

Polymerization of Methyl Methacrylate Initiated by the Redox System Mn^{3+} /Thioglycollic Acid

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Synopsis

The kinetics of aqueous polymerization of methyl methacrylate initiated by the redox system Mn^{3+} -thioglycollic acid was studied in sulfuric acid in the temperature range of 35–50°C, and the rates of polymerization R_p and Mn^{3+} disappearance, etc., were measured. The effect of certain water-miscible organic solvents, neutral electrolytes, and complexing agents on the rates of polymerization has been investigated. A mechanism involving the formation of a complex between Mn^{3+} and thioglycollic acid whose decomposition yields the initiating free radical with the polymerization being terminated by the metal ion has been suggested.

INTRODUCTION

Sulfur compounds such as thiourea,^{1–12} thioacetamide,¹³ 2-mercaptoethanol,¹⁴ 2-mercaptoethylamine,¹⁵ and thioglycollic acid,^{16,17} coupled with suitable catalysts, have been reported to be useful redox pairs toward vinyl polymerization in aqueous medium. The generation of complex thio free radicals by the above redox systems have been observed to initiate vinyl polymerization quite smoothly and effectively. Thioglycollic acid possessing both the thiol and carboxylic groups appear to make it an efficient and tempting activator when coupled with a suitable catalyst.

In a series of communications Nayak et al.^{1,13,18–21} have reported the polymerization of a number of vinyl monomers using Mn^{3+} and a multitude of organic substrates as the redox components. Singh et al.²² and Namasivayam et al.²³ 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.²⁴ have reported the Mn^{3+} -initiated graft copolymerization of vinyl monomers onto collagen. 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 methyl methacrylate (MMA) initiated by the Mn^{3+} -thioglycollic acid redox system. From the experimental observations, a suitable reaction scheme has been suggested, and various kinetic parameters have been evaluated.

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EXPERIMENTAL

Methyl methacrylate was purified according to our previous method. Thioglycollic acid used was BDH Anala R grade. Mn^{2+} sulfate was an E. Merck G.R. product. All other reagents like ferrous ammonium sulfate, *o*-phenanthroline, etc., were commercial products—either BDH, Anala R, or E. Merck G.R. Mn^{3+} stock solutions were prepared by electrolytic oxidation of appropriate Mn^{2+} salt solutions (0.4–0.6M) in 3.5–6N sulfuric acid at a platinum anode^{25,26} and were analyzed for Mn^{3+} content by EDTA titration.²⁷ Water distilled thrice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. The nitrogen (Indian Oxygen Co., Calcutta, India) used was purified by passage through several columns of Fieser's solution, a column of saturated lead acetate, and finally a wash bottle containing distilled water. The polymerization reactions were heterogeneous, with the polymer precipitating continuously. Rates of polymerization (initial rates) were obtained gravimetrically, and the rate of oxidant consumption was obtained by cerimetry on reaction mixtures arrested by addition of excess ferrous ammonium sulfate solution. The ionic strength (μ) was maintained by adding requisite amount of $NaHSO_4$. The appearance of turbidity is taken as the point of initiation.

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid solution at 35–50°C in the presence of the redox system Mn^{3+} –thioglycollic acid. A typical set of time conversion curves at 40°C and at various thioglycollic acid concentrations (0.00025–0.0025M) is shown in Figure 1. Methyl methacrylate has also been polymerized under identical conditions with Mn^{3+} in presence of glycollic acid. The results are recorded in Table I, which shows that under identical conditions, the reactivity, of the acids are thioglycollic acid > glycollic acid.

The generation of the initiating free radical in this system takes place by the abstraction of the loosely bonded hydrogen atom attached to the sulfur atom of the thiol group through complex formation with Mn^{3+} and subsequent decomposition. The initiation of polymerization takes place by the interaction of the initiating free radical with the vinyl monomer, leading to the formation

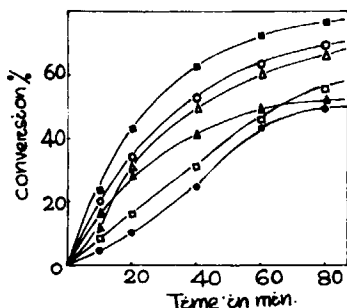


Fig. 1. Plots of conversion % vs. time at different activator concentrations. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.7M$, $[MMA] = 0.09388M$, $\mu = 1.9M$, temperature = 40°C. (●) $[TGA] = 0.25 \times 10^{-3}M$, (▲) $[TGA] = 0.5 \times 10^{-3}M$, (■) $[TGA] = 1 \times 10^{-3}M$, (○) $[TGA] = 1.5 \times 10^{-3}M$, (△) $[TGA] = 2 \times 10^{-3}M$, (□) $[TGA] = 2.5 \times 10^{-3}M$.

