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Effect of Glycerol in the Polymerization of Methyl Methacrylate by Mn(III) Acetate

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ABSTRACT

The kinetics of the mechanism of the polymerization of methyl methacrylate initiated by the glycerol/Mn(III) acetate redox system has been investigated in aqueous sulfuric acid medium in the temperature range of 40 to 50°C. The effects of glycerol, methyl methacrylate, metal ion, acetic acid, and sulfuric acid on the rates of polymerization have been studied. One striking observation is that the increase in monomer concentration steadily decreases the rate of polymerization, contrary to what was observed in the case of acrylonitrile. On the basis of these observations, an appropriate kinetic scheme and rate expression have been developed.

INTRODUCTION

Much work has been done on redox polymerization initiated by the metal ions Co(III), Fe(III), Ce(IV), V(V), Cr(VI), etc. [1-7]. Trivalent manganese has been used as an oxidant in the process of polymerization

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by different workers [8-11]. Previously we have reported the polymerization of acrylonitrile initiated by the Mn(III) acetate/glycerol redox system. The surprising observation that an increase in MMA (monomer) concentration caused a decrease in polymerization, contrary to that found in the case of AN, prompted us to investigate the detailed kinetics of the present system. On the basis of the experimental findings, a suitable reaction scheme and rate expression have been suggested.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was a BDH product. It was first purified by washing with 5% NaOH solution to remove the stabilizer, then washed several times with conductivity water, and then dried over anhydrous $CaCl_2$. The manganese(II) acetate, potassium permanganate, acetic acid, sulfuric acid, and glycerol used were either BDH (AnalaR) or E. Merck (G.R.) products. Manganic(III) acetate was prepared by the usual method as described in the literature [12]. Water, distilled twice over alkaline permanganate in an all-glass Corning unit, was used for the preparation of reagents and solutions. The nitrogen (Indian Oxygen Co., Calcutta) used to deaerate the reaction mixture was freed from oxygen by passing through Fieser's solution, a saturated solution of lead acetate, and finally through conductivity water.

Polymerization

Appropriate quantities of monomer, glycerol, solution, acetic acid, sulfuric acid, and conductivity water (to make the solution 30% v/v HAc) were taken in reaction vessels provided with an inlet and outlet for nitrogen, and deaerated for 25 min, thermostated at the desired temperature. Manganic(III) acetate solution, previously deaerated, was added immediately and polymerization was allowed to continue for a specified time. After the desired time interval, the polymerization was arrested by the addition of an excess of ferrum(II) ammonium sulfate solution. The polymethyl methacrylate was filtered off through previously weighed Gooch crucibles, washed with water, and dried in an oven at 60°C to constant weight. The rate of polymerization (R_p) was calculated gravimetrically.

RESULTS AND DISCUSSION

Rate Dependence on Glycerol Concentration

Plots of R_p^2 at varying concentrations of glycerol at fixed concentrations of manganese(III) acetate, sulfuric acid, and monomer are shown in Fig. 1. The rate of polymerization increases with an increase of glycerol concentration (5×10^{-3} to 25×10^{-3} mol/L) (Table 1). This is probably due to the greater yield of initiating free radicals with an increasing concentration of glycerol.

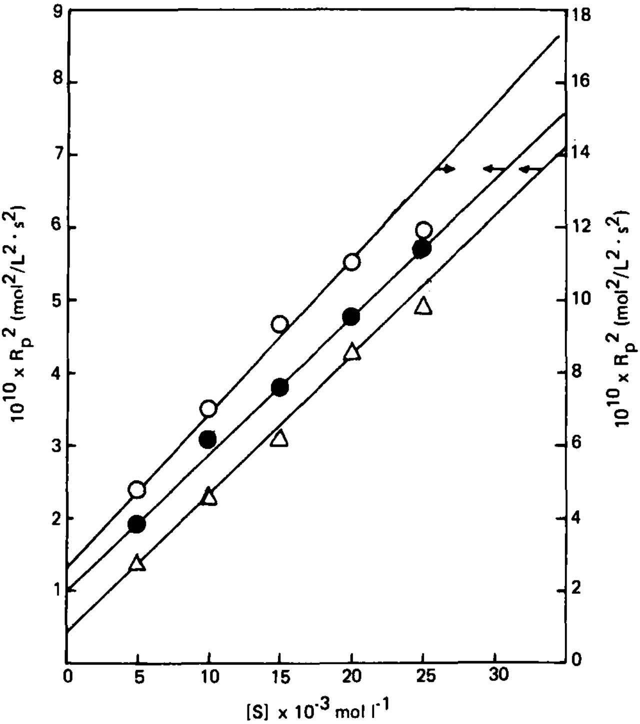

FIG. 1. Effect of [glycerol] on rate (R_p) at different temperatures. [Mn(III)] = 1×10^{-3} mol/L, [MMA] = 0.9349 mol/L, [H_2SO_4] = 0.075 mol/L, acetic acid = 30% (v/v), (○) at 50°C, (●) at 45°C, (△) at 40°C.

