Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3525-3531

Kinetic Studies on the Polymerization of Some Vinyl Monomers by Mn(III)-Tartaric Acid Redox System

T.V. RAJENDIRAN* and S. SUBBU
Postgraduate and Research Department of Chemistry
Pachaiyappa's College, Chennai-600 030, India
E-mail: dr_v_r@yahoo.com

Kinetic studies on the polymerization of methylacrylate and acrylamide initiated by the redox system Mn(III)-tartaric acid have been carried out in aqueous sulphuric acid medium at 15ºC. The effects of [monomer], [Mn (III)], [tartaric acid], [H^+] and ionic strength on the rates of polymerization and Mn(III) ion disappearance have been studied. A mechanism consistent with the experimental observations has been suggested. The rate parameters k_i/k_o and k_p/k_t have been calculated and correlated to monomer and polymer radical reactivities, respectively. Methyl acrylate has been found to have higher monomer and polymer radical reactivities than acrylamide.

Key Words: Kinetics, Polymerization, Methylacrylate, Acrylamide, Reactivity.

INTRODUCTION

Manganese(III) salts in combination with a number of reducing agents such as diglycolic acid[1], ethoxy acetic acid[2], L-threonine[3], *etc.*, have been employed as initiators of vinyl polymerization. Literature survey showed that Mn(III) salts-organic substrate redox systems have been used as initiators in a systematic study of reactivities of monomers and polymer radicals only in a few cases[4,5]. In present work, the kinetics of polymerization of methyl acrylate (MA) and acrylamide (AAM) initiated by Mn(III)-tartaric acid (TTA) redox system has been reported. An attempt to compare the reactivities of the two vinyl monomers and polymer radical reactivities in homopolymerization have also been made.

EXPERIMENTAL

Methylacrylate was purified by distillation under reduced pressure (20ºC/65 mm) and acrylamide was recrytallised from chloroform. Mn(III) acetate dihydrate was prepared and purified by the method of Andrulis *et al.*[6]. Other chemicals such as tartaric acid, sulphuric acid, sodium bisulphate, *etc.* used were of AnalaR grade.

The polymerization experiment was conducted in a reaction tube under nitrogen atmosphere. The rate of polymerization was determined by bromometric method and the rate of Mn(III) ion disappearance by iodometric method.

RESULTS AND DISCUSSION

The polymerization of methylacrylate and acrylamide initiated by the redox system Mn(III)-tartaric acid takes place at measurable rates at 15ºC. No induction period is observed under deaerated conditions. In the polymerization of two monomers, the steady state rate is attained in 5 min.

The rate of polymerization R_p increases with the increasing concentration of monomer. R_p shows first order dependence in the case of both methyl acrylate and acrylamide. The plots of R_p *vs.* $[M]^1$ give straight lines passing through the origin (Fig. 1A-B).

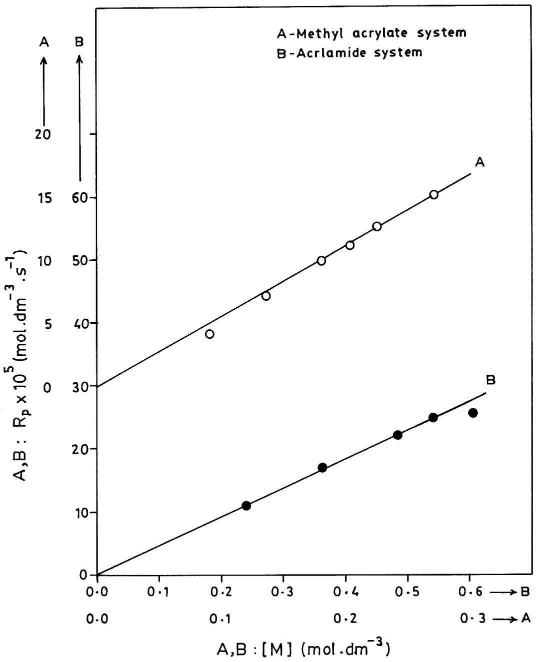


Fig. 1. Mn(III)-Tartaric acid-monomer systems [monomer] variation

In the polymerization of methyl acrylate R_p is found to be almost independent of the concentration of tartaric acid while in the polymerization of acrylamide a small increase in R_p is observed.

There is no significant change in R_p with the increase in concentration of Mn(III) in the polymerization of both methyl acrylate and acrylamide. This observation indicates that the termination of polymerization may be caused either by Mn(III) ion or Mn(III)-tartaric acid complex.

In both the systems, R_p remains unaltered with the variation [H$^+$] and ionic strength of the medium.

The rate of Mn(III) ion disappearance (-R_m) is directely proportional to the first power of [Mn(III)] in both the monomers. The plots of -R_m *vs.* [Mn(III)] give straight lines passing through origin [Figs. 2B and 3B]. -R_m increases uniformly with increase in [TTA] in the polymerization of both methylacrylate and acrylamide. The plots of 1/-R_m *vs.* 1/[TTA] give straight lines with an intercept on 1/-R_m axis [Figs. 2A and 3A] indicating the formation of a weak complex between Mn(III) ion and tartaric acid. There is no significant change in -R_m with the change in [H$^+$] and ionic strength of the medium.