TABLE I
Polymerization of Methyl Methacrylate Initiated by Mn^{3+} -Acid Systems at 40°C^a

[Substrate] = 1×10^{-3} ml ⁻¹	$R_p \times 10^4$ ml ⁻¹ sec ⁻¹
Thioglycollic acid	18.1472
Glycollic acid	6.520

^a Recipe: $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.85M$, $\mu = 1.9M$, $[MMA] = 0.09388M$, temperature = 40°C.

of more stable simple macroradical. The propagation follows the successive addition of the macroradicals with vinyl monomeric units continuously till the dead polymers are formed by termination.

Rate of Manganic Ion Disappearance

The rates of manganic ion disappearance ($-d[Mn^{3+}]/dt$) were first order in $[Mn^{3+}]$ and independent of monomer $[MMA]$ concentration. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[TGA]^{-1}$ were linear with intercept on the rate axis, which shows Lineweaver-Burk kinetics²⁸ for complex formation (Fig. 2). Similar complex formation has been illustrated by Waters and co-workers²⁹ in the case of the Mn^{3+} oxidation of malonic acid.

Rate of Polymerization

The rate of polymerization was found to increase linearly with increasing monomer concentration (0.04644–0.1877M). The plots of R_p vs. $[MMA]$ were linear, passing through the origin (Fig. 3), showing that the order with respect to $[MMA]$ was unity. The rate of polymerization was found to increase with increasing the concentration of thioglycollic acid (Fig. 4), but at higher concentrations deviation from the normal has been observed. Similar observation has been noted by us in the case of the polymerization of AN by the $V(V)$ /ethane-1,2-diol system³⁰ and MMA by the Mn^{3+} /glycerol redox system.²⁰ This might be due to chain transfer and increase in polarity of the medium.

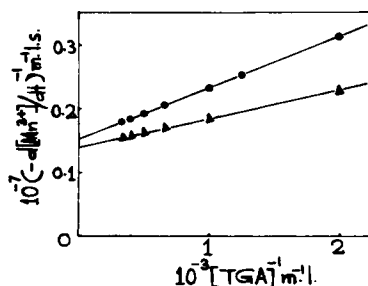


Fig. 2. Variation of R_p with activator concentration. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[TGA]^{-1}$ at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.85M$, $\mu = 2.7M$, $[MMA] = 0.09388M$. (●) Temperature = 35°C, (▲) temperature = 40°C.

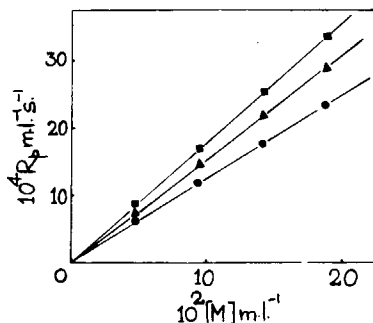


Fig. 3. Plots of R_p vs. $[MMA]$ at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.85M$, $\mu = 2.7M$, $[TGA] = 1 \times 10^{-3}M$. (●) Temperature = $35^\circ C$, (▲) temperature = $40^\circ C$, (■) temperature = $45^\circ C$.

Effect of Water-Miscible Organic Solvents

Addition of 10% (v/v) water-miscible organic solvents such as acetic acid, acetone, chloroform, and DMF etc. is found to depress considerably the rate of polymerization as well as the maximum conversion (Fig. 5). The retardation of the rate by the solvents might be due to the following reasons:

(1) Solvent molecules might decrease the area of shielding of the strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain.

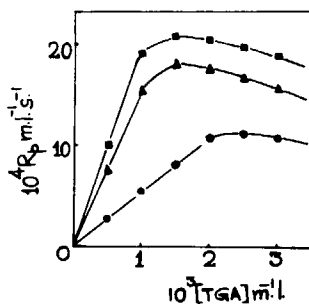


Fig. 4. Plot of R_p vs. $[TGA]$ at different temperatures. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.85M$, $\mu = 2.7M$, $[MMA] = 0.09388M$. (●) Temperature = $35^\circ C$, (▲) temperature = $40^\circ C$, (■) temperature = $45^\circ C$.

