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P. L. Nayak^a; R. K. Samal^a; N. Baral^a

^a Department of Chemistry, Ravenshaw College, Cuttack, India

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Aqueous Polymerization of Methyl Methacrylate Initiated by the Mn(III)-Fructose Redox System

P. L. NAYAK, R. K. SAMAL, and N. BARAL

Department of Chemistry
Ravenshaw College
Cuttack 753003, India

A B S T R A C T

The kinetics of vinyl polymerization of methyl methacrylate initiated by the redox system Mn^{3+} -fructose were investigated in aqueous sulfuric acid in the temperature range of 20-25°C, and the rates of polymerization and disappearance of Mn^{3+} were measured. The effect of certain water-miscible organic solvents and certain cationic and anionic surfactants on the rate of polymerization has been investigated. A mechanism involving the formation of a complex between Mn^{3+} and fructose whose decomposition yields the initiating free radical with the polymerization being terminated by the metal ion has been suggested.

Waters and co-workers [1] have reported the kinetics and mechanism of oxidation of a multitude of organic substrates involving trivalent manganese. Singh et al. [2] and Namasivayam et al. [3] have reported that manganic sulfate in excess sulfuric acid may form an effective redox system for grafting of poly(methyl methacrylate) on cellulose and poly(vinyl alcohol). Very recently, Nayudamma

et al. [4] have reported manganese (III)-initiated graft copolymerization of vinyl monomers onto collagen. Iwakura and Imai [5, 6] have reported the graft copolymerization onto ovalbumin using ceric ion method. It was indicated from the studies on the grafting site, that the carbohydrate residue is a possible grafting site on ovalbumin. We have reported the aqueous polymerization of acrylonitrile [7-11], methyl acrylate, and methyl methacrylate [12] using quinquevalent vanadium and a multitude of organic substrates. As a part of the research program, this communication presents results of the studies of vinyl polymerization of methyl methacrylate (MMA) initiated by the redox system Mn(III)-fructose. Various kinetic parameters were evaluated. From the experimental observations, a suitable reaction scheme is suggested.

EXPERIMENTAL

Methyl methacrylate (MMA) was purified according to our previous method [11]. Fructose used was of Analar grade. Mn(II) sulfate was an EM-GR product. All other reagents were AR grade. Manganese (III) stock solutions were prepared by electrolytic oxidation of the appropriate Mn^{2+} salt solution (0.4-0.6 M) in 4-6 M sulfuric acid at a platinum anode [11, 12]. Freshly prepared solutions which were immediately used were analyzed for Mn^{3+} content by cerimetry and for the 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 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 polymer precipitating continuously. Rates of polymerization were obtained gravimetrically, while rates of oxidant consumption were obtained by cerimetry on reaction mixtures arrested by addition of excess standard ferrous sulfate solution.

RESULTS AND DISCUSSION

A set of time-conversion plots have been drawn for different concentrations of the activator (FR) and the monomer (MMA) at a constant temperature (Fig. 1). The rates of disappearance of manganic ion ($-d[Mn^{3+}]/dt$) were of first order in $[Mn^{3+}]$ and independent of monomer concentration $[M]$. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[FR]^{-1}$ were linear with intercept on the rate axis, showing Lineweaver-Burk