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

[Glycerol] = [S] (10^{-3} × mol/L)	$10^5 \times R_p$ mol/L·s		
	40°C	45°C	50°C
5	1.1951	1.3841	2.1943
10	1.5356	1.7772	2.6483
15	1.7642	1.9502	3.0584
20	2.0815	2.2007	3.3057
25	2.2320	2.4025	3.4437

Effect of Monomer Concentration

A regular decrease in rate (R_p) was noticed with an increase in monomer concentration (0.4675 to 1.4022 mol/L) (Table 2). $R_p^2/[M]^2$ vs [M] was linear as shown in Fig. 2. A decrease in the rate of polymerization with increasing monomer concentration in the case of methyl

TABLE 2. Effect of [Monomer]. [Mn(III)] = 10^{-3} × 1 mol/L, HAc = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [S] = 10 × 10^{-3} mol/L

[M] (mol/L)	$10^5 \times R_p$ mol/L·s		
	40°C	45°C	50°C
0.4675	2.9776	2.5143	1.7998
0.7012	1.6646	0.9204	0.8323
0.9349	1.6063	0.8538	0.8115
1.1686	1.4343	0.7983	0.7040
1.4022	1.3573	0.7005	0.6936

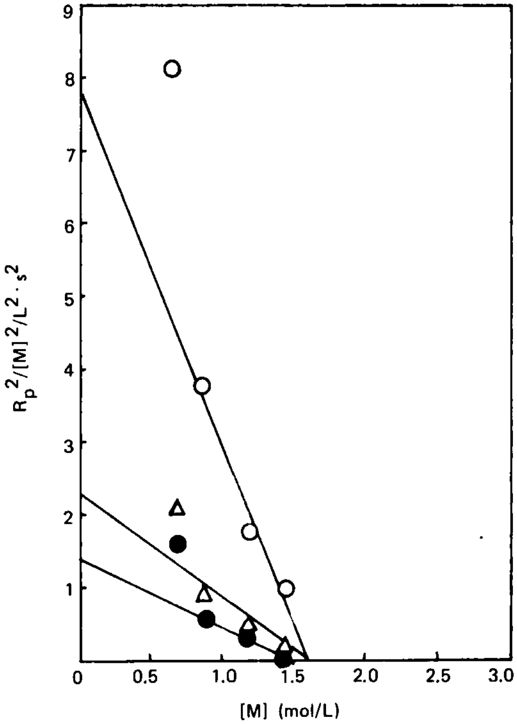

FIG. 2. Effect of [monomer] on rate (R_p) at different temperatures. [Glycerol] = 10 × 10^{-3} mol/L, [Mn(III)] = 1 × 10^{-3} mol/L, [H_2SO_4] = 0.075 mol/L, acetic acid = 30% (v/v), (○) at 40°C, (△) at 45°C, (●) at 50°C.

methacrylate is in contrast with the behavior of acrylonitrile, where the polymerization rate runs parallel to the monomer concentration. This may be due to a chain-transfer mechanism where the free radical center is transferred from a growing chain to another molecule [13]. It has been reported that the growing PMMA chains are more compatible with MMA monomer than are PAN chains with AN monomer in aqueous polymerizations [14].

Effect of Metal Ion on Rate of Polymerization

The plot of R_p^2 versus metal ion concentration was linear with a zero intercept, as shown in Fig. 3. The rate of polymerization increases

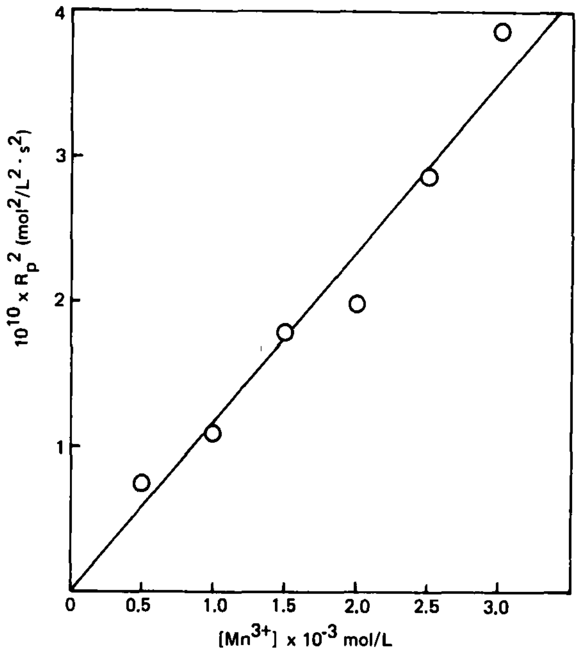

FIG. 3. Effect of [initiator] on rate (R_p) at 45°C. [Glycerol] = 10×10^{-3} mol/L, [MMA] = 0.9349 mol/L, [H_2SO_4] = 0.075 mol/L, acetic acid = 30% (v/v), (○) at 45°C.

