn^{3+} with variety of organic substrates. The present communication presents the results of the studies of vinyl polymerization of acrylonitrile (AN) initiated by the Mn^{3+}/mannitol redox system. From the experimental observations, a suitable reaction scheme is proposed which involves initial complex formation between the hydroxyl group of the polyhydroxy alcohol and the metal ion; decomposition of this complex generates 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 purified according to the method of Bamford et al [15]. It was further purified by distillation in a nitrogen atmosphere under reduced pressure. Mn(II) sulfate and mannitol were EM-GR products. All other reagents, like ferrous ammonium sulfate, o-phenanthroline, etc., were commercial products. Mn(III) stock solutions were prepared by electrolytic oxidation of the appropriate Mn^{2+} solution (0.4-0.6 $\underline{M}$) in 4-6 $\underline{M}$ sulfuric acid at a platinum anode. Freshly prepared solutions which were immediately used were analyzed for Mn^{3+} content by cerimetry and 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 (Indian Oxygen Ltd., Calcutta) used for dearation of the experimental systems was purified by passing through several columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle containing distilled water. Heterogeneity is the characteristic feature of polymerization of acrylonitrile in aqueous media. Rates of polymerization were determined from the weight of the polymer obtained, while the rates of oxidant consumption were obtained by cerimetry on reaction mixtures arrested by the addition of excess standard ferrous ammonium sulfate solution.

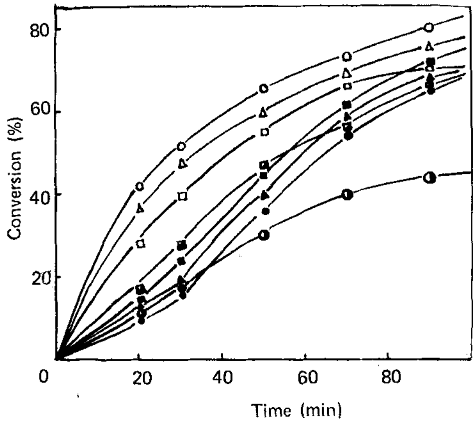

FIG. 1. Percentage conversion vs. time for polymerization of acrylonitrile initiated by mannitol/Mn^{3+} redox system at various activator concentrations and temperatures: (●) [ML] = 0.5×10^{-3} M, 40°C; (▲) [ML] = 1×10^{-3} M, 40°C; (■) [ML] = 1.25×10^{-3} M, 40°C; (○) [ML] = 1.5×10^{-3} M, 40°C; (△) [ML] = 2×10^{-3} M, 40°C; (□) [ML] = 2.5×10^{-3} M, 40°C; (●) [ML] = 1×10^{-3} M, 35°C; (◪) [ML] = 1×10^{-3} M, 45°C. [Mn^{3+}] = 7×10^{-3} M, [H^+] = 0.85 M, μ = 2.2 M, [AN] = 0.754 M.

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous sulfuric acid solution at temperatures of 35-50°C in presence of the Mn^{3+}/mannitol redox system. A set of time conversion curves at 40°C and various mannitol concentrations (0.0005-0.0025 M) at constant [Mn^{3+}] concentration (7×10^{-3} M) are shown in Fig. 1.

Rate of Disappearance of Manganic Ion

The rates of manganic ion disappearance (-d[Mn^{+3}]/dt) were first order in [Mn^{3+}] and independent of monomer concentration. Plots of (-d[Mn^{3+}]/dt) versus 1/[ML] (where ML is mannitol) were linear with intercept on the rate axis (Fig. 2) showing Lineweaver-Burk [16] kinetics for complex formation. Similar complex formation between Mn^{3+} and malonic acid has been shown by waters et al. [5]. The rate of the reaction is catalyzed both by sulfuric acid and perchloric acid.

