

Kinetics of Polymerization of Acrylamide and Methylacrylate Initiated by Mn³⁺-3-ketoglutaric Acid Redox System

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The kinetics of two vinyl monomers acrylamide and methylacrylate by using redox system Mn³⁺-ketoglutaric acid at 20 °C has been investigated. The result indicates that the methylacrylate has higher monomer reactivity than acrylamide with respect to each of ketoglutaric acid, Mn(III) and H⁺. Negligible effect of ionic strength variations on reaction rate was observed. The rate of polymerization has a first order dependence on concentration of monomers was observed. A suitable mechanism with kinetic results has been proposed.

Key Words: Kinetics, Mn(III) acetate, Excellent initiator of free radical polymerization, Acrylamide, Methylacrylate, Ketoglutaric acid.

INTRODUCTION

Free radical polymerization can be initiated by ionizing radiations like α , β , γ rays, heat, light, *etc.* It can be simplified by using transition elements like Fe(III)¹, Co(III)², Cu(II)³, Mn(III)⁴ as redox initiators. Mn(III) can initiate vinyl polymerization by themselves, therefore redox potential of metal ion alone is not the deciding factor in determining its capacity to initiate vinyl polymerization. The advantage of polymerization reaction initiated by redox system are of short induction period and relatively low energy of activation⁵⁻¹⁰. Therefore, it is imperative to compare the kinetics of polymerization of acrylamide and methylacrylate using Mn³⁺-3-ketoglutaric acid redox system in aqueous sulphuric acid medium at 20 °C. In the present communication we report the results of polymerization of acrylamide and methylacrylate initiated by Mn³⁺-3-ketoglutaric acid redox system in sulphuric acid medium at 20 °C.

EXPERIMENTAL

The reagents employed were acrylamide (E. Merck), methylacrylate (E. Merck), nitrogen gas (Sundaram Enterprises, Chennai), ketoglutaric acid, manganese(III) acetate (E. Merck) and all the other reagents used

were of AR grade. All the solutions were prepared in doubly distilled water. The solution of acrylamide and methylacrylate was prepared by direct weighing and was standardized bromometrically.

Preparation of manganese(III) acetate: A mixture of manganese(II) acetate (30.3 g) and acetic acid (450 mL) was refluxed for 2 h. Potassium permanganate (3.4 g) was added and then refluxing was continued for another 45 min, then it was cooled and water (75 mL) was added in drops. After 3 d, the crude Mn(III)acetate dihydrate was separated by filtration and recrystallized from a mixture of distilled acetic acid (210 mL) and water (45 mL). It was standardized iodometrically. The stock solution of Mn(III) acetate, acrylamide, methylacrylate, ketoglutaric acid and all other reagents were stored in brown bottles to prevent photochemical decomposition. A thermostatic water bath was used to maintain the desired temperature (20 °C) within ± 0.1 °C. The reaction were initiated by the addition of manganese(III) acetate in the polymerization experiments. The final strength of acrylamide is 0.2125 M, methylacrylate is 0.2125 M, ketoglutaric acid is 1.25×10^{-3} M, manganic ion is 5.03×10^{-3} M, $[H^+]$ is 1.0 M, μ is 1.2 M and temperature at 20 °C. The progress of the reaction was carried by deaeration technique.

RESULTS AND DISCUSSION

The mixture of monomer (either acrylamide or methylacrylate), ketoglutaric acid, sulphuric acid and sodium bisulphate was taken in the reaction tube and kept in the thermostat to maintain at 20 °C. Purified nitrogen gas was passed through the above reaction mixture for about 0.5 h, at the end of deaeration, manganese(III) acetate solution was added into the reaction mixture, then the contents were mixed by shaking the reaction tube and was closed with rubber gaskets to ensure inert atmosphere. At the end of reaction time, the polymer tube was cooled in ice to arrest the polymerization reaction, then 5 mL of the reaction mixture is taken in iodine flask and titrated bromometrically to determine the rate of disappearance of monomer and simultaneously 5 mL of reaction mixture is taken in conical flask and titrated iodometrically to determine the disappearance of manganic ion during polymerization reaction.

