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Polymerization of Methyl Methacrylate by Mn(III) Acetate/Ethylene Glycol Redox System in Acetic-Sulfuric Acid Mixture

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ABSTRACT

A kinetic study of the thermal polymerization of methyl methacrylate initiated by the Mn(III) acetate/ethylene glycol redox system in sulfuric acid and acetic acid was made in the temperature range of 40 to 50°C under nitrogen atmosphere. The effects of the concentrations of 1) monomer, 2) metal ion, 3) ethylene glycol, and 4) acid on the kinetics of polymerization have been investigated. It has been observed that with an increase of monomer concentration, the rate is progressively decreased. A kinetic scheme has been proposed involving the production of initiating radicals formed by the oxidation of ethylene glycol by Mn^{3+} ions and termination exclusively by the growing PMMA chain. The scheme conforms to the experimental findings.

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INTRODUCTION

Several reports [1-5] have appeared on the mechanism and kinetics of redox polymerization initiated by different metal ions. Mn(III) in the form of sulfate [6], perchlorate [7], pyrophosphate [8, 9], and acetate [10] has been used as the oxidant in case of vinyl polymerization. Since the behavior of acrylonitrile and methyl methacrylate in the Mn(III) acetate initiated polymerization in the presence of glycerol was different, it was considered worthwhile to study the present system in detail.

EXPERIMENTAL

Materials

Methyl methacrylate, manganous acetate, acetic acid, sulfuric acid, and potassium permanganate were either E. Merck, G.R. grade, or BDH AnalaR quality. The nitrogen used for deaeration of the experimental system was purified by passing it through several columns of Fieser's solution, a saturated solution of lead acetate, and finally through conductivity water. Mn(III) acetate was prepared according to the method reported in the literature [11].

Polymerization Procedure

Appropriate quantities of monomer, ethylene glycol, sulfuric acid, acetic acid, and conductivity water [to make 30% (v/v) HAc] were placed in the reaction vessel (80 mL capacity and provided with an inlet and outlet for nitrogen), deaerated for 25 min, and maintained at the desired temperature by a thermostat. The requisite quantity of initiator solution, previously deaerated, was quickly introduced and the polymerization was allowed to continue. After a specified interval of time, further polymerization was quenched by the addition of a known excess of Fe(II) ammonium sulfate solution. The polymers were then filtered through previously weighed Gooch crucibles and oven dried at 60°C to a constant weight. The rate of polymerization (R_p) was calculated gravimetrically.

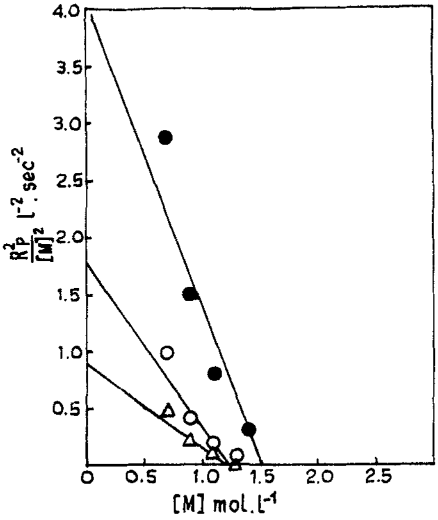

FIG. 1. Effect of monomer. [Mn(III)] = 1 × 10^{-3} mol/L, acetic acid = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [EG] = 10 × 10^{-3} mol/L. Temperatures: (●) 40°C, (○) 45°C, (△) 50°C.

RESULTS AND DISCUSSION

Rate of Polymerization (R_p)

Effect of Monomer

The value of R_p steadily decreased with an increase in monomer concentration. Figure 1 and Table 1 show the dependence of $R_p^2/[M]^2$ versus [M]. This is probably due to chain transfer. Flory [12] has explained the kinetics of chain transfer where the reactivity of a radical can be transferred to another speices, i.e., solvent/monomer, the growth of the chain previously bearing the free radical being thereby terminated. Similar observations have been made in the case of glycerol/Mn(III) acetate-MMA redox system, which will be reported elsewhere.