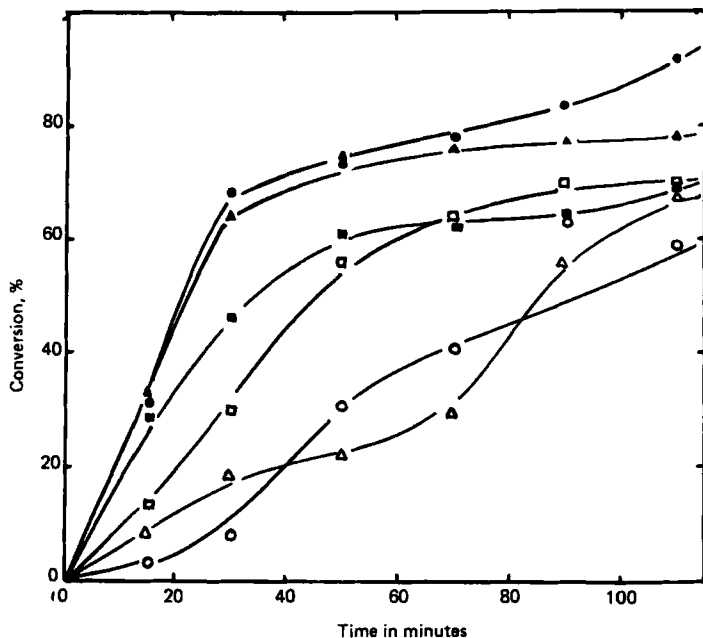


FIG. 1. Variation of percentage conversion with time (\circ , Δ , \square) at various fructose concentrations and (\bullet , \blacktriangle , \blacksquare) various monomer concentrations in polymerization of methyl methacrylate initiated by fructose-Mn(III) redox system: (\circ) $[\text{Fru}] = 3 \times 10^{-3} \text{ M}$, $[\text{MMA}] = 0.09388 \text{ M}$; (Δ) $[\text{Fru}] = 6 \times 10^{-3} \text{ M}$, $[\text{MMA}] = 0.09388 \text{ M}$; (\square) $[\text{Fru}] = 9 \times 10^{-3} \text{ M}$, $[\text{MMA}] = 0.09388 \text{ M}$; (\bullet) $[\text{MMA}] = 0.04694 \text{ M}$; (\blacktriangle) $[\text{MMA}] = 0.14082 \text{ M}$; (\blacksquare) $[\text{MMA}] = 0.18766 \text{ M}$. $[\text{Mn(III)}] = 1.75 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 1.83 \text{ M}$; $\mu = 1.957 \text{ M}$; 20°C .

kinetics [13] for complex formation (Fig. 2). Similar complex formation by malonic acid and manganese(III) has been illustrated by Waters and colleagues [1]. The rate of the reaction is catalyzed both by sulfuric acid and perchloric acids.

Rate of Polymerization

The rate of polymerization R_p increased with increasing monomer concentrations (0.04694–0.5632 M). The plots of R_p versus $[\text{MMA}]$ were linear and passed through the origin (Fig. 3); therefore, the order with respect to $[\text{MMA}]$ was unity. The rate of polymerization

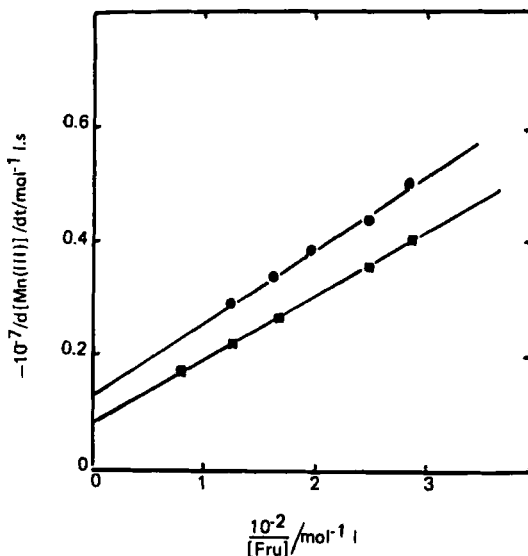


FIG. 2. Variation of $1/(-d[\text{Mn(III)}]/dt)$ vs. $1/[\text{FR}]$ at different temperatures for polymerization of methyl methacrylate initiated by fructose-Mn(III) redox system: (●) at 20°C; (■) at 25°C. $[\text{Mn(III)}] = 1.75 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 1.83 \text{ M}$; $\mu = 1.957 \text{ M}$; $[\text{MMA}] = 0.09388 \text{ M}$.

is independent of $[\text{Mn(III)}]$. The rate is increased with increasing fructose concentration. Linear plots of $\log R_p$ versus $\log [\text{FR}]$ with unit slopes as well as R_p versus $[\text{FR}]$ plots with zero intercepts (Fig. 4) indicated that the order with respect to $[\text{FR}]$ was unity.

Effect of Water-Miscible Organic Solvents

Water-miscible organic solvents are found to depress considerably the rate of polymerization as well as the maximum conversion (Fig. 5). Solvents of the type of ethanol, methanol, etc. decrease the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chains. These solvents increase 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. Palit and co-workers [14] have reported a similar observation even for a homogeneous medium in which water is the additive.