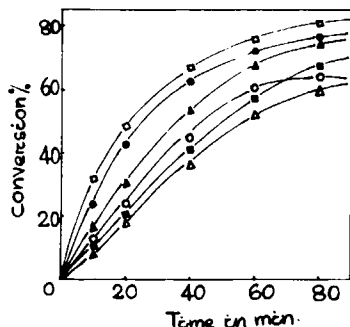


Fig. 5. Plots of conversion % vs. time in presence of 10% water miscible organic solvents and solid substances. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.7M$, $[TGA] = 1 \times 10^{-3}M$, $\mu = 1.9M$, $[MMA] = 0.09388M$. (●) Control, (▲) [acetic acid] = 10% (v/v), (■) [acetone] = 10% (v/v), (○) [DMF] = 10% (v/v), (△) [chloroform] = 10% (v/v), (□) silica = 1 g.

(2) These solvents might increase the regulated rate of production of primary radicals, which, under existing experimental conditions, render the termination rate relatively fast as compared with the rate of growth of the polymer chain. This is in agreement with the views of Kern et al.³¹

(3) Further, the interchain hydrogen bonding interlocking the polymer chain is not rigid (strong), thereby the tendency of mutual termination of the polymer chain increases.

Effect of Complexing Agents

Upon addition of 0.02M complexing agents such as NaF, succinic acid, pyridine, and lutidine, the initial rate and the maximum conversion were depressed considerably (Fig. 6), 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 consumption of the H⁺ ion by the amines and that activity of the Mn³⁺ ion is reduced greatly because of complex formation with amines behaving as ligands.

Effect of Catalyst Concentration

The initial rate and maximum conversion were found to increase with increase in concentration of the catalyst up to $7 \times 10^{-3}M$ (Fig. 7). At concentrations of the catalyst above $7 \times 10^{-3}M$, a decreasing trend in the rate was noted. This might be due to the fact that at a 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.³²

Effect of Solid Substances

Addition of silica to the reaction mixture increases the initial rate as well as the maximum conversion (Fig. 5). Similar observation was noted by Mustafa et al.³³ in the polymerization of methyl methacrylate in the presence of graphite. The behavior of silica in the polymerization of MMA is complex and the catalytic effect may be attributed to the fact that it decreases the apparent activation energy for the polymerization of methyl methacrylate and increases the active centers present at certain spots.

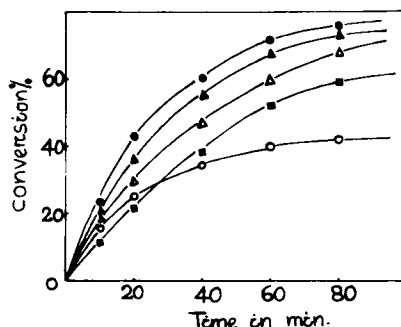


Fig. 6. Plots of conversion % vs. time in presence of complexing agents. $[Mn^{3+}] = 7 \times 10^{-3}M$, $[H^+] = 0.85M$, $[TGA] = 1 \times 10^{-3}M$, $\mu = 1.9M$, $[MMA] = 0.09388M$, temperature = 40°C. (●) Control, (▲) $[NaF] = 0.02M$, (■) $[succinic\ acid] = 0.02M$, (○) $[pyridine] = 0.02M$, (△) $[lutidine] = 0.02M$.

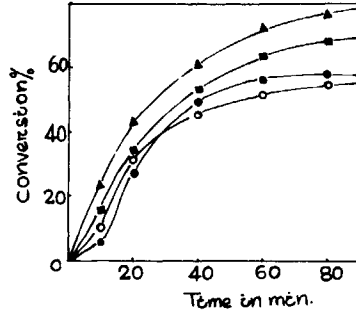
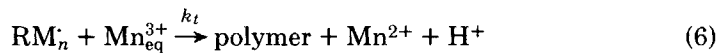
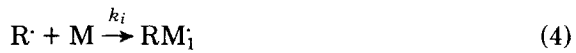
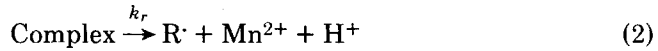
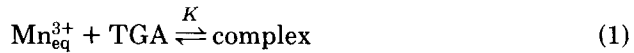


Fig. 7. Plots of conversion % time at different catalyst concentrations. $[H^+] = 0.85M$, $[TGA] = 1 \times 10^{-3}M$, $[MMA] = 0.09388M$, $\mu = 1.9M$, temperature = $40^\circ C$. (●) $[Mn^{3+}] = 3.5 \times 10^{-3}M$, (▲) $[Mn^{3+}] = 7 \times 10^{-3}M$, (■) $[Mn^{3+}] = 10.05 \times 10^{-3}M$, (○) $[Mn^{3+}] = 10.4 \times 10^{-3}M$.

