Polymerization of Methyl Methacrylate: Kinetics of the Reaction Initiated by the Mn(III)-1,2-Propanediol Redox System

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Polymerization of Methyl Methacrylate: Kinetics of the Reaction Initiated by the Mn(III)–1,2-Propanediol Redox System

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ABSTRACT

Kinetics of polymerization of methyl methacrylate initiated by
Mn^{3+}/1,2-propanediol has been investigated in aqueous sul-
furic acid at the temperature range of 25-35°C. The rate of
polymerization (R_p) and the rate of manganic ion disappearance
$(-R_{Mn})$ have been computed. The effects of organic solvents,
certain cationic and anionic detergents, added electrolytes on
the initial rate of polymerization, and maximum conversion
have been examined. Depending on the kinetic results, a reac-
tion scheme has been suggested involving the formation of a
complex between Mn^{3+} and the alcohol, which subsequently

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decomposed in an unimolecular step to generate the initiating free-radical which initiates polymerization and termination of the growing polymer chain by metal ion.

INTRODUCTION

Waters' school [1] has investigated the oxidation kinetics of a multitude of organic substrates involving trivalent manganese. The reaction between Mn^{3+} and alcohols has been pictured as proceeding via a complex between the hydroxyl group of the alcohol and the metal ion. This complex then decomposes by an internal oxidation switch to generate a free radical which initiates polymerization. Singh et al. [2] and Namasivayam et al. [3] have reported that manganic sulfate in excess of sulfuric acid may form an effective redox system for grafting of polymethyl methacrylate onto cellulose and PVA. Nayudamma et al. [4] have reported manganese(III) initiated graft copolymerization of vinyl monomers onto collagen.

During the recent past we have reported the kinetics of vinyl polymerization using a number of transition metal ions [5-16] coupled with suitable activators. The present report is a microscopic aspect of our research program on kinetics and mechanism of vinyl polymerization and graft copolymerization of vinyl monomers onto wool, silk, nylon 6, PVA, etc. using transition metal ion in their higher valency states [i.e., Cr(IV), Ce(IV), Mn(III), Mn(IV), V(V), Co(III), etc.].

EXPERIMENTAL

Methyl methacrylate (MMA) was washed with 5% NaOH to remove the inhibitor. The inhibitor-free sample was washed thrice with deionized water to remove the trace of alkali. Water used for the preparation of solutions was obtained by redistilling distilled water over alkaline permanganate and was deionized by passing through Biodeminrolit resin (Permutit Co. U.K.). Mn(III) stock solutions were prepared by electrolytic oxidation of appropriate Mn(II) salt solution (0.4-0.6 M) in 4-6 M H_2SO_4 at a platinum anode [17, 18] and was analyzed for $\overline{Mn}^{3+}$ content by EDTA titration. Nitrogen used for deaeration of the experimental system was purified by passing through Feiser's solution, saturated lead acetate solution, and finally through distilled water containing a little MMA in order to avoid loss of monomer from the experimental vessel during deaeration. Sulfuric acid (GR or AR, 18 M) was used for polymerization purposes. Sodium bisulfate (AR) was used to maintain the ionic strength. Other reagents such as ferrous ammonium sulfate, o-phenanthroline, 1,2-propanediol, glycerol, 1,4-butanediol, 1-propanol, isobutyl alcohol,

ethylene glycol, cyclopentanol, cyclohexanol, and cycloheptanol were of commercial products (either BDH, AR, or E. Merke GR) and were used after the usual purification.

The polymerization process was the same as described in our previous communication [10]. After desired intervals the reactions were arrested by addition of a known excess of Fe(II) salt solution, and the unconsumed Fe(II) was determined by cerimetry from which the rate of manganic ion disappearance $(-R_{Mn})$ were computed. The precipitated polymers were filtered, washed repeatedly with distilled water, and dried to constant weight at 70°C. From the weights of polymer, the rates of polymerization (R_p) values were computed. The molecular weights $\overline{M}_w$ of the purified polymers were determined by viscometry using the appropriate Mark-Houwink relationship. The viscosities of the polymer solutions (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer in acetone at 30°C, using the relationship [19]

$$[\eta] = 7.7 \times 10^{-3} \overline{M}_w^{0.7}$$

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid solution at 25-35°C in the presence of the redox system $Mn^{3+}/1,2$-propanediol. A set of conversion plots at 25°C for various concentrations of 1,2-propanediol has been computed in Fig. 1.

