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

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

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### ABSTRACT

The vinyl polymerization of acrylonitrile initiated by the redox system  $Mn^{3+}$ -glucose has been studied in aqueous sulfuric acid at 30-50°C. The rate of polymerization, the rate of  $Mn^{3+}$  disappearance, etc. were measured. The effect of certain water miscible organic solvents, inorganic salts, dyes, solvent composition, solid substances, and inhibitors on the rate of polymerization has been investigated. Based on the experimental results, a suitable reaction mechanism involving the formation of a complex between  $Mn^{3+}$  and the substrate molecule, whose

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decomposition yields the initiating free radical with the polymer chain being terminated by the mutual combination of growing chains, has been suggested.

## INTRODUCTION

Detailed kinetic investigations of vinyl polymerization initiated by metal ions in their higher valence states,  $\text{Co}^{3+}$ ,  $\text{V}^{5+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Cr}^{6+}$ , have provided valuable information regarding the mechanistic details of individual steps [1-8]. In a series of interesting communications, Waters et al. [9] have reported the mechanism of oxidation of a multitude of organic substrates involving trivalent manganese. Singh et al. [10] and Namsivayam et al. [11] have reported that manganic sulfate in an excess of sulfuric acid may form an effective redox system for the grafting of polymethyl methacrylate onto cellulose and polyvinyl alcohol (PVA). Recently Nayudamma and colleagues [12] have reported the  $\text{Mn}^{3+}$ -initiated graft copolymerization of vinyl monomers onto collagen. Nayak et al. have reported the graft copolymerization of acrylamide [13] onto nylon 6 fibers in the presence of  $\text{Mn}^{3+}$  ion and the aqueous polymerization of acrylonitrile and methyl methacrylate [14-18] using  $\text{Mn}^{3+}$  and a multitude of organic substrates. We have reported the vinyl polymerization of acrylonitrile [19, 20] using  $\text{Mn}^{3+}$ -mannitol and tartaric acid redox systems. We have an ambitious research program to carry out chemical initiation graft copolymerization of vinyl monomers onto wool, silk, cellulose, nylon 6, etc. by the use of  $\text{Mn}^{3+}$  ion. As a part of the research program this article presents the results of studies of vinyl polymerization of acrylonitrile initiated by the redox system  $\text{Mn}^{3+}$ -glucose. From the experimental observations a suitable reaction scheme has been suggested involving the initial complex formation between the glucose molecule and the metal ion whose decomposition 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. [21].  $\text{Mn}^{2+}$  sulfate was an EM-GR product. All other reagents, e.g., ceric ammonium sulfate, ferrous ammonium sulfate, O-phenanthroline, glucose, fructose, and galactose, were A.R. grade.  $\text{Mn}^{3+}$  stock solutions were prepared by electrolytic oxidation of the appropriate  $\text{Mn}^{2+}$  salt solution (0.4-0.6 M) in 4-6 M sulfuric acid at a platinum anode [22, 23]. Freshly prepared solutions which were immediately used were analyzed for  $\text{Mn}^{3+}$  content by cerimetry

for total manganese content by EDTA titration [24]. Water distilled three times over alkaline permanganate and deionized by passage through a column of Biodeminrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing through several columns of Fieser's [14] 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 rates of oxidant consumption were determined by cerimetry on reaction mixtures arrested by the addition of excess standard ferrous ammonium sulfate solution.

The molecular weight  $\bar{M}_w$  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

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

## RESULTS AND DISCUSSION

Acrylonitrile (AN) was polymerized in aqueous sulfuric acid solution at 35–50°C and in the presence of the  $Mn^{3+}$ -glucose redox system. A typical set of time conversion curves at 35°C and at various glucose concentrations (0.0025 to 0.02 M) at constant  $[Mn^{3+}]$  concentration ( $7 \times 10^{-3}$  M) are shown in Fig. 1. Acrylonitrile was also polymerized under identical conditions with  $Mn^{3+}$  in the presence of other monosaccharides, e.g., fructose and galactose. The results are recorded in Table 1 which shows, under identical conditions, that the reactivity of the monosaccharides are fructose > glucose > galactose.

### 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 plots of  $(-d[Mn^{3+}]/dt)^{-1}$  versus  $[Glu]^{-1}$  (where Glu stands for glucose) were linear with the intercept on the rate axis (Fig. 2) showing Lineweaver-Burke kinetics [26] for complex formation. A similar complex formation between  $Mn^{3+}$  and malonic acid has been shown by Waters et al. [9]. The rate of reaction is catalyzed both by sulfuric and perchloric acid.

