

Polymerization of Vinyl Monomers by Mn(III)-L-methionine Redox System - A Kinetic Study

S. KAVITHA* and S. SUBBU†

Department of Chemistry, Pachaiyappa's College for Men
Kanchipuram-600 501, India

E-mail: kavithasankar_chem@rediffmail.com

The polymerization of methyl acrylate and methacrylic acid initiated by Mn(III)-L-methionine redox system in aqueous sulphuric acid medium has been investigated. The effects of variation of [monomer], [Mn(III) ion], [L-methionine], [H⁺] and ionic strength on the rates of polymerization and Mn³⁺ ion disappearance have also been studied. The effect of temperature on the polymerization rate was studied and the thermodynamic parameters were determined. An appropriate mechanism consistent with the kinetic observations has been suggested. A comparative study of the reactivities of two vinyl monomers has been made on the basis of the rate coefficients of the monomers.

Key Words: Kinetics, Redox system, Polymerization, Methyl acrylate, Methacrylic acid.

INTRODUCTION

The rate of vinyl polymerization can be enhanced by employing a mixture of oxidant and reductant as initiator. A number of redox systems have been used for the initiation of vinyl polymerization. Manganic salts in combination with a number of organic substrates such as isobutyric acid¹, ascorbic acid², aspartic acid³, L-threonine⁴, *etc.* were used as redox systems for the polymerization of several vinyl monomers. Mn(III)-substrate redox systems have been used as initiators in the study of reactivities of vinyl monomers only in a few cases^{5,6}. In this paper, we report the results of the kinetic investigation of the polymerization of two vinyl monomers namely methyl acrylate (MA) and methacrylic acid (MAA) using the redox system Mn³⁺-L-methionine (MTN) in aqueous sulphuric acid medium. An attempt has been made to compare the reactivities of the two monomers in homopolymerization.

†Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India.

EXPERIMENTAL

Manganese(III) acetate dihydrate was obtained by adopting the procedure described in literature⁷. Both methyl acrylate (20 °C/65 mm) and methacrylic acid (50 °C/7 mm) were purified by distillation under reduced pressure. AnalaR Grade chemicals such as L-methionine, sulphuric acid and sodium bisulphate were used.

The polymerization experiments were carried out in aqueous sulphuric acid medium in a polymerization reaction tube in nitrogen atmosphere. The rates of polymerization and Mn(III) ion disappearance were determined by bromometry and iodometry, respectively.

RESULTS AND DISCUSSION

The radical polymerization of the two vinyl monomers methyl acrylate and methacrylic acid was studied at 30 °C in aqueous sulphuric acid medium. The induction period was not observed in deaerated conditions. The steady state rate of polymerization was attained in 5 min in the polymerization of both the monomers.

The rates of polymerization of both the monomers are observed to be dependent on the first power of monomer concentration [M]. The plot of R_p vs. [M] is a straight line passing through the origin in both the systems (Fig. 1A and 1B). This confirms that the order with respect to the monomer concentration is unity in the polymerization of both the monomers.

In the polymerization of both the monomers, the rate of polymerization increases only slightly with the increase in [Mn(III)]. There is no significant change in R_p with increase in [MTN] in the polymerization of both methyl acrylate and methacrylic acid. R_p is observed to be almost independent on the variation of ionic strength and hydrogen ion concentration.

The rate of Mn(III) ion disappearance ($-R_m$) is directly proportional to the first power of [Mn(III)] in both the monomers. The plot of $-R_m$ vs. $[Mn^{3+}]$ is a straight line passing through the origin in both the systems. (Fig. 2A and 2B).

There is a regular increase in $-R_m$ with the increase in the concentration of L-methionine in the polymerization of both methyl acrylate and methacrylic acid. The plot of $-R_m^{-1}$ vs. $[MTN]^{-1}$ gives a straight line with an intercept on $-R_m^{-1}$ axis (Fig. 3A and 3B). There is no significant change in $-R_m$ values with increase in concentration of monomers. In both the systems, increase in $[H^+]$ and ionic strength do not have appreciable effect on $-R_m$.

The rate of polymerization increases regularly with the increase of temperature in both the systems. The energy of activation (ΔE^\ddagger) for the overall rate of polymerization is calculated from a plot of $\log R_p$ vs. $1/T$ K (Fig. 4A and 4B) and it is found to be 11.9714 kJ mol⁻¹ for methyl acrylate

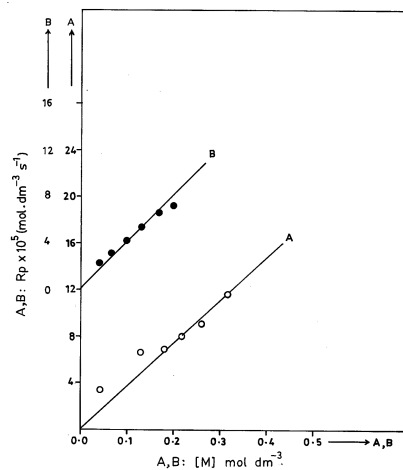


Fig. 1. Mn(III)-L-methionine-monomer systems, [M] variations (A) methyl acrylate system (B) methacrylic acid system