Methyl methacrylate was also polymerized under identical conditions with Mn^{3+} in the presence of other alcohols (1-propanol, ethylene glycol, 1-butanol, isobutyl alcohol, glycerol, 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 of R_p in each case are recorded in Table 1, which shows that under identical conditions the reactivities of the alcohols are 1-propanol > glycerol > ethylene glycol > isobutyl alcohol > 1-butanol > 1,2-propanediol > cycloheptanol > cyclohexanol cyclopentanol.

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 concentration [M]. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ versus $[Pd]^{-1}$ (PD = 1,2-propanediol) were linear with intercepts on the rate axis (Fig. 2) showing Lineweaver-Burk kinetics [20] formation.
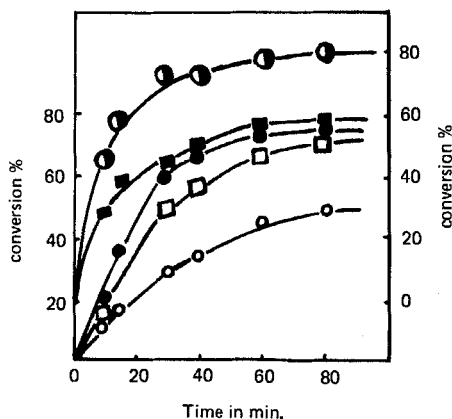
FIG. 1. (a) Variation of rate with time, effect of activator concentration: $[Mn^{3+}]$ = 1.75 × 10^{-3} $\underline{M}$, $[H^+]$ = 2 $\underline{M}$, μ = 2.1 M, $[MMA]$ = 0.0939 M, temperature = 25°C. Plots: (○) $[PD]$ = 0.$\overline{0}$25 $\underline{M}$, (□) $[PD]$ = $\overline{0}$.075 $\underline{M}$, (●) $[PD]$ = 0.2 M. (b) Variation of rate with time, effect of catalyst concentration: μ = 1.96 $\underline{M}$, $[PD]$ = 0.2 $\underline{M}$, $[MMA]$ = 0.0939 $\underline{M}$, temperature = 25°C. Plots: (■) $[Mn^{3+}]$ = 1.0$\overline{5}$ × 10^{-3} $\underline{M}$, (◑) $[Mn^{3+}]$ = 2.45 × 10^{-3} $\underline{M}$.

TABLE 1. Polymerization of Methyl Methacrylate Initiated by Mn^{3+}/ Alcohols System at 35°C. $[Mn(III)]$ = 3.5 × 10^{-3} $\underline{M}$, $[H^+]$ = 2 $\underline{M}$, μ = 2.3 $\underline{M}$, $[MMA]$ = 0.094 $\underline{M}$, $[alcohol]$ = 0.272 $\underline{M}$.