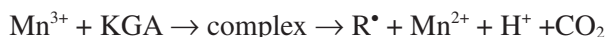
The kinetic investigation shows that the steady state rate of polymerization was reached in 5 min in both acrylamide and methylacrylate (Table-1 and Fig. 1). In case of varying concentration of monomer, the rate of polymerization of both the monomer are found to be dependent on the first power of monomer concentration. This confirms that the order with respect to monomer concentration is unity. In polymerization of acrylamide the rate of polymerization decreases slightly with increase in concentration of ketoglutaric acid but there is no significant change in methylacrylate

TABLE-1
MANGANIC ION-KETOGLUTARIC ACID-ACRYLAMIDE AND
METHYLACRYLATE SYSTEM STEADY STATE RATE OF
POLYMERIZATION

Experimental conditions: Monomer (Acrylamide and Methylacrylate) = 0.2125 M, [KGA] = 1.25×10^{-3} M, $[\text{Mn}^{3+}] = 5.04 \times 10^{-3}$ M, $[\text{H}^+] = 1.0$ M, $\mu = 1.2$ M and at temperature 20 °C

Monomers	Time (min)	$R_p \times 10^5 \text{ m dm}^{-3} \text{ s}^{-1}$
Acrylamide	5	8.433
	10	5.816
	15	4.944
	20	4.500
	30	4.072
	40	3.860
Methylacrylate	5	8.33
	10	5.00
	15	3.88
	20	2.91
	30	1.80
	40	1.14

polymerization. The rate of polymerization is not affected appreciably by changes in ionic strength of the medium. In present experiments, Mn(III) ion are not oxidized by the vinyl monomers therefore the rate of disappearance of manganic ion increases with increase in concentration of manganic ion. The rate of disappearance of manganic ion is linearly related to ketoglutaric acid concentration and has first order dependence on Mn(III) ion concentration. The rate of polymerization increases regularly with increase of temperature in both the system. The overall reaction is as follows:

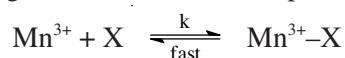


KGA = 3-ketoglutaric acid; complex = $\text{Mn}^{3+} - \text{X}$.

The significant features observed in these two systems are R_p (rate of polymerization) has a first order dependence on the concentration of monomers and $-R_m$ (rate of disappearance of manganic ion) is linearly related to [KGA] and has first order dependence on $[\text{Mn}^{3+}]$. All these experimental observation are in agreement with the mechanism and the reaction scheme (*i.e.*, initiation by primary radical and termination by the Mn^{3+} -ketoglutaric acid complex) given below:

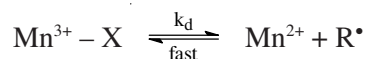
Reaction scheme:

Formation of manganic ion-substrate complex



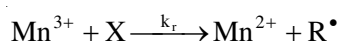
X = ketoglutaric acid.

Dissociation of manganic ion-substrate complex

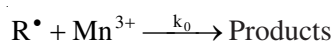


R[•] is the primary radical generated from organic substrate.

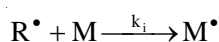
Production of primary radical without the formation of the intermediate complex.



Reaction of primary radical with Mn³⁺ ion

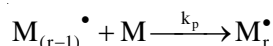
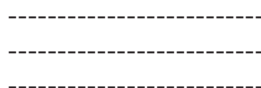
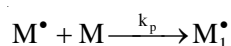


Initiation: Initiation of polymerization by primary radical.



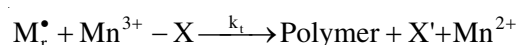
where, M = Monomer M[•] = radical formed from monomer.

Propagation of polymerization



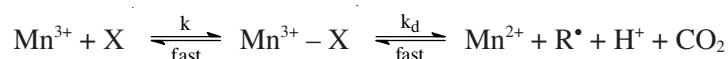
where M₁[•], M_(r-1)[•] and M_r[•] are polymer radicals.