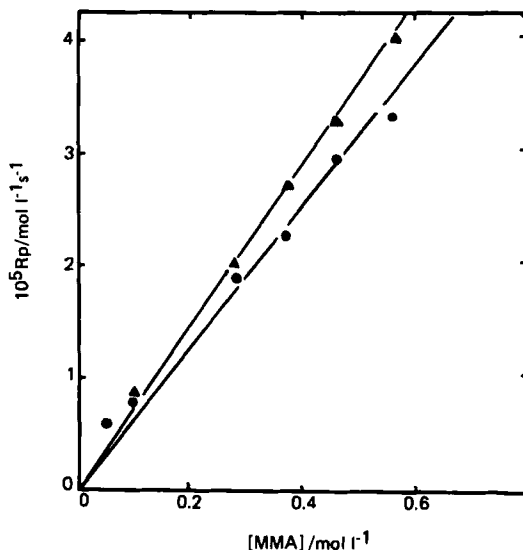


FIG. 3. Variation of rate of polymerization R_p with monomer concentration at different temperatures for polymerization of MMA initiated by fructose-Mn(III) redox system: (●) at 20°C; (▲) at 25°C. $[Mn(III)] = 1.75 \times 10^{-3} M$; $[H^+] = 1.83 M$; $\mu = 1.957 M$; $[Fru] = 0.004 M$.

Effect of Surfactants

The rate of polymerization has been investigated in the presence of micelles of certain cationic, anionic, and nonionic surfactants. Cationic micelles of cetyltrimethylammonium bromide (CTABr) retard the rate, and anionic micelles of sodium lauryl sulfate (NaLS) accelerate the rate, but a nonionic surfactant (Triton-100) has no effect. The catalysis of the rate of polymerization by NaLS can be explained on the assumption that the organic substrate, when incorporated by the anionic micelles of NaLS, is in an electrostatically favorable environment [15-17] for attack by the tripositive manganese ion, and hence the formation of free radical occurs more easily, as a result of which the polymerization rate increases. The retardation of the reaction in the micelles of cationic nature may be explained in terms of incorporation of the substrate into the cationic micelle, where it is shielded electrostatically from attack by the tripositive manganese ions.

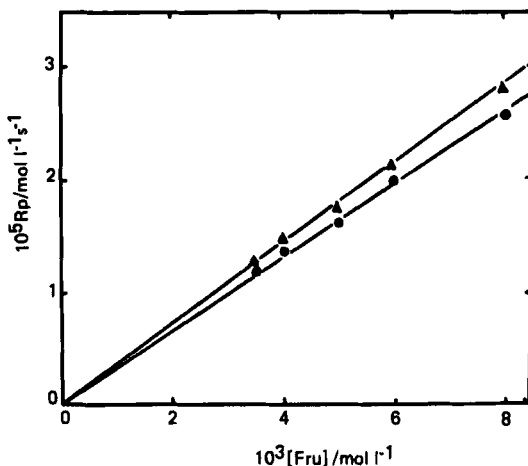
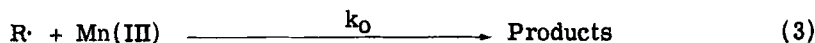
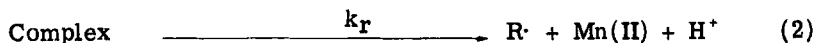
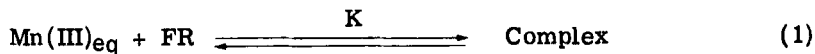


FIG. 4. Variation of rate of polymerization with fructose concentration at different temperatures for polymerization of methyl methacrylate initiated by fructose-Mn(III) redox system: (●) at 20°C; (▲) at 25°C. $[\text{Mn(III)}] = 1.75 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 1.83 \text{ M}$; $\mu = 1.957 \text{ M}$; $[\text{MMA}] = 0.09388 \text{ M}$.

Reaction Mechanism and Rate Law

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

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme is suggested involving initiation by organic free radical produced by the interaction of Mn^{3+} with fructose and termination by Mn^{3+} ion. Termination of vinyl polymerization by metal ions is now well recognized [7-12].