Alcohols	Induction period (min)	$10^5 R_p$ m·L^{-1}·s^{-1}
1-Propanol	3	2.46
1-Butanol	6	1.12
Isobutyl alcohol	4	1.58
Ethylene glycol	5	1.599
1,2-Propanediol	8	1.106
Glycerol	8	1.919
Cyclopentanol	58	0.105
Cyclohexanol	22	0.388
Cycloheptanol	50	0.853
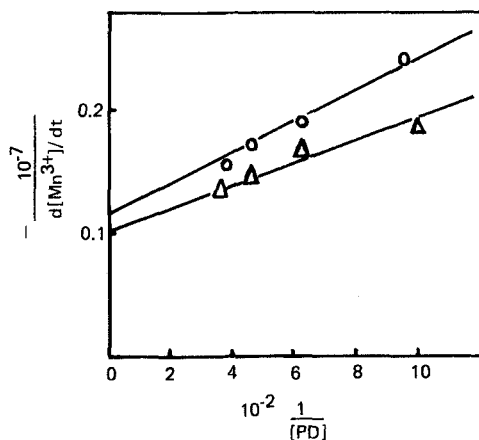
FIG. 2. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs $[PD]^{-1}$. $[Mn^{3+}] = 3.5 \times 10^{-3}$ $\underline{M}$, $[H^+] = 2$ $\underline{M}$, $\mu = 2.1$ $\underline{M}$, $[MMA] = 0.0939$ $\underline{M}$. Plots: (●) temperature = 25°C, (▲) temperature = 30°C.
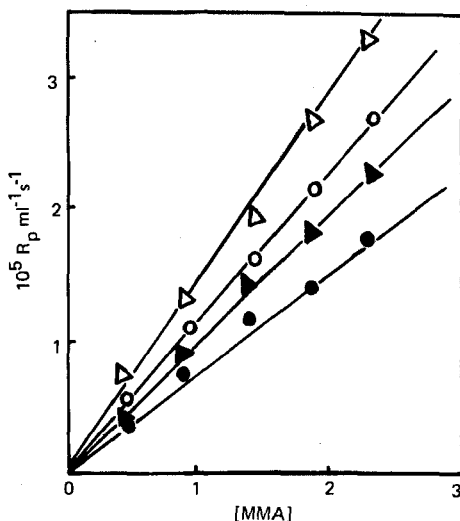
FIG. 3. Variation of rate of polymerization (R_p) with MMA at various temperatures. (a) $[Mn^{3+}] = 3.5 \times 10^{-3}$ $\underline{M}$, $[H^+] = 2$ $\underline{M}$, $\mu = 2.1$ $\underline{M}$, $[PD] = 0.21$ M. Plots: (○) temperature = 25°C, (△) temperature = 30°C. (b) $[Mn^{3+}] = 4.2 \times 10^{-3}$ $\underline{M}$, $\mu = 2.1$ $\underline{M}$, $[PD] = 0.21$ M. Plots: (●) temperature = 25°C, (▲) temperature = 30°C.
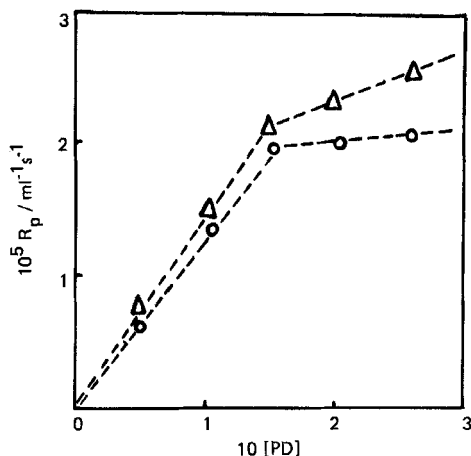
FIG. 4. Variation of rate of polymerization (R_p) with $[PD]$ at various temperatures. $[Mn^{3+}] = 3.5 \times 10^{-3}$ $\underline{M}$, $[H^+] = 2$ $\underline{M}$, $\mu = 2.1$ $\underline{M}$, $[MMA] = 0.0939$ $\underline{M}$. Plots: ($\bullet$) temperature $= 25°C$, ($\blacktriangle$) temperature $= 30°C$.

Rate of Polymerization

The rates of polymerization increased linearly with increasing monomer concentration ($0.0469-0.2347$ $\underline{M}$). Plots of R_p versus $[MMA]$ are linear and pass through the origin (Fig. 3), showing that the order with respect to $[MMA]$ is unity. The rate of polymerization (R_p) increases on increasing $[Mn^{3+}]$ up to a certain concentration of Mn^{3+} ion, after which the rate has a decreasing trend. The rate increases linearly with increasing PD concentrations in the low concentration range, but at higher concentrations, deviation from normal behavior is noticed (Fig. 4). A similar observation has been made by Samal et al. [21] in the case of polymerization of acrylonitrile initiated by the Cr(VI)/1,2-propanediol redox system. These are probably caused by accompanying changes in the polarity of the system, which changes with an increasing diol proportion in the reaction mixture.

Effect of Organic Solvents

Addition of 5% (v/v) organic solvents such as methanol, ethanol, acetic acid, and acetone to the reaction mixture decreases the initial rate of polymerization as well as the maximum conversion (Fig. 5b).
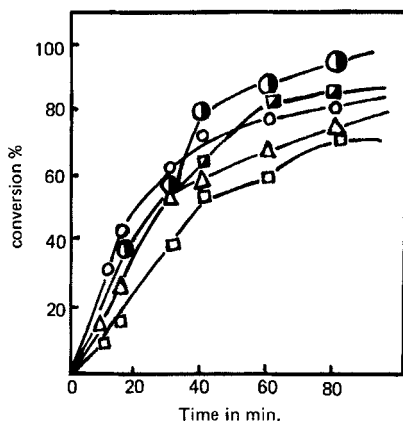
FIG. 5. (a) Variation of rate with time, effect of anionic surfac-
tants: $[Mn^{3+}]$ = 1.75 × 10⁻³ M, $[H^+]$ = 1.9 M, μ = 2 M, [PD] = 0.2 M,
[MMA] = 0.0939 M, temperature = 30°C. Plots: (○) Control, (△)
[SLS] = 3 × 10⁻³ M, (□) [SLS] = 5 × 10⁻³ M, (◑) [SLS] = 9.05 × 10⁻³
M, (■) [SLS] = 10.025 × 10⁻³ M. (b) Variation of rate with time,
effect of organic solvents: $[Mn^{3+}]$ = 1.75 × 10⁻³ M, $[H^+]$ = 1.9 M,
μ = 2 M, [PD] = 0.2 M, [MMA] = 0.0939 M, temperature = 30°C.