Termination: Termination by manganic ion-substrate complex



where X' may be reducing agent itself or an inactive substance.

Overall reaction:



where X = 3 - ketoglutaric acid; Mn³⁺ - X = complex.

Kinetic expressions

R_p is given by the equation

$$R_p = \frac{K_p k_d [M]^2}{K_t \{ [M] + (k_0/k_i) [\text{Mn}^{3+}] \}} \quad (1)$$

Increase in [Mn³⁺] does not have significant effect on the value of R_p in the polymerization of monomers. Therefore the term (k₀/k_i) (Mn³⁺) in eqn. 1 is not significant.

Taking the reciprocal of the eqn. 1 and then multiplying by [M]² on both sides, the following equation is obtained.

$$\frac{[M]^2}{R_p} = \frac{k_t[M]}{k_p k_d} + \frac{k_t(k_0/k_i)[Mn^{3+}]}{k_p k_d} \quad (2)$$

From the intercept and slope of the plot $[M^2]/R_p$ vs. $[M]$ (Tables 2 and 3) the value of $(k_0/k_i) [Mn^{3+}]$ for the polymerization of vinyl monomers are obtained. This is found to be acrylamide (0.025) and methylacrylate (0.013). This is negligible in comparison with the value of $[M]$ in eqn. 1, *i.e.*, the term $(k_0/k_i) [Mn^{3+}]$ is ignored in eqn. 1. Then it reduces to:

$$R_p = \frac{K_p k_d [M]}{k_t} \quad (3)$$

TABLE-2
Mn³⁺-KETOGLUTARIC ACID-ACRYLAMIDE SYSTEM EFFECT OF MONOMER CONCENTRATION ON RATES OF POLYMERIZATION
Experimental conditions: [KGA] = 1.25 × 10⁻³ M, [Mn³⁺] = 5.04 × 10⁻³ M, [H⁺] = 1.0 M, μ = 1.2 M, Reaction time = 15 min at 20 °C

[M] (m dm ⁻³)	2 + log [M]	R _p × 10 ⁵ (m dm ⁻³ s ⁻¹)	5 + log R _p	-R _m × 10 ⁷ (m dm ⁻³ s ⁻¹)	(M ² /R _p) × 10 ⁻² (m dm ⁻³ s)
0.2125	1.3273	04.67	0.6693	08.88	09.66
0.3187	1.5033	08.74	0.9415	08.40	11.62
0.4250	1.6283	12.55	1.0986	08.05	14.39
0.5312	1.7252	15.28	1.1841	10.00	18.46
0.6375	1.8044	18.30	1.2624	07.80	22.20

TABLE-3
Mn³⁺-KETOGLUTARIC ACID-METHYLACRYLATE SYSTEM EFFECT OF MONOMER CONCENTRATION ON RATES OF POLYMERIZATION
Experimental conditions: [KGA] = 1.25 × 10⁻³ M, [Mn³⁺] = 5.04 × 10⁻³ M, [H⁺] = 1.0 M, μ = 1.2 M, Reaction time = 15 min at 20 °C

[M] (m dm ⁻³)	2 + log [M]	R _p × 10 ⁵ (m dm ⁻³ s ⁻¹)	5 + log R _p	-R _m × 10 ⁷ (m dm ⁻³ s ⁻¹)	(M ² /R _p) × 10 ⁻² (m dm ⁻³ s)
0.1035	1.0150	01.22	0.0871	11.11	08.78
0.2070	1.3159	03.83	0.5832	07.77	11.18
0.3106	1.4922	05.90	0.7708	06.94	16.35
0.4141	1.6171	07.95	0.9003	06.11	21.56
0.5177	1.7140	10.00	1.0000	05.50	26.80
0.6212	1.7932	11.80	1.0718	05.00	32.70

This equation explains well the experimental observations in this system.