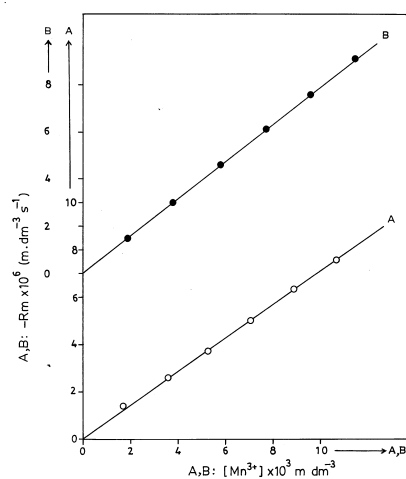


Fig. 2. Mn(III)-L-methionine-monomer systems, $-R_m$ vs. $[M^{3+}]$ plot (A) methyl acrylate system (B) methacrylic acid system

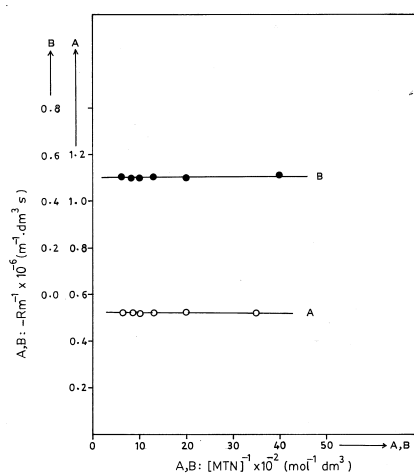


Fig. 3. Mn(III)-L-methionine-monomer systems, $-R_m^{-1}$ vs. $[MTN]^{-1}$ plot (A) methyl acrylate system (B) methacrylic acid system

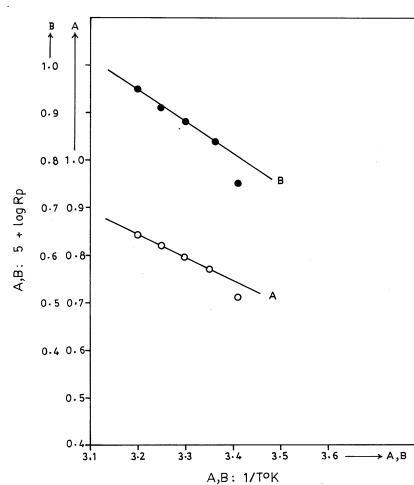


Fig. 4. Mn(III)-L-methionine-monomer systems, $5 + \log R_p$ vs. $1/T$ (K) plot (A) methyl acrylate system (B) methacrylic acid system

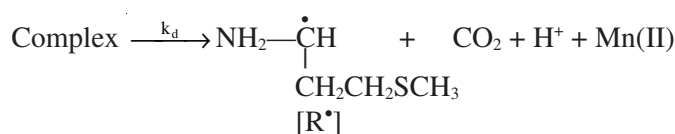
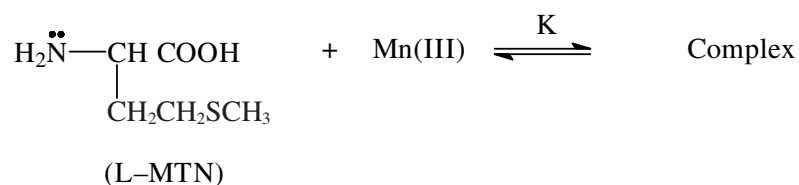
and $15.9605 \text{ kJ mol}^{-1}$ for methacrylic acid. The other thermodynamic parameters such as the entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) have also been evaluated for the polymerization of both the monomers (Table-1).

TABLE-1

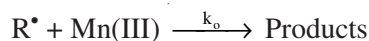
Monomer	ΔE^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (kJ mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
Methyl acrylate	11.9714	-286.39	98.747
Methacrylic acid	15.9605	-271.36	98.186

The following mechanism has been proposed to account for the kinetic features observed in the polymerization of both the monomers.

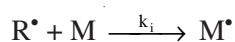
Formation of primary radical (R[•]) *via* complex formation



Oxidation of primary radical with Mn(III):

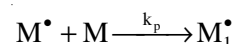


Initiation:

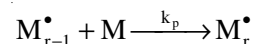


where M is the vinyl monomer

Propagation:



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where M_r[•] and M_{r-1}[•] are polymer radicals.

Termination:



where X is an inactive product.

The following kinetic expressions were derived by assuming stationary state concentration of free radicals and adopting the principle of non-dependence of rate constants on the chain lengths.

$$R_p = \frac{k_p k_d [M]}{k_t}$$

$$-R_m = \frac{2Kk_d [Mn^{3+}]_{total} [MTN]}{1 + K[MTN]}$$

Comparison of monomer reactivity

Since oxidation step is common to both the systems, the values of (k_i/k_o) may be taken as the measure of relative reactivities of the monomers with the primary radical.

The value of k_i/k_o for methyl acrylate (0.2778) is greater than that of the methacrylic acid (0.1792). This shows clearly that methyl acrylate has greater monomer reactivity than methacrylic acid. Thus, the order of monomer reactivities of the two vinyl monomers is

methyl acrylate > methacrylic acid.

A comparison of R_p values of the two monomers under similar experimental conditions shows that the rate of polymerization of methyl acrylate is higher than that of the methacrylic acid (Table-2). This also confirms that methyl acrylate is more reactive than methacrylic acid towards the redox system Mn^{3+} -L-methionine.

TABLE-2

Monomer	k_o/k_i	k_i/k_o	$R_p \times 10^5$ (mol dm ⁻³ s ⁻¹)
Methyl acrylate	3.600	0.2778	6.605
Methacrylic acid	5.581	0.1792	5.620

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