Reaction Mechanism and Rate Law

Heterogeneity is a characteristic feature of the polymerization of methyl methacrylate in an aqueous medium. The reaction mixture though homogeneous before initiation of polymerization becomes heterogeneous as soon as the polymerization starts, owing to the insolubility of the polymer in the aqueous phase.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme has been suggested involving initiation by organic free radical produced by the interaction of Mn^{3+} with thioglycollic acid (TGA) and termination by Mn^{3+} ion. The termination by metal ions has been suggested in our previous communication²⁰:



Making the usual steady-state approximation, we can arrive at the following expressions:

$$\frac{d[R\cdot]}{dt} = k_r [\text{complex}] - k_i [R\cdot] [M] - k_0 [R\cdot] [Mn^{3+}]_{eq} = 0 \quad (7)$$

$$[R\cdot] = k_r [\text{complex}] / (k_i [M] + k_0 [Mn^{3+}]_{eq}) \quad (8)$$

$$= k_r K [Mn^{3+}]_{eq} [TGA] / (k_i [M] + k_0 [Mn^{3+}]_{eq}) \quad (9)$$

The steady-state expression for RM_n will be

$$[RM_n] = k_i k_r K [TGA] [M] / (k_i [M] + k_0 [Mn^{3+}]_{eq}) k_t \quad (10)$$

If $k_p[\text{RM}_n][\text{M}] \gg k_i[\text{R}^\cdot][\text{M}]$, rates of polymerization would be given by

$$\frac{-d[\text{M}]}{dt} = k_p k_i k_r K [\text{M}]^2 [\text{TGA}] / k_t (k_i [\text{M}] + k_0 [\text{Mn}^{3+}]_{\text{eq}}) \quad (11)$$

Equation (11) requires that R_p will be second order with respect to monomer, which decreases with increasing $[\text{Mn}^{3+}]$. If, on the other hand, reaction step (3) were unimportant, with the primary radical being effectively scavenged by the monomer ($k_i [\text{M}] \gg k_0 [\text{Mn}^{3+}]_{\text{eq}}$), we could get

$$[\text{RM}_n] = k_r K [\text{TGA}] / k_t \quad (12)$$

Hence

$$R_p = k_p k_r K [\text{TGA}] [\text{M}] / k_t \quad (13)$$

Further, the rates of oxidant consumption would be given by

$$\frac{-d[\text{Mn}^{3+}]}{dt} = k_r K [\text{Mn}^{3+}]_{\text{eq}} [\text{TGA}] + k_t [\text{RM}_n] [\text{Mn}^{3+}]_{\text{eq}} \quad (14)$$

Substitution of the above values of RM_n from eq. (12), gives

$$\frac{-d[\text{Mn}^{3+}]}{dt} = 2k_r K [\text{Mn}^{3+}]_{\text{eq}} [\text{TGA}] \quad (15)$$

Since $[\text{Mn}^{3+}]_{\text{total}} = [\text{Mn}^{3+}]_{\text{eq}} (1 + K [\text{TGA}])$,

$$\frac{-d[\text{Mn}^{3+}]}{dt} = 2k_r K [\text{Mn}^{3+}]_T [\text{TGA}] / (1 + K [\text{TGA}]) \quad (16)$$

Equation (16) can be rearranged as follows:

$$\left(\frac{-d[\text{Mn}^{3+}]}{dt} \right)^{-1} = \frac{1}{2k_r K [\text{Mn}^{3+}]_T [\text{TGA}]} + \frac{1}{2k_r [\text{Mn}^{3+}]_T} \quad (17)$$

According to eq. (17), the plots of $(-d[\text{Mn}^{3+}]/dt)^{-1}$ vs. $[\text{TGA}]^{-1}$ (Fig. 2) are linear with the intercept on the ordinate.

From the intercepts and the intercept-slope ratio of these plots, the rate of unimolecular decomposition of the complex k_r and its formation constant K were computed. Values of $k_r = 5.03 \times 10^{-3}$ and $9.995 \times 10^{-3} \text{ sec}^{-1}$ at 35 and 40°C and values of $K = 5.6$ and 10.8 at 35 and 40°C, respectively.

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