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

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ABSTRACT

The vinyl polymerization of acrylonitrile initiated by the redox system Mn^{3+}-cyclohexanol 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 effects of certain water-miscible organic solvents and certain anionic, cationic, and nonionic surfactants on the rate of polymerization were investigated. Based on the results obtained, a suitable reaction mechanism involving the formation of a complex between Mn^{3+} and the alcohol, whose decomposition yields the initiating free radical with the polymer chain being terminated by the mutual combination of growing chains is suggested.

INTRODUCTION

Detailed kinetic studies 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 [1-4]. Waters and his co-workers [5] have reported the mechanism of oxidation of a multitude of organic substrates involving trivalent manganese. Singh et al. [6] and Namsivayam 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] have reported the Mn^{3+}-initiated graft copolymerization of vinyl monomers onto collagen. We have reported the aqueous polymerization of acrylonitrile [9-16], methyl acrylate and methyl methacrylate [17], acrylamide [18], and methyl methacrylate [19, 20] using V(V), Cr(VI), and Mn^{3+} and a multitude of organic substrates. In this laboratory there is an ambitious research program to use trivalent manganese either in the form of pyrophosphate or sulfate for grafting of vinyl monomers onto some natural and synthetic macromolecules such as wool, silk, nylon 6, etc. 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+}-cyclohexanol redox system. From the experimental observation, a suitable reaction scheme involving the initial complex formation between the hydroxyl group of the alcohol and the metal ion, whose decomposition generates the initiating free radical with the polymerization being terminated by mutual combination of the growing chains has been suggested. 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 E. Merck-GR product. All other reagents, i.e., ferrous ammonium sulfate, o-phenanthroline, 1-propanol, ethyl alcohol, glycerol, isobutyl alcohol, tert-butyl alcohol, 1,2-propanediol, 1-butanol, sec-butyl alcohol, cyclopentanol cyclohexanol, and cycloheptanol, were commercial products. 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 [21, 22]. Freshly prepared solutions which were immediately used, were analyzed for Mn^{3+} content by cerimetry and for total manganese content by EDTA titration. Water used to prepare all solutions was triply distilled over alkaline permanganate and deionized by passage through a column of Biodeminrolit resin (Permutit Co., U. K.). Nitrogen used for deaeration of the experimental systems was purified by passage through several columns of Fieser's 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 were determined from the weight of the polymer obtained, while the rate of oxidant consumption was determined by cerimetry on reaction mixtures arrested by the addition of excess standard ferrous ammonium sulfate solution.

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous sulfuric acid solution at temperatures of 30-40°C in the presence of the redox system Mn^{3+}-cyclohexanol. A typical set of time conversion curves at 25°C and various cyclohexanol concentration (0.005-0.09 M) at constant Mn^{3+} concentration ($[Mn^{+3}] = 1.75 \times 10^{-3}$ M) are shown in Fig. 1.

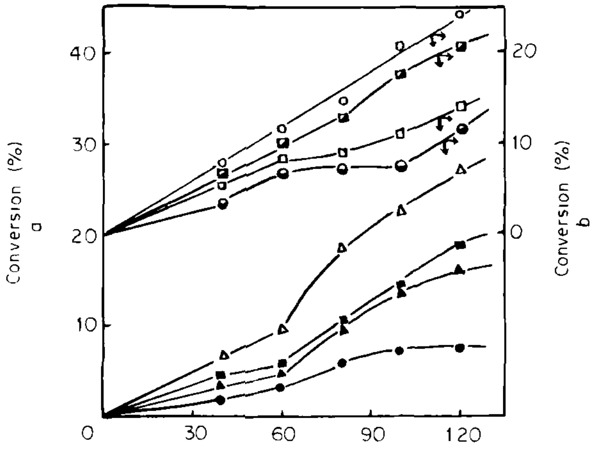

FIG. 1. Plots of conversion vs. time for showing (right ordinate) the effect of activator concentration at $[Mn^{3+}] = 1.75 \times 10^{-3}$ M, $[H^+] = 1.9$ M, $\mu = 1.96$ M, [AN] = 0.754 M, 25°C: (●) [CH] = 0.005 M, (▲) [CH] = 0.03 M, (■) [CH] = 0.06 M, and (△) [CH] = 0.12 M; and (left ordinate) the effect of addition of water-miscible organic solvents at $[Mn^{3+}] \approx 1.75 \times 10^{-3}$ M, $[H^+] = 1.9$ M, $\mu = 1.96$ M, [CH] = 0.09 M, [AN] = 0.754 M, 30°C: (○) control, (□) 5% CH_3OH, (□) 5% C_2H_5OH, and (○) 5% CH_3COCH_3.