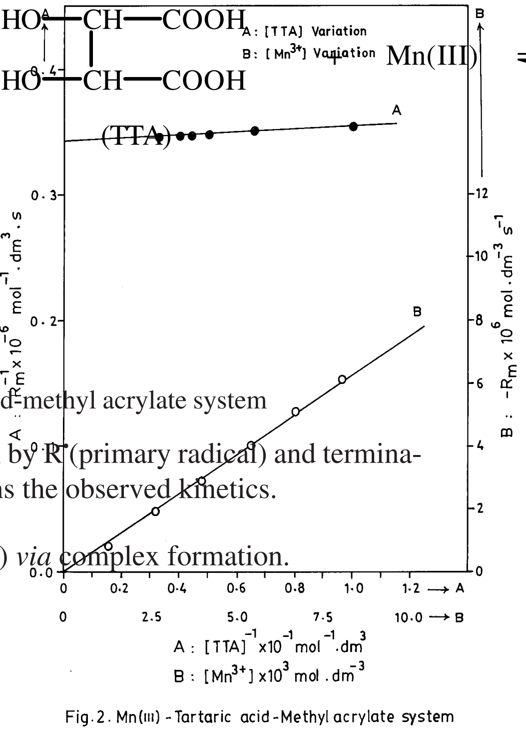


Fig. 2. Mn(III)-Tartaric acid-methyl acrylate system

A mechanism involving initiation by R$^\bullet$ (primary radical) and termination by Mn(III)-TTA complex explains the observed kinetics.

Production of primary radical (R$^\bullet$) *via* complex formation.

$$\begin{array}{l} \text{HO}-\text{CH}-\text{COOH} \\ \quad\;\;| \\ \text{HO}-\text{CH}-\text{COOH} \\ \quad\text{(TTA)} \end{array} + \text{Mn(III)} \overset{K}{\rightleftharpoons} \text{Complex}$$

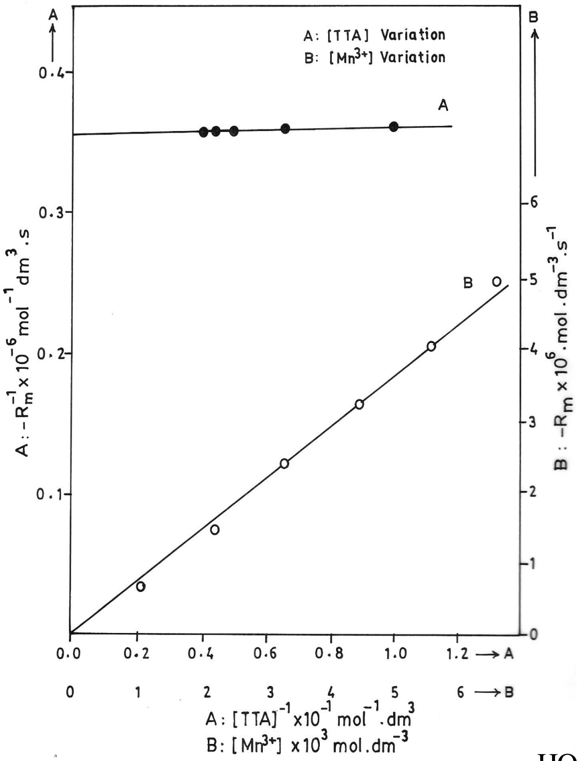
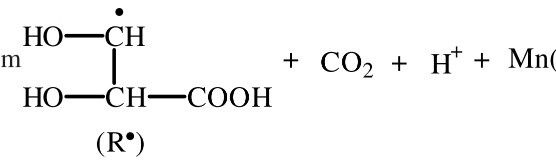


Fig. 3. Mn(III)-Tartaric acid-acrylamide system



$$\text{Complex} \xrightarrow{k} \begin{array}{l} \text{HO—}\dot{\text{C}}\text{H} \\ \quad\;\;\; | \\ \text{HO—CH—COOH} \\ \quad\;\; (\text{R}^\bullet) \end{array} + CO_2 + H^+ + \text{Mn(}$$

Reaction of primary radical ($R^\bullet$) with Mn(III):

$$R^\bullet + \text{Mn(III)} \xrightarrow{k_o} \text{Products}$$

Initiation:

$$R^\bullet + M \xrightarrow{k_i} \text{Products}$$

where M is the monomer.

Propagation:

$$M^\bullet + M \xrightarrow{k_p} M_1^\bullet$$

....

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$$M_{r-1}^\bullet + M \xrightarrow{k_p} M_r^\bullet$$

where $M_{r-1}^\bullet$ and $M_r^\bullet$ are polymer radicals.