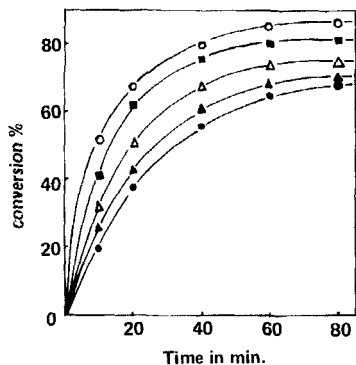


FIGURE 1.

TABLE 1. Polymerization of Acrylonitrile (AN) Initiated by Various  $Mn^{3+}$ -Monosaccharides Redox Systems at  $35 \pm 0.1^\circ C$ 

Monosaccharides	Concentration (M)	$R_p \times 10^4$ ( $min^{-1}$ )
Glucose	$1 \times 10^{-2}$	10.9508
Fructose	$1 \times 10^{-2}$	11.6065
Galactose	$1 \times 10^{-2}$	9.9341

<sup>a</sup> Recipe:  $[Mn^{3+}] = 7 \times 10^{-3} M$ ,  $[H^+] = 0.7 M$ ,  $\mu = 1.8 M$ ,  $[AN] = 0.754 M$ .

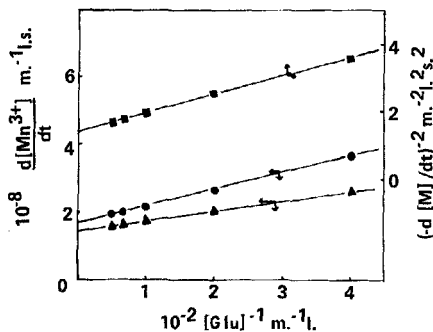


FIGURE 2.

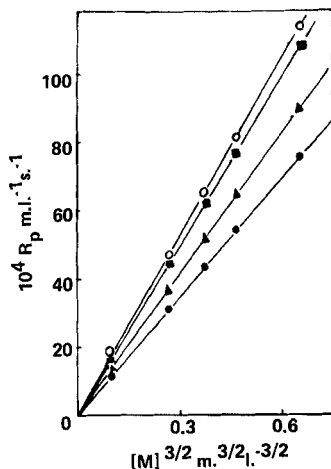


FIGURE 3.

### Rate of Polymerization

The rate of polymerization ( $R_p$ ) was found to increase linearly with an increase of monomer concentration (0.1508-0.754 M). 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 three halves.  $R_p$  also increased linearly with an 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 glucose concentration. Plots of  $1/R_p^2$  versus  $[Glu]^{-1}$  were linear with the intercept on the rate axis (Fig. 4).

### Effect of Water-Miscible Organic Solvents

Addition of 10% (v/v) water-miscible organic solvents such as acetic acid, acetone, ethanol and chloroform to the reaction mixture depresses the initial rate as well as maximum conversion (Fig. 5). This is probably caused by a decrease in the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain or an increase in the regulated rate of production of primary radicals caused by the solvents, which under existing experimental conditions renders the termination rate relatively fast compared to the rate of growth of polymer chains, as pointed out by Kern et al. [27]. Palit et al. [28] have noticed similar

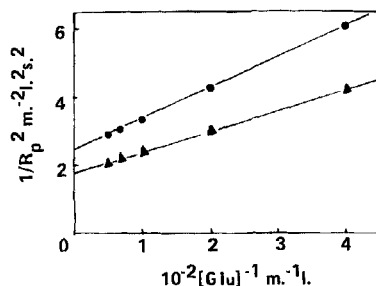


FIGURE 4.

observations even for a 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. The addition of a higher percentage of the solvent causes a decrease in the initial rate as well in the maximum conversion.

#### Effect of Added Electrolytes

The addition of certain neutral electrolytes such as  $\text{CuSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$ , and  $\text{ZnSO}_4$  to the reaction mixture reduces both the initial rate of polymerization and the maximum conversion to a considerable extent. This might be due to (1) the ionic dissociation of the added electrolytes 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. The higher concentration of  $\text{NaCl}$  decreases the initial rate as well as the maximum conversion (Fig. 5b).

#### Effect of Complexing Agents

On addition of 0.02 M complexing agents like  $\text{NaF}$ , Succinic acid, lutidine, and  $\alpha$ -picoline, the initial rate and maximum conversion were depressed considerably, 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  $\text{H}^+$  ion by the amines and that the activity of the  $\text{Mn}^{3+}$  ion is greatly reduced due to the complex formation with amines behaving as ligands.