The retardation of the rate by these 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.

(2) These solvent molecules might 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 chain. This is in agreement with
the view of Kern et al. [22].

(3) Further, the interchain hydrogen bonding interlocking the poly-
mer chain is not rigid, and therefore the tendency of mutual termi-
nation of the polymer chain increases. Similar observations have
been made by Mishra et al. [23] in the case of polymerization of
acrylamide and by Samal et al. [24] in the polymerization of
acrylonitrile.

Effect of Surfactants

Recently, much interest has been shown in the kinetics and mech-
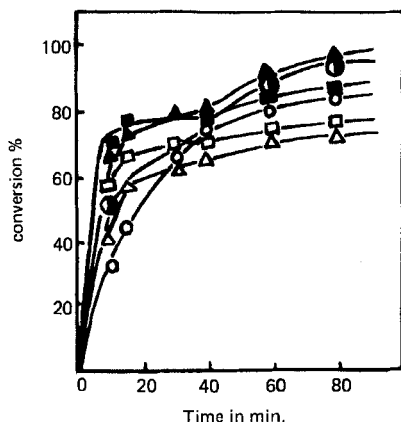anism of polymerization reaction in the presence of micelles [25, 26].

FIG. 6. Variation of rate with time, effect of cationic surfactants on the rate: $[Mn^{3+}]$ = 1.75 × 10^{-3} $\underline{M}$, $[H^+]$ = 1.9 $\underline{M}$, μ = 2 $\underline{M}$, $[PD]$ = 0.2 $\underline{M}$, $[MMA]$ = 0.0939 $\underline{M}$, temperature = 30°C. Plots: (o) Control, (△) $[CTABr]$ = 5 × 10^{-4} $\underline{M}$, (□) $[CTABr]$ = 7 × 10^{-4} $\underline{M}$, (▲) $[CTABr]$ = 10 × 10^{-4} $\underline{M}$, (■) $[CTABr]$ = 12 × 10^{-4} $\underline{M}$, (◑) $[CTABr]$ = 14 × 10^{-4} $\underline{M}$.
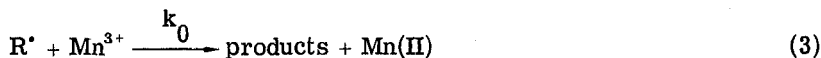
The hydrophobic interaction and electrostatic attractions are mainly responsible for the spectacular rate enhancement or inhibition exhibited by micelles on polymerization reactions. The rate of polymerization has been investigated in the presence of micelles of certain cationic and anionic surfactants. The cationic surfactant of cetyltrimethyl-ammonium bromide (CTABr) enhances the initial rate and maximum conversion (Fig. 6). The rate was affected seriously on increasing the concentration of the anionic surfactants sodium lauryl sulfate below CMC (Fig. 5). The retarding effect of anions may be under-stood by assuming specific ion-pair coupling of the cation Mn^{3+} with the anion RSO$_4^-$, which might lower the rate of primary radical gener-ation. Alexander and co-workers [26] have assumed such ion-pair coupling between cationic and S$_2$O$_8^{2-}$ ions only above CMC, leading to the formation of an insoluble complex, which could be dissolved or dispersed by further addition of the cationics and hence reducing the rate. As expected, the rate is not affected in the presence of micelles of a nonionic surfactant or Triton-X-100.