steadily with an increase in metal ion concentration, thus confirming the validity of the proposed scheme (Table 3).

Effect of H_2SO_4

The rate of polymerization was found to be dependent on H_2SO_4 acid concentration because polymerization does not occur in the absence of H_2SO_4. The rate of polymerization increases up to a particular concentration of H_2SO_4 (7.5×10^{-2} to 30×10^{-2} mol/L) and then decreases (Table 4). Similar observations have been reported in the case of acrylonitrile glycerol/Mn(III) acetate.

Effect of Acetic Acid (Table 5)

It has been reported by Singh et al. [15] in the case of Mn^{3+} ions as initiator for grafting onto polysaccharides that disproportionation of

TABLE 3. Effect of [Metal Ion]. [S] = 10 × 10^{-3} mol/L, HAc = 30% (v/v), [H_2SO_4] = 0.075 mol/L, [MM] = 0.9349 mol/L, 45°C

10^{-3} × [Mn(III)] (mol/L)	$10^5 \times R_p$ mol/L·s
0.5	0.8913
1.0	1.0688
1.5	1.3435
2.0	1.4156
2.5	1.7175
3.0	1.9802

TABLE 4. Effect of [H_2SO_4]. [S] = 10 × 10^{-3} mol/L, [MMA] = 0.9349 mol/L, [Mn(III)] = 1 × 10^{-3} mol/L, HAc = 30% (v/v), 45°C

10^{-2} × [H_2SO_4] (mol/L)	$10^5 \times R_p$ mol/L·s
7.5	0.9086
15.0	0.9350
22.5	0.9447
30.0	1.2013
37.5	0.3614
45.0	0.188

TABLE 5. Effect of [HAc]. [S] = 10 × 10^{-3} mol/L, [MMA] = 0.9349 mol/L, [Mn(III)] = 1 × 10^{-3} mol/L, [H_2SO_4] = 0.075 mol/L

	$10^5 \times R_p$ mol/L·s	
% of HAc	40°C	45°C
10	0.9183	1.4427
20	0.7463	1.4371
30	0.6610	0.9266
40	2.0274	3.941
50	1.5280	2.7751
60	1.3872	1.9967

these ions due to instability occurs in H_2SO_4 media of low acidity. Therefore, high acidity is necessary to prevent disproportionation of Mn^{3+} ions. It seems that Mn^{3+} ions suffer instability and disproportionation in acetic acid because of the low acidity.

PROPOSED KINETIC SCHEME AND RATE EXPRESSION

The following kinetic scheme has been proposed for deriving the various rate expressions:

Reaction of Mn(III) ion with organic substrate S:

$$\mathrm{Mn(III)} + \mathrm{S} \xrightarrow{K} \text{complex} \xrightarrow{K} \mathrm{S}^\bullet + \mathrm{Mn(II)}$$

Initiation of polymerization by Mn(III) ion:

$$\mathrm{Mn(III)} + \mathrm{M} \xrightarrow{K_1} \mathrm{M}^\bullet + \mathrm{Mn(III)}$$

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

$$\mathrm{S}^\bullet + \mathrm{M} \xrightarrow{K_2} \mathrm{M}^\bullet + \mathrm{R}$$

Propagation:

$$\mathrm{M}^\bullet \overset{K_p}{\rightsquigarrow} \mathrm{Mx}^\bullet$$

Termination by combination of growing polymer radicals (mutual termination):

$$\mathrm{Mx}^\bullet + \mathrm{Mx}^\bullet \xrightarrow{K_{tm}} \mathrm{P}$$

$$\mathrm{S}^\bullet + \mathrm{Mn(III)} \xrightarrow{K_o} \text{oxidation product}$$

Considering the termination to be mutual and making the usual assumptions for steady-state concentrations, the following expressions may be derived:

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

Therefore:

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

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

Therefore:

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

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

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

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

The rate of polymerization R_p is given by

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

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

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

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

The proposed rate expression satisfactorily explains the kinetic result obtained in the present study.

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