Rate Dependence of Metal Ion

The rate of polymerization increased with increasing concentration of the metal ion. The plot of R_p^2 vs [Mn(III)] is linear and

TABLE 1. Effect of Monomer[a]

[M] (mol/L)	$10^5 \times R_p$ (mol/L·s)		
	40°C	45°C	50°C
0.4675	1.7284	1.1675	1.6974
0.7012	1.0232	0.5909	0.4892
0.9349	1.0140	0.5618	0.3935
1.1686	0.9543	0.5012	0.3606
1.4022	0.7768	0.4485	0.2113

[a] [Mn(III)] = 1×10^{-3} mol/L, HAc = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [EG] = 10×10^{-3} mol/L.

TABLE 2. Effect of Metal Ion[a]

$10^3 \times$ [Mn(III)] (mol/L)	$10^5 \times R_p$ (mol/L·s), 45°C
0.2	0.4901
0.4	0.6579
0.6	1.0246
0.8	1.1499
1.0	1.7460

[a] [EG] = 10×10^{-3} mol/L, HAc^- = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [MMA] = 0.9349 mol/L.

passes through the origin, thus confirming the termination to be mutual (Table 2, Fig. 2).

Effect of Substrate

The rate of polymerization progressively increases with an increase of substrate concentration (5×10^{-3} to 25×10^{-3} mol/L) at a constant concentration of Mn(III)acetate, H_2SO_4, and monomer. This is shown in Table 3 and Fig. 3. Similar observations were made in the case of the Mn(III) acetate-acrylonitrile-ethylene glycol system.

Effect of H_2SO_4

Polymerization does not occur in the absence of H_2SO_4. The rate of polymerization was found to increase up to a particular concentration

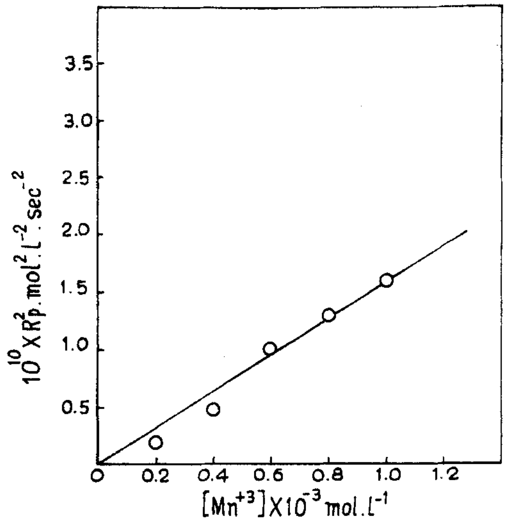

FIG. 2. Rate dependence of metal ion. [EG] = 10 × 10^{-3} mol/L, acetic acid = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [MMA] = 0.9349 mol/L, temperature = 45°C.

TABLE 3. Effect of Substrate[a]

	$10^5 \times R_p$ (mol/L·s)		
[EG] × 10^{-3} (mol/L)	40°C	45°C	50°C
5	0.4402	1.0838	1.7275
10	0.5345	1.2914	1.7566
15	1.0084	1.3363	1.9971
20	1.3418	1.5199	2.1224
25	1.4265	1.6447	2.2960

[a] [Mn(III)] = 1 × 10^{-3} mol/L, HAc = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [MMA] = 0.9349 mol/L.

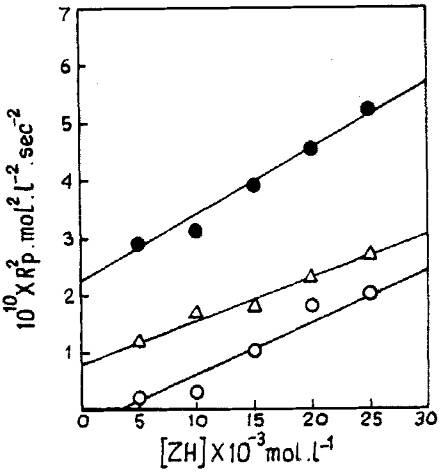

FIG. 3. Effect of substrate. [Mn(III)] = 1 × 10^{-3} mol/L, acetic acid = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [MMA] = 0.9349 mol/L. Temperatures: (○) 40°C, (△) 45°C, (●) 50°C.

of H_2SO_4 (7.5×10^{-2} to 22.5×10^{-2} mol/L) and then gradually falls (Table 4). Exactly the same result had been obtained in the Mn(III) acetate-acrylonitrile-ethylene glycol system. This is probably due to inactivation of the active initiator species which brings about premature termination of polymerization. Similar observations have been reported by Santappa et al. [5].