Rates of Polymerization

The rate of polymerization (R_p) was found to increase linearly

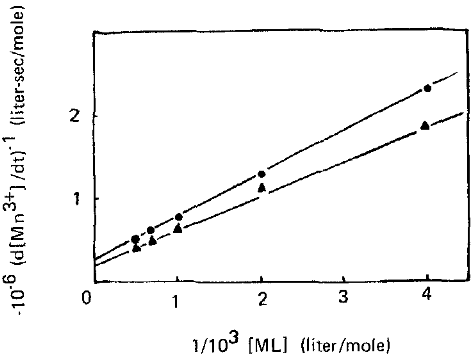

FIG. 2. Variation of $-d[Mn^{3+}]/dt$ with [ML] at different temperatures for polymerization of acrylonitrile initiated by the mannitol/ Mn^{3+} redox system: (●) 35°C; (▲) 40°C. $[Mn^{3+}] = 7 \times 10^{-3}$ M, [H] = 0.85 M, μ = 2.2 M, [AN] = 0.754 M.

with increase of monomer concentration (0.1508-0.9048). The plots of R_p versus $[AN]^{3/2}$ were linear and passed through the origin (Fig. 3), indicating that the order with respect to [AN] was 3/2. The rate of polymerization also increased with increase of the catalyst concentration up to a certain limit, after which a decreasing trend was noticed. The rate of polymerization was found to increase linearly with increasing mannitol concentration (0.5×10^{-3} - 2.5×10^{-3} M). The plots of $1/R_p^2$ versus 1/[ML] were linear, with intercept on the rate axis (Fig. 4).

Effect of Water-Miscible Organic Solvents

Addition of 10% (v/v) water-miscible organic solvents such as C_2H_5OH, CH_3COCH_3, CH_3COOH, and $CHCl_3$ to the reaction mixture decreases the initial rate as well as the maximum conversion. These are probably due to the decrease in area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain, and also an increase by these solvents in the regulated rate of production of primary radicals, which under the existing experimental conditions renders the termination rate relatively fast as compared to the rate of growth of the polymer chains, as pointed out by Kern et al. [17]. Palit and co-workers [18] have noticed similar observation even for the homogeneous medium in which water is the additive. Further, the interchain hydrogen bonding interlocking polymer chain is not rigid, and therefore a tendency of mutual termination of the polymer chain occurs. The

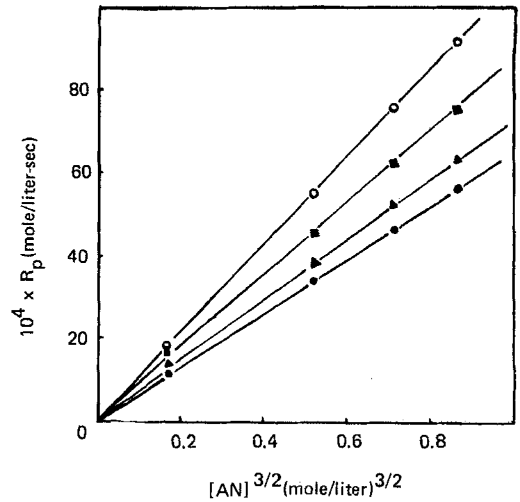

FIG. 3. Variation of R_p with monomer at different temperature for polymerization of acrylonitrile (AN) initiated by the mannitol/ Mn^{3+} redox system: (●) 35°C; (▲) 40°C; (■) 45°C; (○) 50°C. $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 2.2$ M.

effect of higher solvent composition of acetic acid results in a still further decrease in the initial rate as well as maximum conversion (Fig. 5).

Effect of Added Electrolytes

The addition of certain electrolytes, such as $CuSO_4$, Na_2SO_4 etc. 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 electrolyte produces ions of opposite character among which the positive ion arrests the radical end of the growing chains, for which the rate is depressed; (2) the activity of the manganic ion is greatly reduced due to the interference of the added salts on the normal dissociation of manganic sulfate.

