



KINETICS OF POLYMERIZATION OF METHYLMETHACRYLATE INITIATED BY THE Mn (III)-CITRIC ACID REDOX SYSTEM

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ABSTRACT

The kinetics and mechanism of polymerization of Methylmethacrylate (MMA) initiated by Manganese(III) acetate - Citric acid (CA) redox system in aqueous acetic acid and sulphuric acid medium were studied over the temperature range of 30-50^o C. The overall rate of polymerisation (R_p), disappearance of Manganic ion ($-R_m$) and Degree of polymerization (X_n) were measured with variation in [Monomer], [CA], [H⁺] and temperature. The polymerization is initiated by the organic free radical arising from the dissociation of Mn(III)-CA complex and the termination is by the metal ions. The various rate parameters were evaluated and discussed.

Key words: Redox Polymerization, Methylmethacrylate, Citric acid, Manganese(III) acetate, Degree of Polymerization, Initiation, Propagation, Termination

INTRODUCTION

The trivalent manganese(III) when coupled with reducing agents was found to be an effective initiator for vinyl polymerisation. Mn(III)/glycolic acid¹, Mn(III)/isobutyric acid², Mn(III)/pinacol³, Mn(III)/malonic acid⁴, Mn(III)/Citric acid⁵ and Mn(III)/ascorbic acid⁶ redox systems were employed in the polymerization of various vinyl monomers. The Mn(III) ion forms a complex with all the reducing agents and the complex decomposes to give radicals, which initiate vinyl polymerization. The termination is affected by different ways. This paper reports the results of the kinetics of thermal polymerization of MA initiated by Mn(III)-Citric acid redox system. A suitable reaction scheme has been proposed based on the experimental results and various kinetic parameters were evaluated.

EXPERIMENTAL

Experimental conditions were similar to those reported in the previous paper⁵. The rate of monomer disappearance (R_p) was determined iodometrically using the method of Wallace and Young⁷. The rate of monomer disappearance was computed from the change in monomer concentration during the polymerization. The rate of disappearance of Mn(III) ($-R_m$) was followed iodometrically by determining the concentration of manganic ion in the reaction mixture before and after polymerization.

RESULTS AND DISCUSSION

The photochemical initiation of MMA was not noticed under these experimental conditions. No polymerization of MMA by the reducing agent alone took place. Same was the case with Mn(III) ions. Oxidation of citric acid by manganese (III) acetate has been reported earlier⁵. No induction period was observed under deaerated conditions, whereas in non-deaerated conditions an induction period of 5 minutes was usually noticed; it was therefore obvious that polymerization was initiated by free radicals. The steady state was reached with in 20 minutes. [Mn(III)] was kept nearly 20 times higher than Mn(III) in order to prevent the disproportionation of Mn(III) to Mn(II) and Mn(IV) ions. An increase of [Mn(III)] above this ratio caused no change in rates. Oxidation of water by Mn(III) under these conditions was not noticed.

MMA-CA

Temp (°C)	K x 10 ⁻³ (mols/litre) Oxidation Experiments	K x 10 ⁻³ (mols/litre) Polymerisati on Experiments	K _d x 10 ³ (litre/mol/sec) Oxidation Experiments	K _d x 10 ³ Polymerisation Experiments (litre/mol/sec)	k _p /k _t	(k _o /k _i)
30	2.0000	1.1000	3.8403	1.1549	0.5186	93.15
35	3.0590	2.9217	1.9200	1.2549	0.1995	52.65

Rate of Polymerization (R_p)

The rate of polymerization increase with increase in monomer concentration [M]; the R_p versus [M] plot was linear with zero intercept (Fig.-1) revealed the order with respect to [M] was unity. The rate was found to decrease with increasing Mn(III) concentration. The plot of 1/R_p versus [Mn(III)] is linear and passed through origin. Elayaperumal et al noticed similar type of dependence of R_p on [Mn(III)] in the Mn(III)/ isobutyric acid redox system². The rate increased with the concentration of citric acid; R_p versus [CA] plots are linear with zero intercepts (Fig.-2) indicating that the order with respect to [CA] is unity.