Termination of polymerization by Mn(III)-TTA complex:

$$M_r^{\bullet} + \text{Complex} \xrightarrow{k_t} \text{Polymer} + X^* + \text{Mn II}) + H^+$$

where X* may be an inactive product or reducing agent itself.

On the basis of above mechanism, rate expressions for R_p and $-R_m$ are derived by adopting the stationary state assumption for the free radical concentration and the principle of non-dependence of rate constants (k_p and k_i) on the chain lengths.

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

and $$-R_m = \frac{2K \cdot k_d \cdot [Mn(III)]_{total} \cdot [TTA]}{1 + K[TTA]}$$

where $[Mn(III)]_{total} = [Mn(III)]\ (1+ K[TTA])$

The second order rate constant k_d is calculated from the plots of $1/-R_m$ *vs.* 1/TTA for both the monomers. The kinetic parameters k_i/k_o and k_p/k_t are also computed and presented in Table-1.

TABLE-1

Monomer	k_i/k_o	k_p/k_t	$R_p \times 10^5$ mol dm^{-3} s^{-1}	$k_p \times 10^4$ dm^{-3} mol^{-1} s^{-1}
Methylacrylate	0.6621	1.672	12.56	3.539
Acrylamide	0.4065	1.514	11.28	3.126

The energy of activation (E_a), for the overall rate of polymerization is obtained from a plot of log R_p *vs.* 1/T K (Fig. 4) for both the monomers. The entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) for the overall rate of polymerization are also calculated for the polymerization of both the monomers (Table-2) .

TABLE-2

Monomer	E_a (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1}K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
Methylacrylate	32.55	-217.48	95.186
Acrylamide	42.26	-173.51	92.220

Comparison of monomer reactivity

Since oxidation of primary radical by Mn(III) is a common step for both the monomers, the value k_i/k_o may be considered as a measure of monomer reactivity. The value of k_i/k_o for methylacrylate (0.6621) is greater

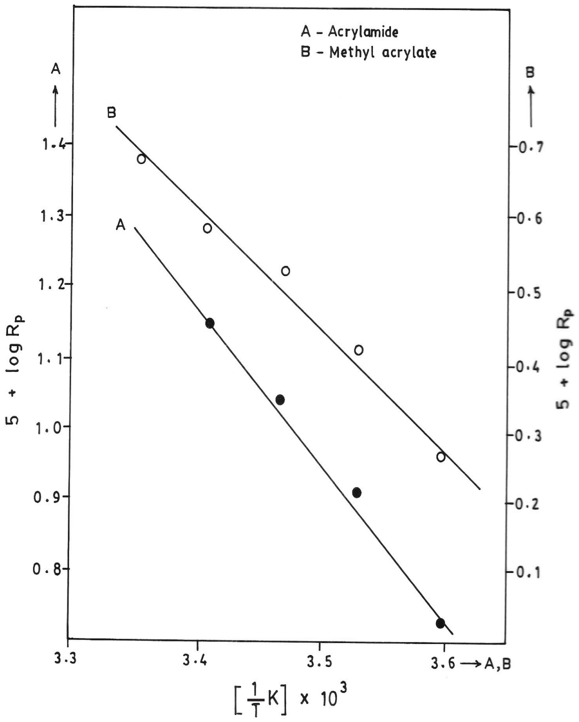

Fig. 4. Mn(III)-tartaric acid momoner system temperature variation

than that for acrylamide (0.4065). This indicates that methylacrylate is more reactive than acrylamide towards Mn(III)-TTA redox system. Hence the monomer reactivities of the two monomers follow the order.

methylacrylate > acrylamide

A comparison of R_p values and activation energies of the two monomers also confirms this order of reactivity.

Comparison of polymer radical reactivity

If a set of monomers follows the same mechanism of initiation and termination, the values of k_p/k_t may be assumed to be a measure of the polymer radical reactivity. The values of k_p/k_t obtained at 15°C for methylacrylate and acrylamide are 1.672 and 1.514, respectively (Table-1). Hence the reactivities of the polymer radicals follow the order

methylacrylate > acrylamide

In accordance with the observation of Otsu[7] polymer radical reactivity varies inversely with the Q-value of the monomers in present investigation. The Q values (resonance stabilisation) of methylacrylate and acrylamide are 0.42 and 1.12, respectively[8]. Hence the polymer radical reactivities of these two monomers should be in the order

methylacrylate > acrylamide

It has been observed that monomers with low e values (polarity) give more reactive polymer radical and *vice versa*. The e values of acrylamide and methylacrylate are 1.19 and 0.6, repectively. Hence it is expected that poly (methylacrylate) radical should be more reactive than poly (acrylamide) radical. This is consistent with the above observation *viz.*, k_p/k_t (polymer radical reactivity) for methylacrylate is higher than that for acrylamide.

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(*Received*: 6 March 2006; *Accepted*: 24 February 2007) AJC-5441