Effect of Complexing Agents

On addition of 0.02 M complexing agents like pyridine or succinic acid, the initial rate and the maximum conversion were depressed considerably (Fig. 6), and with aniline as the complexing agent the

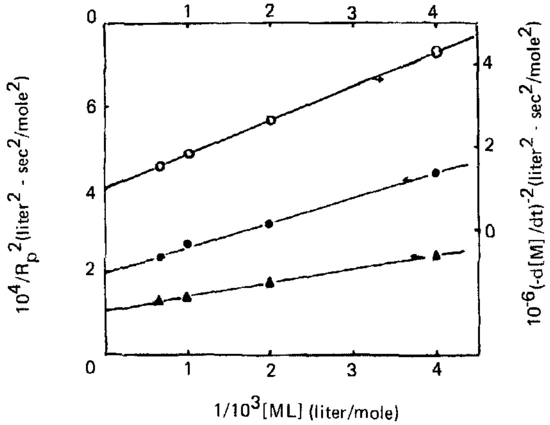

FIG. 4. Polymerization of acrylonitrile initiated by mannitol/ Mn^{3+} redox system: (●, ▲) variation of R_p with activator concentration $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 2.2$ M, [AN] = 0.754 M, as plots of $[ML]^{-1}$ vs. $1/R_p^2$ at (●) 35°C and (▲) 40°C; (○) variation of $-d[Mn^{3+}]/dt$ with [ML]. $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 2.2$ M, [AN] = 0.754 M.

reaction was completely inhibited. The most probable explanations for this type of behavior are that there is a change in pH of the medium 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 complex formation with amines behaving as ligands.

REACTION MECHANISM AND RATE LAW

The aqueous polymerization of acrylonitrile initiated by trivalent manganese ion in the presence of mannitol shows features characteristic of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as the polymerization starts, due to insolubility of the 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 mannitol and termination by mutual combination of the polymer chain has been suggested; this mechanism is summarized in Eqs. (1)-(6).

$$Mn^{3+} + ML \underset{}{\overset{K_1}{\rightleftharpoons}} Complex \qquad (1)$$

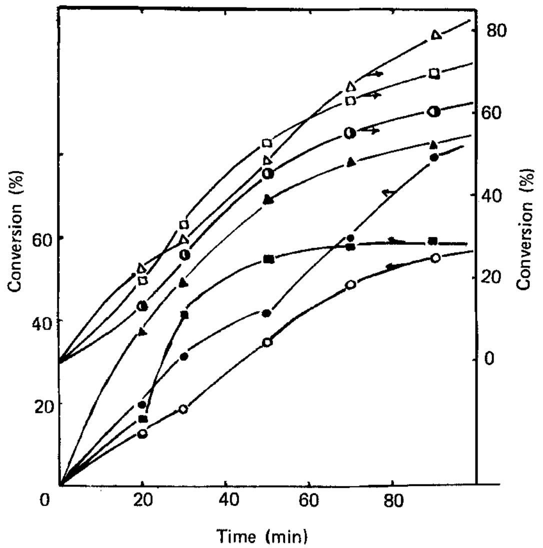

FIG. 5. Effect of acetic acid (HOAc) concentration and of neutral electrolytes on polymerization of acrylonitrile initiated by the mannitol/Mn^{3+} redox system: (●) [HOAc] = 10%; (▲) [HOAc] = 20%; (■) [HOAc] = 30%; (○) [HOAc] = 40%; (△) [$CuSO_4$] = 0.02 M, (□) [$ZnSO_4$] = 0.02 M; (◑) [KCl] = 0.02 M. [Mn^{3+}] = 7×10^{-3} M, [H^+] = 0.85 M, [ML] = 1×10^{-3} M, [AN] = 0.754 M, μ = 2.2 M, 40°C.