Rate of Mn(III) disappearance (- R_m)

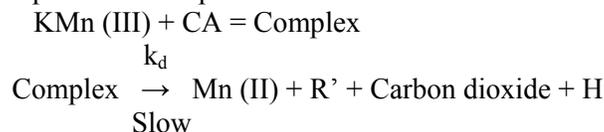
The rate of disappearance of Mn(III) was not affected by the change in monomer concentration. This is the evidence for the absence of monomer oxidation by Mn(III) ions. -R_m increased linearly with [Mn(III)]; a linear plot of - R_m versus [Mn(III)] with zero intercept (Fig.-3) shows that the order with respect to [Mn(III)] is unity. A rise in [LA] increased the rate; the plot of 1/-R_m versus 1/[CA] was linear with an intercept on the ordinate (Fig.-4) thereby suggesting the formation of a complex involving Mn(III)-CA. The rate was found to be more or less constant with increase in Hydrogen ion concentration and with increase of ionic strength which suggests that the reactive species is Mn(III) and not Manganic Hydroxide.

Degree of Polymerization (X_n)

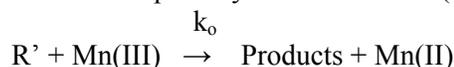
The degree of polymerization is directly proportional to [M]. The plot of X_n versus [M] was linear with zero intercept (Fig.-5). The degree of polymerization decreased with increase in concentration of [Mn(III)]. A plot of X_n versus 1/[Mn(III)] gave a straight line also passing through the origin (Fig 6). X_n was found to be independent of reducing agent concentration.

Based on the results a reaction scheme was suggested involving the initiation of polymerization by the organic free radical produced by the decomposition of the Mn(III)/ CA complex and termination by the Mn(III) ions.

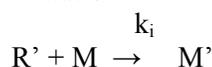
- i. Primary radical production step



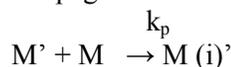
- ii. Reaction of primary radical with Mn(III)

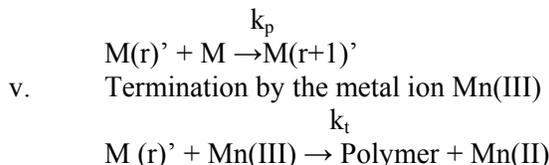


- iii. Initiation



- iv. Propagation





Applying the stationary state principle for radicals and assuming the non-dependence of rate constants k_p and k_t on chain length we derived the following rate expression for R_p , $-R_m$ and X_n based on the above scheme.

$$R_p = k_p k_d [\text{CA}] [\text{M}] [\text{M}] / k_t [\text{M}] + (k_o/k_i) [\text{Mn(III)}] \quad (1)$$

$$-R_m = 3 K k_d [\text{Mn(III)}] [\text{CA}] \quad (2)$$

Since the measured rate $-d[\text{Mn(III)}] / dt$ applied to the total $[\text{Mn(III)}]$ regardless of the species and since

$$[\text{Mn(III)}]_t = \text{Mn(III)} \times (1 + K [\text{CA}])$$

the following was obtained

$$-d[\text{Mn(III)}] / dt = 2K k_d [\text{Mn(III)}]_t [\text{CA}] / (1 + K[\text{CA}]) \quad (3)$$

$$\bar{X}_n = k_p [\text{M}] / k_t [\text{Mn(III)}] \quad (4)$$

The dependence of R_p on $[\text{M}]$ $[\text{LA}]$ and of $1/R_p$ on $[\text{Mn(III)}]$; $-R_m$ on $[\text{Mn(III)}]$ and of $1/-R_m$ of $1/[\text{CA}]$, all of which were observed favor the above scheme. Hence mutual termination by radicals and termination by complex were treated as unimportant reactions in the present investigations.