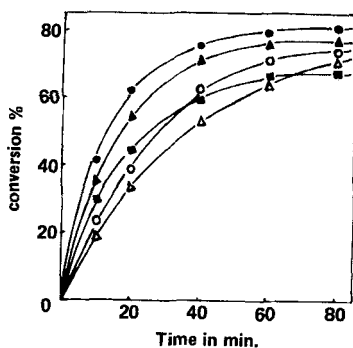


FIGURE 5a.

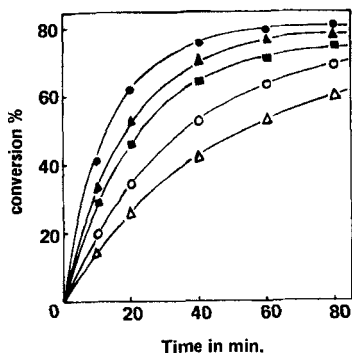


FIGURE 5b.

### Effect of Inhibitor Concentration

Addition of hydroquinone ( $0.5 \times 10^{-3} \text{ M}$  to  $2.5 \times 10^{-3} \text{ M}$ ) to the reaction mixture causes a marked decrease (Fig. 6) in the initial rate as well as in the maximum conversion. The effect can be explained in at least two ways: (1) the inhibitor may combine with the metal ion and prevent it from operating, and (2) the chain is broken by the inhibitor. This process would be expected to be first order in the chain carrier and first order in the inhibitor. The exact mode of action of inhibitors is still uncertain as pointed out by Hamilton et al. [29] and Bollard et al. [30]. Among the probable mechanisms, one is the combination of the chain carrier with the inhibitor to form



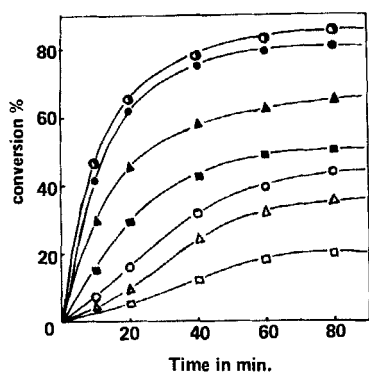


FIGURE 6.

an unreactive free radical and the metal ion, or hydrogen abstraction from the inhibitor to produce the same effect.

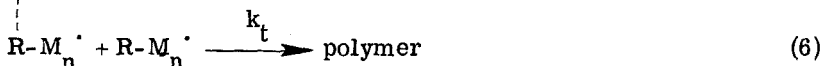
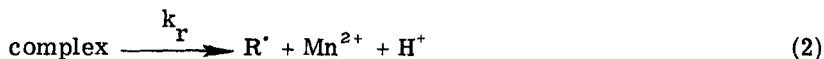
#### Effect of Solid Substances

In the presence of silica the initial rate as well as the maximum conversion were increased (Fig. 5b). Similar observation was noticed by Moustafa et al. [31] 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  $Mn^{3+}$  ions in the presence of glucose 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 initiation by the organic free radical produced by the interaction of  $Mn^{3+}$  with glucose and termination by mutual combination of the polymer chain has been suggested:



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

$$-d[\text{Mn}^{3+}]/dt = k_r K [\text{Mn}^{3+}] [\text{Glu}] + k_0 k_r K [\text{Mn}^{3+}]^2 [\text{Glu}] / (k_0 [\text{Mn}^{3+}] + k_i [\text{M}]) \quad (7)$$

The second term in Eq. (7) is due to Reaction (3).

If  $k_0 [\text{Mn}^{3+}] \gg k_i [\text{M}]$ , this term reduces to

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

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

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

we obtain

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

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

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

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

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

Equation (10) can be rearranged to

$$\begin{aligned} (-d[M]/dt)^{-2} &= k_t k_0 / K k_p^2 k_i k_r [Glu][M]^3 + k_t / k_p^2 k_r K [Mn^{3+}]_T [Glu][M]^2 \\ &+ k_t / k_p^2 k_r [Mn^{3+}]_T [M]^2 \end{aligned} \quad (12)$$

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

From the intercepts and the intercept-slope ratio of these plots, the rate of unimolecular decomposition of the complex ( $k_t$ ) and the formation constant ( $K$ ) were computed. Values of  $k_r$  were  $3.86 \times 10^{-3}$  and  $6.08 \times 10^{-3} \text{ s}^{-1}$  at 35 and 40°C and values of  $K$  were 3.9 and 13.2 L/mol at 35 and 40°C, respectively.

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