TABLE 1. Polymerization of Acrylonitrile Initiated by Various Mn^{3+}-alcohol Redox Systems at 25 ± 0.1 C[a]

Alcohol	Induction period (min)	10^5 R_p (mole/liter-sec)
1,2-Propanediol	10	7.0236
Isobutyl alcohol	30	6.2054
Glycerol	20	3.4612
Cyclohexanol	18	2.9014
1-Propanol	15	2.1780
Cycloheptanol	12	1.4458
1-Butanol	42	1.3438
sec-Butyl alcohol	40	1.0964
Ethyl alcohol	35	0.7840
Cyclopentanol	12	0.1069
tert-Butyl alcohol	120	0.1012

[a] Recipe: [Alcohol] = 0.272 $\underline{M}$, $[Mn^{3+}]$ = 1.75 × 10^{-3} $\underline{M}$; $[H^+]$ = 1.9 $\underline{M}$, μ = 2 $\underline{M}$, [AN] = 0.754 $\underline{M}$.

Acrylonitrile was also polymerized under identical conditions with Mn^{3+} in the presence of other alcohols like 1-propanol, 1-butanol, 1,2-propanediol, ethyl alcohol, glycerol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, cyclopentanol, cyclohexanol, and cycloheptanol. There is an induction period involved in each case, and the point of appearance of turbidity in the reaction solution is taken as the starting point of polymerization. The results, recorded in Table 1, show that under identical conditions, the reactivity of the alcohols decreases in the order: 1,2-propanediol > isobutyl alcohol > glycerol > cyclohexanol > 1-propanol > cycloheptanol > 1-butanol > sec-butyl alcohol > ethanol > cyclopentanol > tert-butyl alcohol.

Rate of Manganic Ion Disappearance

The rates of disappearance of manganic ion $(-d[Mn^{3+}]/dt)$ were first-order in $[Mn^{3+}]$ (Fig. 2) and independent of monomer concentration [AN]. The plots of $(-d[Mn^{3+}]/dt)^{-1}$ versus $[CH]^{-1}$ were

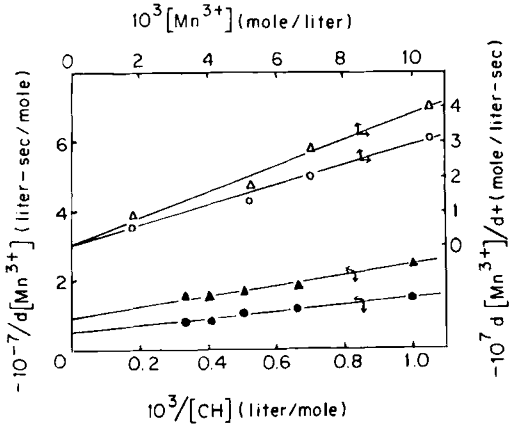

FIG. 2. Plots of (right ordinate) -d[Mn^{3+}]/dt vs. [Mn^{3+}] at μ = 1 M, [CH] = 0.06 M, [AN] = 0.754 M: (○) at 35°C and (△) at 40°C; and plots of (left ordinate) $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[CH]^{-1}$ at [Mn^{3+}] = 3.25×10^{-3} M, [H^+] = 1.94 M, μ = 2 M, [AN] = 0.754 M: (▲) at 30°C and (●) at 40°C.

linear, with the intercept on the rate axis showing Lineweaver-Burk kinetics [23] for complex formation (Fig. 2). Similar complex formation between Mn^{3+} and malonic acid has been shown by Waters and colleagues [5]. 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 with increase of monomer concentration (0.1507-0.9042 M). 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 an increase of the catalyst concentration up to a certain limit, after which a decreasing trend was noted. The rate of polymerization was found to increase linearly with increasing cyclohexanol concentration (0.5×10^{-3}-3×10^{-3} M). The plots of $1/R_p^2$ versus $[CH]^{-1}$ were linear with an intercept on the rate axis (Fig. 4).