Evaluation of rate constants

The second-order rate constant k_d and the equilibrium constant K for the production of radicals for the initiation of polymerization are evaluated from the plots of $1/-R_m$ versus $1/[\text{CA}]$ at two different temperatures employing equation (3) (Fig.-4). The plot is linear with an intercept on the Y axis which is equal to $\frac{1}{2} k_d [\text{Mn(III)}]$ and the slope is equal to $\frac{1}{2} K k_d [\text{Mn(III)}]$. Hence the ratio of (intercept/slope) gives the value of the equilibrium constant K . $1/(\text{intercept})[\text{Mn(III)}] \times 2$ gives the value of k_d . The second-order rate constant k_d value obtained from the oxidation experiments was approximately twice that of the oxidation experiments as expected from equation (2).

The value of the ratio of propagation and termination rate constants namely k_p/k_t and the value of the ratio of the oxidation of primary radicals to the initiation rate constants k_o/k_i were evaluated as follows:

$$R_p = k_p K k_d [\text{CA}][\text{M}]^2 / \{ k_t [\text{M}] + (k_o/k_i) [\text{Mn(III)}] \} \quad (5)$$

$$1/R_p = k_t [\text{M}] / k_p K k_d [\text{CA}][\text{M}]^2 + (k_o/k_i) [\text{Mn(III)}] k_p/k_t K k_d [\text{CA}][\text{M}]^2 \quad (6)$$

On rearrangement-

$$1/R_p = k_t / k_p K k_d [\text{CA}] [\text{M}] + (k_o/k_i) [\text{Mn(III)}] k_p/k_t K k_d [\text{CA}] [\text{M}] \quad (7)$$

Taking square of the expression for $1/R_p$ and multiplying with $[\text{M}]^2$ the equation rearranges to $[\text{M}]^2 / R_p^2 = k_t^2 / k_p^2 K k_d [\text{CA}]^2 + (k_o/k_i) [\text{Mn(III)}]^2 k_t^2 / k_p^2 K^2 k_d^2 [\text{CA}]^2 [\text{M}]^2 \quad (8)$

The above equation requires that plots of $[\text{M}]^2 / R_p^2$ versus $1/[\text{M}]^2$ are linear with an intercept on the $[\text{M}]^2 / R_p^2$ axis (Fig 7). The slope and intercepts of the plot are equal to $k_t^2 (k_o/k_i) [\text{Mn(III)}] / k_p^2 K^2 k_d^2 [\text{CA}]^2$ and $k_t^2 / k_p^2 K^2 k_d^2 [\text{CA}]^2$ respectively. Therefore $\{(\text{slope}/\text{intercept}) (1/[\text{Mn(III)}]^2)\}^{0.5}$ gives k_o/k_i . The k_p/k_t value is obtained from $\{(1/\text{intercept}) (1/K^2 k_d^2 [\text{CA}]^2)\}^{0.5}$. All the rate parameters are presented in the following table. From the values of the rate constants at different temperatures, the thermodynamic parameters Activation Energy (E_a), Entropy change dS and Free energy change dG are calculated. E_a for k_d was -13.87 k cal/mol and for k_p/k_t was -8.468 k cal/mol, Entropy change for k_d was -116.92

eu/mol and for k_p/k_t was - 89.31 eu/mol and Free Energy change for k_d was 21.53 k cal/mol and for k_p/k_t was 18.43 k cal/mol respectively.