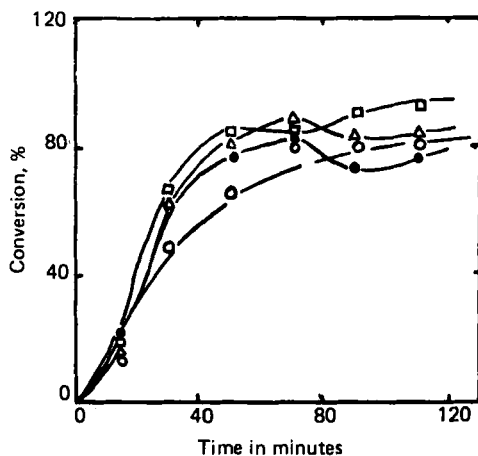
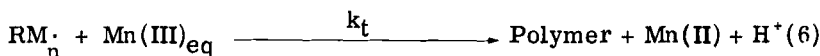
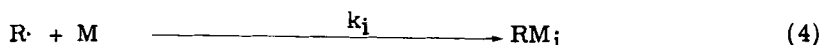


FIG. 5. Variation of percentage conversion with time in the presence of 5% water-miscible organic solvents in polymerization of methyl methacrylate initiated by fructose-Mn(III) redox system: (○) control; (△) 5% ethanol; (□) 5% acetic acid; (●) 5% acetone. $[Mn(III)] = 1.75 \times 10^{-3} M$; $[H^+] = 1.83 M$; $\mu = 1.957 M$; $[Fru] = 9.0 \times 10^{-3} M$.



Making the usual assumptions regarding the radical reactivity being independent of radical size, we can apply the steady-state approximation and arrive at the expressions (7)-(9).

$$d[R\cdot]/dt = k_r[Complex] - k_i[R\cdot][M] - k_o[R\cdot][Mn(III)]_{eq} = 0 \quad (7)$$

$$[R\cdot] = \frac{k_r[Complex]}{\{k_i[M] + k_o[Mn(III)]_{eq}\}} \quad (8)$$

$$= \frac{k_r K [Mn(III)]_{eq} [FR]}{\{k_i[M] + k_o[Mn(III)]_{eq}\}} \quad (9)$$

The steady-state expression for $RM_{\dot{n}}$ will be

$$[RM_{\dot{n}}] = \frac{k_i k_r K [FR] [M]}{\{k_i [M] + k_o [Mn(III)]\} k_t} \quad (10)$$

If $k_p [RM_{\dot{n}}] [M] \gg k_i [R\cdot] [M]$, rates of polymerization would be given by

$$\frac{-d[M]}{dt} = \frac{K k_p k_i k_r [M]^2 [FR]}{k_t (k_i [M] + k_o [Mn(III)])_{eq}} \quad (11)$$

Equation (11) requires that R_p is second-order with respect to monomer while decreasing with increasing $[Mn(III)]$. If, on the other hand, reaction step (3) were unimportant with primary radical being effectively scavenged by monomer ($k_i [M] \gg k_o [Mn(III)]$), we would get

$$[RM_{\dot{n}}] = k_r K [FR] / k_t \quad (12)$$

Hence

$$R_p = k_p k_r K [FR] [M] / k_t \quad (13)$$

Further, the rate of oxidant consumption would be given by Eq. (14):

$$-d[Mn(III)]/dt = k_r K [Mn(III)]_{eq} [FR] + k_t [RM_{\dot{n}}] [Mn(III)]_{eq} \quad (14)$$

Substituting for $[RM_{\dot{n}}]$ from Eq. (12) yields

$$-d[Mn(III)]/dt = 2 k_r K [Mn(III)] [FR]$$

Since

$$[Mn(III)]_{total} = [Mn(III)]_{eq} (1 + K [FR])$$

$$\frac{-d[Mn(III)]}{dt} = \frac{2 k_r K [Mn(III)]_T [FR]}{(1 + K [FR])} \quad (16)$$

Equation (16) can be rearranged to Eq. (17):

$$(-d[\text{Mn(III)}]/dt)^{-1} = \frac{1}{2k_r K [\text{Mn(III)}]_T [\text{FR}]} + \frac{1}{2k_r [\text{Mn(III)}]_T} \quad (17)$$

According to Eq. (17), the plot of left-hand side of Eq. (17) versus reciprocal of $[\text{FR}]$ (Fig. 2) is linear with an intercept on the ordinate. From the slope and the intercept, the values of k_r and K have been computed (Table 1).

TABLE 1. Mean Values of the Rate Parameters in the Polymerization of Methyl Methacrylate (MMA) Initiated by the System Fructose-Mn(III)

Monomer	K (liter/mole)		$k_r \times 10^4$ (sec ⁻¹)		k_p/k_t	
	20°C	25°C	20°C	25°C	20°C	25°C
MMA	80	100.2	2.20	3.57	0.93	0.69

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