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

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

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

$$R-\dot{M}_1 + M \xrightarrow{k_p} R-\dot{M}_2 \tag{5}$$

$$R-\dot{M}_n + R-\dot{M}_m \xrightarrow{k_t} \text{Polymer} \tag{6}$$

Applying the steady-state principle (i. e., the rate of initiation is equal to rate of termination) to the primary radical $R^{\cdot}$ as well as to the growing radical $R-M_n^{\cdot}$ and making the usual assumption that the radical reactivity is independent of radical size, we arrive at the rate expression (7):

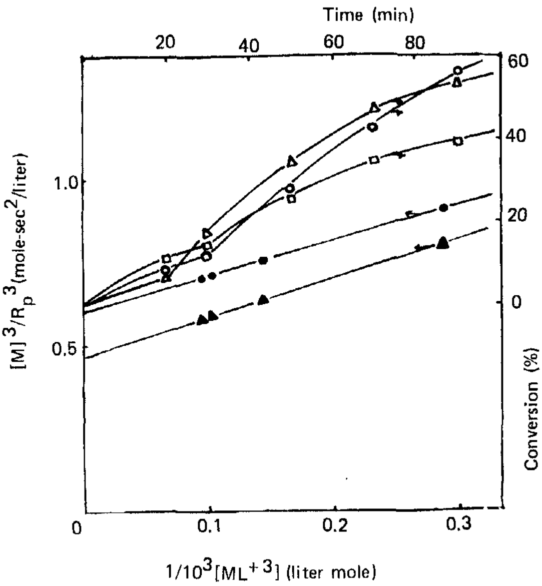

FIG. 6. Polymerization of acrylonitrile initiated by the mannitol/Mn^{3+} redox system. (a) Variation of R_p with oxidant at different temperature as plots of $[Mn^{3+}]^{-1}$ vs. $[M]^3/R_p^2$ at (●) 35°C, and (▲) 40°C at $[ML] = 1 \times 10^{-3}$ M, $[AN] = 0.754$ M, $\mu = 3.2977$ M. (b) Effect of the complexing agents on conversion vs. time: (○) [NaF] = 0.02 M, (△) [Succinic acid] = 0.02 M, (□) [Pyridine] = 0.02 M, all at $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $[ML] = 1 \times 10^{-3}$ M, $[AN] = 0.754$ M, $\mu = 2.2$ M, 40°C.

$$-d[Mn^{3+}]/dt = k_rK[Mn^{3+}][ML] + \frac{k_0k_rK[Mn^{3+}]^2[ML]}{(k_0[Mn^{3+}] + k_i[M])} \qquad (7)$$

The second term in Eq. (7) is due to reaction (3). If $k_0[Mn^{3+}] \gg k_i[M]$, this equation reduces to Eq. (8):

$$-d[Mn^{3+}]/dt = 2\,k_rK[Mn^{3+}][ML] \qquad (8)$$

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

$$[Mn^{3+}]_T = [Mn^{3+}]\,(1 + K[ML])$$

we have

$$-d[Mn^{3+}]/dt = \frac{2k_rK[Mn^{3+}]_T[ML]}{(1 + K[ML])}$$

or

$$\left(\frac{-d[Mn^{3+}]}{dt}\right)^{-1} = \frac{1}{2k_rK[Mn^{3+}]_T[ML]} + \frac{1}{2k_r[Mn^{3+}]_T} \qquad (9)$$

The polymerization rates are given by

$$-d[M]/dt = k_p[M][R - \dot{M}n]$$

for $k_p[R\dot{M}] \gg k_i[R^{\cdot}]$

$$-\frac{d[M]}{dt} = \frac{k_pk_i^{1/2}(k_rK[Mn^{3+}][ML])^{1/2}[M]^{3/2}}{k_t^{1/2}(k_0[Mn^{3+}] + k_i[M])^{1/2}} \qquad (10)$$

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

$$\frac{-d[M]}{dt} = \frac{k_pk_i^{1/2}(k_rK[ML])^{1/2}[M]^{3/2}}{k_0^{1/2}k_t^{1/2}} \qquad (11)$$

Now Eq. (10) can be rearranged to

$$\left(\frac{-d[M]}{dt}\right)^{-2} = \frac{k_tk_0}{Kk_p^2k_ik_r[ML][M]^3} + \frac{k_t}{k_p^2k_rK[Mn^{3+}][ML][M]^2} + \frac{k_t}{k_p^2k_r[Mn^{3+}][M]^2} \qquad (12)$$

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

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