Effect of Acetic Acid

In the case of acetic acid, because of the low acidity, Mn^{3+} ions acquire instability and suffer disproportionation (Table 5) as reported by Singh et al. [13]. Similar observations have been reported in the case of the polymerization of methyl methacrylate initiated by the Mn(III)acetate/glycerol redox system.

PROPOSED KINETIC SCHEME AND RATE EXPRESSION

The proposed scheme satisfactorily explains all the kinetic results obtained.

(a) Reaction of Mn(III) ions with substrate:

$$\mathrm{Mn(III)} = \mathrm{S} \overset{k}{\rightleftharpoons} \text{complex} \xrightarrow{k} \mathrm{S}^{\bullet} + \mathrm{Mn(II)}$$

TABLE 4. Effect of H_2SO_4[a]

$[H_2SO_4) \times 10^{-2}$ (mol/L)	$10^5 \times R_p$ (mol/L·s), 45°C
7.5	1.7506
15.0	1.9911
22.5	2.2084
30.0	1.6577
37.5	1.3793
45.0	1.1532

[a] [EG] = 10×10^{-3} mol/L, [MMA] = 0.9349 mol/L, [Mn(III)] = 1×10^{-3} mol/L, HAc = 30% (v/v).

TABLE 5. Effect of Acetic Acid[a]

	$10^5 \times R_p$ (mol/L·s)	
% of HAc	40°C	45°C
10	1.2970	1.3973
20	1.2600	1.3520
30	1.0348	1.0121
40	2.7637	3.1383
50	1.7104	2.8160
60	1.1925	1.9097

[a] [EG] = 10×10^{-3} mol/L, [MMA] = 0.9349 mol/L, [Mn(III)] = 1×10^{-3} mol/L, $[H_2SO_4]$ = 0.075 mol/L.

(b) Initiation of polymerization by Mn(III) ion:

$$\mathrm{Mn(III)} + \mathrm{M} \xrightarrow{k_1} \mathrm{M}^{\bullet} + \mathrm{Mn(II)}$$

(c) Initiation of polymerization by primary radical $S^{\bullet}$:

$$\mathrm{S}^{\bullet} + \mathrm{M} \xrightarrow{k_2} \mathrm{M}^{\bullet} + \mathrm{R}$$

(d) Propagation:

$$M^{\bullet} \sim\sim \xrightarrow{k_p} M_x^{\bullet}$$

(e) Termination:
By combination of growing polymer radicals (mutual termination):

$$Mx^{\bullet} + Mx^{\bullet} \xrightarrow{k_{tm}} P$$

By applying the steady-state kinetics, the following expressions may be derived:

$$\frac{d[Mx^{\bullet}]}{dt} = K_2[M][S^{\bullet}] + K_1[Mn(III)][M] - K_{tm}[Mx^{\bullet}]^2 = 0$$

Therefore

$$[Mx^{\bullet}] = \left(\frac{K_1[M][Mn(III)] + K_2[M][S^{\bullet}]}{K_{tm}}\right)^{1/2} \quad (1)$$

$$\frac{d[S^{\bullet}]}{dt} = K[Mn(III)][S] - K_2[M][S^{\bullet}] - K_0[S^{\bullet}][Mn(III)] = 0$$

Therefore

$$[S^{\bullet}] = \frac{K[Mn(III)][S]}{K_2[M] + K_0[Mn(III)]} \quad (2)$$

Substituting the value of $[S^{\bullet}]$ from Eq. (2) in Eq. (1), neglecting both the terms involving K_0 (K_0 is of the order of 10^{-3}) and K_1K_2 (which is of the order of 10^2), and combining the constant terms:

$$[Mx^{\bullet}] = \left(\frac{A[M]^2[Mn(III)] + B[M][S][Mn(III)]}{C[M]}\right)^{1/2} \quad (3)$$

where $K_1K_2 = A$, $KK_2 = B$, and $K_{tm} = C$.

R_p is given by

$$R_p = K_p[M][Mx^{\cdot}] \tag{4}$$

$$R_p{}^2 = K_p{}^2[M]^2[Mx^{\cdot}]^2 \tag{5}$$

Substituting the value of $[Mx^{\cdot}]$ from Eq. (3) and again combining the constant terms:

$$\frac{R_p{}^2}{[M]^2} = X[M][Mn(III)] + Y[Mn(III)][S] \tag{6}$$

The proposed rate expression satisfactorily explains all the kinetic results obtained.

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