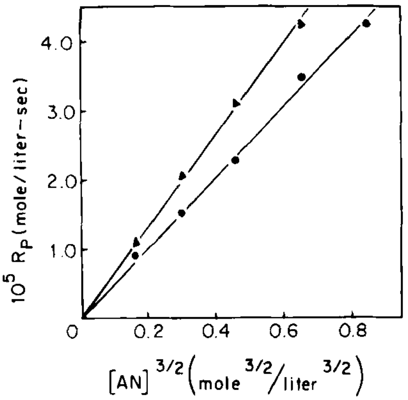

FIG. 3. Plots of R_p vs. $[AN]^{3/2}$ at $[Mn^{3+}] = 3.25 \times 10^{-3}$ $\underline{M}$, $[H^+] = 1.94$ M, $\mu = 2$ $\underline{M}$, [CH] = 0.09 $\underline{M}$: (●) at 35°C; (▲) at 40°C.

Effect of Water-Miscible Organic Solvents

Addition of 5% (v/v) water-miscible organic solvents such as C_2H_5OH, CH_3OH, CH_3COCH_3, and CH_3COOH to the reaction mixture decreases the initial rate as well as the maximum conversion (Fig. 1). 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. Moreover, these solvents increase the regulated rate of production of primary radicals 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. [24]. Palit and co-workers [25], have made a similar observation even for the homogeneous medium in which water is the additive. Also, the interchain hydrogen bonding interlocking the polymer chain is not rigid, and therefore a tendency for mutual termination of the polymer chain occurs.

Effect of Added Electrolytes

The addition of certain electrolytes, such as $CuSO_4$ or Na_2SO_4, 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, which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain;

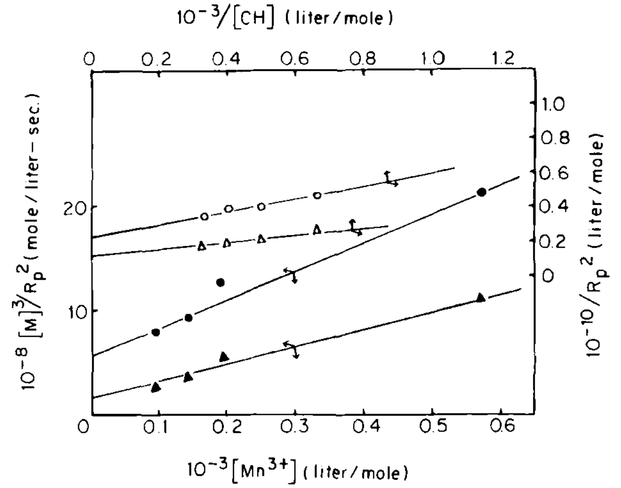

FIG. 4. Plots of $(1/R_p^2)[M]^3$ vs. $1/[Mn^{3+}]$ at $\mu = 1$ M, [CH] = 0.06 M, [AN] = 0.754 M: (●) at 35°C and (▲) at 40°C; and plots of $1/R_p^2$ vs. 1/[CH] at $[Mn^{3+}] = 3.25 \times 10^{-3}$ M, $[H^+] = 1.94$ M, $\mu = 2$M, [AN] = 0.754 M: (○) at 30°C and (△) at 35°C.

(2) the activity of the manganic ion is greatly reduced due to ion-pair coupling with the added electrolytes as suggested by Nayak et al. [20].

Effect of Surfactants

In recent years micellar catalysis has played an important role in the kinetics and mechanism of certain polymerization reactions [26, 27]. 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 the anionic surfactant, sodium lauryl sulfate to the reaction mixture below and above the critical micelle concentration (CMC) decreased 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 might lower the rate of primary radical generation. Alexander and co-workers [27] have assumed such ion-pair binding between cationics and $S_2O_8^{2-}$ ions only above the CMC, leading to the formation of an insoluble complex;

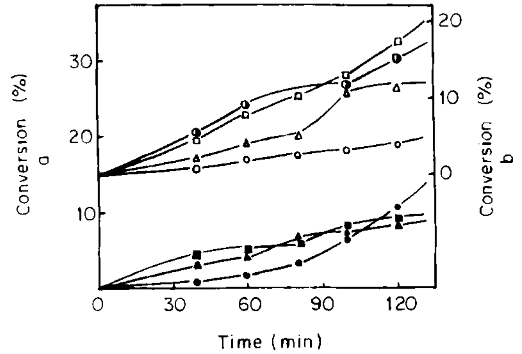

FIG. 5. Plots of conversion vs. time showing (right ordinate) effect of added electrolytes at $[Mn^{3+}] = 1.75 \times 10^{-3}$ M, $[H^+] = 1.9$ M, $\mu = 1.96$ M [CH] = 0.06 M, [AN] = 0.754 M, 30°C: (■) $CuSO_4$, 0.02 M, (▲) Na_2SO_4, 0.02 M, and (●) $AgNO_3$, 0.02 M; and (left ordinate) effect of catalyst at $\mu = 1$ M, [CH] = 0.06 M, [AN] = 0.754 M, 30°C: (○): $[Mn^{3+}] = 1.75 \times 10^{-3}$ M, (△) $[Mn^{3+}] = 5.25$ 10^{-3} M, (□) $[Mn^{3+}] = 7.0 \times 10^{-3}$ M and (◑) $[Mn^{3+}] = 15.0 \times 10^{-3}$ M.