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Table-1: Effect of Monomer Concentration on the Rate of Polymerization

[Monomer]	$R_p \times 10^5 \text{ MS}^{-1}$
0.0890	0.912
0.1288	1.330
0.1778	1.549
0.2830	2.630
0.3548	3.891

Table-2: Effect of Reducing agent concentration on rate of Polymerization

[CA] x 10 ⁴ M	$R_p \times 10^5 \text{ MS}^{-1}$
1.60	1.02
2.00	1.25
2.40	1.50
2.80	1.70
3.20	2.05
3.60	2.40

Table-3: Dependence of $-R_m$ on the Manganic ion Concentration

[Mn ⁺³] x 10 ³ M	$- R_m \times 10^6 \text{ MS}^{-1}$
0.786	0.689
1.574	1.295
2.361	1.895
3.148	2.485

Table-4: Dependence of $-R_m$ on Citric acid Concentration

[CA] x 10 ⁴ M	$1/- R_m \times 10^{-5} \text{ M}^{-1} \text{ S}$ 30 ⁰ c
2.4	5.20
2.8	4.65
3.2	4.10
3.6	3.75
4.0	3.45

Table-5: Effect of Monomer concentration on the Degree of Polymerization

[Monomer] M	$X_n \times 10^{-2}$
0.2656	0.63
0.3542	0.85
0.4428	1.06
0.5314	1.22
0.6199	1.42

Table-6: Effect of Manganic ion concentration on Degree of Polymerization

$1/[Mn^{+3}] \times 10^{-2} M^{-1}$	$X_n \times 10^{-2}$
3.376	2.40
4.501	1.80
5.627	1.37
6.752	1.17
7.877	1.04

Table-7: Variation of $[M]^2 / R_p^2$ with $1/[M]^2$

$1/[M]^2 M^{-2}$	$[M]^2 / R_p^2 (S^2) \times 10^{-8}$
3.56	0.541
4.90	0.586
7.90	0.745
14.50	1.050
20.50	1.245
25.20	1.469