-R_m is given by the equation:

$$-R_m = \frac{2K.k_d[Mn^{3+}]_{total}[KGA]}{1 + K[KGA]} \quad (4)$$

The inverse of eqn. 4 is

$$\frac{1}{-R_m} = \frac{1}{2.K.k_d[Mn^{3+}]_{total}[KGA]} + \frac{1}{2.k_d[Mn^{3+}]_{total}} \quad (5)$$

Eqns. 4 and 5 account for the observed kinetics in present studies satisfactorily.

The second order rate constant k_d is calculated from the plot of $[-R_m]^{-1}$ vs. $[KGA]$ for both the systems (Tables 4 and 5). The values of k_d are found for acrylamide ($0.333 \times 10^{-4} \text{ m}^{-1} \text{ dm}^3 \text{ s}^{-1}$) and for methyl acrylate ($0.3571 \times 10^{-4} \text{ m}^{-1} \text{ dm}^3 \text{ s}^{-1}$), respectively.

TABLE-4
MANGANIC ION-KETOGLUTARIC ACID-ACRYLAMIDE SYSTEM
EFFECT OF KETOGLUTARIC ACID CONCENTRATION
Experimental conditions: Acrylamide = 0.2125 M, $[Mn^{3+}] = 9.971 \times 10^{-3} \text{ M}$,
 $[H^+] = 1.0 \text{ M}$, $\mu = 1.2 \text{ M}$ at 20 °C

$[KGA] \times 10^4$ (m dm^{-3})	$[MGA]^{-1}$ ($\text{m}^{-1} \text{ dm}^3$)	$R_p \times 10^5$ ($\text{m dm}^{-3} \text{ s}^{-1}$)	$-R_m \times 10^7$ ($\text{m dm}^{-3} \text{ s}^{-1}$)	$(-R_m)^{-1} \times 10^7$ ($\text{m}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
5.0	2000	9.36	2.22	0.4504
10.0	1000	8.80	3.33	0.3003
15.0	667	8.52	4.00	0.2500
20.0	500	8.52	4.40	0.2272
25.0	400	8.23	4.66	0.2145
30.0	333	8.23	5.55	0.1801

TABLE-5
MANGANIC ION-KETOGLUTARIC ACID-METHYLACRYLATE
SYSTEM EFFECT OF KETOGLUTARIC ACID CONCENTRATION
Experimental conditions: Methylacrylate = 0.2125 M, $[Mn^{3+}] = 9.971 \times 10^{-3} \text{ M}$,
 $[H^+] = 1.0 \text{ M}$, $\mu = 1.2 \text{ M}$ at 20 °C

$[KGA] \times 10^4$ (m dm^{-3})	$[MGA]^{-1}$ ($\text{m}^{-1} \text{ dm}^3$)	$R_p \times 10^5$ ($\text{m dm}^{-3} \text{ s}^{-1}$)	$-R_m \times 10^7$ ($\text{m dm}^{-3} \text{ s}^{-1}$)	$(-R_m)^{-1} \times 10^7$ ($\text{m}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
5.0	2000	9.10	2.10	0.4761
10.0	1000	8.30	3.33	0.3030
15.0	667	8.05	3.80	0.2220
25.0	400	8.30	4.53	0.2207
35.0	286	7.77	5.10	0.1956
45.0	223	8.05	5.55	0.1800

The values of k_i/k_0 for the polymerization of acrylamide and methylacrylate are computed from the slope and intercept of the plots of $[M]^2/R_p$ vs. $[M]$ and given in the table below.

Monomer	Temp. (K)	k_i/k_0
Acrylamide	293	0.200
Methylacrylate	293	0.375

This observation shows clearly that the methylacrylate has higher monomer reactivity than acrylamide. Hence the order of reactivity is

Methylacrylate > Acrylamide

Hence, a kinetic analysis of the polymerization of acrylamide and methylacrylate using the redox system manganic ion-ketoglutaric acid reveals the following order of reactivity

Methylacrylate > Acrylamide

ACKNOWLEDGEMENTS

The authors are thankful to Dr. S. Subbu, Head, Department of Chemistry and Dr. D. Baskaran, Department of Chemistry, Pachaiyappa's College, Chennai for providing the facilities.

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