Reaction Mechanism and Rate Law

The polymerization of methyl methacrylate (MMA) in aqueous media initiated by Mn^{3+}/1,2-propanediol shows the characteristic features of heterogeneous polymerization. The reaction mixture

becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer (MMA) in the aqueous phase.
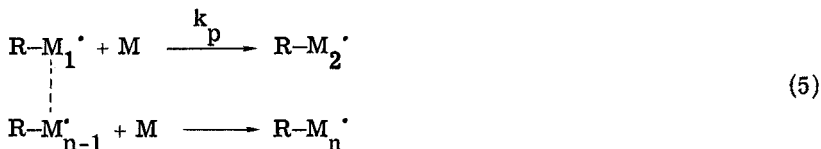
From the kinetic results a reaction scheme has been proposed involving the initiation by organic free radicals generated by the interaction of the Mn^{3+} ion with the OH group of the diol via complex formation and termination by metal ion:
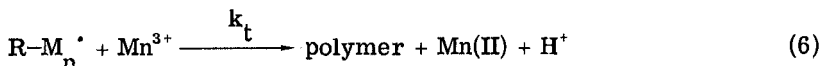
$$Mn^{3+} + PD \overset{K}{\rightleftharpoons} complex \tag{1}$$

$$Complex \xrightarrow{k_r} R^\bullet + Mn(II) + H^+ \tag{2}$$

$$R^\bullet + Mn^{3+} \xrightarrow{k_0} products + Mn(II) \tag{3}$$

Initiation:

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

Propagation:

$$R-M_1^\bullet + M \xrightarrow{k_p} R-M_2^\bullet$$

$$R-M_{n-1}^\bullet + M \longrightarrow R-M_n^\bullet \tag{5}$$

Termination:

$$R-M_n^\bullet + Mn^{3+} \xrightarrow{k_t} polymer + Mn(II) + H^+ \tag{6}$$

Applying the steady-state approximation to the primary radical $(R^\bullet)$ as well as to the growing polymer chain $(R-M_n^\bullet)$, and taking the radical reactivity as independent of radical size, we obtain

$$d[R^\bullet]/dt = k_r[complex] - k_i[R^\bullet][M] - k_0[R^\bullet][Mn^{3+}]_{eq} = 0 \tag{7}$$

$$[R^\bullet] = \frac{k_r[complex]}{(k_i[M] + k_0[Mn^{3+}]_{eq})} = \frac{k_r K[Mn^{3+}]_{eq}[PD]}{(k_i[M] + k_0[Mn^{3+}])} \tag{8}$$

The steady-state expression for $R-M_n^\bullet$ will be

$$[R\text{-}M_n^\bullet] = \frac{k_i k_r K[PD][M]}{(k_i[M] + k_0[Mn^{3+}]_{eq})k_t} \tag{9}$$

If $k_p[R\text{-}M_n^\bullet][M] \gg k_i[R^\bullet][M]$, R_p is given by

$$R_p = \frac{k_p k_i k_r K[M]^2[PD]}{k_t(k_i[M] + k_0[Mn^{3+}]_{eq})} \tag{10}$$

The above equation requires that R_p is second order with respect to monomer, which decreases with increasing $[Mn^{3+}]$. If, on the other hand,

$$k_i[M] \gg k_0[Mn^{3+}]_{eq}$$

we get

$$[R\text{-}M_n^\bullet] = \frac{k_r K[PD]}{k_t} \tag{11}$$

Hence

$$R_p = \frac{k_p k_r K[PD][M]}{k_t} \tag{12}$$

Further, the rates of oxidant consumption would be given by

$$-d[Mn^{3+}]/dt = k_r K[Mn^{3+}]_{eq}[PD] + k_t[R\text{-}M_n^\bullet][Mn^{3+}]_{eq} \tag{13}$$

$$-d[Mn^{3+}]/dt = 2k_r K[Mn^{3+}]_{eq}[PD] \tag{14}$$

Since

$$[Mn^{3+}]_{total} = [Mn^{3+}]_{eq}(1 + K[PD])$$

$$-d[Mn^{3+}]/dt = \frac{2k_r K[Mn^{3+}]_T[PD]}{(1 + K[S])} \tag{15}$$

TABLE 2. Mean Values of Rate Parameters in the Polymerization of Methyl Methacrylate Initiated by the Mn^{3+}/1,2-PD System

Monomer	10^{-2} $K \cdot mol^{-1} \cdot L$		$k_r \times 10^4 / s^{-1}$		10^2 k_p/k_t	
	25°C	30°C	25°C	30°C	25°C	30°C
MMA	7.68	10.06	1.24	1.42	0.6	0.5

Equation (15) can be rearranged as follows:

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

According to Eq. (16), the plots of $(-d[Mn^{3+}]/dt)^{-1}$ versus $[PD]^{-1}$ are linear with intercepts on the ordinate. From the slopes and intercepts, the values of k_r and K can be calculated. Putting the values of k_r and K in Eq. (12), the value of k_p/k_t can be evaluated from the plots of R_p versus $[M]$ (Table 2).

ACKNOWLEDGMENT

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