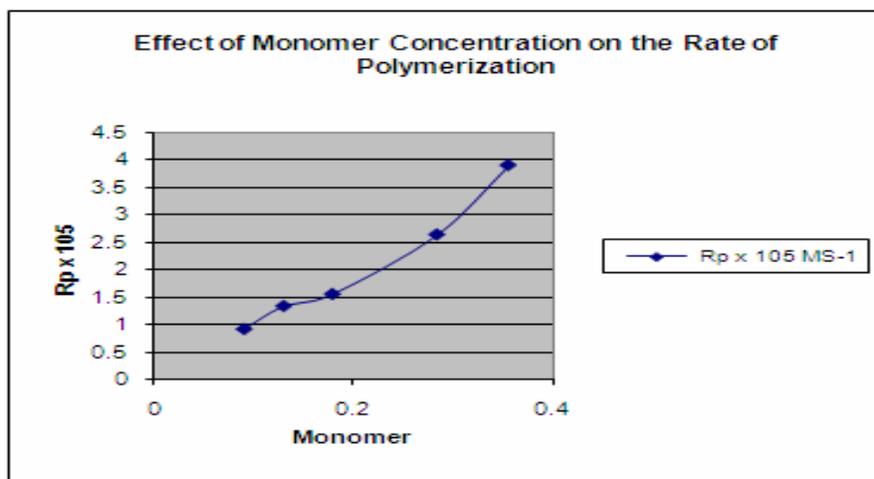


Fig.-1

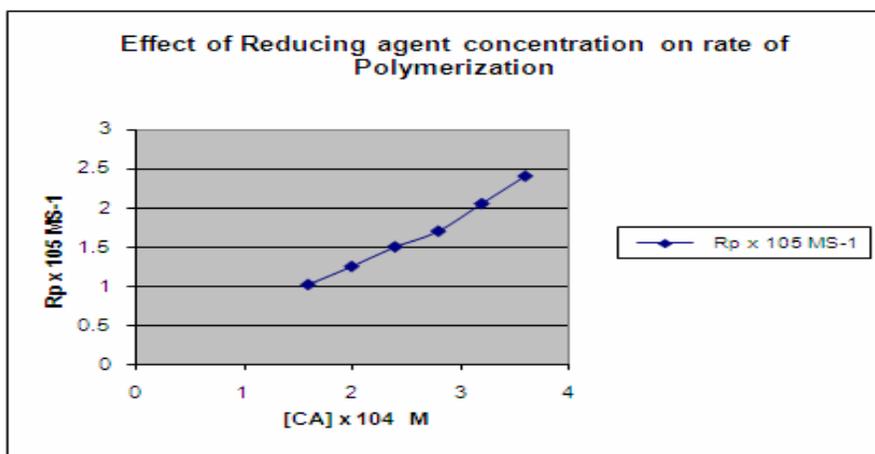


Fig.-2

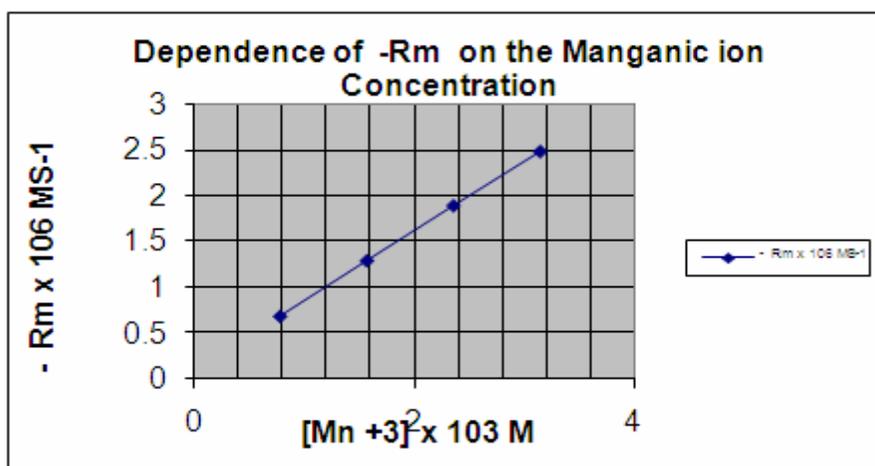


Fig.-3

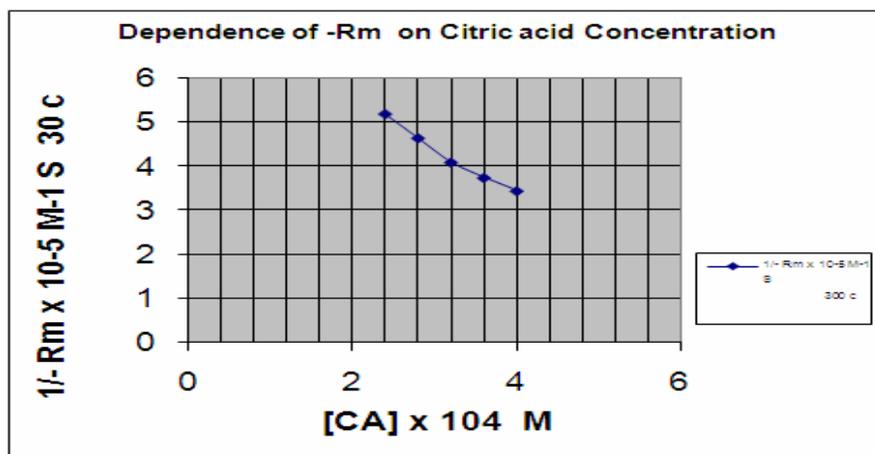


Fig.-4