this binding could be depressed by further addition of cationics and hence lead to a reduction in rate. The nonionic surfactant, Triton X-100, has no effect on the rate of polymerization.

Effect of Catalyst Concentration

The initial rate as well as the maximum conversion were found to increase with the increase in the concentration of the catalyst in the range 1.75×10^{-3}-15×10^{-3} M. Time-conversion plots at a definite temperature are shown in Fig. 5. At concentrations of the catalyst above 15×10^{-3} M, a decreasing trend in the rate was noticed. This might be due to fact that at higher concentration of the metal ion the oxidation rate becomes relatively fast compared to the rate of polymerization, as pointed out by Nayak et al. [14].

Reaction Mechanism and Rate Law

The aqueous polymerization of acrylonitrile initiated by trivalent manganese ion in the presence of cyclohexanol shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the insolubility of the polyacrylonitrile in aqueous phase.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme [Eqs. (1)-(6)] involving the initiation by organic free radical produced by the interaction of Mn^{3+} with cyclohexanol and termination by mutual combination of the polymer chain has been suggested.

$$Mn^{3+} + CH \overset{K}{\rightleftharpoons} \text{Complex} \tag{1}$$

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

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

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

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

$$\vdots$$

$$RM_n^{\cdot} + R\text{-}M_m^{\cdot} \xrightarrow{k_t} \text{Polymer} \tag{6}$$

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

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

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

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

Since the measured rates $-d[Mn^{3+}]/dt$ apply to the total $[Mn^{3+}]$ regardless of the species and since $[Mn^{3+}]_T = [Mn^{3+}] (1 + K[CH])$, we obtain

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

The polymerization rates (for $k_p\,[\mathrm{RM}^\cdot] \gg k_i\,[\mathrm{R}^\cdot]$) are given by Eq. (10):

$$\frac{-d[\mathrm{M}]}{dt} = \frac{k_p k_i^{1/2}\,(k_r K\,[\mathrm{Mn}^{3+}]\,[\mathrm{CH}]^{1/2}\,[\overline{\mathrm{M}}]^{3/2}}{k_t^{1/2}\,(k_0\,[\mathrm{Mn}^{3+}] + k_i\,[\mathrm{M}]^{1/2}} \tag{10}$$

If $k_0\,[\mathrm{Mn}^{3+}] \gg k_i\,[\mathrm{M}]$, Eq. (10) reduces to Eq. (11):

$$-d\,[\mathrm{M}]/dt = k_p k_i^{1/2}(k_r K[\bar{\mathrm{C}}\mathrm{H}])^{1/2}\,[\mathrm{M}]^{3/2}/\,k_0^{1/2}\,k_t^{1/2} \tag{11}$$

Now Eq. (10) can be rearranged to

$$\left(\frac{d[\mathrm{M}]}{dt}\right)^{-2} = \frac{k_t k_0}{k_p^{2}\,k_i k_r\,[\mathrm{CH}]\,[\mathrm{M}]^{3}} = \frac{kt}{k_p^{2}\,k_r K\,[\mathrm{Mn}^{3+}]\,[\mathrm{CH}]\,[\mathrm{M}]^{2}} + \frac{kt}{k_p^{2}\,k_r\,[\mathrm{Mn}^{3+}]\,[\mathrm{M}]^{2}} \tag{12}$$

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

TABLE 2. Values of Rate Parameters in the Polymerization of Acrylonitrile Initiated by the System Mn^{3+}-Cyclohexanol

Temp (°C)	$k_r \times 10^5$ (sec^{-1})	10^{-2} K (liter/mole)
30	1.73	5.30
40	3.07	6.0

Evaluation of K and k_r

The values of K and k_r were computed by plotting ($-d[Mn^{3+}]/dt$) versus $[CH]^{-1}$. From the intercepts and the ratio intercept/slope of these plots the rates of unimolecular decomposition of the complex (k_r) and its formation constant (K) can be calculated. The values are presented in Table 2.

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