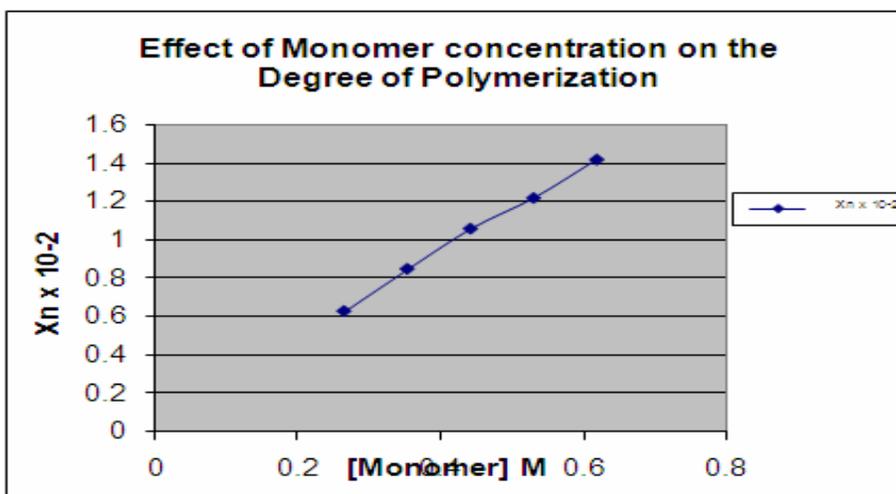


Fig.-5

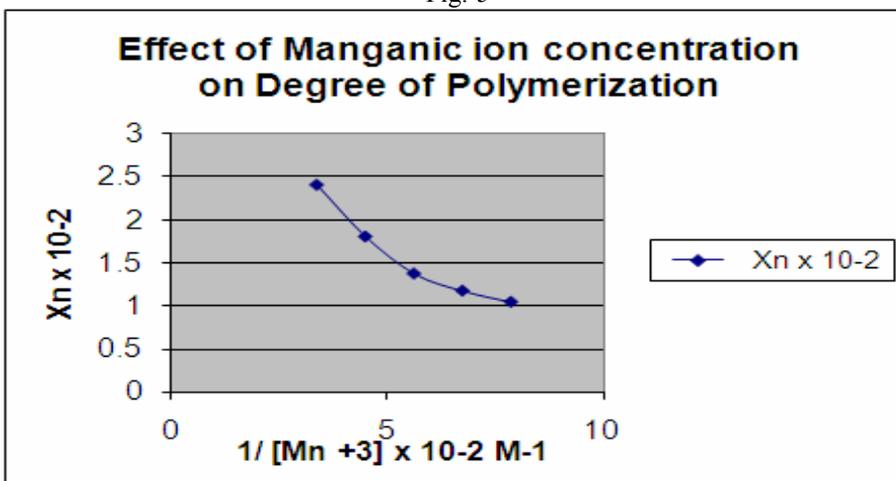


Fig.-6

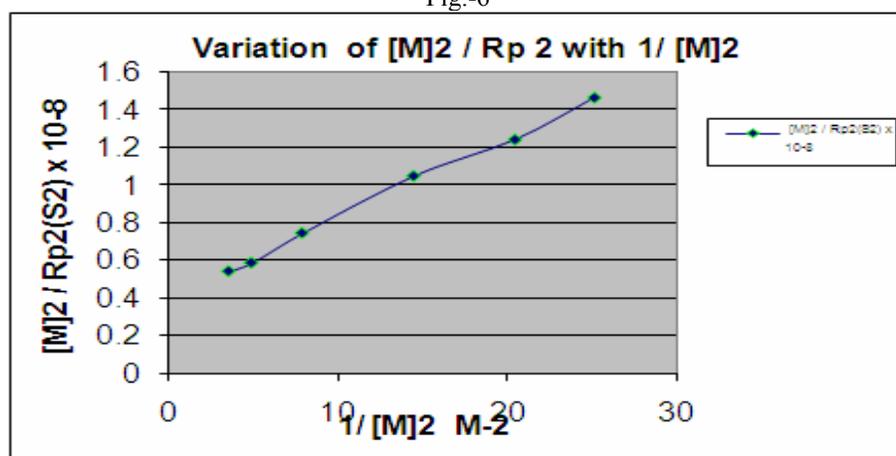


Fig.-7

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